⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 105 690**
A1

⑫
EUROPEAN PATENT APPLICATION

㉑ Application number: **83305726.8**

㉒ Date of filing: **26.09.83**

(51) Int. Cl.^{3}: **C 11 D 3/39**
D 06 L 3/02

㉚ Priority: **30.09.82 US 430562**
16.09.83 US 532456

㊸ Date of publication of application:
18.04.84 Bulletin 84/16

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI NL SE

(71) Applicant: **THE PROCTER & GAMBLE COMPANY**
301 East Sixth Street
Cincinnati Ohio 45201(US)

(72) Inventor: **Dyer, John C.**
9 Darby Heath
Fairfield Ohio 45014(US)

(74) Representative: **Gibson, Tony Nicholas et al,**
Procter & Gamble (NTC) Limited Whitley Road
Longbenton Newcastle upon Tyne NE12 9TS(GB)

(54) Bleaching compositions.

(57) This invention relates to bleaching compositions. More particularly, this invention relates to bleaching compositions that provide effective and efficient solution bleaching and/or surface bleaching performance on textiles. Such bleaching performance is obtained over an extremely wide class of stains and soils and a wide range of bleaching solution temperatures and pH. The bleaching compositions within the invention contain a carboxylic acid and an aromatic sulfonyl halide bleach activator. In a highly preferred embodiment the bleaching compositions within the invention are detergent compositions.

EP 0 105 690 A1

Croydon Printing Company Ltd.

BLEACHING COMPOSITIONS

John C. Dyer

BACKGROUND TO THE INVENTION

This invention relates to bleaching compositions. More particularly, this invention relates to bleaching compositions that provide effective and efficient solution bleaching and/or surface bleaching performance on textiles. Solution bleaching is bleaching wherein the bleaching mechanism takes place in the bleaching solution itself, i.e., the bleach and water mixture, rather than the textile surface, and, thereby, modifies soils that are suspended in the bleaching solution. This prevents soils from being deposited on the textile surface and/or decolorizes soils which are then deposited on the textile surface, but are rendered less objectionable. Surface bleaching is bleaching wherein the bleaching mechanism takes place on the textile surface and, thereby, modifies stains that are on the textile surface. This results in the removal and/or decoloration of such stains. Such bleaching performance is obtained over an extremely wide class of stains and soils and wide range of bleaching solution temperatures and pH. The bleaching compositions within the invention contain a peroxycarboxylic acid and an aromatic sulfonyl halide bleach activator. In a highly preferred embodiment the bleaching compositions within the invention are detergent compositions.

It has long been known that peroxygen bleaches that yield hydrogen peroxide in an aqueous solution provide a desirable level of solution bleaching and/or surface bleaching performance, but that they are also extremely temperature dependent. Such bleaches are essentially only practicable and/or effective in bleaching solutions wherein the solution temperature is above about 60°C. At bleach solution temperatures of about 60°C peroxygen bleaches are only partially effective, due to their low level of reactivity. Therefore, in order to obtain a desirable level of bleaching performance extremely high levels of peroxygen bleach must be added to the system. As the bleach solution temperature is lowered below 60°C, even higher levels of peroxygen bleach must be added to the system in order to obtain a desirable level of bleaching performance. The temperature dependence of peroxygen bleaches is significant because such bleaches are commonly used as a detergent adjuvant in textile wash processes that utilize an automatic household washing machine at wash water temperatures below 60°C. Such wash temperatures are utilized because of textile care and energy considerations. As a consequence of such wash processes, there has been much industrial research to develop substances, generally referred to as bleach activators, that render peroxygen bleaches effective at bleach solution temperatures below 60°C. Numerous substances have been disclosed in the art as effective bleach activators.

Typically, the substances that have been utilized as bleach activators are substances that react with the perhydroxide anion of hydrogen peroxide, which is yielded by the peroxygen bleach in the bleaching solution, to form a peroxy acid. Peroxy acids are more reactive than the peroxygen bleach alone and, therefore, can provide bleaching at bleach solution temperatures below about 60°C. Many of the peroxy acids are peroxycarboxylic acids or persulfonic acids. The peroxycarboxylic acids are derived from bleach activators that contain a carbonyl carbon that reacts with the perhydroxide anion to form the peroxycarboxylic acid. Examples of such bleach activators are disclosed in U.S. Patents 4,248,928, Spadini et al (February 3, 1981); 4,126,573, Johnston (November 21, 1978) and 4,100,095, Hutchins et al (July 11, 1978). The persulfonic acids are derived from bleach activators that contain a sulfonyl group that reacts with the perhydroxide anion to form the persulfonic acid. For example, U.S. Patent 4,292,191, Gray (September 29, 1981) discloses bleaching compositions containing a peroxygen bleach and a sulfonyl halide bleach activator, such as an alkoxybenzenesulfonyl halide. U.S. Patent 4,107,065, Gray (August 15, 1978) discloses bleaching compositions containing a peroxygen bleach and a sulfonyl bleach activator, such as an aromatic sulfonyl halide.

SUMMARY OF THE INVENTION

The present invention comprises a bleaching composition containing:

(a) a peroxycarboxylic acid or salt thereof or precursors thereof; and

(b) an aromatic sulfonyl halide bleach activator;

wherein the molar ratio of each potential and actual peroxycarboxyl group of (a) to each sulfonyl group that can potentially generate an acyl persulfonate is from 10 to 0.05.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to bleaching compositions consisting of a peroxycarboxylic acid and an aromatic sulfonyl halide bleach activator, both of which are defined hereinafter. The bleaching compositions provide very effective and efficient solution bleaching and/or surface bleaching performance on textiles. Solution bleaching is particularly beneficial when the bleaching compositions are detergent compositions. This is because a detergent system may be effective for removing soils from the textiles and into the bleaching solution, but not for preventing such soils from being redeposited onto the textiles. Solution bleaching modifies the soils in the bleaching solution and, thereby, reduces such soil redeposition and/or decolorizes the soils which renders soil redeposition less objectionable. The surface bleaching provided by the bleaching compositions not only provides effective and efficient removal and/or decoloration of stains on textiles, but also provides dingy soil removal. Dingy soils are soils that build up on textiles after numerous cycles of usage and washing and, thus, result in a white textile having a gray tint. These soils tend to be a blend of body lipids and proteinaceous debris. The removal of this type of soil is sometimes referred to as "dingy fabric clean up". Furthermore, such solution bleaching and/or surface bleaching performance is obtained with minimal damage to the textiles and with bleach solution temperatures as low as about 5°C. Bleaching compositions consisting only of a peroxycarboxylic acid or a peroxygen bleach capable of yielding hydrogen peroxide in an aqueous solution plus an aromatic sulfonyl halide bleach activator are also able to provide solution bleaching and/or surface bleaching at temperatures below about 60°C, i.e., the temperature wherein peroxygen bleaches are essentially ineffective; however, they provide neither the effectiveness nor the efficiency of the bleaching compositions within the invention.

The bleaching compositions within the invention are extremely effective. Such compositions provide a superior level of solution bleaching and/or surface bleaching performance over a very wide class of stains. Bleaching compositions consisting of only a peroxycarboxylic acid or, especially, a peroxygen bleach capable of yielding hydrogen peroxide in an aqueous solution plus an aromatic sulfonyl halide bleach activator do not provide the superior level of bleaching performance over a very wide class of stains. Bleaching compositions consisting only of a peroxycarboxylic acid provide, at best, a superior level of bleaching performance for only a narrow class of stains. Such performance is obtained primarily on beverage type stains, e.g., tea and wine. This severely limits the practicability of such compositions because there are numerous other types of common stains. Without being bound by theory, it is believed that this stain specificity is based upon the chemical structure of the stain. Beverage type stains consist essentially of aromatic type compounds. Other common stains, such as grass, ink and tomato, have structures which are very olefinic. This structural difference is believed to be the cause of the stain specificity of such bleaching compositions. Bleaching compositions consisting only of a peroxygen bleach capable of yielding hydrogen peroxide in an aqueous solution plus an aromatic sulfonyl halide bleach activator do not provide the superior level of bleaching performance, regardless of the type of stain. Surprisingly, only the compositions within the invention provide the superior level of solution bleaching and/or surface bleaching performance over a very wide class of stains.

The bleaching compositions within the invention are very efficient. Extremely small quantities of such compositions provide the superior level of solution bleaching and/or surface bleaching performance. Without being bound by theory, it is believed that such efficiency is obtained because a substantial majority of active oxygen, defined below, is utilized for bleaching during the bleaching process. This can be explained as follows.

It is believed that the peroxycarboxylic acid reacts with the aromatic sulfonyl halide bleach activator to form an acyl persulfonate. Since the acyl persulfonate contains an -O-O- group it contains a reactive oxygen atom, generally referred to as an "active oxygen" atom. The active oxygen is the active bleaching component which reacts with and, thereby, modifies stains on textiles and/or soils in the bleaching solution. The acyl persulfonate is sufficiently reactive so that very little active oxygen is present after the bleaching process. However, and just as important, the acyl persulfonate is not too reactive, based upon the superior level of solution bleaching and/or surface bleaching performance observed, so as to decompose rather than provide such bleaching performance. Therefore, the vast majority of the active oxygen is utilized for bleaching during the bleaching process. This enables one to obtain the superior level of bleaching performance with very small amounts of the bleaching compositions within the invention.

