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(54) Title: SULFANIMINES AS BLEACH CATALYSTS

(57) Abstract

Novel bleaches, a method for bleaching substrates using these materials and detergent compositions containing same are reported. The bleaches are sulfanimines. Substrates such as fabrics may be bleached in an aqueous solution containing the sulfanimine and a peroxygen compound.

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SULFANIMINES AS BLEACH CATALYSTS

Field of the Invention

The invention relates to bleach catalysts, compositions containing same and a method for using the catalysts for cleaning substrates, especially fabrics.

Background of the invention and the Related Art

Many household and personal care products are formulated with an active oxygen-releasing material to effect removal of stain and soil. Oxygen-releasing materials have an important limitation; their activity is extremely temperature dependent. Temperatures in excess of 60°C are normally required to achieve any bleach effectiveness in an aqueous wash system. Especially for cleaning fabrics, high temperature operation is both economically and practically disadvantageous.

The art has partially solved the aforementioned problem through the use of activators. These activators, also known as bleach precursors, often appear in the form of carboxylic acid esters. In an aqueous liquor, anions of hydrogen peroxide react with the ester to generate the corresponding peroxyacid which oxidizes the stained substrate. Commercial application of this technology is found in certain fabric bleaching detergent powders incorporating sodium nonanoyloxybenzene sulfonate. This activator is typical of a class that features a phenol sulfonate leaving group; see US Patent 4,412,934.

While carboxylic acid ester activators and the like are often effective, they are not catalytic. Once the ester has been perhydrolyzed it can no longer be recycled.

Accordingly, relatively large amounts of activator are necessary. Amounts as high as 8% may be necessary in a detergent formulation for bleaching fabrics. Cost for these relatively expensive activators is of major concern at such levels.

A significant advance in catalysis was reported utilizing sulfonimines in US Patent 5,041,232, US Patent 5,047,163 and US Patent 5,045,223. Only a few of the reported compounds have been studied in any detail. More investigation needs to be conducted to identify catalysts of even greater activity.

Accordingly, it is an object of the present invention to provide novel bleach catalysts that can operate over a wide temperature range including that of under 60°C.

It is another object of the present invention to provide bleach catalysts which are effective at relatively low concentrations thereby achieving a cost effective stain removal system.

A further object of the present invention is to provide a method for bleaching stained substrates such as clothes, household hard surfaces including sinks, toilets and the like, and even dentures.

Other objects of the present invention will become apparent through the following summary, detailed discussion and examples.

SUMMARY OF THE INVENTION

A bleaching composition is provided including:

(i) from 1 to 60% by weight of a peroxygen compound;

(ii) from 0.01 to 10% of an oxygen transfer agent whose structure is:

$$R^1R^2C=NSO_2-XR^3$$

wherein:

X is a radical selected from the group consisting of oxygen, nitrogen and NR^1 radicals;

R^1 may be hydrogen or a C_1-C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, acyl, heterocyclic ring, alkyl and cycloalkyl radicals;

R^2 may be hydrogen or a C_1-C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, $R^1C=NSO_2XR^3$, nitro, halo, cyano, alkoxy, keto, carboxylic and carboalkoxy radicals;

R^3 may be a C_1-C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nitro, halo and cyano radicals;

R^1 with R^2 and R^2 with R^3 may respectively together independently form a cycloalkyl, heterocyclic, and aromatic ring system; and

(iii) from about 0.5 to 50% of a surfactant.

Additionally, there is provided a method for bleaching a stained substrate comprising the step of applying to the stained substrate an aqueous solution comprising a peroxygen compound and an oxygen transfer agent whose structure is $R^1R^2C=NSO_2-XR^3$, with radical groups as defined above, the mole ratio of peroxygen compound to oxygen transfer agent being from about 250:1 to about 1:2.

Certain novel compounds are also provided whose structure is $R^1R^2C=NSO_2-XR^3$ having radical groups as defined above, with the proviso that at least one of R^1, R^2, R^3 is substituted with a water-solubilizing functional group. Typical water-solubilizing groups include carboxylic acid, phosphoric acid, phosphonic acid, sulfuric acid, sulfonic acid, and, especially, their salt derivatives and quaternary ammonium salts.

