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Laundry bleach product.

A laundry bleaching product comprising a nonparticulate substrate, preferably a flexible sheet, having disposed thereon a composition comprising a peroxyacid bleach and a binder selected from certain types of surfactants, anionic aromatic hydrotropes and mixtures thereof.

EP 0 075 419 A2

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Frank P. Bossu

FIELD OF THE INVENTION

This invention relates to the bleaching of laundry and is especially concerned with bleach products designed for the delivery of a premeasured amount of
5 organic peroxyacid bleach to the laundering bath.

BACKGROUND OF THE INVENTION

Peroxyacids and their utility as laundry bleaches are well-known in the art. See Canadian Pat. No. 635,620, McCune, issued January 30, 1962, and U.S.
10 Pat. No. 4,100,095, Hutchins, issued July 11, 1978.

The addition of premeasured amounts of peroxyacid bleach precursors to a laundry solution which contains an inorganic persalt is disclosed in U.S. Pat. No. 4,179,390, Spadini et al., issued December 18,
15 1979. According to this patent, the peroxyacid bleach precursor is coated onto a substrate (such as a nonwoven cloth). The coated substrate article is then added to the laundry bath where the precursor is released and reacts with the persalt to form the highly reactive
20 peroxyacid bleach. The precursor is coated onto the substrate by forming a melt of the precursor or a dispersion of unmelted precursor in a melt of another organic material such as a surfactant or water-soluble polymer, applying molten material to the substrate, and
25 then cooling the substrate to solidify the melt. According to the patent, the precursor and the inorganic persalt can both be coated onto the substrate, if desired, so long as they are disposed on the substrate in a manner so as to keep them spatially separated from
30 each other, for example as discrete bands on the substrate.

The addition of premeasured amounts of peroxy-
acid bleach to a wash solution by means of a permeable
pouch containing said bleach is disclosed in
the commonly assigned European Patent Applications Nos.
5 82200817.3 and 82200818.1 filed July 1, 1982.

U.S. Ser. No. 297,659 (Kacher), filed August 31,
1981, discloses bleaching articles comprising a sub-
strate carrier (e.g., a woven or nonwoven fabric)
having disposed thereon a urea adduct of a peroxyacid
10 bleach. The urea binds the composition to the sub-
strate. The composition may contain up to 5% of an
anionic surfactant. Approximately 70-75% of the com-
position is urea.

It is an object of the present invention to
15 provide a storage-stable product for direct addition of
a premeasured amount of organic peroxyacid bleach to
the laundry bath, without the need to use substantial
amounts of urea.

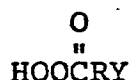
SUMMARY OF THE INVENTION

20 According to the present invention, there is
provided a laundry additive bleach product comprising:

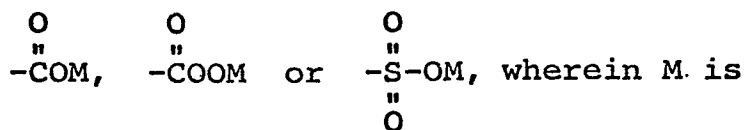
A. a substrate in the form of a nonparticulate
solid article having disposed thereon,

B. a bleach composition comprising:

25 (i) from 1% to 50% of an
organic peroxyacid compound having the
formula:



wherein R is an alkylene group of
30 from 4 to 16 carbon
atoms and Y is hydrogen, halogen
or a radical selected from



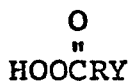
hydrogen, alkali metal or ammonium; and

(ii) from 5% to 98% of a binder selected from anionic surfactants, semi-polar surfactants, N,N-di(C₁-C₃)alkyl fatty acid amide surfactants, zwitterionic surfactants, cationic surfactants, anionic aromatic hydrotropes and mixtures thereof.

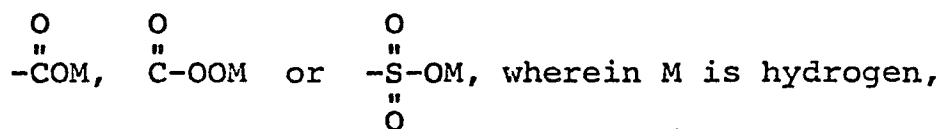
DETAILED DESCRIPTION OF THE INVENTION

The Peroxyacid Bleach

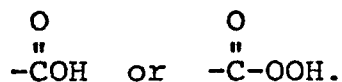
The peroxyacid bleaches used in the present invention have the general formula



wherein R is an alkylene group of from 4 to 16 carbon atoms and Y is hydrogen, halogen or a radical selected from



alkali metal or ammonium, preferably hydrogen. Preferably R contains from 7 to 12 carbon atoms and Y is hydrogen,



Representative compounds of the above formula are peroxydodecanoic acid, peroxyhexanoic acid, peroxyoctanoic acid, monoperoxydodecanedioic acid, diperoxydodecanedioic acid, 12-chloroperoxydodecanoic acid, sodium-12-sulfonatoperoxydodecanoic acid. Preferred compounds

for use herein are diperoxytridecanedioic acid, diperoxy-decanedioic acid, diperoxy-nonanedioic acid and diperoxy-dodecanedioic acid and mixtures thereof. The peroxyacids are present in the compositions herein at levels of from
5 1% to 50%, preferably from 10% to 50%, and most preferably from 20% to 40%. All percentages and ratios herein are "by weight" unless specifically stated otherwise.