Bleaching compositions consisting only of a peroxycarboxylic acid or a peroxygen bleach capable of yielding hydrogen peroxide in an aqueous solution plus an aromatic sulfonyl halide bleach activator are extremely inefficient and/or ineffective. Bleaching compositions consisting only of a peroxycarboxylic acid are very inefficient because a substantial amount of the active oxygen of the peroxycarboxylic acid remains in the bleaching solution after the bleaching process is carried out. This unreacted peroxycarboxylic acid is essentially wasted. Thus, in order to achieve the superior level of bleaching performance very large amounts of such compositions, as compared to the bleaching compositions within the invention, are required. However, it should be noted that regardless of the amount of peroxycarboxylic acid added to the bleaching solution, within practicable limits, the desired superior level of bleaching performance is obtained primarily on beverage type stains. Bleaching compositions consisting of a peroxygen bleach capable of yielding hydrogen peroxide in an aqueous solution plus an aromatic sulfonyl halide bleach activator are very efficient in that very little active oxygen is present after the bleaching process. However, such bleaching compositions do not provide the desired superior level of solution bleaching performance and provide essentially no surface bleaching. Without being bound by theory, it is believed that the persulfonic acid formed is so reactive that it decomposes before it even comes into contact with the textiles. Only the bleaching compositions within the invention are both efficient and provide the superior level of solution bleaching and/or surface bleaching performance over a very wide class of stains.

Another major advantage of the bleaching compositions within the invention is that they provide the superior level of solution bleaching and/or surface bleaching performance over a very wide range of pH's of the bleaching solution. Therefore, for example, when the bleaching compositions are detergent compositions one can adjust the pH of the bleaching solution so as to optimize detergency performance without sacrificing bleaching performance. Typical activated bleaching compositions, i.e., those consisting only of a peroxygen bleach capable of yielding hydrogen peroxide in an aqueous solution and a bleach activator which react in the bleaching solution to form a peroxy acid, are very pH dependent. It is believed that such pH dependence is due to that the active oxygen of the peroxy acid reacts with stains and/or soils via the formation of a dimer by the peroxy acid with its anion. Thus, in order to maximize the amount of the dimer formed it is essential that the pK_a of the peroxy acid be similar to the pH of the bleaching solution. This ensures that there will be similar levels of the peroxy acid and its anion present in the bleaching solution and, therefore maximizes the amount of dimer formed. Otherwise, there will be an excess of peroxy acid as compared to its anion or vice versa; either of such excess is not utilized and, thus, as indicated by experimental evidence, bleaching performance declines. It should be noted that even if the pH of the bleaching solution is similar to the pK_a of the peroxy acid the vast majority of the active oxygen is still present after the bleaching process. It is theorized that the bleaching compositions within the invention do not operate via the formation of a reactive dimer and, therefore, as indicated by experimental evidence, provide the superior level of bleaching performance over a wide range of pH's.

The initial pH of the bleaching solution containing the bleaching compositions within the invention is from 6 to 12, preferably from 7 to 11 and most preferably from 8.5 to 10.

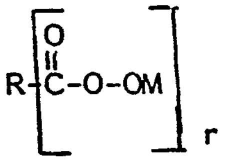
In the compositions within the invention the ratio of the peroxycarboxylic acid to aromatic sulfonyl halide is such that the molar ratio of each actual and potential peroxycarboxyl group of the peroxycarboxylic acid to each sulfonyl group of the aromatic sulfonyl halide that can potentially generate acyl persulfonate is from 10 to 0.05, preferably from 1 to .3 and most preferably from 1 to 0.7. Molar ratios of such components of from 1 to 0.7 are most preferred because vast excesses of either component will result in such excess not interacting with the other component and, therefore, won't provide the superior level of bleaching performance that is obtained by such components that interact with each other. The term "potential peroxycarboxyl group" is meant to define the level of peroxycarboxylic acid that can be present in the bleaching compositions within the invention when the peroxycarboxylic acid is generated <u>in situ</u>, as discussed hereinafter. It should be noted that the ratio is found to vary considerably as a function of pH. For example, if the initial pH of the bleaching solution is greater than 10, then excess aromatic sulfonyl halide would be preferred to make up for the amount lost due to alkaline hydrolysis.

The following is a detailed description of the essential and the optional components of the bleaching compositions within the invention. All percentages, parts or ratios are by weight unless otherwise indicated.

THE PEROXYCARBOXYLIC ACID

Essentially any peroxycarboxylic acid or salt thereof is suitable for use herein. Albeit some peroxycarboxylic acids are more preferred than others, it is believed that the effectiveness and efficiency of solution bleaching and/or surface bleaching performance of essentially any peroxycarboxylic acid will be enhanced by utilizing it in the bleaching compositions within the invention.

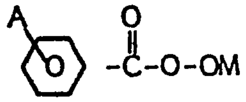
The preferred peroxycarboxylic acids and salts thereof have the general formula:



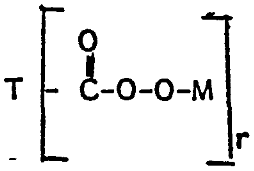
$$R\left[\overset{O}{\overset{\|}{C}}-O-OM\right]_r$$

wherein R is selected from H, a linear or branched alkyl or alkylene group containing from 1 to 18 carbon atoms, a cyclic alkyl, or alkylene group containing from 3 to 18 carbon atoms, an aryl group, an aromatic heterocyclic group, a polyarylene group consisting of two or more annelated benzenoid rings and groups in which two or more aryl or arylene substituents are covalently attached, M is H or a cation which provides water-solubility or dispersibility to the peroxycarboxylic acid and r is from 1 to the total number of hydrogen atoms on R. Preferably, M is H or an alkali metal or an alkaline earth metal, with H, magnesium, sodium and potassium being the most preferred. R can be substituted with essentially any group or groups, including an alkyl group when R is aryl and an aryl group when R is alkyl, so long as they do not interfere with the function of the peroxycarboxylic acid. The preferred alkyl or alkylene group substituents are $-SO_3^-M$ and -COOM and the preferred aryl and arylene substituents are selected from halogens (fluorine, chlorine, or bromine), $-NO_2$, $-OCH_3$ and -COOM wherein M is as defined above. Suitable aromatic heterocyclic groups include furan, thiophene and pyridine. Examples of polyarylene groups consisting of two or more annelated benzenoid rings are the napthyl, phenanthryl and anthracenyl moieties.

The more preferred peroxycarboxylic acids and salts thereof have the general formula:



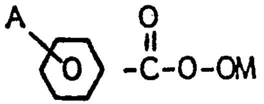
or



$$T\left[-\overset{O}{\overset{\|}{C}}-O-O-M\right]_r$$

wherein A is a halogen (fluorine or chlorine) or $-NO_2$, M is as defined above, T is an alkyl group containing from 5 to 18 carbon atoms and r is one or two.

The most preferred peroxycarboxylic acids and salts thereof have the general formula:



wherein A is a halogen (chlorine or fluorine), preferably Cl, and M is H or magnesium. Surprisingly, when halogen substituted peroxybenzoic acids or salts thereof are utilized within the compositions of the invention, solution bleaching and, especially, surface bleaching performance are exceptional.

Formation of the Peroxycarboxylic Acid In Situ by Utilizing Specific Peroxygen Bleaches and Bleach Activators

As an alternative to directly adding the peroxycarboxylic acid to the bleaching solution, the peroxycarboxylic acid can be formed in situ from its precursors. For example, a two component peroxycarboxylic acid source consisting of a peroxygen bleach capable of yielding hydrogen peroxide in an aqueous solution and a bleach activator that contains a carbonyl carbon that can potentially react with the hydrogen peroxide to form a peroxycarboxylic acid can be utilized. The use of this system within the compositions of the invention provides essentially the same level of effectiveness and efficiency of solution bleaching and/or surface bleaching performance as is obtained by directly utilizing a peroxycarboxylic acid within the compositions of the invention.

An additional advantage of such two component peroxycarboxylic acid source with respect to bleaching compositions consisting solely of such two components is based upon pH. As discussed above, for bleaching compositions that consist solely of such peroxygen bleach and bleach activator, it is believed that the pH of the bleaching solution must be adjusted to be similar to the pK_a of the peroxycarboxylic acid formed in order to maximize the formation of the reactive dimer. However, the pH of the bleaching solution must also be adjusted to ensure that the hydrogen peroxide, yielded by the peroxygen bleach, is to an appreciable extent in the perhydroxide anion form. This maximizes the rate of formation of the peroxycarboxylic acid. Therefore, since there are two pH dependent chemical reactions that must take place, neither one can be maximized. However, when utilizing the two component peroxycarboxylic acid source within the compositions of the invention the pH of the bleaching solution need not be similar to the pK_a of the peroxycarboxylic acid. Therefore, one can adjust the pH of the bleaching solution to maximize the formation of the perhydroxide anion and, thus, maximize the formation of the peroxycarboxylic acid.

