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(71) Applicant:
THE PROCTER & GAMBLE COMPANY
Cincinnati, Ohio 45202 (US)

(72) Inventors:
- **Bianchetti, Giulia Ottavia**
  00144 Roma (IT)
- **Scialla, Stefano, (NMN)**
  00128 Roma (IT)

(74) Representative:
Engisch, Gautier et al
Procter & Gamble
European Technical Center N.V.
Temselaan 100
1853 Strombeek-Bever (BE)

(54) Peracids, stable aqueous compositions comprising peracids, and a process for forming said peracids

(57) The present invention relates to aqueous compositions comprising a peracid of the formula H000C-Ra-Y wherein Ra is a linear or branched alkyl or aryl group of 1 to 30 carbon atoms, and Y is SO_3^-, $N(Rb)_3^+$ or $HO(CH2CH2O)_n$, wherein Rb is a linear or branched alkyl or aryl group of from 1 to 8 carbon atoms, and n is an integer of 1 to 40, or mixtures thereof. The present invention further relates to peracids having the formula H000C-Ra-Y wherein Ra is a linear or branched alkyl or aryl group of 1 to 30 carbon atoms, Y is $HO(CH2CH2O)_n$, and n is an integer of 1 to 40, precursors thereof and to a process for forming such peracids.

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Description

Technical field

The present invention relates to stable aqueous compositions comprising peroxy carboxylic acids (i.e., peracids). These aqueous compositions according to the present invention are particularly suitable to be used in various applications such as in laundry applications, or as hard-surface cleaners or as carpet cleaners, or as denture cleaners or as disinfecting compositions in general.

Background

A great variety of cleaning compositions have been described in the art. Indeed, compositions comprising hydrogen peroxide, and/or water soluble sources thereof including peracids are known. In order to provide such compositions comprising peracids, it is common practice to use peracid precursors as a source of said peracids. Peracids are not commonly commercially available, and if available they may not be used satisfactorily, because they are not stable and tend to decompose dramatically during storage in aqueous compositions.

It is therefore an object of the present invention to provide stable aqueous compositions comprising peracids.

We have now found that this object can be efficiently met by incorporating in an aqueous composition a dual function peracid. By "dual function peracid" it is meant herein a peracid which has both a percarboxylic group and a charged head or a head of higher polarity than the percarboxylic group. Accordingly, it has now been found that improved stability is obtained by incorporating in an aqueous composition a dual function peracid having the general formula of H000C-Ra-Y wherein Ra is a linear or branched alkyl or aryl group of 1 to 30 carbon atoms and Y is SO_3^-, $N(Rb)_3^+$ or HO $(CH2CH2O)_n$, wherein Rb is a linear or branched alkyl or aryl group of from 1 to 8 carbon atoms, and n is 1 to 40.

An advantage of the aqueous compositions herein is that they do not necessarily require the presence of surfactants to perform good cleaning performance. Thus, the present invention encompasses one embodiment wherein the aqueous compositions herein are free of surfactants. Indeed, the dual function peracids according to the present invention not only deliver excellent bleaching performance but also good cleaning performance. In other words, these dual function peracids allow to achieve concomitantly stain removal through solubilization/emulsification of various stains like greasy stains such as make-up, vegetal oil, spaghetti, and bleaching of bleachable stains like coffee, tea and the like.

Different types of peracids or precursors thereof have been described in the art. EP-A-170 386 discloses a bleaching composition which provides in an aqueous solution an amide substituted peroxyacid of the formula R1-CO-N-R2R5-COOOH or R1-N-R5-CO-R2-COOOH, wherein R1 is an aryl or alkaryl group with from 1 to 14 carbon atoms, R2 is an alkylene, arylene or alkarylene group containing from 1 to 14 carbon atoms, and R5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms.