The Binder

10 The binder portion of the compositions of the present invention binds the peroxyacid to the substrate and rapidly dissolves to release the peroxyacid from the substrate when the article is placed in water. The binder is selected from anionic surfac-
15 tants, semi-polar surfactants, N,N-di(C₁-C₃)alkyl fatty acid amides, zwitterionic surfactants, cationic surfactants and anionic aromatic hydrotropes, and mixtures thereof. The preferred classes of binders for use herein are the anionic surfactants and the anionic aro-
20 matic hydrotropes. The binder is present in the compositions herein at levels of from 5% to 98%, preferably from 5% to 50%, most preferably from 5% to 20%.

Anionic surfactants are a well-known class of
25 surface active chemicals and any of those known in the art can be used in the present compositions. Anionic surfactants include the soaps (preferably the alkali metal soaps) of C₈-C₂₀ fatty acids, e.g., sodium stearate and potassium laurate, and synthetic anionic surfactants.
30 The synthetics are preferred.

The most common anionic synthetic surfactants can be broadly described as the water-soluble salts, particularly the alkali metal salts, of organic sulfuric acid reaction products having in their molecular structure
35 an alkyl or alkaryl radical containing from 8 to

22 carbon atoms and a radical selected from sulfonic acid and sulfuric acid ester radicals. (Included in the term "alkyl" is the alkyl portion of higher acyl radicals.) Important examples of the anionic surfactants which can be employed in the practice of the present invention are the sodium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8 - C_{18} carbon atoms); sodium or potassium alkyl benzene sulfonates; in which the alkyl group contains from 9 to 15 carbon atoms, (the alkyl radical can be a straight or branched aliphatic chain); paraffin sulfonate surfactants having the general formula RSO_3M , wherein R is a primary or secondary alkyl group containing from 8 to 22 carbon atoms (preferably 10 to 18 carbon atoms) and M is an alkali metal, e.g., sodium or potassium; sodium or potassium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol (e.g., tallow or coconut oil alcohols) and 1 to 10 moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates with 1 to 10 units of ethylene oxide per molecule and in which the alkyl radicals contain from 8 to 12 carbon atoms; the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of a methyl tauride in which the fatty acids, for example, are derived from coconut oil, and sodium or potassium α -acetoxy or α -acetamido-alkane-sulfonates where the alkane has from 8 to 22 carbon atoms.

Mixtures of anionic surfactants can also be used.

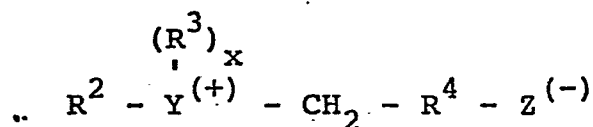
Semi-polar surfactants useful herein include water-soluble amine oxides containing one alkyl moiety of

from 10 to 28 carbon atoms and 2 moieties selected from alkyl groups containing from 1 to 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of

5 10 to 28 carbon atoms and 2 moieties selected from alkyl 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 10 alkyl moieties of from 1 to 3 carbon atoms.

Typical examples of semi-polar surfactants are dodecyldimethylphosphine oxide, octadecylmethyl sulfoxide, dodecylmethyl sulfoxide, tridecylethyl 15 sulfoxide, dimethyldodecylamine oxide, diisopropyltetradecylamine oxide and dimethylhexadecylamine oxide.

The zwitterionic synthetic detergents useful in the compositions of the present invention can be broadly described as derivatives of aliphatic quaternary 20 ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight chain or branched, and wherein one of the aliphatic substituents contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, phosphate, or phosphonate. A 25 general formula for these compounds is:



wherein R^2 contains an alkyl radical of from 8 to 18 carbon atoms; Y is selected from

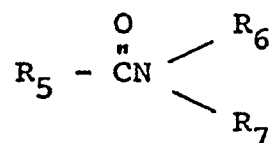
nitrogen, phosphorous, and sulfur atoms; 30 R^3 is an alkyl group containing 1 to 3 carbon atoms; x is 1 when Y is a sulfur atom and 2 when Y is a nitrogen or phosphorous atom, R^4 is an alkylene of from 1 to 4 carbon atoms and Z is a radical selected from 35 carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Examples include:

- 4-[N,N-diethyl-N-octadecylammonio]-butane-1-carboxylate;
 5-[S-isopropyl-S-hexadecylsulfonio]-pentane-1-sulfate;
 3-[P,P-diethyl-P-3,6,9-tetradecylphosphonio]-
 5 propane-1-phosphate;
 3-[N,N-dipropyl-N-dodecylammonio]-propane-1-phosphonate;
 3-[N,N-dimethyl-N-hexadecylammonio]-propane-1-sulfonate;
 3-[N,N-dimethyl-N-hexadecylammonio]-butane-1-sulfonate;
 4-[N,N-diethyl-N-hexadecylammonio]-butane-1-carboxylate;
 10 3-[S-ethyl-S-dodecylsulfonio]-propane-1-phosphate; and
 3-[P,P-dimethyl-P-tetradecylphosphonio]-propane-
 1-phosphonate.