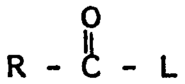
The Peroxygen Bleach

The peroxygen bleaches useful herein are those capable of yielding hydrogen peroxide in an aqueous solution. These bleaches are well known in the art and include hydrogen peroxide and the alkali metal peroxides, organic peroxide bleaching compounds such as urea peroxide, and inorganic persalt bleaches, such as the alkali metal perborates, percarbonates, perphosphates, and the like. Mixtures of two or more such bleaches can also be used, if desired.

Preferred peroxygen bleaches include sodium perborate, commercially available in the form of mono- and tetra-hydrates, sodium carbonate peroxyhydrate, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Particularly preferred are sodium perborate monohydrate and sodium perborate tetrahydrate and mixtures thereof.

The Bleach Activator

The bleach activators that can be utilized for such a purpose are ones capable of generating peroxycarboxylic acids and have the general formula:



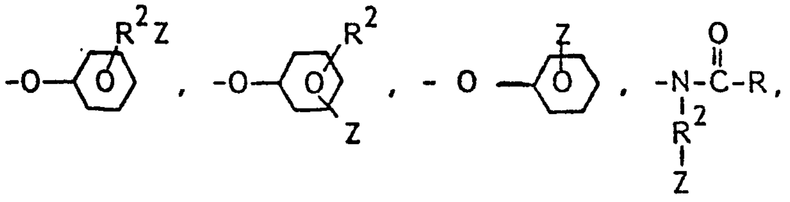
$$R - \overset{O}{\overset{\|}{C}} - L$$

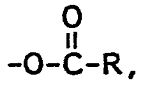
wherein R is as defined above and L is a leaving group, wherein the conjugate acid of the anion formed on L has a pK_a in the range of from 4 to 13.

L can be essentially any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydroxide anion. This, as discussed hereinabove, is the perhydrolysis reaction. Leaving groups that exhibit such behavior are those in which their conjugate acid has a pK_a in the range of from 4 to 13, preferably from 7 to 11 and most preferably from 8 to 11.

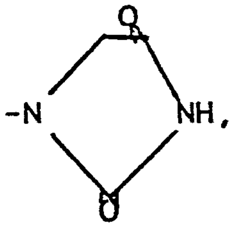
It should be noted that, as an option, R or L can be a group that contains an aromatic sulfonyl halide. Such a system can be utilized in combination with a peroxygen bleach capable of yielding hydrogen peroxide in an aqueous solution and provides the desired level of solution bleaching and/or surface bleaching performance.

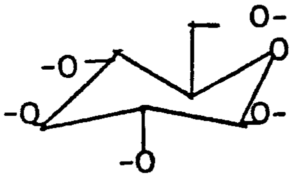
Preferred bleach activators are those of the above general formula wherein R is as defined above and L is selected from

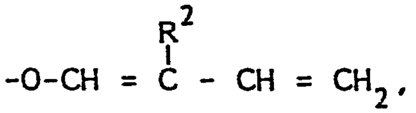




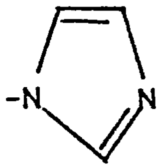
$-O-\overset{\overset{\displaystyle O}{\|}}{C}-R,$

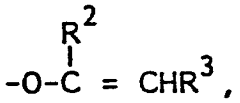






$-O-CH=\overset{\overset{\displaystyle R^2}{|}}{C}-CH=CH_2,$





$-O-\overset{\overset{\displaystyle R^2}{|}}{C}=CHR^3,$

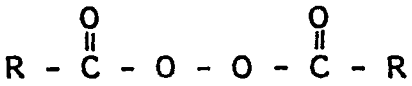
wherein R is as defined above, R^2 is an alkyl chain containing from about 1 to about 8 carbon atoms, R^3 is H or R^2, and Z is H or a solubilizing group. The preferred solubilizing groups are $-SO_3^-M^+$, $-COO^-M^+$, $-SO_4^-M^+$, $(-N^+R_3^4)X^-$ and $O{\leftarrow}NR_2^4$ and most preferably $-SO_3^-M^+$ and $-COO^-M^+$ wherein R^4 is an alkyl chain containing from about 1 to about 4 carbon atoms, M is as defined above and X is an anion which provides solubility to the bleach activator. Preferably, X is a halide (fluorine, chlorine or bromine), hydroxide, methylsulfate or acetate anion. It should be noted that bleach activators with a leaving group that does not contain a solubilizing group should be well dispersed in the bleaching solution in order to assist in their dissolution.

The molar ratio of hydrogen peroxide yielded by the peroxygen bleach to such peroxycarboxylic acid generating bleach activator is from 20 to 0.1, preferably from 3 to 1 and most preferably from 2 to 1. However, it should be noted that the preferred ratio is found to vary considerably if the initial pH of the bleaching solution is below 9. Under such conditions a higher molar ratio of hydrogen peroxide yielded by the peroxygen bleach to peroxycarboxylic acid generating bleach activator is desirable. Preferably, such molar ratio is from 4 to 20.

Formation of The Peroxycarboxylic Acid *In Situ* Utilizing an Organic Peroxide Compound

Another precursor that can be utilized to form the peroxycarboxylic acid *in situ* is an organic peroxide compound. It is believed that such a compound undergoes hydrolysis in the bleaching solution to form the peroxycarboxylic acid. This system is not preferred because the peroxycarboxylic acid formation is often slow and, therefore, it is theorized that during this time some of the aromatic sulfonyl halide bleach activator undergoes hydrolysis to form an inactive sulfonic acid.

The organic peroxide compounds have the general formula:



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-\overset{\overset{\displaystyle O}{\|}}{C}-R$$

wherein each R is as defined above.

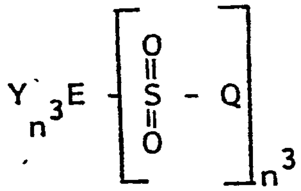
As an option, a peroxygen bleach, such as those described above, can also be added to the bleaching solution with the organic peroxide compound. This results in the potential formation of two moles of peroxycarboxylic acid per mole of organic peroxide and, therefore, only half of the level of organic peroxide is required as would otherwise be necessary without such peroxygen bleach. The molar ratio of such organic peroxide compounds to such peroxygen bleach is from 0.1 to 10, preferably from 0.25 to 4 and most preferably from 1 to 0.3.

The level of peroxycarboxylic acid within compositions of the invention is from 0.1% to 80%, preferably from 5% to 60% and most preferably from 30% to 60%. It should be noted that when a two component peroxycarboxylic acid source is utilized, e.g., a peroxygen bleach capable of yielding hydrogen peroxide in an aqueous solution plus a peroxycarboxylic acid generating bleach activator or such peroxygen bleach plus an organic peroxide compound, the level of each component should be such that it can theoretically produce the levels of peroxycarboxylic acid within the compositions of the invention. When the bleaching compositions within the invention are also detergent compositions it is preferred that the level of peroxycarboxylic acid is from 0.1% to 10% and more preferably from 1% to 3%.

THE AROMATIC SULFONYL HALIDE

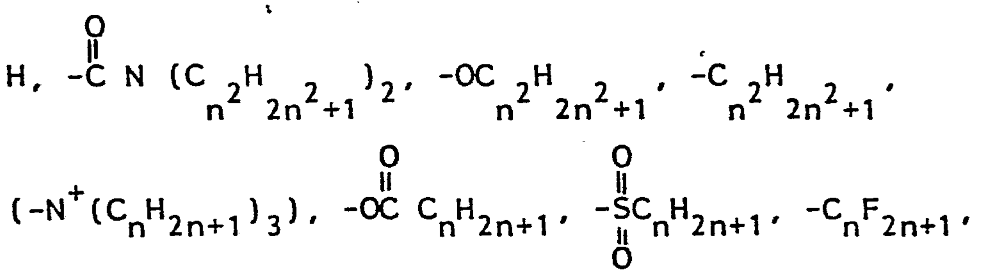
Essentially any aromatic sulfonyl halide bleach activator is suitable for use herein. The aromatic group can contain one or more substituents so long as they do not interfere with the function of the bleach activator.