EP-A-267 047 and EP-A-373 743 disclose a peracid precursor having the formula R-CO-O-C-R'R''-CO-L, wherein R may represent C1-C20 linear or branched alkyl, alkylethoxylated, cycloalkyl, aryl, substituted aryl, R' and R'' may independently represent H, C1-20 alkylaryl, substituted aryl and $NR3^+$, wherein R may represent C1-C30 alkyl and L may represent essentially any useful leaving group which may be displaced in a peroxygen bleaching solution by perhydroxide anion.

EP-A-390 393 discloses polyglycolate peracid precursors of the formula $R\text{-}CO\text{-}(O\text{-}C\text{-}R'R''\text{-}CO)_n\text{-}L$, wherein n is an integer from 2 to 10, R is C1-20 linear or branched alkyl, alkoxylated alkyl, cycloalkyl, aryl alkyaryl, substituted aryl, R' and R'' are independently H, C1-20 alkyl, C1-20 aryl, C1-20 alkylaryl, substituted aryl and $NR3^+$ wherein R may represent C1-C30 alkyl and L may represent essentially any useful leaving group which may be displaced in a peroxygen bleaching solution by perhydroxide anion.

EP-A-267 046 discloses bleaching compositions comprising a source of hydrogen peroxide and as a bleach activator of the general formula (i) $R\text{-}X\text{-}(CH2)_n\text{-}CO\text{-}O\text{-}N\text{-}R1$ wherein R represents C1-20 alkyl, alkoxyl, or cycloalkyl, R1 represents a group which contains at least one carbon atom which is singly bonded directly to N; n represents an integer of from 1 to 6 and X represents methylene or a heteroatom, or (ii) R-X-(CH2)n-COO-N=R2, wherein n is as defined above, R2 represents a group which contains a carbon atom doubly bonded directly to N, and either X represents a heteroatom, R represents C4-C17 alkyl or both.

EP-A-331 229 discloses quaternary ammonium peHOarboxylic acid precursors of formula $R1R2R3N^+\text{-}R4\text{-}CO\text{-}L$, corresponding peracids and compositions comprising them. The bleaching compositions disclosed are powders or non-aqueous liquid compositions.

GB 1147 871 discloses peracid precursors of the formula SO3M-substituted benzene ring-OCOR, wherein R is hydrogen or an alkyl radical having 1-7 carbon atoms and M is an alkali metal, ammonium or substituted ammonium radical, and the corresponding peracid (HOOOCOR). The precursor is said to possess detergent and emulsifying properties comparable to alkylbenzene sulphonate on top of its peracid precursor activity. The corresponding peracids do not have this dual function.

US-4 259 201 discloses granular bleaching compositions with peroxyacid compounds of the formula HO-O-CO-R-Y wherein R is an alkyl or alkylene group containing from 1 to 20 carbon atoms and Y may be SO_3M, M being either hydrogen or a cation which preferably provides a wash-water-soluble and/or water dispersible wash-compound.

Summary of the invention

The present invention encompasses an aqueous composition comprising from 0.1% to 40% by weight of the total composition of a peracid of the formula H000C-Ra-Y wherein Ra is a linear or branched alkyl or aryl group of 1 to 30 carbon atoms, and Y is SO_3^-, $N(Rb)_3^+$ or $HO(CH2CH2O)_n$, wherein Rb is a linear or branched alkyl or aryl group of from 1 to 8 carbon atoms, and n is an integer of 1 to 40, or mixtures thereof.

In another embodiment the present invention encompasses a peracid, suitable for use in an aqueous composition according to the present invention, said peracid having the formula H000C-Ra-Y wherein Ra is a linear or branched alkyl or aryl group of 1 to 30 carbon atoms and Y is $HO(CH2CH2O)_n$, wherein n is an integer of 1 to 40.

The present invention further encompasses a process for forming a peracid having the formula H000C-Ra-Y wherein Ra is a linear or branched alkyl or aryl group of 1 to 30 carbon atoms and Y is $HO(CH2CH2O)_n$, wherein n is an integer of 1 to 40, said process comprising the step of reacting in an aqueous medium the corresponding peracid precursor with hydrogen peroxide or a water-soluble source thereof.

