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3,245,913

BLEACHING COMPOSITIONS CONTAINING ACYL SULFONAMIDES

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The present application is a continuation-in-part of patent application Serial No. 181,449, filed March 21, 1962, now abandoned.

The present invention relates to novel compositions containing oxygen releasing compounds, and more particularly relates to washing compositions, containing bleaching agents with or without detergent agents. The present invention further relates to improved bleaching and/or laundering compositions containing oxygen releasing agents, which compositions may be used for bleaching and/or laundering operations, or for removing stains from textile materials.

Detergent compositions containing an oxygen releasing compound, for example, an inorganic per salt such as an alkali metal perborate, or percarbonate or peroxide such as urea peroxide, have been disclosed heretofore as useful for bleaching and sanitizing purposes. Although such compositions provide a satisfactory bleaching action when they are used in water which is at or near the boiling point (e.g., 95° C.-100° C.), the bleaching activity is unsatisfactory when the water is at lower temperatures, that is temperatures below 75° C. Detergent and/or sanitizing compositions containing oxygen releasing compounds thus have the disadvantages of being unsatisfactory for many uses such as the washing and/or bleaching of textiles and fabrics which cannot withstand higher temperatures, that is temperatures above about 70° C. Compositions containing these oxygen releasing compounds are also unsatisfactory in that they cannot be efficiently employed in modern automatic washing machines and laundering devices utilizing water at relatively low temperatures such as 50° C. to 70° C.

Such disadvantages have been recognized and the prior art indicates that attempts have been made to formulate compositions containing oxygen-releasing compounds such as per salts and peroxides with the goal of providing more effective bleaching and sanitizing activity at temperatures as low as 50° C., usually between 50° C. and 75° C.

As examples of prior art compositions are the following: U.S. Patent 2,898,181, issued August 4, 1959, discloses certain carboxylic acid amides such as acetamide and acrylamide in washing compositions containing inorganic per salts and surfactants to promote or accelerate the release of oxygen from the inorganic per salt; U.S. Patent 2,955,905, issued October 11, 1960, discloses the addition of esters such as the benzoyl ester of alkali metal phenol sulfonates and glucose penta acetate as oxygen releasing promoters to washing compositions containing inorganic per salts; German Patent 1,018,181, published July 8, 1955, discloses the addition of certain compounds such as malo-nitrile or ethylene dicyanide in compositions containing inorganic per salts; and German Patent 1,038,693, published November 22, 1956, discloses certain carboxylic anhydrides such as benzoic anhydride and phthalic anhydride in compositions containing sodium perborate to promote or accelerate the release of oxygen therefrom.

However, compositions containing the promoter compounds of the above-mentioned patents have certain disadvantages in that they either do not bleach efficiently in water at temperatures of between 50° C. or 75° C. or tend to render such compositions unstable, that is, cause

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a loss of available oxygen from the inorganic per salts, when the compositions are stored under normal storage conditions for periods of from one week to several months. Compositions which have lost available oxygen are usually inefficient or ineffective for bleaching and washing purposes.

It has presently been found, however, that compositions containing oxygen-releasing compounds and certain hereinafter defined sulfonamides will effectively bleach and whiten textiles and fabrics in water at temperatures as low as 40° C. when used under standard laundering conditions. Additionally compositions containing these sulfonamides are stable for prolonged periods of time under ordinary storage conditions.

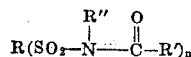
Accordingly, it is one object of the present invention to provide novel compositions containing oxygen releasing compounds.

It is another object of the present invention to provide stable bleaching compositions containing an oxygen releasing agent.

It is a further object of this invention to provide stable bleaching and detergent compositions containing an oxygen releasing compound, which compositions are capable, when employed in water at temperatures as low as 50° C., of good bleaching activity and oxygen releasing properties.

Still further objects and advantages of this invention are disclosed in or will become apparent from the following description and the appended claims.

The present invention provides a composition comprising a mixture of an oxygen releasing compound, for example, sodium perborate, and an acyl sulfonamide, particularly a compound having the general formula:



wherein R and R' are organic radicals and R'' is an organic radical and n is an integer of from 1 to 3. Generally, these compositions can be readily formulated as bleaching and sanitizing agents which are effective under a wide variety of conditions, when used with water at temperatures of from about 50° C. to 100° C. The preferred compositions are generally stable with respect to loss of available oxygen when stored under ordinary storage conditions for prolonged periods of time, that is, for periods of six-months and longer.

In the formula referred to above n is preferably 1 and the organic radicals may be any of a wide variety of substituted or unsubstituted aliphatic or aromatic radicals. Thus, in the above general formula R, R', and R'' may be like or dissimilar aliphatic or aromatic radicals and may be any combination of a wide variety of substituted and unsubstituted aliphatic or aromatic radicals.

The aliphatic radicals preferably contain from 1 to 10 carbon atoms in the aliphatic group. Although such radicals may contain more than 10 carbon atoms, compounds containing them often have limited solubility. Thus, the unsubstituted aliphatic hydrocarbon radicals in the above structure may include, for example, alkyl radicals having a straight or branched chain, e.g., methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl, n-amyl, isoamyl, n-hexyl, isohexyl, n-heptyl, isoheptyl, n-octyl, iso-octyl, 2-ethyl-hexyl groups or radicals.

The substituents of substituted aliphatic radicals may be halogen atoms, sulfo, nitro, carboxy, methoxy-, carbethoxy-, amino, ethyl, carboxyl groups or radicals to provide the aforementioned substituted aliphatic radicals. The unsubstituted aromatic radicals may be phenyl, pyridyl, benzyl, alpha- and beta-naphthyl, quinolyl, anthryl, phenanthryl, benzquinolyl and the like. The substituents of substituted aromatic radicals include halo-,

nitro-, sulfo-, and alkyl substituted groups or radicals and the alkyl substituted aromatic radicals may contain from 1 to 20 carbon atoms in the alkyl group.