The preferred aromatic sulfonyl halide bleach activators within the compositions of the invention have the general formula:



$$Y_{n^3}E\left[\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - Q\right]_{n^3}$$

wherein each Y is selected from



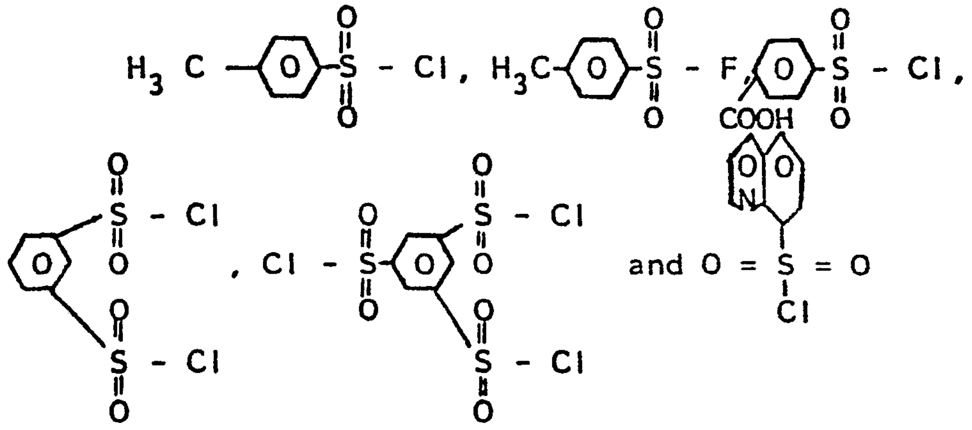
$$H,\ -\overset{\overset{O}{\|}}{C}\,N\,(C_{n^2}H_{2n^2+1})_2,\ -OC_{n^2}H_{2n^2+1},\ -C_{n^2}H_{2n^2+1},$$

$$(-N^+(C_nH_{2n+1})_3),\ -O\overset{\overset{O}{\|}}{C}\,C_nH_{2n+1},\ -\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}C_nH_{2n+1},\ -C_nF_{2n+1},$$

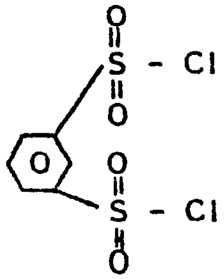
halogens and any group which provides an anionic moiety in aqueous solution wherein each n is from 0 to 12 and each n^2 is from 0 to 18, E is selected from the group consisting of an aryl arylene group, an aromatic heterocyclic group.

two or more annelated benzenoid rings and groups in which two or more aryl arylene substituents are covalently attached, Q is a halogen (fluorine, chlorine, or bromine) preferably chlorine, and each n^3 is from 1 to 3. Suitable aromatic heterocyclic groups include furan, thiophene, quinoline and pyridine. Examples of polyarylene groups consisting of two or more annelated groups are the napthyl, phenanthryl and anthracenyl moieties.

The preferred aromatic sulfonyl halide bleach activators are selected from



The most preferred aromatic sulfonyl halide bleach activator has the formula:



The level of aromatic sulfonyl halide within the compositions of the invention is from .1% to 70%, preferably from 5% to 70% and most preferably from 40% to 70%. When the bleaching compositions within the invention are also detergent compositions it is preferred that the level of aromatic sulfonyl halide is from 0.1% to 10% and more preferably from 1% to 3%.

OPTIONAL COMPONENTS

As a preferred embodiment, the bleaching compositions of the invention can be detergent compositions. Thus, the bleaching compositions can contain typical detergent composition components such as detergency surfactants and detergency builders. In such preferred embodiments the bleaching compositions are particularly effective. The bleaching compositions of this invention can contain all of the usual components of detergent compositions including the ingredients set forth in U.S. Patent 3,936,537, Baskerville et al. Such components include color speckles, suds boosters, suds suppressors, antitarnish and/or anticorrosion agents, soil-suspending agents, soil-release agents, dyes, fillers, optical brighteners, germicides, alkalinity sources, hydrotropes, antioxidants, enzymes, enzyme stabilizing agents, perfumes, etc.

The detergent surfactants can be any one or more surface active agents selected from anionic, nonionic, zwitterionic, amphoteric and cationic classes and compatible mixtures thereof. Detergent surfactants useful herein are listed in U.S. Patent 3,664,961, Norris, issued May 23, 1972, and in U.S. Patent 3,919,678, Laughlin et al, issued December 30, 1975. Useful cationic surfactants also include those described in U.S. Patent 4,222,905, Cockrell, issued September 16, 1980, and in U.S. Patent 4,239,659, Murphy, issued December 16, 1980. The following are representative examples of detergent surfactants useful in the present compositions.

Water-soluble salts of the higher fatty acids, i.e., "soaps", are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylammonium salts of higher fatty acids containing from 8 to 24 carbon atoms, and preferably from 12 to 18 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 soap.

Useful anionic surfactants also include the water-soluble salts, preferably the alkali metal, ammonium and alkylammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from 10 to 20 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 are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8-C_{18} carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkylbenzene 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. Patents 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as C_{11-13}LAS.

Other anionic surfactants herein are 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; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates containing from 1 to 10 units of ethylene oxide per molecule and wherein the alkyl groups contain from 8 to 12 carbon atoms; and sodium or potassium salts of alkyl ethylene oxide ether sulfates containing 1 to 10 units of ethylene oxide per molecule and wherein the alkyl group contains from 10 to 20 carbon atoms.

Other useful anionic surfactants herein include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from 6 to 20 carbon atoms in the fatty acid group and from 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxyalkane-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; water-soluble salts of olefin and paraffin sulfonates containing from 12 to 20 carbon atoms; and beta-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.

Water-soluble nonionic surfactants are also useful in the compositions of the invention. Such nonionic materials include compounds produced by the condensation of alkyl or alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature.

The length of the polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Suitable nonionic surfactants include the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from 6 to 15 carbon atoms, in either a straight chain or branched chain configuration, with from 3 to 12 moles of ethylene oxide per mole of alkyl phenol.

Preferred nonionics are the water-soluble and water-dispersible condensation products of aliphatic alcohols containing from 8 to 22 carbon atoms, in either straight chain or branched configuration, with from 2 to 12 moles of ethylene oxide per mole of alcohol. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 9 to 15 carbon atoms with from 4 to 8 moles of ethylene oxide per mole of alcohol.

Semi-polar nonionic surfactants include water-soluble amine oxides containing one alkyl moiety of from 10 to 18 carbon atoms and two moieties selected from the group of alkyl and hydroxyalkyl moieties of from 1 to 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of 10 to 18 carbon atoms and two 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 18 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 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 one of the aliphatic substituents contains from 8 to 18 carbon atoms.

The level of detergent surfactant that can be employed is from 0% to about 50%, preferably from 1% to 30% and most preferably from 10% to 25% by weight of the total composition.

In addition to detergent surfactants, detergency builders can be employed in the bleaching compositions. Water-soluble inorganic or organic electrolytes are suitable builders. The builder can also be water-insoluble calcium ion exchange materials; non-limiting examples of suitable water-soluble, inorganic detergent builders include: alkali metal carbonates, borates, phosphates, bicarbonates and silicates. Specific examples of such salts include sodium and potassium tetraborates, bicarbonates, carbonates, orthophosphates, pyrophosphates, tripolyphosphates and metaphosphates.

Examples of suitable organic alkaline detergency builders include: (1) water-soluble amino carboxylates and aminopolyacetates, for example, nitrilotriacetates, glycinates, ethylenediamine tetraacetates, N-(2-hydroxyethyl)nitrilo diacetates and diethylenetriamine pentaacetates; (2) water-soluble salts of phytic acid, for example, sodium and potassium phytates; (3) water-soluble polyphosphonates, including sodium, potassium, and lithium salts of ethane-1-hydroxy-1, 1-diphosphonic acid; sodium, potassium, and lithium salts of ethylene diphosphonic acid; and the like; (4) water-soluble polycarboxylates such as the salts of lactic acid, succinic acid, malonic acid, maleic acid, citric acid, carboxymethyloxysuccinic acid, 2-oxa-1,1,3-propane tricarboxylic acid, 1,1,2,2-ethane tetracarboxylic acid, mellitic acid and pyromellitic acid; (5) water-soluble polyacetals as disclosed in U.S. Patents 4,144,266 and 4,246,495 and (6) water-soluble polyacrylates.

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 preferably in combination with a crystallization seed which is capable of providing growth sites for said reaction product. Such "seeded builder" compositions are fully disclosed in British Patent Specification No. 1,424,406.

A further class of detergency builder materials useful in the present invention are insoluble sodium aluminosilicates, particularly those described in U.S. Patent 4,303,556 issued December 1, 1981. This patent discloses and claims detergent compositions containing sodium aluminosilicates having the formula:

$$Na_z(AlO_2)_z(SiO_2)_yXH_2O$$

wherein z and y are integers equal to at least 6, the molar ratio of z to y is in the range of from 1.0:1 to 0.5:1, and X is an integer from 15 to 264, said aluminosilicates having a calcium ion exchange capacity of at least 200 milligrams equivalent/gram and a calcium ion exchange rate of at least 2 grains/ minute/gram. A preferred material is Zeolite A which is:

$$Na_{12}(SiO_2AlO_2)_{12}27H_2O$$

The level of detergency builder of the bleaching compositions is from 0% to about 70%, preferably from 10% to 60% and most preferably from 20% to 60%.

Buffering agents can be utilized to maintain the desired alkaline pH of the bleaching solutions. Buffering agents include, but are not limited to many of the detergency builder compounds disclosed hereinbefore. Buffering agents suitable for use herein are those well known in the detergency art.