In yet another embodiment the present invention further encompasses a peracid precursor of the formula $HO\text{-}(CH2\text{-}CH2O)_n\text{-}Ra\text{-}CO\text{-}O\text{-}CO\text{-}Ra\text{-}(OCH2\text{-}CH2)_n\text{-}OH$ or $HO\text{-}(CH2\text{-}CH2O)_n\text{-}Ra\text{-}CO\text{-}OH$, wherein Ra is a linear or branched alkyl or aryl group of 1 to 30 carbon atoms, wherein n is an integer of 1 to 40.

Finally, the present invention also encompasses a bleaching composition comprising a peracid precursor as defined above and hydrogen peroxide or a water-soluble source thereof.

Detailed description of the invention

Aqueous compositions comprising the peracids

In one embodiment the present invention is an aqueous composition comprising a dual function peracid.

Thus, the aqueous compositions of the present invention comprise as an essential ingredient a peracid according to the formula

H000C-Ra-Y

wherein Ra is a linear or branched alkyl or aryl group of 1 to 30 carbon atoms, preferably 1 to 20, more preferably 2 to 18 and most preferably 4 to 16, Y is SO_3^-, $N(Rb)_3^+$ or $HO(CH2CH2O)_n$, wherein Rb is a linear or branched alkyl or aryl group of from 1 to 8 carbon atoms, preferably 1 to 6 and more preferably from 2 to 4, and n is an integer of 1 to 40, preferably from 2 to 20 and more preferably 2 to 12.

Particularly suitable peracids to be used herein include

$HOOOC\text{-}(CH_2)_5\text{-}SO_3\text{-}$, $HOOOC\text{-}(CH_2)_7N(CH_3)_3^+$,
$HOOOC\text{-}(CH_2)_3\text{-}(OCH_2CH_2)_3\text{-}OH$, $HOOOC\text{-}(CH_2)_9\text{-}(OCH_2CH_2)_{10}OH$,
$HOOOC\text{-}(CH_2)_{15}\text{-}(OCH_2CH_2)_3\text{-}OH$ or mixtures thereof.

The aqueous compositions of the present invention comprise from 0.1% to 40% by weight of the total composition of said dual function peracid or mixtures thereof, preferably from 1 % to 20%, more preferably from 1.5% to 18% and most preferably from 2% to 15%.

It has now been found that the aqueous compositions of the present invention comprising such a dual function peracid exhibit improved chemical stability upon storage.

Indeed, the aqueous compositions according to the present invention comprising a peracid as described hereinabove generally do not undergo more than 30% available oxygen loss, in one month at 20 °C, more preferably not more than 50% available oxygen loss. Peracid concentration can be measured by analysing the peracid available oxygen (often abbreviated to Avox). Test method to evaluate peracid Avox is done via chromatography (see F. Di Furia et. alt., Gas-liquid chromatography method for determination of peracids, Analyst, vol. 109, August 1984, p. 985-987; or ibidem vol. 113, May 1988, p. 793-795).

It is believed that in aqueous medium the dual function peracids form micelles. In these micelles, the charged head or the head of higher polarity (e.g. ethoxylated groups) than the percarboxylic group of the dual function peroxide is oriented towards the water phase while the percarboxylic group is oriented towards the inner part of the micelles. This results in percarboxylic groups that are protected, i.e., they are less subject to hydrolysis.

Another advantage of the aqueous compositions of the present invention is that they exhibit at the same time excellent bleaching performance as well as excellent cleaning performance on different types of stains including greasy stains due to the presence of one single ingredient, the dual function peracid.

However, in applications where it is intended to clean heavily soiled surfaces, the aqueous compositions according to the present invention may further comprise optional ingredients including surfactants, as well as other optional ingredients selected from the group consisting of hydrogen peroxide or a water-soluble source thereof, soil suspending agents, builders, chelants, bleach activators, radical scavengers, pigments, enzymes, dye transfer inhibitors, solvents, buffering agents, suds suppressing agents, photobleaching agents, dyes, perfumes and mixtures thereof.