The cationic surfactants useful in the compositions of the present invention can be broadly defined
 15 as quaternary ammonium compounds having 1 long alkyl
 chain containing from 8 to 18 carbon atoms
 such as lauryl trimethylammonium chloride; cetyl pyridinium
 chloride; cetyl trimethylammonium bromide;
 coconutalkyltrimethylammonium nitrite; cetyl pyridinium
 20 bromide; etc.

The N,N-di(C₁-C₃)alkyl fatty acid amides suitable for use herein have the formula



wherein R₅ is a fatty alkyl group of 10 to
 25 22 (preferably 10 to 14) carbon atoms and
 R₆ and R₇ are selected from C₁ to C₃ alkyl groups.
 Examples of these materials are N,N-dimethyl lauramide;
 N,N-diethyl capramide; N,N-dimethyl myristamide and
 N,N-diisopropyl lauramide.

30 The surfactants used as binders herein should
 not contain primary or secondary hydroxyl groups or substantial
 amounts of unsaturation because of reactivity
 of these moieties with the peroxyacid.

Generally, ethoxylated nonionic surfactants such as ethoxylated alkyl alcohols, ethoxylated alkyl phenols, ethoxylated amines, etc., should not be used as binders in the compositions herein since the peroxy-
 5 acid bleaches are not sufficiently stable in the presence of substantial quantities of these materials. Likewise, polyethylene glycols, poly(ethylene oxide) resins and primary and secondary fatty alcohols should not be present in substantial quantities in the compositions herein. Preferably, the compositions are
 10 substantially free of these materials.

Additional examples from the types of surfactants suitable for use herein are disclosed in McCutcheon's Detergents and Emulsifiers, North American
 15 Ed. (1980).

The anionic aromatic hydrotropes are well-known materials. They can be described as alkyl substituted benzene and naphthalene sulfonic acid salts, wherein the alkyl contains from 1 to 4 carbon
 20 atoms and wherein there are from 1 to 3 alkyl substituents on the benzene or naphthalene nucleus. The salt-forming cation can be any metal ion which renders the hydrotrope molecule soluble in water. The alkali metal ions are preferred. Specific examples of
 25 anionic aromatic hydrotropes are sodium toluene sulfonate, sodium xylene sulfonate, potassium cumene sulfonate, calcium toluene sulfonate, magnesium cumene sulfonate, sodium-1-methyl naphthalene-4-sulfonate, sodium-1,6-dimethyl naphthalene-4-sulfonate, potassium-
 30 1-butyl naphthalene-4-sulfonate and sodium-1-methyl-4-ethyl naphthalene-2-sulfonate.

Preferred anionic surfactant binders are the alkali metal C₁₀-C₁₈ alkyl sulfates and the alkali metal C₉-C₁₅ linear alkyl benzene sulfonates, especially
 35 the C₁₁-C₁₃ linear alkyl benzene sulfonates.

Preferred hydrotrope binders are the alkali metal salts of toluene, xylene and cumene sulfonic acids.

Mixtures of the various binders herein can be used. A particularly preferred mixture of binders is sodium C₁₂ linear alkyl benzene sulfonate and sodium lauryl sulfate.

The binders are present in the compositions herein at levels of from 5% to 98%, preferably from 5% to 50%, and most preferably from 5% to 20%. The ratio of peroxyacid bleach to binder is generally from 1:1 to 5:1.

The Substrate

The present invention requires that the peroxyacid bleach composition be disposed on a substrate which is a nonparticulate solid article. The substrate may itself be water-soluble or water-insoluble and in the latter case it should possess sufficient structural integrity under laundering conditions to be recovered from the laundered fabrics at the end of the laundering process, which may include drying in a hot air clothes dryer. Structures which are water-disintegrable, i.e., that break down in aqueous media to individual fibers or insoluble particles, or structures which disintegrate in a hot air clothes dryer, are not considered satisfactory for the purposes of the present invention.

Water-soluble materials include certain cellulose ethers, alginates, polyvinyl alcohol and water-soluble polyvinyl pyrrolidone polymers, which can be formed into nonwoven and woven fibrous structures or onto
5 films.

Suitable water-insoluble materials include, but are not restricted to, natural and synthetic woven and nonwoven fabrics, foams, sponges and films.

The substrate may have any one of a number of
10 physical forms such as sheets, blocks, rings, balls, rods or tubes. Such forms should be amenable to unit usage by the consumer, i.e., they should be capable of addition to the laundry bath in measured amounts, such as individual sheets, blocks or balls and unit lengths
15 of rods or tubes. Certain of these substrate types can also be adapted for single or multiple uses, and can be provided with loadings of peroxyacid bleach compositions up to a composition:substrate ratio of 15:1 by weight.

20 One such article comprises a sponge material releasably enclosing enough peroxyacid bleach composition to provide bleaching action during several washing cycles. This multi-use article can be made by impregnating a sponge ball or block with 30-60 grams of the composition.
25 In use, the bleach composition leaches out through the pores of the sponge into the wash liquor. Such a filled sponge can be used to treat several loads of fabrics in conventional washing machines, and has the advantage that it can remain in the washer after use.