Preferred optional ingredients include suds modifiers particularly those of suds suppressing types, exemplified by silicones, and silica-silicone mixtures. U.S. Patents 3,933,672, issued January 20, 1976 to Bartolotta et al, and 4,136,045, issued

January 23, 1979 to Gault et al, disclose silicone suds controlling agents. Particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in U.S. Patent 4,073,118, Gault et al, issued February 21, 1978. An example of such a compound is DB-544, commercially available from Dow Corning, which is a siloxane/glycol copolymer. Suds modifiers as described above are used at levels of up to approximately 2%, preferably from 0.1 to 1½% by weight of the surfactant.

Microcrystalline waxes having a melting point in the range from 35°C-115°C and a saponification value of less than 100 represent additional examples of preferred suds control components for use in the subject compositions, and are described in detail in U.S. Patent 4,056,481, Tate, issued November 1, 1977, The microcrystalline waxes are substantially water-insoluble, but are water-dispersible in the presence of organic surfactants. Preferred microcrystalline waxes have a melting point from about 65°C to 100°C, a molecular weight in the range from 400-1,000; and a penetration value of at least 6, measured at 25°C by ASTM-D1321. Suitable examples of the above waxes include: microcrystalline and oxidized microcrystalline petroleum waxes; Fischer-Tropsch and oxidized Fischer-Tropsch waxes; ozokerite; ceresin; montan wax; beeswax; candelilla; and carnauba wax.

Alkyl phosphate esters represent an additional preferred suds control agent for use herein. These preferred phosphate esters are predominantly monostearyl phosphate which, in addition thereto, can contain di- and tristearyl phosphates and monooleyl phosphate, which can contain di- and trioleyl phosphate.

Other suds control agents useful in the practice of the invention are the soap or the soap and nonionic mixtures as disclosed in U.S. Patents 2,954,347 and 2,954,348, Fluorescent or optical brighteners can be utilized within the bleaching compositions of the invention. Surprisingly, such brighteners exhibit acceptable compatibility with such compositions. Suitable anionic brighteners are disclosed in U.S. Patents 3,537,993 Coward et al (November 3, 1970) and 3,953,380 Sundby (April 27, 1976). Nonionic brighteners can also be utilized within the compositions of the invention.

The following examples are given to illustrate the parameters of and compositions within the invention. All percentages, parts and ratios are by weight unless otherwise indicated.

EXAMPLE I

The following granular detergent composition was prepared:

	%
Sodium C_{16-18} alkyl sulfate	5.5
Sodium C_{12} linear alkylbenzene sulfonate	3.5
C_{14-16} alkyl polyethoxylate$_{2.25}$	5.5
Sodium tripolyphosphate	24.4
Zeolite A	17.6
Sodium carbonate	10.5
Sodium silicate (2.0r)	1.9
Sodium sulfate	21.0
Water	8.9
Miscellaneous	1.2

Two sets of six 12.5 x 12.5cm swatches consisting of five polycotton swatches each stained with one of the following stains - chili, RAGU spaghetti sauce, mustard, ink and tea - and one denim swatch stained with grass were prepared.

A laundry load consisting of one set of the six swatches, four clean terry cloth towels and one terry cloth towel soiled with 1.5 grams of a mixture of artificial body soil and vacuum cleaner soil was placed in a mini-wash system. This laundry load was then washed with 8.5 grams of the above granular detergent composition in 5.5 liters of water. This mini-wash system with such a load and granular detergent concentration simulates a conventional automatic wash process. The wash water temperature was 37°C and the wash water contained ~136 ppm water hardness. The initial pH of the wash water was about 9.7.

After drying, each of the swatches was visually graded by comparing it to its unwashed counterpart. A grading scale of 0 to 5 was used, with 0 indicating no stain removal and 5 indicating 100% stain removal. Each swatch was graded by three graders and then the average grade for each swatch was calculated. This average was then scaled from 0 to 100, with 100 being 100% stain removal. Also, the mean for the set of swatches was calculated.

The entire procedure was repeated numerous times, but each time a different bleaching system was added to the mini-wash system one minute after the start of the wash process.

The results were as follows:

	% Stain Removal		
Bleaching System	Chili	Spaghetti	Mustard
1. None	62	60	64
2. m-chloroperoxybenzoic acid (3)[i]	60	50	63
3. p-chloroperoxybenzoic acid (3)	63	53	63
4. p-nitroperoxybenzoic acid (3)	63	57	63
5. m-chloroperoxybenzoic acid (3) + 1,3-benzene disulfonyl chloride (6)[ii]	83	83	63
6. p-chloroperoxybenzoic acid (3) + 1,3-benzenedisulfonyl chloride (6)	90	90	77
7. p-nitroperoxybenzoic acid (3) + 1,3-benzenedisulfonyl chloride (6)	77	57	67
*8. p-fluoroperoxybenzoic acid (3)	73	60	50

*

9. p-fluoroperoxybenzoic acid (3) + 1,3-benzenedisulfonyl chloride (3)	80	73	60

		% Stain Removal		
Bleaching System	Ink	Tea	Grass	Mean
1. None	61	62	58	61
2. m-chloroperoxybenzoic acid (3)[i]	60	77	67	63
3. p-chloroperoxybenzoic acid (3)	60	80	50	62
4. p-nitroperoxybenzoic acid (3)	57	83	60	64
5. m-chloroperoxybenzoic acid (3) + 1,3-benzenedisulfonyl chloride (6)[ii]	70	73	67	73
6. p-chloroperoxybenzoic acid (3) + 1,3-benzenedisulfonyl chloride (6)	73	83	57	78
7. p-nitroperoxybenzoic acid (3) + 1,3-benzene disulfonyl chloride (6)	60	87	53	67
*8. p-fluoroperoxybenzoic acid (3)	57	73	60	62
*9. p-fluoroperoxybenzoic acid (3) + 1,3-benzenedisulfonyl chloride (3)	67	67	70	70

[i] - indicates the parts per million of active oxygen available in the wash water from m-chloroperoxybenzoic acid. This same denotation is utilized in all the examples.

[ii] - indicates the potential parts per million of active oxygen in the wash water available as an acyl persulfonate.

* - The initial pH of the wash water was about 10.

Bleaching systems 5-7 and 9 which are within the compositions of the invention, provided significantly more stain removal and, therefore, surface bleaching than bleaching systems 2-4 and 8 which are outside the compositions of the invention because they did not contain an aromatic sulfonyl halide bleach activator.

The above procedure was carried out with other bleaching systems consisting only of a peroxycarboxylic acid, which are not within the compositions of the invention, and bleaching systems consisting of such peroxycarboxylic acids plus 1,3-benzenedisulfonyl chloride, which are within the compositions of the invention. The data indicate that the surface bleaching performance obtained with each peroxycarboxylic acid plus 1,3-benzenedisulfonyl chloride bleaching system was improved on some of the above stains as compared to the same bleaching system, but containing only the peroxycarboxylic acid. However, it is believed that solution bleaching performance of all the bleaching systems consisting solely of the peroxycarboxylic acid is improved by the addition of 1,3-benzenedisulfonyl chloride.

EXAMPLE II

Surface bleaching performance capabilities were determined as in EXAMPLE I with various bleaching systems. The results were as follows:

		% Stain Removal	
Bleaching System	Chili	Spaghetti	Mustard
1. None	57	63	63
2. m-chloroperoxybenzoic acid (3)	60	50	63
*3. m-chloroperoxybenzoic acid (3) + 1,3-benzenedisulfonyl chloride (3)	83	70	90
*4. m-chloroperoxybenzoic acid (3) + 1,3,5-benzenetrisulfonyl chloride (3)	73	53	90
*5. m-chloroperoxybenzoic acid (3) + p-acetaminobenzenesulfonyl chloride (3)	63	63	83

*

6. m-chloroperoxybenzoic acid (3) + p-toluenesulfonyl chloride (3)	77	60	90
*7. m-chloroperoxybenzoic acid (3) + m-chlorosulfonylbenzoic acid (3)	87	80	80
*8. m-chloroperoxybenzoic acid (3) + p-toluenesulfonyl fluoride (3)	80	70	80
9. m-chloroperoxybenzoic acid (3) + 8-quinolinesulfonyl chloride (3)	90	90	73
10. m-chloroperoxybenzoic acid (3) + d-camphorsulfonyl chloride (3)	70	53	57
11. m-chloroperoxybenzoic acid (3) + dodecanesulfonyl chloride (3)	60	50	63

		% Stain Removal		
Bleaching System	Ink	Grass	Tea	Mean
1. None	57	73	60	62
2. m-chloroperoxybenzoic acid (3)	60	77	67	63
*3. m-chloroperoxybenzoic acid (3) + 1,3-benzenedisulfonyl chloride (3)	67	77	73	77
*4. m-chloroperoxybenzoic acid (3) + 1,3,5-benzenetrisulfonyl chloride (3)	57	70	77	70
*5. m-chloroperoxybenzoic acid (3) + p-acetaminobenzenesulfonyl chloride (3)	57	63	60	65
*6. m-chloroperoxybenzoic acid (3) + p-toluenesulfonyl chloride (3)	67	73	73	73