Illustrative examples of some specific acyl sulfonamide compounds falling within the scope of the above formula and which may be used in the compositions of this invention are:

N - phenyl, N - benzoyl - p - toluenesulfonamide,
 N - methyl, N - acetyl - methanesulfonamide,
 N - phenyl, N - acetyl - benzenesulfonamide,
 N - methyl, N - acetyl - p - toluenesulfonamide,
 N - phenyl, N - acetyl - methanesulfonamide,
 N - methyl, N - acetyl - p - nitrobenzenesulfonamide,
 N - methyl, N - benzoyl - p - toluenesulfonamide,
 N - methyl, N - benzoyl - benzenesulfonamide,
 N - methyl, N - benzoyl - methanesulfonamide,
 N - ethyl, N - acetyl - o - toluenesulfonamide,
 N - n - propyl, N - benzoyl - 2 - butenylsulfonamide,
 N - phenyl, N - (p - cyanobenzoyl) - 8 - quinolinesulfonamide,
 N - hydroxymethyl, N - benzoyl - 5 - hydroxy - 4 - pyrimidinesulfonamide,
 N - isopropyl, N - chloroacetyl - m - xylene - 2 - sulfonamide,
 N - ethyl, N - beta - phenylacetyl - p - trimethylammonium - benzenesulfonamide,
 N - methyl, N - hydrocinnamoyl - p - sulfobenzenesulfonamide,
 N - hydroxyethyl, N - benzoyl - 2,4 - dinitrobenzenesulfonamide,
 N - 4 - hydroxycyclohexyl, N - trichloroacetyl - alpha - naphthylsulfonamide,
 N - (beta - carboxymethyl), N - (benzoyl) - O - toluenesulfonamide,
 N - (4 - pyridyl), N - propionylethanesulfonamide,
 N - formyl, N - (p - bromobenzoyl) - cyclohexanesulfonamide,
 N - methyl, N - benzoyl - 3,5 - disulfobenzenesulfonamide disodium salt,
 N - carbethoxymethyl, N - (alpha - naphthoyl) - p - toluenesulfonamide,
 N - methyl, N - (p - nitrobenzoyl) - 4 - carboxybenzenesulfonamide, sodium salt,
 N - acetyl - p - hydroxymethylbenzenesulfonamide,
 N - phenyl, N - butyrylvinylnsulfonamide,
 N - N' - diphenyl - N, N' - dibenzoyl - butane - 1,4 - disulfonamide,
 N - methyl, N - benzoyl - p - nitrobenzenesulfonamide,
 N - nitroethyl, N - acetyl - o - bromobenzenesulfonamide.

A particularly suitable group of acyl sulfonamides of the above formula are those wherein R is a substituted aromatic radical, preferably an alkyl phenyl, a paratolyl or a paranitrophenyl radical, R' is an unsubstituted aromatic radical, preferably a phenyl radical and R'' is an aliphatic hydrocarbon radical having from 1 to 10 carbon atoms, preferably from 1 to 4 carbon atoms, more preferably a methyl or an ethyl radical.

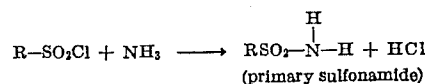
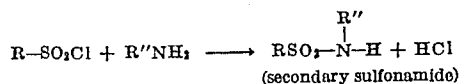
Preferred compounds falling within this group are:

N - methyl, N - benzoyl - dodecylbenzenesulfonamide;
 N - methyl, N - benzoyl - paratoluenesulfonamide;
 N - ethyl, N - benzoyl - paratoluenesulfonamide; and
 N - methyl, N - benzoyl - para - nitrobenzenesulfonamide.

The acyl sulfonamides suitable for inclusion in the compositions of this invention may be prepared by several well-known methods, such as for example the methods in General Chemistry of USSR, pages 2706-2708, 1957 (C. B. translation).

A particularly advantageous method for preparing the acyl sulfonamides comprises a two-step reaction, the first step of which comprising reacting one mol of a sulfonyl chloride having the formula $R-SO_2Cl$ wherein R is an organic radical as hereinbefore described with at least one mol of ammonia or an amine having the formula $R''NH_2$, where R'' is an organic radical, as hereinbefore described,

to form the acyl sulfonamides. The following equations exemplify these reactions:



The reactions are usually exothermic and are carried out in a liquid alkaline medium for example in an organic medium such as pyridine or in an inorganic liquid medium such as a 2% to 20% by weight aqueous solution of a water soluble alkaline metal salt. The exotherm may be controlled by standard procedures, such as by cooling, using well-known cooling techniques or by the controlled addition of the reactants. The acyl sulfonamides may then be readily obtained by the second step which comprises acylating the primary and secondary sulfonamides and refluxing and reacting the primary or secondary sulfonamide in an excess of an acyl halide or an acid anhydride, the excess acyl compound being appropriately removed by distillation or extraction. By so proceeding primary sulfonamides can be suitably mono- or di-acylated and secondary sulfonamides can be suitably mono-acylated.

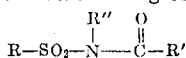
The primary and secondary sulfonamides may be suitably acylated to obtain the acyl sulfonamides useful in the compositions of this invention by heating and reacting 1 mol of either the primary or secondary sulfonamide with at least 1.1 mol of an acyl halide in at least 1.2 molar equivalents of an alkaline solvent such as pyridine at 100° C. to 120° C. for at least 4 hours. At the end of the reaction the reaction product is preferably taken up in an organic solvent such as chloroform and the hydrohalide, formed by the reaction of the acid produced in the alkaline solvent, is extracted with an aqueous acid solution. If any unacylated product remains such unacylated material may be extracted with an aqueous alkaline solution of a metal hydroxide.