30 Other devices and articles that can be adapted for use in dispensing the bleach composition in a washing liquor include those described in U.S. Pat. No. 3,736,668,

Dillarstone, issued June 5, 1973; U.S. Pat. No. 3,701,202, Compa et al., issued October 31, 1972; U.S. Pat. No. 3,634,947, Furgal, issued January 18, 1972; U.S. Pat. No. 3,633,538, Hoeflin, issued January 11, 1972; and
5 U.S. Pat. No. 3,435,537, Rumsey, issued April 1, 1969.

A highly preferred article herein comprises the peroxyacid bleach composition in combination with a
10 sheet and this should be flexible so as to make it compatible with the movement of the fabrics in the washing machine and to facilitate its handling during manufacture of the product. Preferably the sheet is water pervious, i.e., water can pass from one surface
15 of the sheet to the opposite surface.

If the substrate is a film-type material, perforation of the sheet is desirable. The most preferred form of the substrate is a sheet of woven or nonwoven fabric or a thin sheet of cellular plastic
20 material (e.g., polyurethane foam). Woven fabric sheets can take the form of a plain weave natural or synthetic fiber of low fiber count/unit length, such as is used for surgical dressings, or of the type known as cheesecloth. Loading limitations of nonwoven sheet
25 type substrates limit the amount of composition that can be applied to the sheet. Typically the weight ratio of composition:sheet is 5:1. Generally a ratio of from 2:1 to 12:1 is preferable. For a one-time-use article, the size of the article and
30 the amount of composition disposed thereon should be chosen such that the article contains from 0.1g to 2.5g, preferably from 0.2g to 1.0g available oxygen.

A desirable feature of a substrate to be
35 utilized in the present invention herein is that it be absorbent in nature. It is known that most substances

are able to absorb a liquid substance to some degree; however, the term "absorbent", as used herein, is intended to mean a substance with an absorbent capacity (i.e., values representing a substrate's ability to take up and retain a liquid) of up to approximately 25 times its weight of water.

Determination of absorbent capacity values is made by using the capacity testing procedures described in U.S. Federal Specification UUT-595b modified as follows:

1. Tap water is used instead of distilled water;
2. The specimen is immersed for 30 seconds instead of 3 minutes;
3. Draining time is 15 seconds instead of 1 minute; and
4. The specimen is immediately weighed on a torsion balance having a pan with turned-up edges.

Absorbent capacity values are then calculated in accordance with the formula given in said specification. Based on this test, one-ply, dense, bleached paper (e.g., kraft or bond having a basis weight of 52 g/m²), has an absorbent capacity of 3.5 to 4; commercially available household one-ply towelling paper has a value of 5 to 6; and commercially available two-ply household towelling paper (a paper structure preferred herein) has a value of 7 to 9.5. See U.S. Pat. No. 3,686,025, Morton, issued August 22, 1972.

The substrate of this invention can also be defined in terms of "free space." Free space, also called "void volume," as used herein is intended to mean that space within a structure that is unoccupied. For example, certain multi-ply paper structures comprise plies embossed with protuberances, the ends of

which are mated and jointed; such a paper structure has a void volume of free space between the unembossed portion of the plies, as well as between the fibers of the paper sheet itself. A nonwoven cloth also has such
5 space between each of its fibers. The free space of nonwoven cloth or paper, having designated physical dimensions, can be varied by modifying the density of the paper or nonwoven cloth. Substances with a high amount of free space generally have low fiber density;
10 high density substrates generally have a low amount of free space. Preferred substrates of the invention herein have up to about 90% free space based on the overall volume of the substrate's structure.

As stated above, suitable materials which can
15 be used as a substrate in the invention herein include, among others, sponges, foamed cellular plastic sheets, paper, and woven and nonwoven cloth.

A preferred paper substrate is a compressible, laminated, calendered, multi-ply absorbent paper structure. Preferably, the paper structure has 2 or 3 plies
20 and a total basis weight of from 23 to 146 g/m² and absorbent capacity values within the range of 7 to 10. Each ply of the preferred paper structure has a basis weight of 11 to
25 49 g/m² and the paper structure can consist of plies having the same or different basis weights. Each ply is preferably made from creped, or otherwise extensible, paper with crepe percentage of 15% to 40% and a machine direction (MD) tensile
30 and cross-machine (CD) tensile of from 40 to 600 g/cm of paper width. The two outer plies of a 3-ply paper structure of each ply of a 2-ply paper structure are embossed with identical repeating patterns consisting of 2.5 to 310
35 discrete protuberances per square cm, raised to a height of from 0.25 mm to 11 mm above the

surface of the unembossed paper sheet. From 10% to 60% of the paper sheet surface is raised. The distal ends (i.e., the ends away from the unembossed paper sheet surface) of the protuberances on each ply are mated and adhesively joined together, thereby providing a preferred paper structure exhibiting a compressive modulus of from 200 to 800 inch-grams per cubic inch and Handle-O-Meter (HOM) MD and CD values of from 10 to 130.

10 The compressive modulus values which define the compressive deformation characteristics of a paper structure compressively loaded on its opposing surfaces, the HOM values which refer to the stiffness or handle of a paper structure, the MD and CD HOM values which
15 refer to HOM values obtained from paper structure samples tested in a machine and cross-machine direction, the methods of determining these values, the equipment used, and a more detailed disclosure of the above paper structure, as well as methods of its preparation, can
20 be found in Wells, U.S. Pat. No. 3,415,459, issued December 3, 1968.