DETAILED DESCRIPTION

It has been found that sulfanimines operate even more effectively than sulfonimines as catalysts for activating peroxygen compounds to transfer active oxygen to stains. Consumer and industrial articles can effectively be bleached to remove stains present on such articles. Sulfanimines covered by the present invention are those whose structure is:

$$R^1R^2C=NSO_2-XR^3$$

wherein:

X is a radical selected from the group consisting of oxygen, nitrogen and NR^1 radicals;

R^1 may be hydrogen or a C_1-C_{40} substituted or unsubstituted radical selected from the group the group consisting of phenyl, aryl, acyl, heterocyclic ring, alkyl and cycloalkyl radicals;

R^2 may be hydrogen or a C_1-C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, $R^1C{=}NSO_2{-}XR^3$, nitro, halo, cyano, alkoxy, keto, carboxylic and carboalkoxy radicals;

R^3 may be a C_1-C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nitro, halo and cyano radicals; and

R^1 with R^2 and R^2 with R^3 may respectively together independently form a cycloalkyl, heterocyclic or aromatic ring system.

Often advantageous are sulfanimines having at least one of R^1, R^2, R^3 substituted with a water-solubilizing functional group. These functional groups may be selected from carboxylates, phosphates, phosphonates, sulfates, sulfonates in acid and salt form and quaternary ammonium salts. Suitable salts include those whose counterions are selected from alkali metal, ammonium, and C_2-C_6 alkanolammonium cations.

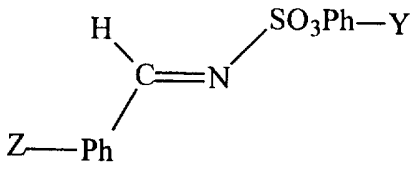
Amine functional groups may also be incorporated into R^1, R^2 or R^3 to provide water-solubilization of the sulfanimines. An example combining the amine and heterocyclic structure is that of pyridine.

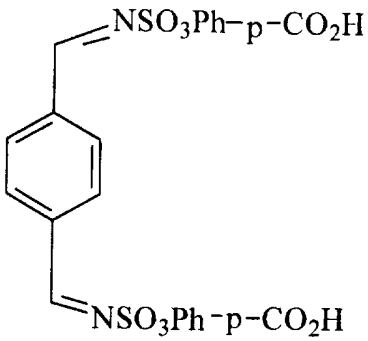
A water-solubilizing functional group is one which renders the sulfanimines soluble to the extent of at least 2 mg/l, preferably at least 25 mg/l, optimally at least 250 mg/l by weight in water at 25°C.

Heterocyclic rings according to this invention include cycloaliphatic and cycloaromatic type radicals incorporating an oxygen, sulfur and/or nitrogen atom within the ring system. Representative nitrogen heterocycles include pyridine, morpholine, pyrrole, imidazole, triazole, tetrazole, pyrrolidine, piperidine and piperazine. Suitable oxygen heterocycles include furan, tetrahydrofuran and dioxane. Sulfur heterocycles may include thiophene and tetrahydrothiophene. Among the various heterocycles, it has been found that those incorporating nitrogen are the most active.

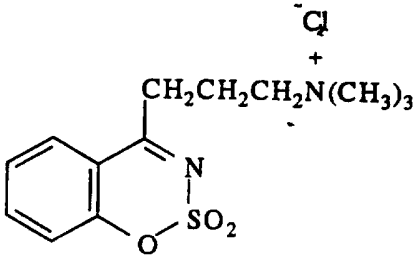
The term "substituted" is defined in relation to R^1, R^2, R^3 as a substituent which is a nitro, halo, cyano, C_1-C_{20} alkyl, acyl, amino, aminoalkyl, thioalkyl, sulfoxyalkyl, carboxyester, hydroxy, C_1-C_{20} alkoxy, polyalkoxy and C_1-C_{40} quaternary di- or trialkylammonium function.

Novel sulfanimine compounds are described below wherein R^1 is hydrogen, R^2 is phenyl with a Z substitutent, and R^3 is phenyl with a Y substituent. Very often Z and Y groups are water-solubilizing groups, most commonly being carboxylic acid or salts thereof. Representative structures are as follows:

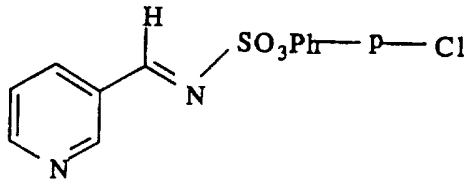


	Z	Y
O-SULF 1	4-CO_2H	4-Cl
O-SULF 2	4-CO_2H	4-CO_2H
O-SULF 3	4-Cl	4-CO_2H
O-SULF 4	H	4-CO_2H
O-SULF 5	4-CH_2H	4-CH_2H
O-SULF 6	4-CO_2H	3-NO_2
O-SULF 7	4-CN	4-CO_2H
O-SULF 8	4-OMe	4-CO_2H
O-SULF 9	3-OH	4-Cl
O-SULF 10		

Illustrative of cycloaromatic and of heterocyclic nitrogen ringen sulfanimines are the respective O-SULF 11 and O-SULF 12 whose structures are outlined below.