Any of the hereinbefore defined acyl sulfonamides may be mixed with a wide variety of organic and/or inorganic oxygen releasing compounds to provide the compositions of the present invention. Examples of organic oxygen releasing compounds include organic peroxides such as urea peroxide, benzoyl peroxide, methylethyl ketone peroxide and the like. Examples of inorganic oxygen releasing compounds include inorganic peroxides such as, alkaline earth metal peroxides, for example, calcium, magnesium, zinc and barium peroxides. Other suitable inorganic peroxides include alkali metal carbonate peroxides such as sodium carbonate peroxide and alkali metal pyrophosphate peroxides such as sodium pyrophosphate peroxide. Particularly suitable inorganic oxygen releasing compounds include inorganic per salts such as metal and ammonium persulfates, perchlorates and perborates. Of these per salts, water soluble alkali metal persulfates, and perborates are preferred, and alkali metal perborates especially sodium and potassium perborates are particularly preferred.

The compositions of this invention comprise, as noted above, a mixture of an oxygen releasing compound and an acyl sulfonamide. These ingredients can be used in the compositions in various proportions depending upon whether the composition is to be used as a bleaching composition or a washing composition or both. However, in most instances, the compositions contain either an organic or an inorganic oxygen releasing compound and from about 0.1 to about 2.0 mols, per mol of the oxygen releasing compound, of any of the acyl sulfonamides hereinbefore described.

In one embodiment of this invention the compositions comprise a mixture of an inorganic per salt such as an alkali metal perborate and from about 0.1 to about 2.0

mols per mol of perborate of an acyl sulfonamide preferably an acyl sulfonamide having the general formula:



wherein R is a substituted aromatic radical such as, an alkyl benzene or a paratoluene or paranitrophenyl group or radical, R' is an unsubstituted aromatic radical and R'' is an aliphatic hydrocarbon radical having from 1 to 10 carbon atoms.

In a preferred embodiment of this invention the compositions comprise sodium perborate and from about 0.1 to about 2.0 mols, per mol of sodium perborate, of N-methyl, N-benzoyl-dodecylbenzene sulfonamide; N-methyl, N-benzoyl-para-toluenesulfonamide, N-methyl, N-benzoyl-para-nitrobenzenesulfonamide or N-ethyl, N-benzoyl-para-toluenesulfonamide or a mixture of such sulfonamides. Such compositions are stable and are useful as commercial laundry bleaches and for bleaching textiles and generally will effectively bleach textile and other materials in water at temperatures as low as 50° C.

The compositions of the present invention may also contain, in addition to the oxygen releasing compound and acyl sulfonamide, a variety of inorganic compounds of a class different from the inorganic oxygen releasing compounds. Examples of such different inorganic compounds include alkaline water soluble, alkali metal inorganic salts, preferably those alkaline inorganic salts of this class which are employed as detergent builders. Illustrative of such salts are trialkali metal phosphates such as trisodium phosphate and tripotassium phosphate; di-alkali metal hydrogen phosphates such as di-sodium hydrogen phosphate and di-potassium hydrogen phosphate; alkaline, water soluble, molecularly dehydrated alkali metal phosphate salts such as alkali metal pyrophosphates, for example, tetra sodium pyrophosphate, trisodium hydrogen pyrophosphate and tetrapotassium pyrophosphate, and the alkali metal tripolyphosphates such as sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$) and potassium tripolyphosphate; alkaline, water soluble alkali metal metaphosphates such as sodium hexametaphosphate; water soluble, alkali metal silicates such as sodium silicates having and Na_2O to SiO_2 mol ratio of 1:1 to 1:3.6, preferably 1:1 to 1:1.35, and the corresponding potassium silicates, water soluble, alkali metal borates such as calcined sodium tetraborate or borax; water soluble alkali metal carbonates or bicarbonates such as sodium or potassium carbonates or bicarbonates; and the like. These salts can be used alone or in various combinations with each other or with water soluble, neutral, inert diluents, which may also have some detergent building properties, for example, water soluble inert neutral alkali metal salt diluents such as neutral alkali metal sulfates or chlorides, for example, sodium sulfate or sodium chloride.

The proportions of the aforementioned alkaline or neutral salts which may be employed in the compositions of this invention can be varied considerably, depending upon the end use of the composition. However, when used, such salts comprise in excess of about 40% and up to about 90% by weight of the dry solids content of the composition. Of this the alkaline alkali metal salts usually comprise about 10% to 95% of the total salts, other than the oxygen releasing compounds, and the inert diluent neutral salts usually comprise about 90% to about 5% of the total salts other than the oxygen releasing compounds.

Although the compositions of this invention may comprise an oxygen releasing compound, an N-substituted acyl sulfonamide and the above-described alkaline salts or combination thereof with inert diluent neutral salts hereinbefore referred to, the compositions may also contain, alone or in combination with the above-described salts, relatively minor amounts, usually less than 15% by weight, preferably 1 to 10% by weight, on a solids basis, an organic surface active agent such as a foaming agent, emulsifier, detergent surfactant or the like. Examples of

organic surface active agents include anionic surfactants such as sulfated alkyl and sulfonated alkyl, aryl, and alkyl aryl hydrocarbons and alkali metal salts thereof, for example, sodium salts of long chain alkyl sulfates, sodium salts of alkyl naphthalene sulfonic acids, sodium salts of sulfonated abietenes, sodium salts of alkyl benzene sulfonic acids particularly those in which the alkyl group contains from 8-24 carbon atoms; sodium salts of sulfonated mineral oils and sodium salts of sulfosuccinic acid esters such as sodium dioctyl sulfosuccinate.