 The preferred nonwoven cloth substrates usable in the invention herein can generally be defined as adhesively bonded fibrous or filamentous products,
25 having a web or carded fiber structure (where the fiber strength is suitable to allow carding) or comprising fibrous mats, in which the fibers or filaments are distributed haphazardly or in random array (i.e., an array of fibers in a carded web wherein partial orienta-
30 tion of the fibers is frequently present, as well as a completely haphazard distributional orientation) or substantially aligned. The fibers or filaments can be natural (e.g., wool, silk, jute, hemp, cotton, linen, sisal, or ramie) or synthetic (e.g., rayon, cellulose,
35 or polyesters) or blends thereof.

Methods of making nonwoven cloths are not a part of this invention and being well known in the art, are not described in detail herein. Generally, such cloths are made by air or water laying processes in which the fibers or filaments are first cut to desired lengths from long strands, passed into a water or air stream, and then deposited onto a screen through which the fiber-laden air or water is passed. The deposited fibers or filaments are then adhesively bonded together, dried, cured and otherwise treated as desired to form the nonwoven cloth. Nonwoven cloths made of polyesters, polyamides, vinyl resins, and other thermoplastic fibers can be spunbonded, i.e., the fibers are spun out onto a flat surface and bonded (melted) together by heat or by chemical reactions.

The absorbent properties desired herein are particularly easy to obtain with nonwoven cloths and are provided merely by building up the thickness of the cloth, i.e., by superimposing a plurality of carded webs or mats to a thickness adequate to obtain the desired absorbent properties, or by allowing a sufficient thickness of the fibers to deposit on the screen. Any diameter or denier of the fiber (generally up to about 10 denier) can be used, inasmuch as it is the free space between each fiber that makes the thickness of the cloth directly related to the absorbent capacity of the cloth, and which further makes the nonwoven cloth especially suitable for impregnation with an adducted peroxyacid bleach by means of intersectional or capillary action. Thus, any thickness necessary to obtain the required absorbent capacity can be used.

The choice of binder-resins used in the manufacture of nonwoven cloths can provide substrates possessing a variety of desirable traits. For example, the absorbent capacity of the cloth can be increased, decreased, or regulated by respectively using a hydro-

philic binder-resin, a hydrophobic binder-resin or a mixture thereof in the fiber bonding step. Moreover, the hydrophobic binder-resin, when used singly or as the predominant compound of a hydrophobic-hydrophilic mixture, provides nonwoven cloths which are especially useful as substrates when the bleach composition-substrate combinations disclosed herein are used in an automatic washer.

When the substrate herein is a nonwoven cloth made from fibers, deposited haphazardly or in random array on the screen, the substrate exhibits excellent strength in all directions and is not prone to tear or separate when used in the washer. Apertured nonwoven substrates are also useful for the purpose of the present invention. The apertures, which extend between opposite surfaces of the substrate can be in a pattern which can be formed during laydown of the fibers to produce the substrate, or by machine-aperturing of the substrate after it is formed. Exemplary apertured nonwoven substrates are disclosed in U.S. Pat. Nos. 3,741,724, Harmon, issued June 26, 1973; 3,930,086, Harmon, issued December 30, 1975; 3,750,237 Kalwaites, issued August 7, 1973; and 3,956,556, McQueary, issued May 11, 1976.

Preferably, the nonwoven cloth is water-laid or air-laid and is made from cellulosic fibers, particularly from regenerated cellulose or rayon, which are lubricated with standard textile lubricant. Preferably, the fibers are from 4.7 mm to 50 mm in length and are from 1.5 to 5 denier (Denier is an internationally recognized unit in yarn measure, corresponding to the weight in grams of a 9,000 meter length of yarn). Preferably, the fibers are at least partially oriented haphazardly, particularly substantially haphazardly, and are adhesively bonded together with hydrophobic or

substantially hydrophobic binder-resin, particularly with a nonionic self-crosslinking acrylic polymer or polymers. Conveniently, the cloth comprises 70% fiber and 30% binder-resin polymer by weight and has a basis weight of from 12 to 120, preferably 24 to 72 g/m².

One preferred example is an air-laid nonwoven cloth comprising 70% regenerated cellulose (American Viscose Corporation) and 30% hydrophobic binder-resins (Rhoplex HA-8 on one side of the cloth, Rhoplex HA-16 on the other; Rohm and Haas Co.). The cloth has a thickness of 4 to 5 mils., a basis weight of 29 g/m², and an absorbent capacity of 6. 30 cm of the cloth 23 cm wide, weighs 2.0 grams. The fibers are 6.5 mm in length, 1.5 denier, and are oriented substantially haphazardly. The fibers are lubricated with sodium oleate.

A further preferred substrate is a mechanically laid, nonwoven cloth commercially available from Chicopee Mills, Inc., New Brunswick, New Jersey 08903. The fibers are rayon of 1.5 denier and the composition of the nonwoven fabric is 78% rayon and 22% binder. The fabric is uniformly patterned with diamond-shaped holes at 17 holes/cm². The substrate has a basis weight of 34.7 g/m². 30 cm length of the substrate, 23 cm wide, weighs 2.4 grams. The cloth is sold under the name "Chicopee Keyback 147" by Chicopee Manufacturing Co., Milltown, New Jersey.