O-SULF 11



O-SULF 12

The following further compounds are illustrative of sulfanimes of the present invention:

N-Benzylidenebenzenesulfamate

N-(3-Pyridinylmethylene)benzenesulfamate

N-(4-Pyridinylmethylene)benzenesulfamate

N-(2-Pyridinylmethylene)benzenesulfamate

N-(N-Methyl-3-pyridinylmethylene)benzenesulfamate chloride salt

N-(2-Furfurylidene)benzenesulfamate

N-(2-Furfurylidene)-4-carboxybenzenesulfamate sodium salt

N-(2,6-Dicarboxy-4-pyridinylmethylene)benzenesulfamate disodium salt

N-(4-Cholyloxycarbonylbenzylidene)benzenesulfamate chloride salt

N-Benzylidene-4-cholyloxycarbonylbenzenesulfamate chloride

salt
N-Cyclohexylidenebenzenesulfamate
N-(4-Trifluoromethylbenzylidene)benzenesulfamate
N-(4-Methylsulfonylbenzylidene)benzene sulfamate
N-(4-Trimethylammoniobenzylidene)benzenesulfamate chloride salt
N-Benzylidene-4-trimethylammoniobenzenesulfamate chloride salt
4-Trimethylammoniomethyl-1,2,3-benzoxathiazine-2,2-dioxide chloride salt
4-Carboxymethyl-1,2,3-benzoxathiazine-2,2-dioxide sodium salt
4-Trifluoromethyl-1,2,3-benzoxathiazine-2,2-dioxide
5-Hydroxy-4-phenyl-1,2,3-benzoxathiazine-2,2-dioxide
6,7-Dimethoxy-4-methyl-1,2,3-benzoxathiazine-2,2-dioxide
N',N'-Dimethyl-N-(4-Trimethylammoniobenzylidene)sulfamide chloride salt
N',N'-Dimethyl-N-(4-Carboxybenzylidene)sulfamide sodium salt
N',N'-Dimethyl-N-(4-Trifluoromethylbenzylidene)sulfamide
N',N'-Dimethyl-N-(4-Cholyloxycarbonylbenzylidene)sulfamide chloride salt
1-Phenyl-4-trimethylammoniomethyl-2,1,3-benzthiadiazine-2,2-dioxide chloride salt
4-Methyl-1-Trifluoromethyl-2,1,3-benzthiadiazine-2,2-dioxide
1-Acetyl-4-methyl-2,1,3-benzthiadiazine-2,2-dioxide

The foregoing oxygen transfer agents may be incorporated into detergent bleach compositions along with a further essential component which is a peroxygen compound capable of yielding peroxide anion or peroxyacid in an aqueous solution.

Amounts of oxygen transfer agent suitable for the present invention may range from 0.01 to 10%, preferably from 0.1 to 5%, optimally between 0.5 and 1.5% by weight of the composition.

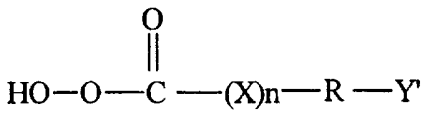
The peroxygen compound may be present from 1% to 65%, preferably from 1.5 to 25%, optimally between about 2 and 10% by weight.

The molar ratio of peroxygen compound to oxygen transfer agent will range from about 250:1 to 1:2, preferably 100:1 to 1:1, optimally between about 25:1 to 2:1.

Peroxyacid and peroxide anion sources are well known in the art. They include the alkali metal peroxides, organic peroxides such as urea peroxide, and inorganic persalts, such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulfates (e.g. Oxone®). Mixtures of two or more such compounds may also be suitable. Particularly preferred are sodium percarbonate, Oxone® and sodium perborate monohydrate.

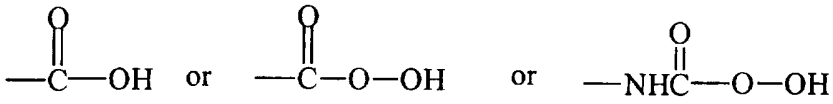
Alkylhydroperoxides are another suitable class of peroxygen compounds. Examples of these materials include cumene hydroperoxide and t-butyl hydroperoxide.