Advantageous anionic surfactants include the higher alkyl aryl sulfonic acids and their alkali metal and alkaline earth metal salts such as for example sodium dodecyl benzene sulfonate, sodium tridecyl benzene sulfonate, magnesium dodecyl benzene sulfonate, potassium tetradecyl benzene sulfonate, ammonium dodecyl toluene sulfonate, lithium pentadecyl benzene sulfonate, sodium dioctyl benzene sulfonate, desodium dodecyl benzene disulfonate, disodium di-isopropyl naphthalene disulfonate and the like as well as the alkali metal salts of fatty alcohol esters of sulfuric and sulfonic acids, the alkali metal salts of alkyl aryl (sulfothioic acid) ethers and the alkyl thiosulfuric acid, etc. Preferred anionic organic surface active agents are, as noted hereinbefore, sodium salts of alkyl benzene sulfonic acids and particularly preferred sodium salts of alkyl benzene sulfonic acids are those in which the alkyl group or radical contains 10 to 18 carbon atoms in a straight (i.e., unbranched) chain.

Examples of nonionic surfactants include products formed by condensing one or more alkylene oxides of 2 to 4 carbon atoms, such as ethylene oxide or propylene oxide, preferably ethylene oxide alone or with other alkylene oxides, with a relatively hydrophobic compound such as a fatty alcohol, fatty acid, sterol, a fatty glyceride, a fatty amine, an aryl amine, a fatty mercaptan, tall oil etc. Nonionic surface active agents also include those products produced by condensing one or more relatively lower alkyl alcohol amines (such as methanolamine, ethanolamine, propanolamine, etc.) with a fatty acid such as lauric acid, cetyl acid, tall oil fatty acid, abietic acid etc. to produce the corresponding amide.

Particularly advantageous nonionic surface active agents are condensation products of a hydrophobic compound having at least 1 active hydrogen atom and a lower alkylene oxide (for example, the condensation product of an aliphatic alcohol containing from about 8 to about 18 carbon atoms) and from about 3 to about 30 mols of ethylene oxide per mol of the alcohol, or the condensation product of an alkyl phenol containing from about 8 to about 18 carbon atoms in the alkyl group and from about 3 to about 30 mols of ethylene oxide per mole of alkyl phenol. Other advantageous nonionic detergents include condensation products of ethylene oxide with a hydrophobic compound formed by condensing propylene oxide with propylene glycol.

Other typical examples of these categories of the anionic and nonionic surface active agents are described in Schwartz and Perry, "Surface Active Agents," Interscience Publishers, New York (1949), and the Journal of American Oil Chemists Society, volume 34, No. 4, pages 170-216 (April 1957).

The various ingredients employed in the compositions of this invention can be used in various proportions depending upon whether the composition is to be used as a bleaching composition, a detergent composition or the like. However, when all four types of ingredients are used the compositions preferably contain, on a dry basis, from about 1% to about 40% by weight of the oxygen releasing compound, preferably an alkali metal perborate, and from about 0.1 to about 2.0 mols, per mol of said oxygen releasing compound of any of the hereinbefore described acyl sulfonamides, from about 0.05 to about 10% of organic surface active agent, and the remainder consisting substantially of the alkaline, alkali metal salts and/or the inert diluent salts. In the case

of aqueous compositions, the ingredients are normally present in the compositions of the same solids basis, but the compositions may contain from 50% to 99% by weight of water.

In a particularly preferred embodiment of this invention the compositions comprise, on a solids basis, from about 3% to 15% by weight of sodium perborate and from about 0.1 to about 2.0 mols per mol of sodium perborate of an acyl sulfonamide such as N-methyl, N-benzoyl-para-toluenesulfonamide, from about 10% to 60% by weight of sodium tripolyphosphate or a mixture of such phosphate and sodium silicate and the remainder consisting essentially of sodium sulfate. Such compositions are useful as bleaching and washing compositions in commercial laundering operations.

In another embodiment of this invention the compositions comprise, on a solids basis, about 3% to 15% by weight of sodium perborate, from about 0.1 to 1.0 mol per mol of perborate of an acyl sulfonamide such as N-methyl, N-benzoyl-para-toluenesulfonamide, about 10% to 60% by weight of an anionic wetting agent, preferably sodium dodecyl benzene sulfonate and the remainder consisting substantially of sodium sulfate. Such compositions are useful as household bleaches and sanitizers.

In still another embodiment of this invention, the compositions comprise from about 3% to 15% of sodium perborate, from about 0.1 to 1.0 mol per mol of perborate of a compound such as N-methyl, N-benzoyl-para-toluenesulfonamide, N-methyl, N-benzoyl-dodecyl-benzenesulfonamide, or N-methyl, N-benzoyl-para-nitrobenzene sulfonamide and the remainder consisting substantially of sodium carbonate or mixtures thereof with sodium tripolyphosphate. These compositions are useful as washing and sanitizing agents particularly in cleaning and sanitizing food processing equipment and containers.

In most instances the proportion and kind of ingredients in the formulation employed will depend on the purpose for which the formulation or composition is being used, that is whether it is being used for bleaching, sanitizing, laundering etc. Regardless of the use involved, however, the compositions containing the oxygen releasing compound and any of the compounds of the class of acyl sulfonamides herein described have the definite properties of bleaching and sanitizing in aqueous solution at temperatures well below the boiling point of water and these compositions also have the tendency to retain their original available oxygen content under ordinary storage conditions for prolonged periods of time, that is for periods up to six months and longer.

A further understanding of the compositions of this invention will be obtained from the following specific examples which are intended to illustrate the invention but not to limit the scope thereof, parts and percentages being by weight unless otherwise indicated.

Example I

Dry mixed compositions containing the following ingredients in the percentages given in Table I were prepared.