4.	Sodium perborate (13.5) + 4-sulfophenyloctanoate, sodium salt (4.5)	67	67	57
5.	Sodium perborate (13.5) + 4-sulfophenyloctanoate, sodium salt (4.5) + 1,3 benzenedisulfonyl chloride (13.5)	87	77	63
6.	Sodium perborate (13.5) + tetracetylethylenediamine (TAED) (4.5)	67	63	57
7.	Sodium perborate (13.5) + TAED (4.5) + 1,3-benzenedisulfonyl chloride (13.5)	77	63	60
8.	Sodium perborate (13.5) + tetracetylglycoluril (TAGU) (4.5)	67	67	57
9.	Sodium perborate (13.5) + TAGU (4.5) + 1,3-benzenedisulfonyl chloride (13.5)	77	60	60

		% Stain Removal			
	Bleaching System	Ink	Tea	Grass	Mean
1.	None	61	62	58	61
2.	Sodium perborate (13.5)	60	63	60	61
3.	Sodium perborate (13.5) + 1,3-benzenedisulfonyl chloride (13.5)	60	67	60	60
4.	Sodium perborate (13.5) + 4-sulfophenyloctanoate, sodium salt (4.5)	63	77	60	65
5.	Sodium perborate (13.5) + 4-sulfophenyloctanoate, sodium salt (4.5) + 1,3 benzenedisulfonyl chloride (13.5)	77	77	73	76

6.	Sodium perborate (13.5) + tetracetylethylenediamine (TAED) (4.5)	60	70	60	63
7.	Sodium perborate (13.5) + TAED (4.5) + 1,3-benzenedisulfonyl chloride (13.5)	67	73	70	68
8.	Sodium perborate (13.5) + tetracetylglycoluril (TAGU) (4.5)	60	70	60	64
9.	Sodium perborate (13.5) + TAGU (4.5) + 1,3-benzenedisulfonyl chloride (13.5)	60	77	70	67

Bleaching systems 5, 7 and 9, which are within the compositions of the invention, generally provided significantly more surface bleaching than bleaching systems 2-4, 6 and 8, which are without the compositions of the invention. Bleaching system 2 contained neither a peroxycarboxylic acid source nor an aromatic sulfonyl halide bleach activator. Bleaching system 3 did not contain a peroxycarboxylic acid source and bleaching systems 4, 6 and 8 did not contain an aromatic sulfonyl halide bleach activator.

EXAMPLE IV

The following granular detergent composition was prepared:

	%
Sodium C_{12} linear alkylbenzene sulfonate	10.2
Sodium C_{14-15} alkyl polyethoxylate$_{2.25}$sulfate	4.4
C_{12-13} alkyl polyethoxylate$_{2.5T^*}$	2.2
Fatty acid from menhaden oil	1.1
Sodium tripolyphosphate	68.9
Protease (Anson units/gram)	0.036
Amylase (Amylase units/gram)	990
Sodium silicate (2.0r)	3.3
Water	5.5
Miscellaneous	3.5

Surface bleaching performance was determined as in Example I, but with 3.8 grams of the above granular detergent composition and various bleaching systems. Also, the initial pH of the wash water after addition of the bleach system was about 8.1. The results were as follows:

	% Stain Removal		
Bleaching System	Chili	Spaghetti	Mustard
1. None	53	53	47
2. m-chloroperoxybenzoic acid (2)	53	60	43
3. m-chlorobenzoic acid (2) + 1,3-benzenedisulfonyl chloride (2)	83	87	43

	% Stain Removal			
Bleaching System	Ink	Tea	Grass	Mean
1. None	50	53	57	53
2. m-chloroperoxybenzoic acid (2)	60	90	63	63
3. m-chlorobenzoic acid (2) + 1,3-benzenedisulfonyl chloride (2)	67	89	63	74

Bleaching system 3, which is within the compositions of the invention, provided significantly more surface bleaching than bleaching composition 2, which is without the compositions of the invention because it did not contain an aromatic sulfonyl halide bleach activator. Also, it should be noted that since the pK_a of m-chloroperoxybenzoic acid is 7.57, the pH of the wash water was optimum for bleaching performance of the m-chloroperoxybenzoic acid alone.

EXAMPLE V

7.00 milliliters of a one molar solution of methylene blue dye in methanol was added to a beaker containing 1.00 liter of distilled water. 5.1 grams of sodium carbonate and 1.3 grams of boric acid was added to the beaker which resulted in the pH of the solution being about 10.00. The temperature of the solution was maintained at 37°C.

A quantity of m-chloroperoxybenzoic acid was added to the solution to give a 1.25 x 10^{-4} molar concentration. After 20 minutes, the percent transmittance (T) was measured with a Brinkman Colorimeter Model PC700 equipped with a 440 nm filter. This measurement indicates the amount of methylene blue dye that is destroyed in the solution; a higher change in percent T indicates a larger amount of dye that is destroyed. Immediately after this measurement a quantity of 1,3-benzenedisulfonyl chloride was added to the solution to give a 6.25 x 10^{-5} molar concentration, which is an equivalent amount to the m-chloroperoxybenzoic acid. The percent T was measured after 30 seconds. This entire procedure was repeated but benzoyl peroxide was substituted for the m-chloroperoxybenzoic acid. The results were as follows:

		Bleaching System (Minutes)	Change in % T
1.	i.	m-chloroperoxybenzoic acid (20)	1
	ii.	m-chloroperoxybenzoic acid + 1,3-benzenedisulfonyl chloride (20.5)	59
2.	i.	Benzoyl peroxide (20)	1
	ii.	Benzoyl peroxide + 1,3-benzene-disulfonyl chloride (21)	17

The addition of 1,3-benzenedisulfonyl chloride to either m-chloroperoxybenzoic acid or benzoyl peroxide, which are compositions within the invention, rapidly increases the destruction of the methylene blue dye as compared to the m-chloroperoxybenzoic acid alone, which is without the compositions of the invention. It is believed that increased methylene blue dye destruction corresponds to increased solution bleaching efficacy on soils.

EXAMPLE VI

1.5 Grams of the granular detergent composition of Example I and a quantity of m-chloroperoxybenzoic acid equivalent to 15 parts per million of available oxygen were dissolved in a tergotometer containing one liter of 37°C. water containing 120 ppm water hardness. Then six 12.5 x 12.5 cm swatches, three of which were dyed with methylene blue dye and three of which were undyed, were placed in the tergotometer. The tergotometer was agitated for 10 minutes and then the swatches were removed and dried.

ΔE for the three dyed and three undyed swatches was measured. ΔE is a measurement of the change in color of the swatch resulting from the treatment in the tergotometer. The greater the ΔE value, the greater the change in color. It is believed that a larger ΔE value for the dyed swatches represents better surface bleaching performance and a smaller ΔE value for the undyed swatches represents better solution bleaching.

The above procedure was repeated with numerous bleaching systems. The results were as follows:

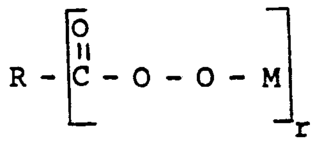
		ΔE	
	Bleaching System	Dyed	Undyed
1.	m-chloroperoxybenzoic acid (15)	3.7	5.9
2.	m-chloroperoxybenzoic acid (15) + p-toluenesulfonyl chloride (15)	12.8	1.9
3.	peroxylauric acid (5) + p-toluenesulfonyl chloride (5)	8.4	1.6
4.	Diperoxydodecanedoic acid (15) + p-toluenesulfonyl chloride (5)	8.5	1.7
5.	p-nitroperoxybenzoic acid (5) + p-toluenesulfonyl chloride (5)	8.1	1.9
6.	m-chloroperoxybenzoic acid (5)	5.3	7.2
7.	m-chloroperoxybenzoic acid (5) + p-toluenesulfonyl chloride (5)	6.9	2.4
8.	m-chloroperoxybenzoic acid (5) + methylsulfonyl chloride (5)	4.6	4.5
9.	m-chloroperoxybenzoic acid (5) + dodecanesulfonyl chloride (5)	4.0	5.8
10.	o-carboxyperoxybenzoic acid (2)	9.8	4.4
11.	o-carboxyperoxybenzoic acid (2) + p-toluenesulfonyl chloride (8)	12.0	2.4

Bleaching systems 2-5, 7 and 11, which are within the compositions of the invention, provided significantly more surface bleaching and solution bleaching than was obtained with bleaching systems 1, 6, and 8-10, which are without the compositions of the invention because they did not contain an aromatic sulfonyl halide bleach activator.

CLAIMS

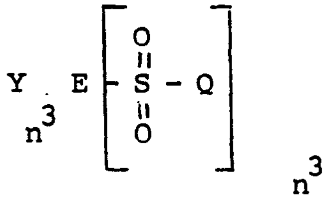
1. A bleaching composition comprising:
(a) a peroxycarboxylic acid or salt thereof; and
(b) an aromatic sulfonyl halide bleach activator;
wherein the molar ratio of each potential and actual peroxycarboxyl group of (a) to each sulfonyl group that can potentially generate acyl persulfonate is from 10 to 0.05.