A further class of substrate material that can be used in the present invention comprises an absorbent foam-like material in the form of a sheet. The term "absorbent foam-like material" is intended to encompass three dimensional absorptive materials such as "gas blown foams," natural sponges and composite fibrous based structures such as are disclosed in U.S. Pat. Nos. 3,311,115, Mueller et al., issued March 28,

1967, and 3,430,630, Megison et al., issued March 4, 1969.

Synthetic organic polymeric plastics material such as polyether, polyurethane, polyester, polystyrene, polyvinylchloride, nylon, polyethylene and polypropylene are most often employed and a particularly preferred material of this type is a hydrophilic polyurethane foam in which the internal cellular walls of the foam have been broken by reticulation. Foams of this type are described in detail in U.S. Pat. No. 3,794,029, Dulle, issued Feb. 26, 1974.

A specific example of this foam type comprises a hydrophilic polyurethane foam of density 0.036 g/cm^3 with a cell count of between 8 and 40 cells per cm, preferably 24 to 32 per cm available from the Scott Paper Company, Eddystone, Pennsylvania, USA, under the Registered Trade Mark "Hydrofoam."

The size and the shape of the substrate sheet are a matter of choice and are determined principally by factors associated with the convenience of its use. Thus the sheet should not be so small as to become trapped in the crevices of the machine or the clothes being washed or so large as to be awkward to package and dispense from the container in which it is sold. For the purposes of the present invention sheets ranging in area from 129 cm^2 to 1290 cm^2

are acceptable, the preferred area lying in the range of from 516 cm^2 to 1032 cm^2 for nonwoven substrates and 193 cm^2 to 322 cm^2 for foamed sheets.

Such a size has the additional advantage of being too large to be swallowed by, e.g., small children, thereby minimizing the risk of internal tissue damage from ingestion of the materials absorbed on the substrate.

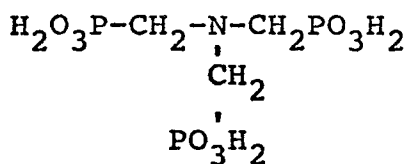
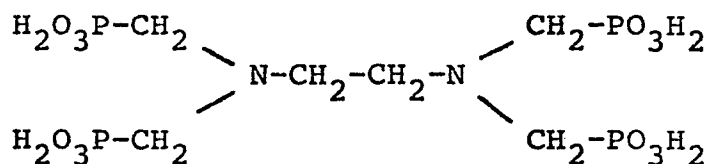
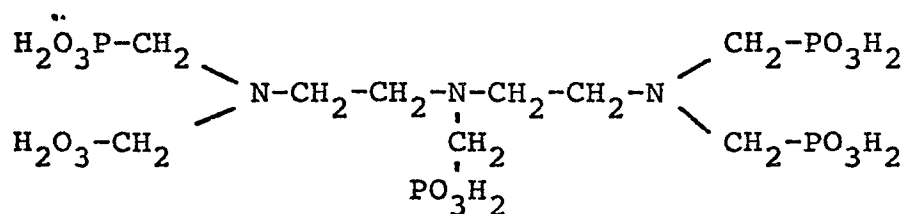
Optional Ingredients

Many optional ingredients can be used in the compositions of the present invention.

A caveat is that when an optional material which is inherently incompatible with the peroxyacid bleach of this invention is included, such incompatible material should be separated from the peroxyacid component. Means for separation include: coating either the peroxyacid or the optional component, or disposing the components on separate portions of the substrate (See U.S. Pat. 4,179,390, Spadini et al., supra). Optional ingredients include stabilizers, exotherm control agents, pH control agents, and the like. These will be discussed in more detail below.

Particularly useful stabilizers are the amino-phosphonate chelators, 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 2000Dequest 2041Dequest 2060

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. Preferably the acid form is used.

Additional stabilizers can also be used, primarily to protect the peroxyacids against decomposition which is catalyzed by heavy metals such as iron and copper. 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, are also 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.

Stabilizers, when used in the compositions herein, are generally present at levels of from 0.005% to 2%.

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 highly desirable to include a substantial amount of an exotherm control agent in peroxyacid bleaching compositions. Suitable materials include 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.

Additional agents which may be used to aid in giving good bleaching performance include such things as pH adjustment agents, detergent builders, bleach activators and minors such as coloring agents, dyes, soil suspending agents and perfumes. Typical pH adjustment agents are used to alter or maintain aqueous solutions of the instant compositions within the 5 to 10 pH range in which peroxyacid bleaching agents are generally most useful. Depending upon the nature of other optional composition ingredients, pH adjustment agents can be either of the acid or base type. Examples of acidic pH adjustment agents designed to compensate for the presence of other highly alkaline materials include normally solid organic and inorganic acids, acid mixtures and acid salts. Examples of such acidic pH adjustment agents include adipic acid, citric acid, glycolic acid, tartaric acid, gluconic acid, glutamic acid, sulfamic acid, sodium bisulfate, potassium bisulfate, ammonium bisulfate and mixtures of citric acid and lauric acid. Citric acid is preferred by virtue of its low toxicity and hardness sequestering capability. Also preferred is adipic acid. Some of the unreacted parent acid used in making the peroxyacid is generally also present in the compositions. Typically, it is present at one-fifth the level of the peroxyacid.