TABLE I

Composition Number	1	2	3	4	5	6	7	8	9	10
Ingredient:										
Sodium perborate	6	6	6	6	6	6	6	6	6	6
N-methyl, N-benzoyl-dodecylbenzenesulfonamide	15	0	0	0	0	15	0	0	0	0
N-methyl, N-benzoyl-para-toluenesulfonamide	0	11	0	0	11	0	11	0	0	0
N-methyl, N-benzoyl-para-nitrobenzenesulfonamide	0	0	15	0	0	0	0	0	0	0
N-ethyl, N-benzoyl-para-toluenesulfonamide	0	0	0	15	0	0	0	0	0	0
Sodium tripolyphosphate	40	30	30	40	40	40	30	40	30	25
Sodium sulfate	39	41	30	0	43	30	20	54	52	30
Sodium carbonate	0	0	19	27	0	0	10	0	0	25
Sodium silicate	0	0	0	0	0	0	10	0	0	14
Sodium dodecylbenzene sulfonate	0	12	0	12	0	9	13	0	12	0

The bleaching capacity of each of Compositions 1 through 10 was determined by dissolving 0.25% by weight of each composition in 1 liter of water in separate cylindrical receptacles. The receptacles were provided with mechanical agitation and the solutions therein were maintained at a temperature of 60° C. Each solution had an available oxygen concentration of about 11.5 parts per million. The solutions containing Compositions 1 through 7 respectively contained a mol ratio of sodium perborate to acyl sulfonamide of 1:1.

Twenty 5" x 5" swatches of unbleached naturally yellowed muslin were analyzed for reflectance (Rd) and (a)+(b) color values on a Gardner Automatic Color Difference Meter. Two swatches were placed in each of the ten receptacles containing the dissolved compositions and washed for 10 minutes. After this period the swatches were dried, pressed and again analysed on the Gardner Automatic Colorimeter. The reflectance ΔR_d (brightening) and bleaching efficiency $\Delta(a)$ and $\Delta(b)$ were calculated by subtracting the differences in the readings before and after the washing operation. The loss of available oxygen was also determined for each solution. The results are summarized in Table II.

The Gardner Automatic Color Difference Meter is a tristimulus colorimeter, that is, it contains three photocells which measure (1) reflectance (Rd); (2) green to red color, (a); (3) blue to yellow color, (b).

TABLE II

Composition Number	Loss of available oxygen (percent)	ΔR_d^2	$\Delta(a)^3$	$\Delta(b)^3$
1	83	+7.6	-0.1	-1.9
2	86	+8.0	-0.4	-2.5
3	74	+6.2	-0.1	-1.5
4	77	+6.5	-0.1	-1.5
5	86	+8.0	-0.4	-2.4
6	76	+6.5	-0.1	-1.4
7	85	+8.1	-0.4	-2.4
8	3	+4.0	+0.1	-1.2
9	4	+4.6	+0.1	-1.3
10	3	+4.2	+0.1	-1.2

¹ Determined by iodometric titration of spent wash solutions.

² Positive values indicate degree of increase in reflectance or brightening.

³ Negative values indicate degree of color disappearance or bleaching.

The above values for loss of available oxygen indicate that the acyl sulfonamides in Compositions 1 through 7 promote the release of the oxygen in the oxygen releasing compounds sodium perborate in aqueous solution and that such oxygen was consumed in bleaching and brightening the fabric. Also these results show that the acyl sulfonamides promote the bleaching and brightening of the yellow unbleached muslin. In contrast, solutions of Compositions 8 through 10 which contain sodium perborate, but no acyl sulfonamides, did not lose or release oxygen and did not bleach or brighten the muslin to any appreciable extent.

Four compositions each containing mixtures of sodium perborate and one of the acyl sulfonamides described in this example were prepared in which the mol ratio of sodium perborate to acyl sulfonamide was 1:1. These

compositions were dissolved in water in concentrations 0.1% by weight and evaluated for bleaching and brightening ability using the procedures as above-described. In all instances the results obtained, that is the bleaching of unbleached muslin, were similar to those obtained with solutions containing 0.25% by weight of Compositions 1 through 7 using the washing and bleaching procedures previously described.

Four additional compositions were prepared in which 5.0% weight based on the weight of the composition of sodium dodecyl benzene sulfonamide were incorporated in the sodium perborate-acyl sulfonamide mixtures described in the preceding paragraph. These compositions when dissolved in water in concentrations of 0.12% by weight effectively bleached the unbleached muslin swatches under the washing and bleaching procedures described above.

Compositions similar to Compositions 1 through 7 were prepared except that urea peroxide was used in place of sodium perborate. These compositions when dissolved in water in concentrations of 0.25% effectively bleached and brightened unbleached muslin swatches under the conditions and using the procedures described in Example I.

When compositions similar to those of Compositions 1-7 were prepared using acrylamide, acetamide, malonitrile, benzoic anhydride, phenyl cinnamate, or glucose penta acetate instead of the acyl sulfonamides, 0.25% aqueous solutions of these compositions did not substantially brighten or bleach unbleached muslin until the temperature of the solution was raised about 90° C. although the bleaching procedures were otherwise as described.

Example II

Twenty 5" x 5" swatches of Indian head 80 x 80 cotton fabric, bleached and de-sized were stained by immersing the swatches in a tea prepared by dissolving 48 grams of soluble tea in 8 liters of distilled water at 70° C. After the temperature of the tea stain had dropped to 65° C. the twenty 5" x 5" swatches of fabric were immersed and agitated in the tea for 3 minutes. The swatches were removed, permitted to drain and immersed in 4 liters of distilled water for 15 seconds. The swatches were then dried by a heat pressing and analyzed for reflectance and color values as in Example I.

Two swatches of the fabric were then immersed respectively in fresh solutions of the compositions prepared as described in Example I and evaluated for bleaching effectiveness as described in that example. The results including loss of available oxygen are summarized in Table III.

TABLE III

Composition Number	Loss of available oxygen (percent)	ΔR_d^2	$\Delta(a)^3$	$\Delta(b)^3$
1.....	86	+9.6	-1.7	-8.7
2.....	90	+10.9	-1.8	-9.4
3.....	83	+9.5	-1.7	-8.6
4.....	85	+9.5	-1.7	-9.1
5.....	97	+9.7	-1.7	-9.5
6.....	82	+9.4	-1.7	-9.1
7.....	94	+9.8	-1.7	-9.4
8.....	3	+8.2	-1.5	-8.2
9.....	4	+8.5	-1.5	-8.2
10.....	3	+8.0	-1.5	-8.2

¹ Determined by iodometric titration of spent wash solutions.