Organic peroxy acids may also be suitable as the peroxygen compound. Such materials have a general formula:

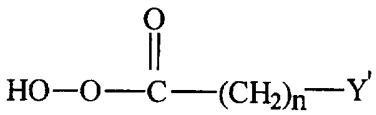


wherein X is oxygen or nitrogen, n=0 or 1, R is an alkylene or substituted alkylene group containing from 1 to about 22

carbon atoms or a phenylene or substituted phenylene group, and Y' is hydrogen, halogen, alkyl, aryl or

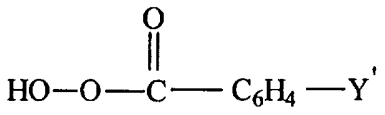


The organic peroxy acids usable in the present invention can contain either one or two peroxy groups and can be either aliphatic or aromatic. When the organic peroxy acid is aliphatic, the unsubstituted acid has the general formula:



where Y' can be, for example, H, CH_3, CH_2Cl, COOH, NHCOOOH or COOOH; and n is an integer from 0 to 20.

When the organic peroxy acid is aromatic, the unsubstituted acid has the general formula:



wherein Y' is hydrogen, alkyl, alkylhalogen, halogen, COOH, NHCOOOH or COOOH.

Typical monoperoxy acids useful herein include alkyl peroxy acids and aryl peroxy acids such as:

(i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy-α-naphthoic acid;

(ii) aliphatic, substituted aliphatic and arylalkyl monoperoxy acids, e.g. peroxylauric acid, peroxystearic acid, and N,N-phthaloylaminoperoxycaproic acid (PAP).

Typical diperoxy acids useful herein include alkyl diperoxy acids and aryldiperoxy acids, such as:

(iii) 1,12-diperoxydodecanedioic acid;

(iv) 1,9-diperoxyazelaic acid;

(v) diperoxybrassylic acid; diperoxysebacic acid and diperoxyisophthalic acid;

(vi) 2-decyldiperoxybutane-1,4-dioic acid;

(vii) 4,4'-sulfonylbisperoxybenzoic acid;

(viii) N,N'-terephthaloyl-di(6-aminoperoxycaproic acid).

Particularly preferred organic acids are N,N-phthaloylaminoperoxycaproic acid, peracetic acid, monoperoxyphthalic acid (magnesium salt hexahydrate), and diperoxydodecanedioic acid. Under certain circumstances, hydrogen peroxide itself may directly be employed as the peroxygen compound.

Optionally, compositions of the present invention may further include a pre-bleach precursor that reacts with peroxide anion or peroxyacid and forms therewith a peracid, percarbonic acid or perimidic acid.

The preferred precursors are N,N,N',N'-tetraacetylethylene diamine (TAED), tetraacetyl-glycoluril (TAGU), glucose pentaacetate, xylose tetraacetate, sodium acetyloxybenzene sulfonate (SABS) and sodium nonanoyloxybenzene sulfonate (SNOBS). Levels of precursor may range from 0.1 to 40%, preferably from 1 to 10%, optimally from 2 to 8% by weight.

Bleach systems of the present invention may be employed for a wide variety of purposes, but are especially useful in the cleaning of laundry. When intended for such purpose, the peroxygen compound and oxygen transfer agent of the present invention will usually also be combined with surface-active materials, detergency builders and other known ingredients of laundry detergent formulations.

The surface-active material may be naturally derived, or synthetic material selected from anionic, nonionic, amphoteric, zwitterionic, cationic actives and mixtures thereof. Many suitable actives are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. The total level of the surface-active material may range up to 50% by weight, preferably being from 0.5 to 40% by weight of the composition, most preferably 4 to 25%.

Synthetic anionic surface-actives are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms.

Examples of suitable synthetic anionic detergent compounds are sodium and ammonium alkyl sulphates, especially those obtained by sulphating higher (C_8-C_{18}) alcohols produced for

example from tallow or coconut oil; sodium and ammonium alkyl (C_9-C_{20}) benzene sulphonates, sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium and ammonium salts of sulphuric acid esters of higher (C_9-C_{18}) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralized with sodium hydroxide; sodium and ammonium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C_8-C_{20}) with sodium bisulphite and those derived by reacting paraffins with SO_2 and Cl_2 and then hydrolyzing with a base to produce a random sulphonate; sodium and ammonium C_7-C_{12} dialkyl sulfosuccinates; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C_{10}-C_{20} alpha-olefins, with SO_3 and then neutralizing and hydrolyzing the reaction product. The preferred anionic detergent compounds are sodium (C_{11}-C_{15}) alkylbenzene sulphonates, sodium (C_{16}-C_{18}) alkyl sulphates and sodium (C_{16}-C_{18}) alkyl ether sulphates.