The aqueous compositions according to the present invention may be used as laundry detergent, as laundry pretreaters, i.e., compositions which are dispensed and left to act onto fabrics before they are washed, or as laundry additives to be used together with detergents to boost their performance. These compositions may also be particularly suitable as dishwashing compositions to be used either in the dishwashing machines or by hand, or as carpet cleaners to be used either by direct application onto the carpets or in carpet cleaning machines, or as toilet bowl cleaners or as hard surface cleaners or as denture cleaners.

Particular peracids

In another embodiment the present invention is a particular dual function peracid, suitable for use in the aqueous compositions herein. Said dual function peracid according to the present invention has the general formula H000C-Ra-Y wherein Ra is a linear or branched alkyl or aryl group of 1 to 30 carbon atoms, preferably from 1 to 20, more preferably from 2 to 18 and most preferably from 4 to 16, and Y is HO (CH2CH2O)$_n$, wherein n is an integer of 1 to 40, preferably is 2 to 20 and more preferably 2 to 12.

Preferred peracids herein are:

$HOOOC\text{-}(CH_2)_3\text{-}(OCH_2CH_2)_3\text{-}OH$; $HOOOC\text{-}(CH_2)_9\text{-}(OCH_2CH_2)_3OH$;
$HOOOC\text{-}(CH_2)_{15}\text{-}(OCH_2CH_2)_3\text{-}OH$; $HOOOC\text{-}(CH_2)_{11}\text{-}(OCH_2CH_2)_3\text{-}OH$;
$HOOOC\text{-}(CH_2)_3\text{-}(OCH_2CH_2)_{10}OH$; $HOOOC\text{-}(CH_2)_9\text{-}(OCH_2CH_2)_{10}OH$;
$HOOOC\text{-}(CH_2)_{15}\text{-}(OCH_2CH_2)_{10}\text{-}OH$; $HOOOC\text{-}(CH_2)_{11}\text{-}(OCH_2CH_2)_{10}\text{-}OH$;
$HOOOC\text{-}(CH_2)_{15}\text{-}(OCH_2\text{-}CH_2)_7\text{-}OH$; $HOOOC\text{-}(CH_2)_9\text{-}(OCH_2\text{-}CH_2)_{14}\text{-}OH$,
$HO\text{-}(CH_2\text{-}CH_2O)_{14}\text{-}(CH_2)9\text{-}COOOH$ or mixtures thereof.

Said peracids have the advantage to act both as a surfactant, i.e., that they possess detergent and emulsifying properties comparable to ethoxylated nonionic surfactants and as peracids.

The process for forming the particular peracids

The dual function peracids hereinbefore may be formed by a process comprising the step of reacting in an aqueous medium the corresponding peracid precursor with hydrogen peroxide or a water-soluble source thereof. Thus, the present invention also encompasses a process for forming such a peracid.

As a first essential element, the process of the present invention requires the use of the corresponding peracid precursor or mixtures thereof. By "the corresponding peracid precursor" it is meant herein a compound that allows to obtain the desired peracid by reaction in an aqueous medium with hydrogen peroxide or a source thereof. Peroxidation is the reaction which occurs when the peracid precursor is combined in an aqueous reaction medium, preferably an acidic aqueous medium, with hydrogen peroxide or a source thereof.

Accordingly, the present invention also encompasses the peracid precursors of the formula

$$HO\text{-}(CH_2\text{-}CH_2O)_n\text{-}Ra\text{-}CO\text{-}O\text{-}CO\text{-}Ra\text{-}(OCH_2\text{-}CH_2)_n\text{-}OH, \text{ or } HO\text{-}(CH_2\text{-}CH_2O)_n\text{-}Ra\text{-}CO\text{-}OH,$$

wherein Ra a linear or branched alkyl or aryl group of from 1 to 30 carbon atoms, preferably from 1 to 20, more preferably from 2 to 18, and n is an integer of 1 to 40 and preferably from 2 to 20.