² Positive values indicate degree of increase in reflectance or brightening.

³ Negative values indicate degree of color disappearance or bleaching.

The above results clearly demonstrate the oxygen releasing efficiency of solutions of Compositions 1 through 7 containing the acyl sulfonamides at temperatures of 60° C. When compositions similar to Compositions 1 through 7 were prepared using the amides, esters, nitriles, and anhydrides instead of the acyl sulfonamides and such compositions were dissolved in water and the bleaching effectiveness determined as above described, the solution

did not function as efficient brightening and bleaching agents to remove tea stains until the temperature of the bath was increased to 90° C.

Example III

Cotton fabric swatches were stained with a grass stain prepared by adding 30 grams of grass cuttings to a Waring Blendor jar containing 250 ml. of 2 B alcohol, mixing the resultant dispersion at high speeds for 5 minutes and filtering the resultant mixture. The filtrate consisted of a solution of green stain. The swatches were immersed in the staining solution for 3 minutes, drained, and immersed in 500 ml. of distilled water for 15 seconds. The swatches were then dried and bleaching evaluation of Compositions 1 through 10 were conducted as in Example II.

The results are summarized in Table IV.

TABLE IV

Composition Number	Loss of available oxygen (percent)	ΔR_d^2	$\Delta(a)^3$	$\Delta(b)^3$
1.....	41	+13.5	-11.8	-12.9
2.....	61	+14.2	-12.9	-13.8
3.....	44	+13.6	-11.9	-12.8
4.....	49	+13.7	-12.0	-13.1
5.....	62	+14.3	-13.0	-13.8
6.....	51	+13.6	-12.2	-12.9
7.....	63	+14.3	-13.0	-13.8
8.....	0	+12.7	-10.6	-11.4
9.....	0	+12.7	-10.4	-11.2
10.....	0	+12.7	-10.6	-11.2

¹ Determined by iodometric titration of spent wash solutions.

² Positive values indicate degree of increase in reflectance or brightening.

³ Negative values indicate degree of color disappearance or bleaching.

The above results demonstrate the bleaching and brightening efficiency of the acyl sulfonamide containing compositions of this invention. Compositions similar to the compositions of Compositions 1 through 7 were prepared using the prior art compounds referred to in Examples I through III in place of the acyl sulfonamides were inefficient when dissolved in water, in brightening and bleaching the grass stains from the cotton fabric at temperatures of 60° C. and did not efficiently bleach such cotton fabrics until the temperature was increased to about 90° C.

Example IV

Five gram samples of compositions identical to those described in Example I were stored in open glass vials in a humidity cabinet maintained at 90° F. and a relative humidity of 85% for 8 days. Available oxygen determinations were conducted on a portion of these samples every second day. The results are given in the following table.

TABLE V

Composition Number	Loss of available oxygen (percent)			
	2 days	4 days	6 days	8 days
1.....	0	3	5	7
2.....	0	2	4	5
3.....	0	3	5	7
4.....	0	3	5	7
5.....	0	3	5	6
6.....	0	2	4	5
7.....	0	3	5	7
8.....	0	2	5	8
9.....	2	4	7	9
10.....	3	5	7	11

By way of contrast when compositions similar to Compositions 1 through 7 were prepared using acrylamide, acetamide, malonitrile, benzoic anhydride, phthalic anhydride, phenyl cinnamate and glucose penta acetate in place of the acyl sulfonamide of Compositions 1 through 7, such compositions containing these prior art compounds lost at least 49% of available oxygen after 8 days of storage, under the above described conditions.

Example V

The bleach promoting properties of the following acyl sulfonamides were evaluated in accordance with the procedure set forth hereinafter.

Formula	Name
(1) $\text{C}_8\text{H}_{17}-\text{SO}_2-\text{N}(\text{H})-\text{C}(=\text{O})-\text{C}_6\text{H}_5$ -----	N-benzoyl-iso-octyl sulfonamide.
(2) $\text{C}_6\text{H}_{13}-\text{SO}_2-\text{N}(\text{H})-\text{C}(=\text{O})-\text{C}_6\text{H}_5$ -----	N-benzoyl-n-hexyl sulfonamide.
(3) $\text{C}_3\text{H}_7-\text{SO}_2-\text{N}(\text{H})-\text{C}(=\text{O})-\text{C}_6\text{H}_5$ -----	N-benzoyl-n-propyl sulfonamide.
(4) $\text{C}_{10}\text{H}_{21}-\text{SO}_2-\text{N}(\text{H})-\text{C}(=\text{O})-\text{C}_6\text{H}_5$ -----	N-benzoyl-n-dodecyl sulfonamide.
(5) $\text{C}_3\text{H}_7-\text{SO}_2-\text{N}(\text{CH}_3)-\text{C}(=\text{O})-\text{C}_6\text{H}_5$ -----	N-methyl-N-benzoyl-n-propyl sulfonamide.

To one liter of standard full strength borate-carbonate, pH 10 buffer solution there was added the following (1) 0.460 grams of Orange-II [p(2-hydroxy-1-naphthylazo)-benzene sulfonic acid-sodium salt], (2) two grams of a detergent solution of the composition:

Ingredient:	Percent
Sodium dodecylbenzene sulfonate -----	25
Lauryl isopropanol amide -----	3
Sodium silicate -----	6.0
Sodium tripolyphosphate -----	28.0
Tetra sodium pyrophosphate -----	12.0
Anhydrous sodium sulfate -----	17.3
Sodium carboxymethylcellulose -----	0.7
Moisture -----	8.0

A 100 ml. portion of this solution was added to each of 7 individually numbered tubes which were mechanically shaken in a water bath maintained at 60° C. The initial color concentration was determined in a Bausch and Lomb Spectrophotometer by measuring the intensity of its absorption maximum at 483 millimicrons. While recording the time, the compounds indicated in the following table were added to the numbered tubes containing the Orange-II detergent.