Examples of suitable nonionic surface-active compounds which may be used, preferably together with the anionic surface-active compounds, include in particular the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C_6-C_{22}) phenols, generally 5-25 EO, i.e. 5-25 units of ethylene oxide per molecule; the condensation products of aliphatic (C_8-C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, generally 2-30 EO, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylene diamine. Other so-called

nonionic surface-actives include alkyl polyglucosides, long chain tertiary amine oxides, and fatty amido polyols such as methyl glucamines.

Amphoteric or zwitterionic surface-active compounds such as alkylamidopropyl betaines can also be used in the compositions of the invention. If any amphoteric or zwitterionic detergent compounds are used, it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and nonionic actives.

Soaps may also be incorporated into the compositions of the invention, preferably at a level of less than 30% by weight. They are particularly useful at low levels in binary (soap/anionic) or ternary mixtures together with nonionic or mixed synthetic anionic and nonionic compounds. Soaps which are used are preferably the sodium, or less desirably potassium, salts of saturated or unsaturated C_{10}-C_{24} fatty acids or mixtures thereof. The amount of such soaps can be varied between 0.5 and 25% by weight, with lower amounts of 0.5 to 5% being generally sufficient for lather control. Amounts of soap between 2 and 20%, especially between 5 and 15, are used to give a beneficial effect on detergency. This is particularly valuable in compositions used in hard water where the soap acts as a supplementary builder.

The detergent compositions of the invention will normally also contain a detergency builder. Builder materials may be selected from (1) calcium sequestrant materials, (2) precipitating materials, (3) calcium ion-exchange materials and (4) mixtures thereof.

In particular, the compositions of the invention may contain any one of the organic or inorganic builder materials, such

as sodium or potassium tripolyphosphate, sodium or potassium pyrophosphate, sodium or potassium orthophosphate, sodium carbonate, the sodium salt of nitrilotriacetic acid, sodium citrate, carboxymethylmalonate, carboxymethyloxysuccinate, tartrate mono- and di- succinate, oxydisuccinate, crystalline or amorphous aluminosilicates and mixtures thereof.

Polycarboxylic homo- and co-polymers may also be included as builders and to function as powder structurants or processing aids. Particularly preferred are polyacrylic acid (available under the trademark Acrysol from the Rohm and Haas Company) and acrylic-maleic acid copolymers (available under the trademark Sokalan from the BASF Corporation) and alkali metal or other salts thereof.

These builder materials may be present at a level of, for example, from 1 to 80% by weight, preferably from 10 to 60% by weight.

Upon dispersal in a wash water, the initial amount of peroxygen compound should range anywhere from 0.05 to 250 ppm active oxygen per liter of water, preferably from 1 to 50 ppm. Within the wash media the amount of oxygen transfer agent initially present should be from 0.01 to 300 ppm, preferably from 5 to 100 ppm. Surfactant should be present in the wash water from 0.05 to 1.0 grams per liter, preferably from 0.15 to 0.20 grams per liter. When present, the builder amount will range from 0.1 to 3.0 grams per liter.

Apart from the components already mentioned, the detergent compositions of the invention can contain any of the conventional additives in the amounts in which such materials are normally employed in detergent compositions. Examples of these additives include dye transfer inhibition agents (e.g.

polymers based on N-vinylpyrrolidone and N-vinylimidazole), lather boosters such as alkanolamides, particularly the monoethanolamides derived from palmkernel fatty acids and coconut fatty acids, lather-depressants such as alkyl phosphates and silicones, anti-redeposition agents such as sodium carboxymethylcellulose and alkyl or substituted alkylcellulose ethers, stabilizers such as ethylene diamine tetraacetic acid and phosphonic acid derivatives (Dequest®), fabric softening agents, inorganic salts such as sodium sulphate, and, usually present in very small amounts, fluorescent agents, perfumes, enzymes such as proteases, cellulases, lipases and amylases, germicides and colorants.

The oxygen transfer agents in combination with a peroxygen compound may be useful for removing stains both in consumer type products and for industrial applications. Among consumer products incorporating this invention are laundry detergents, laundry bleaches, hard surface cleaners, toilet bowl cleaners, automatic dishwashing compositions and even denture cleaners. Stained consumer products benefiting from treatment with compositions of this invention may include clothes and other fabrics; household fixtures and applicants such as sinks, toilet bowls and oven ranges; tableware such as drinking glasses, dishes, cookware and utensils; and even dentures. Hair colorants may also be formulated with the bleach composition of this invention. The bleaching system of this invention may also be applied to industrial uses such as for the bleaching of wood pulp.