2. A composition according to claim 1 wherein the peroxycarboxylic acid or salt thereof has the general formula:



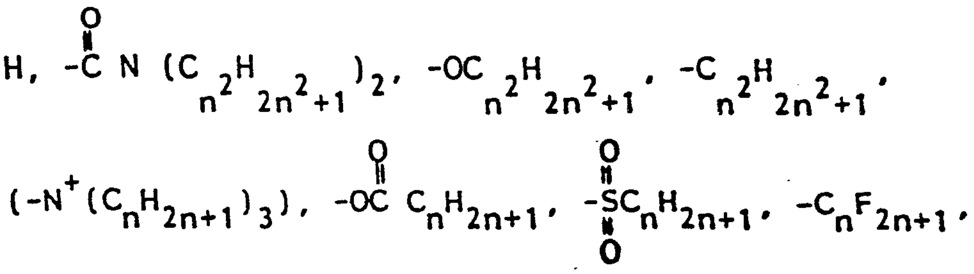
$$R-\left[\overset{O}{\overset{\|}{C}}-O-O-M\right]_r$$

wherein R is selected from H, a linear or branched alkyl or alkylene group containing from 1 to 18 carbon atoms, a cyclic alkyl or alkylene group containing from 3 to 18 carbon atoms, an aryl group, an aromatic heterocyclic group, a polyarylene group consisting of 2 or more annelated benzenoid rings and groups in which 2 or more aryl arylene substituents are covalently attached, M is H or a cation which provides water solubility or dispersibility to the peroxycarboxylic acid and r is from 1 to the total number of hydrogen atoms on R; and the aromatic sulfonyl halide bleach activator has the general formula:



$$Y_{n^3}\;E\left[-\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-Q\right]_{n^3}$$

wherein each Y is selected from

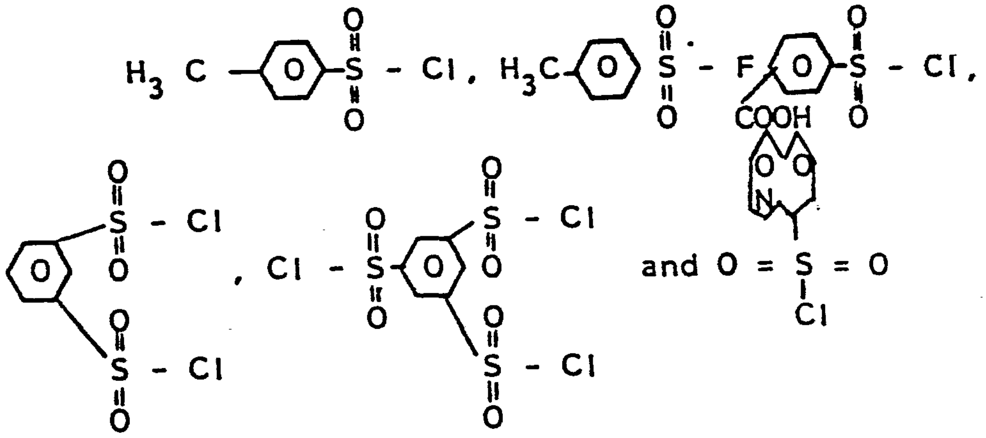


H, $-\overset{O}{\overset{\|}{C}}N(C_{n^2}H_{2n^2+1})_2$, $-OC_{n^2}H_{2n^2+1}$, $-C_{n^2}H_{2n^2+1}$,

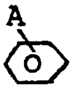
$(-N^+(C_nH_{2n+1})_3)$, $-O\overset{O}{\overset{\|}{C}}C_nH_{2n+1}$, $-\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}C_nH_{2n+1}$, $-C_nF_{2n+1}$, fluorine, chlorine, bromine and any group which provides an anionic moiety in aqueous solution wherein each n is from 0 to 12 and each n^2 is from 0 to 18, E is selected from an aryl or arylene group, an aromatic heterocyclic group, a polyarylene group consisting of two or more annelated benzenoid rings and groups in which two or more aryl arylene substituents are covalently attached, Q is chlorine, fluorine, or bromine, and each n^3 is from 1 to 3.

3. A composition according to either one of claims 2 and 3 wherein the molar ratio of each potential and actual peroxycarboxylate group of (a) to each sulfonyl group that can potentially generate acyl persulfonate is from 1 to 0.3.

4. A composition according to any one of claims 1-3 wherein the aromatic sulfonyl halide bleach activator is selected from:



5. A composition according to any one of claims 1-4 wherein the peroxycarboxylic acid or salt thereof has the general formula:



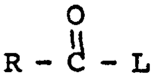
$$-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{O}-\mathrm{O}-\mathrm{M} \quad \text{or} \quad \mathrm{T}\left[-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{O}-\mathrm{O}-\mathrm{M}\right]_r$$

wherein A is fluorine, chlorine, bromine, or $-NO_2$, M is selected from H, magnesium, sodium and potassium, T is an alkyl group containing from 5 to 18 carbon atoms, r is 1 or 2 and the molar ratio of each potential and actual peroxycarboxyl group of (a) to each sulfonyl group that can potentially generate acyl persulfonate is from 1 to 0.7.

6. A bleaching composition comprising:

(a) a peroxygen bleaching compound capable of yielding hydrogen peroxide in an aqueous solution;

(b) a bleach activator having the general formula:

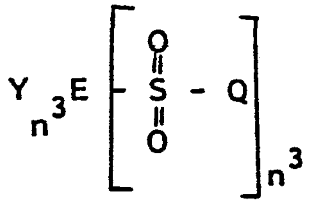


$$\mathrm{R}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{L}$$

wherein R is selected from H, a linear or branched alkyl or alkylene group containing from 1 to 18 carbon atoms, a cyclic alkyl or alkylene group containing from 3 to 18 carbon atoms, an aryl group, an aromatic heterocyclic group, a polyarylene group consisting of 2 or more annelated benzenoid rings and groups in which 2 or more aryl arylene substituents are covalently attached, and L is a leaving group, wherein the conjugate acid of the anion formed on L has a pKa in the range of from 4 to 13;

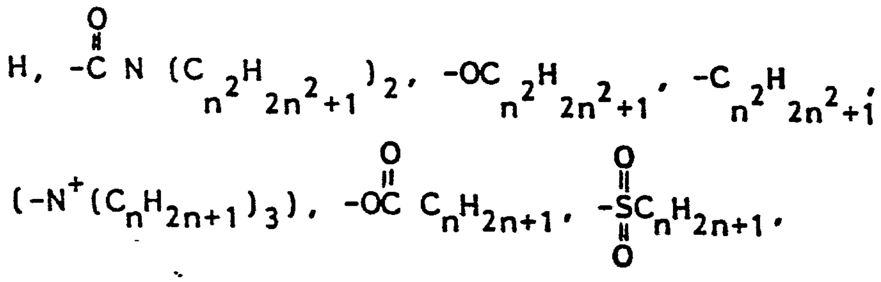
wherein the molar ratio of hydrogen peroxide yielded by (a) to (b) is from 20 to 0.1;

(c) an aromatic sulfonyl halide bleach activator having the general formula:



$$Y_{n^3}E\left[-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-Q\right]_{n^3}$$

wherein each Y is selected from:

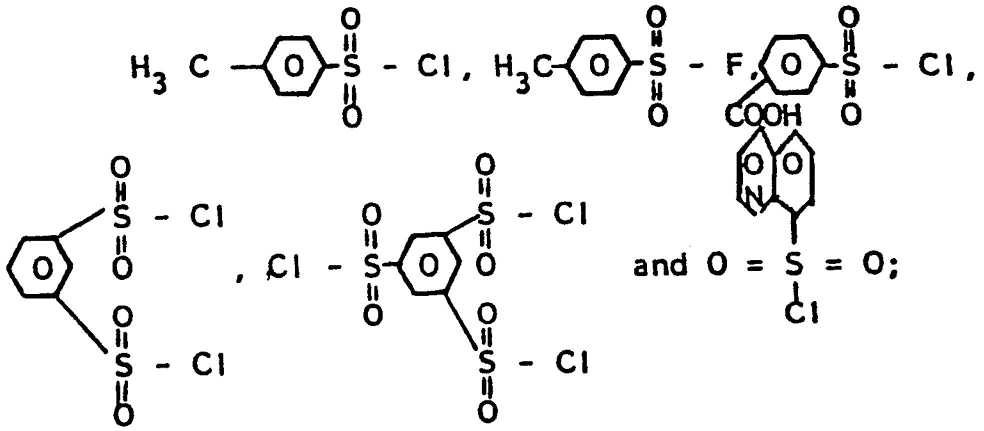


$$H,\ -\overset{\overset{O}{\|}}{C}N(C_{n^2}H_{2n^2+1})_2,\ -OC_{n^2}H_{2n^2+1},\ -C_{n^2}H_{2n^2+1},$$
$$(-N^+(C_nH_{2n+1})_3),\ -O\overset{\overset{O}{\|}}{C}C_nH_{2n+1},\ -\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}C_nH_{2n+1},$$