Optional alkaline pH adjustment agents include the conventional alkaline buffering agents. Examples of such buffering agents include such salts as carbonates, bicarbonates, silicates, pyrophosphates and mixtures thereof. Sodium bicarbonate and tetrasodium pyrophosphate are highly preferred.

Product Manufacture

In a preferred method of manufacturing, the products of the present invention an aqueous slurry of the peroxyacid bleach compound and binder is first prepared. This can be done by simply mixing the peroxyacid, water and binder (along with optional ingredients such as exotherm agents and stabilizers, if used) at a temperature between 25°C and 45°C. The peroxyacid should be 20% to 40% of the total solids of the slurry. The exotherm control agent (boric acid preferred) should be 15% to 45% of the total solids of the slurry. The binders should be 5% to 50%, preferably 5% to 20%, of the total solids of the slurry. The stabilizers should be 0.01% to 2.0% of the total solids of the slurry. The concentration of solids should be chosen so as to use the least amount of water necessary to provide a slurry which gives good coating and efficient operation of the coating process, since water must be removed from the coated product in the final step of the process. Typically the ratio of solids to water in the slurry will be from 1:1 to 4:1.

The slurry can be applied to the substrate by any conventional method used to apply a fluid composition to a substrate, e.g., by spraying, brushing, spreading with a doctor blade, etc.

A particularly preferred mode of application when the substrate is an absorbent sheet-type material

(e.g., absorbent paper or nonwoven cloth) is that which is known as padding. In this method the slurry (and any optional materials) is placed into a pan or trough. A roll of absorbent substrate is then set up on an apparatus so that it can unroll freely. As the substrate unrolls, it travels downwardly and, submersed, passes through the pan or trough containing the slurry at a slow enough speed to allow sufficient impregnation. The absorbent substrate then travels, at the same speed, upwardly and through a pair of rollers which squeeze off excess slurry. The impregnated substrate is then passed through a drying atmosphere to remove most or all of the water. After the drying step, the substrate can be folded, cut or perforated at uniform lengths, and subsequently packaged and/or used.

The rollers used resemble "squeeze rolls" used by those in the paper and papermaking art; they can be made of hard rubber or stainless steel. Preferably, the rollers are adjustable with direction and speed controlled, so that the orifice between their respective surfaces can be adjusted to control the amount of the slurry on the substrate.

In another exemplary mode of applying composition to the substrate, the slurry of peroxyacid bleach composition is sprayed onto absorbent substrate as it unrolls. The unrolled substrate web is arranged to move under the spray nozzle at a predetermined speed so as to receive a uniform coating of the slurry.

After the coating steps, the product is subjected to an evaporative drying step (preferably via a moving stream of air) to remove substantially all of the water. By removal of "substantially all of the water" is meant that the product is dried to the point where it is no longer damp to the touch. Generally, the amount of water left on the article will be less than 0.5% by weight of the article.

EXAMPLE I

This example illustrates a product of the present invention, designed to deliver 10 ppm of available oxygen (AvO) to a wash from diperoxydodecanedioic acid (DPDA). Anionic surfactant is used as the binder and also serves to help disperse and dissolve the peroxyacid bleach into the wash liquor.

A. Preparation of Bleach Product

A coating slurry was made at room temperature, 22°C, by mixing 75gm of a 41% aqueous slurry of DPDA and unreacted dodecanedioic acid in a ratio of 5.5:1 with 30gm of a 30% solution of sodium lauryl sulfate, 10gm of a 40% solution of sodium C₁₂ linear alkyl benzene sulfonate, 1.5gm of ethylenediamine- (tetramethylene phosphonic acid) stabilizer, 25gm of boric acid exotherm agent and 15gm adipic acid. This slurry was 55% solids. The pH of the slurry was measured to be 2.3. 40gm of the slurry was spread onto a 254 mm x 356 mm apertured substrate (Chicopee Keyback 147) with a small roller. The coated substrate was then fan-dried at ambient conditions for 16 hours.

The level of AvO in the coating was 3.8%. The gross weight of the coating plus substrate was 20gm with a 16gm net coating weight. This article, when added to a typical 64.4 litre laundry detergent solution, is intended to provide 10 ppm AvO when all the bleach is released from the sheet. The nominal composition of the dry coating is listed below (Table I-A).

TABLE I-A
BLEACH COATING NOMINAL COMPOSITION

	<u>Ingredient</u>	<u>Wt. %</u>
	1,12-Diperoxydodecanedioic acid	33.3
5	1,12-Dodecanedioic acid	6.0
	Sodium lauryl sulfate	10.1
	Sodium linear alkylbenzenesulfonate	3.9
	Ethylenediamine(tetramethylene phosphonic acid)	1.7
10	Adipic acid	16.9
	Boric acid	<u>28.1</u>
	Total	100.0%

B. Preparation of Bleach Solution
and Bleach Release Measurements

15 The bleach solution was prepared using a standard top-loading washing machine filled with 64.4 litres of 37.8°C water of 120 parts per million hardness. A 2.2 kg bundle of clothes was added to the tub to simulate realistic agitation effects in a normal wash. A phosphate-

20 built detergent (TIDE®) was used at recommended levels and a single sheet was added to the wash. Wash aliquots were obtained at specified times into the wash cycle. The concentration of peroxyacid in the wash is reported in Table I-B for different times throughout

25 the wash in ppm AvO. The data indicates complete release of the coating and AvO into the wash liquor.