TABLE VI

Tube No.	Compound	Dye concentration (percent of original)			
		Minutes			
		0	20	60	160
1-----	Solution only-----	100	100	100	100
2-----	0.080 g. sodium perborate-----	100	83	64	53
3-----	0.080 g. sodium perborate plus Compound 1-----	100	85	68	55
4-----	0.080 g. sodium perborate plus Compound 2-----	100	83	65	53
5-----	0.080 g. sodium perborate plus Compound 3-----	100	85	69	59
6-----	0.080 g. sodium perborate plus Compound 4-----	100	85	66	55
7-----	0.080 g. sodium perborate plus Compound 5-----	100	69	47	12

In the above table the N-acyl alkyl-sulfonamides were added in equimolar amounts with respect to the sodium perborate. Thus, 0.00052 gram mol of each compound was added to the tube indicated. The figures under the column headed "Dye Concentration (percent of original) (minutes)" indicate the percentage of dye which was unbleached by the perborate-bleach promoter combinations at the time periods indicated.

Compounds 1 through 4 incorporated respectively in Groups 3 through 6 which contain a hydrogen atom

bonded to the nitrogen atom of the sulfonamide group did not significantly promote the bleaching or remove the dye color from solutions to a greater extent than that of tube No. 2 which contained sodium perborate without an acyl sulfonamide. On the other hand Compound 5 in tube No. 7 which contained a methyl group in place of a hydrogen atom chemically bound to the nitrogen atom was substantially effective in promoting the bleaching activity, e.g. the disappearance of the colored dye from the solution, at 20, 60 and 160 minutes.

Example VI

The bleach promoting properties of the following additional acyl sulfonamide compounds were determined in accordance with the procedure described in Example V.

Formula	Name
(A) $\text{C}_2\text{H}_5-\text{SO}_2-\text{N}(\text{C}_6\text{H}_5)-\text{C}(=\text{O})-\text{C}_6\text{H}_5$ -----	N-phenyl, N-benzoyl-ethyl sulfonamide.
(B) $\text{C}_2\text{H}_5-\text{SO}_2-\text{N}(\text{C}_6\text{H}_5)-\text{C}(=\text{O})-\text{CH}_3$ -----	N-phenyl, N-acetyl-ethyl sulfonamide.
(C) $\text{C}_{10}\text{H}_{22}-\text{SO}_2-\text{N}(\text{H})-\text{C}(=\text{O})-\text{C}_6\text{H}_5$ -----	N-benzoyl-n-dodecanesulfonamide.
(D) $\text{C}_2\text{H}_5-\text{SO}_2-\text{N}(\text{CH}_3)-\text{C}(=\text{O})-\text{C}_6\text{H}_5$ -----	N-methyl, N-benzoyl-ethyl sulfonamide.

The buffer solution Orange-II detergent solution prepared as described in Example V was added in 100 ml. portions to each of six individually numbered tubes which were mechanically shaken in a water bath maintained at 60° C. As in Example V the initial color concentration was determined in a Bausch and Lomb Spectrophotometer by measuring the intensity of the absorption maximum of the solution at 483 millimicrons. While recording the time the compounds indicated in the following table were added to the numbered tubes containing the Orange-II detergent.

TABLE VII

Tube No.	Compound	Dye concentration (Percent of original)			
		Minutes			
		0	20	60	160
1-----	Solution only-----	100	100	100	100
2-----	0.080 g. sodium perborate-----	100	82	64	54
3-----	0.080 g. sodium perborate plus Compound A-----	100	88	58	32
4-----	0.080 g. sodium perborate plus Compound B-----	100	70	51	38
5-----	0.080 g. sodium perborate plus Compound C-----	100	81	65	55
6-----	0.080 g. sodium perborate plus Compound D-----	100	69	46	11

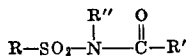
From the above table the N-substituted, N-acyl alkyl-sulfonamides were added to the tubes in equimolar amounts with respect to the sodium perborate. Thus, 0.00052 gram mol of each compound was added to the tube indicated. The figures under the column headed "Dye Concentration (percent of original) (minutes)" indicated the percentage of dye which was unbleached by the bleach promoter combination at the time periods indicated. The results of this example show that Compounds A, B and D were effective in promoting bleaching whereas Compound C was ineffective in promoting bleaching.

Surprisingly when acyl sulfonamide compounds which are unsubstituted, e.g., contain hydrogen attached to the nitrogen atom in addition to having an acyl group attached to said nitrogen atom are employed in compositions containing the oxygen releasing agents, but not the

sulfonamides of this invention; the compositions do not bleach effectively at temperatures below 75° C. but are slightly more effective as bleaching compositions when used in water, which is at or near the boiling point, e.g., 95–100° C., than the compositions containing oxygen releasing compounds without the addition of such unsubstituted acyl sulfonamides. However, when the N-substituted, N-acyl sulfonamides are used in the compositions of this invention such compositions are effective bleaching agents when dispersed in water at temperatures below 70° C.

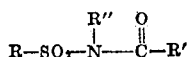
What is claimed is:

1. An oxygen-releasing composition consisting essentially of a mixture of an alkali metal perborate and an acyl sulfonamide having the general formula



wherein R is selected from the group consisting of (a) a substituted phenyl radical selected from the group consisting of halo-, nitro-, sulfo-, and alkyl-substituted phenyl radicals, said alkyl-substituted phenyl radical having 1 to 20 carbon atoms in the alkyl group, and (b) unsubstituted aliphatic radical having from 1 to 10 carbon atoms, R' is selected from the group consisting of unsubstituted phenyl radical and unsubstituted aliphatic radical having from 1 to 10 carbon atoms, and R'' is selected from the group consisting of unsubstituted phenyl radical and unsubstituted aliphatic radical having 1 to 10 carbon atoms; said acyl sulfonamide being present in an amount of from about 0.1 to about 2.0 mols per mol of said perborate.