$-C_nF_{2n+1}$, fluorine, chlorine, or bromine and any group which provides an anionic moiety in aqueous solution wherein each n is from 0 to 12 and each n^2 is from 0 to 18, E is selected from an aryl or arylene group, an aromatic heterocyclic group, a polyarylene group consisting of two or more annelated benzenoid rings and groups in which two or more aryl or arylene substituents are covalently attached, Q is fluorine, chlorine, or bromine, and each n^3 is from 1 to 3;

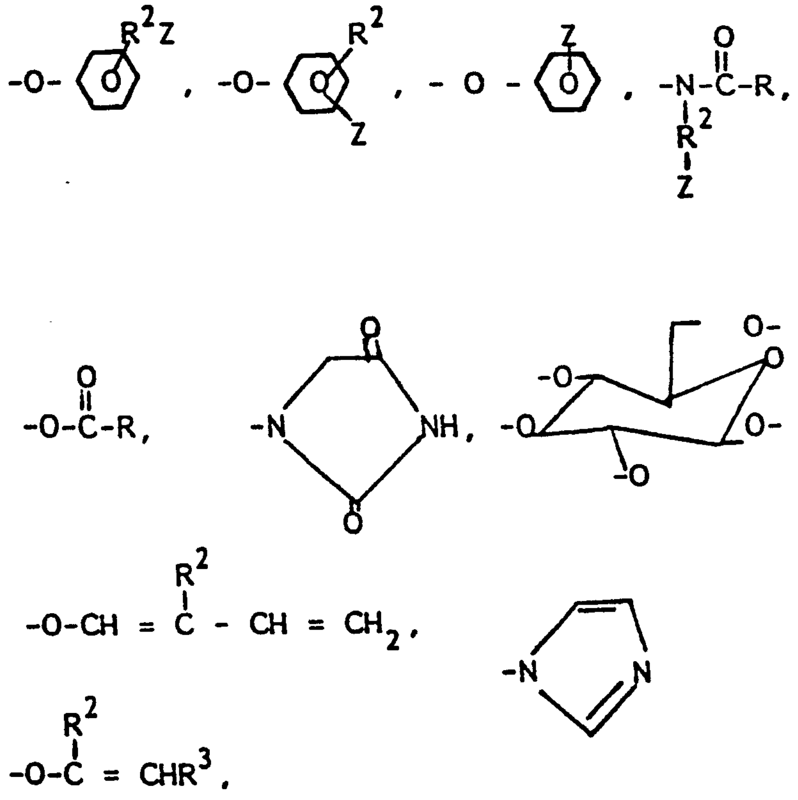
wherein the molar ratio of each potential peroxycarboxyl group formed by (a) + (b) to each sulfonyl group that can potentially generate an acyl persulfonate is from 10 to 0.05.

7. A composition according to claim 6 wherein (a) is selected from from sodium perborate monohydrate, sodium perborate tetrahydrate sodium carbonate peroxyhydrate, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, sodium peroxide and mixtures thereof; L is a leaving group, wherein the conjugate acid of the anion formed on L has a pKa in the range of from 8 to 11; (c) is selected from:



the molar ratio of hydrogen peroxide yielded by (a) to (b) is from 3 to 1 and the molar ratio of each potential peroxycarboxyl group formed by (a) + (b) to each sulfonyl group that can potentially generate acyl persulfonate is from 1 to 0.3.

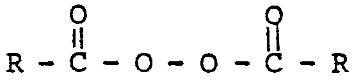
8. A composition of claim 9 wherein according to either one of claims 6 & 7; L is selected from:



wherein R is as defined above, R^2 is an alkyl chain containing from 1 to 8 carbon atoms, R^3 is H or R^2, and Z is H or a solubilizing group, and the molar ratio of each potential peroxycarboxyl group formed by (a) + (b) to each sulfonyl group that can potentially generate an acyl persulfonate is from 1 to 0.7.

9. A bleaching composition comprising:

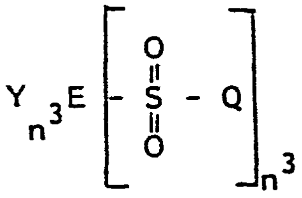
(a) an organic peroxide compound having the general formula:



$$R-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-R$$

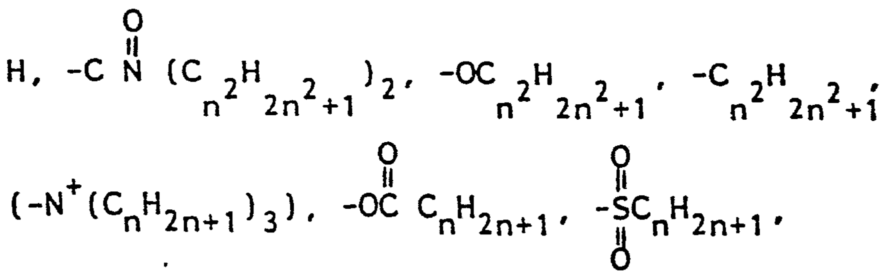
wherein each R is selected from H, a linear or branched alkyl or alkylene group containing from 1 to 18 carbon atoms, a cyclic alkyl or alkylene group containing from 3 to 18 carbon atoms, an aryl group, an aromatic heterocyclic group, a polyarylene group consisting of 2 or more annelated benzenoid rings and groups in which 2 or more aryl or arylene substituents are covalently attached; and

(b) an aromatic sulfonyl halide bleach activator having the general formula:



$$Y_{n^3}E\left[-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-Q\right]_{n^3}$$

wherein each Y is selected from:



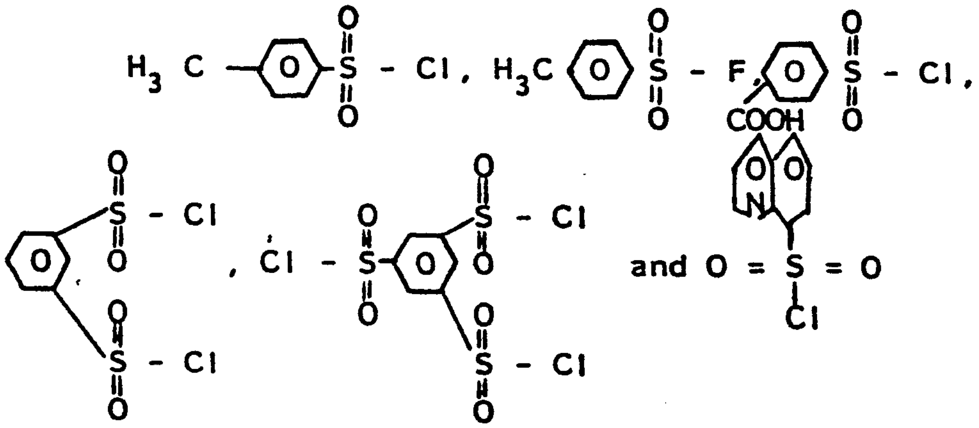
$$H,\ -C\overset{O}{\overset{\|}{N}}(C_{n^2}H_{2n^2+1})_2,\ -OC_{n^2}H_{2n^2+1},\ -C_{n^2}H_{2n^2+1},$$

$$(-N^+(C_nH_{2n+1})_3),\ -\overset{O}{\overset{\|}{OC}}\ C_nH_{2n+1},\ -\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}C_nH_{2n+1},$$

$-C_nF_{2n+1}$, fluorine, chlorine, or bromine and any group which provides an anionic moiety in aqueous solution wherein each n is from 0 to 12 and each n^2 is from 0 to 18, E is selected from an aryl arylene group, an aromatic heterocyclic group, a polyarylene group consisting of two or more annelated benzenoid rings and groups in which two or more aryl or arylene substituents are covalently attached, Q is a halogen and each n^3 is from 1 to 3;

wherein the molar ratio of each potential carboxyl group formed by (a) to each sulfonyl group that can potentially generate acyl persulfonate is from 10 to 0.05.

10. A composition according to claim 9 wherein the aromatic sulfonyl halide bleach activator is selected from



and the molar ratio of each potential peroxycarboxyl group formed by (a) to each sulfonyl group that can potentially generate acyl persulfonate is from 1 to 0.3, preferably from 1 to 0.7.

11. A composition according to either one of claims 9 & 10 further comprising a peroxygen bleaching compound capable of yuielding hydrogen peroxide in an aqueous solution wherein the molar ratio of (a) to said peroxygen bleaching compound is from 0.1 to 10.

0105690

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 83 30 5726

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
D,A	US-A-4 292 191 (F.W. GRAY) * Abstract; claims 1, 10 * ---		C 11 D 3/39 D 06 L 3/02
D,A	US-A-4 107 065 (F.W. GRAY) * Abstract; claims 1, 4 * ---		
A	DE-A-2 737 865 (PROCTER & GAMBLE CO.) * Claims 1, 6 * -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl. ³)
			C 11 D 3/00 D 06 L 3/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	07-12-1983	SCHULTZE D

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document
T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document