TABLE I-B
BLEACH RELEASE MEASUREMENTS

	<u>Time (Minutes)</u>	<u>AvO (ppm)</u>
	1.4	10.4
5	3.6	9.4
	5.9	9.7
	11.0	8.4

EXAMPLE II

This example illustrates the use of an anionic hydrotrope (sodium cumene sulfonate), as a binder in a product of the present invention.

A. Preparation of Bleach Product

A coating slurry was made at room temperature, 22°C, by mixing 75gm of a 41% aqueous slurry of DPDA and unreacted dodecanedioic acid in a ratio of 6:1 with 40gm of a 40% solution of sodium cumene sulfonate, 1.5gm of ethylenediamine(tetramethylene phosphonic acid) stabilizer, 25 gm of boric acid exotherm agent and 20gm of adipic acid. The pH of the slurry was measured to be 2.3. This slurry was 60% solids. 40gm of the slurry was applied to a 254 mm x 356 mm apertured substrate (Chicopee Keyback 147) with a small roller. The coated substrate was then fan-dried at ambient conditions for 16 hrs. The level of AvO in the coating was 3.2%.

The coating plus substrate were 26gm with a 22gm net coating weight. The level of AvO in the coating was analyzed to be 3.14% and was designed to deliver 11 ppm AvO when added to a 64.4 litre laundry detergent solution. The nominal composition of the dry coating is listed in Table II-A.

TABLE II-A

BLEACH COATING NOMINAL COMPOSITION

	<u>Ingredient</u>	<u>Wt. %</u>
	1,12-Diperoxydodecanedioic acid	30.7
5	1,12-Dodecanedioic acid	5.1
	Sodium cumene sulfonate	16.4
	Ethylenediamine(tetramethylene phosphonic acid)	1.5
	Adipic acid	20.5
10	Boric acid	<u>25.6</u>
	Total	100.0%

B. Preparation of Bleach Solution and
Bleach Release Measurements

The bleach solution was prepared in the same
15 manner as in Example I, Item B. The concentration of
peroxyacid in the wash is reported in Table II-B for
different times throughout the wash in ppm AvO. The
data indicates complete release of the coating and AvO
into the wash liquor.

TABLE II-B

BLEACH RELEASE MEASUREMENTS

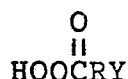
	<u>Time (Minutes)</u>	<u>AvO (ppm)</u>
	0.7	10.5
	2.0	9.9
25	4.0	9.2
	7.1	8.9
..	9.5	8.2

C. Stability

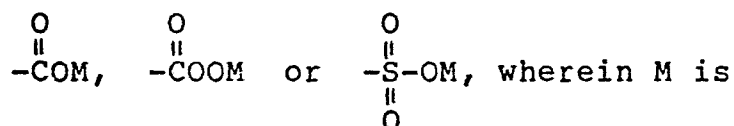
AvO in the coated substrate was measured after
30 storage at 27°C and 38°C. After 6 weeks storage, the
AvO was 98% and 94% of initial level at 27°C and 38°C,
respectively.

CLAIMS

1. A laundry additive bleach product comprising:
 - A. a substrate in the form of a nonparticulate solid article having disposed thereon,
 - B. a bleach composition comprising:
 - (i) from 1% to 50% of an organic peroxyacid compound having the formula:



wherein R is an alkylene group of from 4 to 16 carbon atoms and Y is hydrogen, halogen or a radical selected from



hydrogen, alkali metal or ammonium; and

- (ii) from 5% to 98% of a binder selected from anionic surfactants, semi-polar surfactants, N,N-di(C₁-C₃)alkyl fatty acid amide surfactants, zwitterionic surfactants, cationic surfactants, anionic aromatic hydrotropes and mixtures thereof.
2. The product of Claim 1 wherein the substrate is water-insoluble.
3. The product of either one of Claims 1 and 2 wherein the substrate is a woven or nonwoven fabric.
4. The product of any one of Claims 1-3 wherein the weight ratio of Component B to Component A is from 2:1 to 12:1.
5. The product of Claim 4 wherein in Component B(i) the amount of peroxyacid compound is from 10% to 50%.

6. The product of any one of Claims 1-5 wherein in the peroxy-acid compound R contains from 7 to 12 carbon atoms.

7. The product of any one of Claims 1-6 wherein in the peroxy-acid compound, Y is $\begin{array}{c} \text{O} \\ \parallel \\ -\text{COOH} \end{array}$.

8. The product of Claim 7 wherein the weight ratio of peroxyacid to binder is from 1:1 to 5:1, and the amount of peroxyacid is from 20% to 40%.

9. The product of either one of Claims 7 and 8 wherein the binder is selected from alkali metal C₁₀-C₁₈ alkyl sulfates, alkali metal C₉-C₁₅ linear alkylbenzene sulfonates, alkali metal cumene sulfonates and mixtures thereof.

10. The product of any one of Claims 7-9 wherein the peroxyacid is diperoxydodecanedioic acid.