2. An oxygen-releasing composition consisting essentially of (1) from about 1% to about 40% by weight of an alkali metal perborate, (2) from about 0.1 to about 1.0 mol, per mol of said alkali metal perborate, of an acyl sulfonamide having the general formula



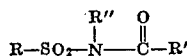
wherein R is selected from the group consisting of (a) a substituted phenyl radical selected from the group consisting of halo-, nitro-, sulfo-, and alkyl-substituted phenyl radicals, said alkyl-substituted phenyl radical having 1 to 20 carbon atoms in the alkyl group, and (b) unsubstituted aliphatic radical having 1 to 10 carbon atoms, R' is selected from the group consisting of unsubstituted phenyl radical and unsubstituted aliphatic radical having from 1 to 10 carbon atoms, and R'' is selected from the group consisting of unsubstituted phenyl radical and unsubstituted aliphatic radical having 1 to 10 carbon atoms, and (3) an inorganic detergent builder salt selected from the group consisting of neutral and alkaline, alkali metal phosphates, alkali metal silicates having an alkali metal oxide to silica mol ratio of 1:1 to 1:3.6, alkali metal sulfates, alkali metal borates, alkali metal carbonates, alkali metal bicarbonates and mixtures thereof, said salt being further characterized as incapable of undergoing an oxidation-reduction reaction with said alkali metal perborate.

3. The composition as in claim 2, wherein the alkali metal perborate is sodium perborate, the acyl sulfonamide is N-methyl, N-benzoyl-para-toluene sulfonamide, and the detergent builder salt is a mixture of sodium triphosphate and sodium sulfate.

4. The composition as in claim 2, wherein the alkali metal perborate is sodium perborate, the acyl sulfonamide is N-methyl, N-benzoyl-dodecylbenzene-sulfonamide, and the detergent builder salt is a mixture of sodium triphosphate and sodium sulfate.

5. An oxygen-releasing composition consisting essentially of (1) a mixture of from about 1% to about 40% by weight of an alkali metal perborate, (2) from about

0.1 to about 1.0 mol per mol of said alkali metal perborate of an acyl sulfonamide having the general formula

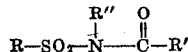


wherein R is selected from the group consisting of (a) a substituted phenyl radical selected from the group consisting of halo-, nitro-, sulfo-, and alkyl-substituted phenyl radicals, said alkyl-substituted phenyl radical having 1 to 20 carbon atoms in the alkyl group, and (b) unsubstituted aliphatic radical having 1 to 10 carbon atoms, R' is selected from the group consisting of unsubstituted phenyl radical and unsubstituted aliphatic radical having from 1 to 10 carbon atoms, and R'' is selected from the group consisting of unsubstituted phenyl radical and unsubstituted aliphatic radical having 1 to 10 carbon atoms, and (3) a non-soap synthetic organic detergent selected from the group consisting of non-soap synthetic anionic surface active agents and non-soap synthetic nonionic surface active agents.

6. The composition as in claim 5, wherein the alkali metal perborate is sodium perborate, the acyl sulfonamide is N-methyl, N-benzoyl-para-toluenesulfonamide, and said organic detergent is a sodium alkyl benzene sulfonate having from about 8 to about 24 carbon atoms in the alkyl group.

7. The composition as in claim 5, wherein the alkali metal perborate is sodium perborate, the acyl sulfonamide is N-methyl, N-benzoyl-dodecylbenzene-sulfonamide, and said organic detergent is a sodium alkyl benzene sulfonate having from about 8 to about 24 carbon atoms in the alkyl group.

8. An oxygen-releasing composition consisting essentially of (1) from about 1% to about 40% by weight of sodium perborate, (2) from about 0.1 mol to about 1.0 mol, per mol of sodium perborate of an acyl sulfonamide having the general formula



wherein R is selected from the group consisting of (a) a substituted phenyl radical selected from the group consisting of halo-, nitro-, sulfo-, and alkyl-substituted phenyl radicals, said alkyl-substituted phenyl radical having 1 to 20 carbon atoms in the alkyl group and (b) unsubstituted aliphatic radical having 1 to 10 carbon atoms, R' is selected from the group consisting of unsubstituted phenyl radical and unsubstituted aliphatic radical having from 1 to 10 carbon atoms, and R'' is selected from the group consisting of unsubstituted phenyl radical and unsubstituted aliphatic radical having 1 to 10 carbon atoms, (3) a detergent builder salt selected from the group consisting of neutral and alkaline, alkali metal phosphates, alkali metal silicates having an alkali metal oxide to silica mol ratio of 1:1 to 1:3.6, alkali metal sulfates, alkali metal borates, alkali metal carbonates, and alkali metal bicarbonates and (4) a non-soap synthetic organic detergent selected from the group consisting of non-soap synthetic anionic surface active agents and non-soap synthetic nonionic surface active agents, said builder salt being incapable of undergoing an oxidation-reduction reaction with said sodium perborate.

9. A composition as in claim 8, wherein the acyl sulfonamide is N-methyl, N-benzoyl-para-toluenesulfonamide, the organic detergent is a sodium alkyl benzene sulfonate wherein the alkyl radical is a straight chain radical having from about 10 to about 18 carbon atoms, and the detergent builder salt is a mixture of sodium triphosphate, sodium sulfate, sodium carbonate, and sodium silicate.

10. A composition as in claim 8, wherein the acyl sulfonamide is N-methyl, N-benzoyl-dodecyl benzene sulfonamide, the organic detergent is a sodium alkyl benzene sulfonate wherein the alkyl radical is a straight chain radical having from about 10 to about 18 carbon atoms,

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and the detergent builder salt is a mixture of sodium tri-
polyphosphate and sodium sulfate.

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