The system of the present invention may be delivered in a variety of product forms including powders, on sheets or other substrates, in pouches, in tablets, in aqueous liquids, or in nonaqueous liquids such as liquid nonionic detergents.

The following examples will more fully illustrate the embodiments of this invention. All parts, percentages and proportions referred to herein and in the appended claims are by weight unless otherwise illustrated.

EXAMPLES

The oxygen transfer agents described below were synthesized according to the procedure of Kamal, A. and Sattur, P.B. , Synthesis, **1981**, pages 272-273.

Synthesis Procedure for Et-O-Sulf

To a stirred solution of the 2-hydroxy propiophenone (46 mmol) in 40 mL of toluene (or xylene) at 108°C (or 135°C) was added chlorosulfonyl isocyanate (46 mmol) 5 mL in toluene (or xylene) over a 20 minute period. After stirring for 3 hours at the reaction temperature, the solvent was removed in vacuum and the residue was added to 50 mL of cold water followed by extraction with hexane. The remaining mass was then recrystallized from ethanol to yield the desired material Et-O-Sulf in about 25% yield.

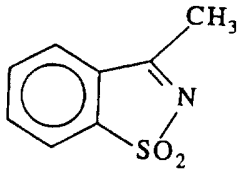
Bleaching Data for the 1,2,3-Benzoxathiazine 2,2-dioxide Class of Molecules

Bleaching studies were conducted by comparing the performance of representative bleaches with and without the presence of sulfanimines. In this regard, the stain removal observed without the intervention of sulfanimines served as an experimental blank and the amount of stain removal by the sulfanimine containing system constituted activation of a given bleach.

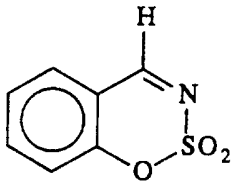
Stain bleaching experiments were conducted in a Terg-O-Tometer in 1000 mL of milli-Q water. These experiments were run employing 0.01M $NaHCO_3$ buffer with the pH adjusted to the reported value with 1N NaOH solution. Four tea stained (BC-1) half cloths were added to each Terg pot. All the runs were performed at 40°C unless otherwise stated. The peracid drivers were either PAP or Oxone® and these were dosed at 7.5 ppm a.o. level. A given peracid was added to the system followed by an appropriate amount of sulfanimine.

Stain bleaching was measured reflectometrically using a Colorgard System/05 Reflectometer. Bleaching was indicated by an increase in reflectance less the effect of oxidant alone, reported as ΔΔR.

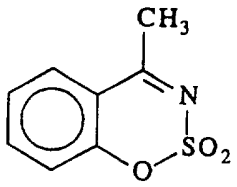
The following molecules were tested in the different experiments described in the tables. Data for SulfD is provided for comparison.



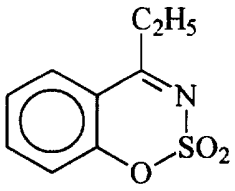
SulfD



O-Sulf



O-SulfD



Et-O-Sulf

TABLE I

Bleaching data for the Different Catalysts at a Concentration of $3x10^{-4}$M and 40°C

pH	SulfD		O-Sulf		O-SulfD	
	Oxone*	PAP**	Oxone	PAP	Oxone	PAP
8	4.9	0.33	11.8	2	12.2	2
9	7.9	5.3	--	--	12.2	7.6
10	10	9.6	7.7	-1.4	13.9	4.6

* $2KHSO_5/KHSO_4/K_2SO_4$ trisalt, ex. DuPont.
** N,N-phthaloylaminoperoxycaproic acid.

TABLE II

Bleaching Data for the Different Catalysts at a Concentration of $6x10^{-5}$M at 40°C with PAP

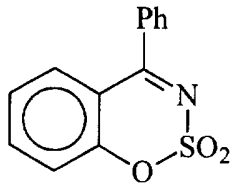
pH	SulfD	O-SulfD	Et-O-Sulf
8	0.8	2.6	3.7
9	4.6	8.6	6.7
10	6.4	6.2	7.8

TABLE III

Bleaching Data for the Different Catalysts at a Concentration of $6x10^{-5}M$ at 20°C with PAP

pH	SulfD	O-SulfD	Et-O-Sulf
8	--	--	3.4
9	2	5.1	3.9
10	3.4	5.5	6.1

Also tested was the Ph-O-Sulf catalyst which showed a small benefit with Oxone and none with PAP as reported in Table IV.



Ph-O-Sulf

TABLE IV

Bleaching with Ph-O-Sulf at 40°C at a Catalyst Concentration of $6x10^{-5}M$

pH	Ph-O-Sulf	
	PAP	Oxone
8	-2.4	0.6
9	-0.6	1.0
10	-0.3	1.1

The foregoing description and Examples illustrate selected embodiments of the present invention. In light thereof, various modifications will be suggested to one skilled in the art all of which are within the spirit and purview of this invention.

WHAT IS CLAIMED IS:

1. A bleaching composition comprising:

(i) from 1 to 60% by weight of a peroxygen compound;

(ii) from 0.01 to 10% of an oxygen transfer agent whose structure is:

$R^1R^2C=NSO_2-XR^3$

wherein:

X is a radical selected from the group consisting of oxygen, nitrogen and NR^1 radicals;

R^1 may be hydrogen or a C_1-C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, acyl, heterocyclic ring, alkyl and cycloalkyl radicals;

R^2 may be hydrogen or a C_1-C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, $R^1C=NSO_2XR^3$, nitro, halo, cyano, alkoxy, keto, carboxylic and carboalkoxy radicals;

R^3 may be a C_1-C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nitro, halo and cyano radicals;

R^1 with R^2 and R^2 with R^3 may respectively together independently form a cycloalkyl, heterocyclic, and aromatic ring system; and

(iii) from about 0.5 to 50% of a surfactant.

2. A composition according to claim 1 further comprising from about 1 to 80% of a detergent builder.

3. A composition according to claim 1 further comprising an effective amount for cleaning of an enzyme selected from the group consisting of proteases, cellulases, lipases, amylases and mixtures thereof.

4. A composition according to claim 1 delivered in a form selected from the group consisting of a powder, sheet, pouch, tablet, aqueous liquid and nonaqueous liquid.

5. A composition according to claim 1 wherein the peroxygen compound is present in an amount from 1.5 to 25% and the oxygen transfer agent is present in an amount from 0.1 to 5% by weight.

6. A composition according to claim 1 wherein the peroxygen compound is an inorganic material selected from the group consisting of perborate, percarbonate, perphosphate, persilicate and monopersulphate salts.

7. A composition according to claim 1 wherein the peroxygen compound is an organic peroxyacid.

8. A composition according to claim 7 wherein the organic peroxyacid is selected from the group consisting of N,N-phthaloylaminoperoxycaproic acid, peracetic acid, monoperoxyphthalic acid and diperoxydodecanedioic acid.

9. A composition according to claim 1 wherein the peroxygen compound is a bleach precursor.

10. A composition according to claim 1 wherein at least one of R^1, R^2 and R^3 is substituted with a water-solubilizing functional group.

11. A composition according to claim 10 wherein the water-solubilizing functional group is selected from the group consisting of carboxylate, phosphate, phosphonate, sulfate, sulphonate in acid and salt forms and quaternary ammonium salts.

12. A composition according to claim 1 wherein said substituent on R^1, R^2 and R^3 is a functional unit selected from the group consisting of nitro, halo, cyano, C_1-C_{20} alkyl, amino, aminoalkyl, thioalkyl, sulfoxyalkyl, carboxyester, hydroxy, C_1-C_{20} alkoxy, polyalkoxy, C_1-C_{40} quaternary di- or tri- alkylammonium functional units and mixtures thereof.

13. A method for bleaching a stained substrate, said method comprising contacting said stained substrate in an aqueous medium with a peroxygen compound, a surfactant in an effective amount to clean said substrate and with an oxygen transfer agent whose structure is:

$$R^1R^2C=NSO_2-XR^3$$

wherein:

X is a radical selected from the group consisting of oxygen, nitrogen and NR^1 radicals;

R^1 may be a hydrogen or a C_1-C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, acyl, heterocyclic ring, alkyl and cycloalkyl radicals;

R^2 may be hydrogen or a C_1-C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, $R^1C=NSO_2XR^3$, nitro, halo, cyano, alkoxy, keto, carboxylic and carboalkoxy radicals;

R^3 may be a C_1-C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nitro, halo, and cyano radicals;

R^1 with R^2 and R^2 with R^3 may respectively together independently form a cycloalkyl, heterocyclic, and aromatic ring system; and said peroxygen compound to oxygen transfer agent being present in a molar ratio ranging from 250:1 to 1:2.

14. A method according to claim 13 wherein the ratio of peroxygen compound to oxygen transfer agent ranges from 100:1 to 1:1.

15. A method according to claim 13 wherein said substrate is selected from the group consisting of fabrics, household fixtures and tableware.

16. A method according to claim 13 wherein said substrate is a denture.

17. A method for bleaching a stained substrate, said method comprising contacting said stained substrate in an aqueous medium with a peroxygen compound and with an oxygen transfer agent whose structure is:

$$R^1R^2C=NSO_2XR^3$$

wherein:

X is a radical selected from the group consisting of oxygen, nitrogen and NR^1 radicals;

R^1 may be a hydrogen or C_1-C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, acyl, heterocyclic ring, alkyl and cycloalkyl radicals;

R^2 may be hydrogen or a C_1-C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, $R^1C{=}NSO_2XR^3$, bitro, halo, cyano, alkoxy, keto, carboxylic and carboalkoxy radicals;

R^3 may be a C_1-C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nitro, halo and cyano radicals;

R^1 with R^2 and R^2 with R^3 may respectively together independently form a cycloalkyl, heterocyclic and aromatic ring system; and

said contacting to achieve bleaching being performed in said medium containing 0.05 to 250 ppm active oxygen from the peroxygen compound, 0.01 to 300 ppm oxygen transfer agent and from 0.05 to 1.0 grams surfactant per liter of medium.

18. A method according to claim 17 wherein the oxygen transfer agent is present from about 5 ppm to about 100 ppm per liter of medium.

19. A bleach whose structure is:

$R^1R^2C=NSO_2-XR^3$

wherein:

X is a radical selected from the group consisting of oxygen, nitrogen and NR^1 radicals;

R^1 may be hydrogen or a C_1-C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, acyl, heterocyclic ring, alkyl and cycloalkyl radicals;

R^2 may be hydrogen or a C_1-C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, $R^1C=NSO_2XR^3$, nitro, halo, cyano, alkoxy, keto, carboxylic and carboalkoxy radicals;

R^3 may be a C_1-C_{40} substituted or unsubstituted radical selected from the group consisting of phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nitro, halo and cyano radicals;

R^1 with R^2 and R^2 with R^3 may respectively together independently form a cycloalkyl, heterocyclic, and aromatic ring system; and

with a proviso that at least one of R^1, R^2, R^3 is substituted with a water-solubilizing functional radical selected from the group consisting of quaternary ammonium salts, carboxylic acid, phosphoric acid, phosphonic acid, sulfuric acid, sulphonic acid and their salt derivatives.

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/EP 97/01831

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/39 C07C307/02 C07C307/06 C07C307/10 C07D291/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D C07C C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 041 232 A (BATAL DAVID J ET AL) 20 August 1991 cited in the application see the whole document ---	1-19
A	EP 0 446 982 A (UNILEVER NV ;UNILEVER PLC (GB)) 18 September 1991 see the whole document ---	1-19
A	US 3 317 523 A (WRIGHT J.B.) 2 May 1967 ---	1,19
A	JOURNAL OF ORGANIC CHEMISTRY, vol. 51, no. 26, 1986, pages 5405-5408, XP002039946 ETTER ET AL. : "An Enolized Sulfonamide Formed by Strong Hydrogen Bonding to Triphenylphosphine Oxide" --- -/--	19

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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1

Date of the actual completion of the international search	Date of mailing of the international search report
5 September 1997	17.09.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Grittern, A

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INTERNATIONAL SEARCH REPORT

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PCT/EP 97/01831

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SYNTHESIS, 1981, pages 272-273, XP002039947 KAMAL ET AL.: cited in the application -----	

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int onal Application No
PCT/EP 97/01831

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5041232 A	20-08-91	AU 636724 B	06-05-93
		AU 7287091 A	19-09-91
		CA 2037800 A	17-09-91
		DE 69104405 D	10-11-94
		DE 69104405 T	09-02-95
		EP 0453003 A	23-10-91
		ES 2061156 T	01-12-94
		IN 171767 A	02-01-93
		JP 4227697 A	17-08-92
		JP 7049597 B	31-05-95
		KR 9502353 B	16-03-95
		NO 177431 B	06-06-95
		US 5463115 A	31-10-95
EP 0446982 A	18-09-91	US 5047163 A	10-09-91
		AU 635620 B	25-03-93
		AU 7287391 A	19-09-91
		CA 2038209 A	17-09-91
		DE 69104751 D	01-12-94
		DE 69104751 T	02-03-95
		ES 2062662 T	16-12-94
		JP 7070597 A	14-03-95
		JP 8000920 B	10-01-96
		KR 9503427 B	12-04-95
		NO 177432 B	06-06-95
US 3317523 A	02-05-67	CH 478138 A	15-09-69
		DE 1620624 A	14-05-70
		FR 1472694 A	25-05-67
		GB 1073836 A	
		NL 6604032 A	30-09-66