In the present invention the peracid precursor reacts with hydrogen peroxide or a source thereof to provide the corresponding peracid. Particularly suitable peracid precursors to be used herein are:

$HO\text{-}(CH_2\text{-}CH_2O)10\text{-}(CH_2)_9\text{-}CO\text{-}O\text{-}CO\text{-}(CH_2)_9\text{-}(OCH_2\text{-}CH_2)_{10}\text{-}OH$,
$HO\text{-}(CH_2\text{-}CH_2O)_3\text{-}(CH_2)_{11}\text{-}CO\text{-}O\text{-}CO\text{-}(CH_2)_{11}\text{-}(OCH_2\text{-}CH_2)_3\text{-}OH$,
$HO\text{-}(CH_2\text{-}CH_2O)_7\text{-}(CH_2)_{15}\text{-}CO\text{-}O\text{-}CO\text{-}(CH_2)_{15}\text{-}(OCH_2\text{-}CH_2)_7\text{-}OH$,
$HO\text{-}(CH_2\text{-}CH_2O)_{14}\text{-}(CH_2)_9\text{-}CO\text{-}O\text{-}CO\text{-}(CH_2)_9\text{-}(OCH_2\text{-}CH_2)_{14}\text{-}OH$,

$HO-(CH_2-CH_2O)_7-(CH_2)_{15}-COOH$,
$HO-(CH_2-CH_2O)_{10}-(CH_2)_{11}-COOH$,
$HO-(CH_2-CH_2O)_{14}-(CH_2)_9-COOH$, or mixtures thereof.

Particularly preferred herein are $HO-(CH_2-CH_2O)_{10}-(CH_2)9-CO-O-CO-(CH_2)9-(OCH_2-CH_2)_{10}-OH$, and $HO-(CH_2-CH_2O)_3-(CH_2)_{15}-COOH$.

As a second essential element, the process of the present invention requires the use of hydrogen peroxide or a water-soluble source thereof or mixtures thereof.

As used herein a hydrogen peroxide source refers to any compound which produces hydrogen peroxide when said compound is in contact with water. Suitable water-soluble sources of hydrogen peroxide for use herein include percarbonates, and perborates. Hydrogen peroxide is most preferred to be used herein.

By "aqueous medium" it is meant herein that the reaction is conducted in presence of water. The amount of water used depends on the end product desired and is at the discretion of the process operator. It is often convenient to use the required amount of water either directly when contacting the precursor and hydrogen peroxide or a source thereof or in a subsequent step so as to provide an aqueous composition that has a peracid concentration of from 0.1% to 40% by weight of the total composition as defined hereinbefore.

Typically, the process according to the present invention requires at least 1.1 moles of hydrogen peroxide or a water-soluble source thereof per molar equivalent of the precursor, preferably at least 1.5 and more preferably at least 2.

Accordingly, in the preferred embodiment where a solution of hydrogen peroxide or a water-soluble source thereof is used in the process of the present invention said solution comprises from 15% to 90% by weight of hydrogen peroxide or a water-soluble source thereof or mixtures thereof, more preferably from 20% to 80% and most preferably from 25% to 70%.

Typically, in the process according to the present invention the peracid precursor is reacted with hydrogen peroxide or a water-soluble source thereof in presence of an aqueous solution of a strong acid or mixtures thereof. By "strong acid" it is meant herein an acid having its first pka below 3, preferably below 2 and more preferably below 1. Said aqueous solution of strong acids may serve as the reaction aqueous medium and as a catalyst. Said strong acids include mineral acids and/or organic sulphonic acid. Preferred strong acids to be used herein are sulphuric acid, phosphonic acid and/or methane sulphonic acid.

In the process according to the present invention said aqueous solution of a strong acid or mixtures thereof, comprises from 90% to 98% by weight of said strong acid, more preferably from 95% to 98% and most preferably from 97% to 98%. Accordingly, the present process is typically conducted in the acidic range at a pH below 7, preferably up to 5, more preferably up to 2, most preferably below 0.5.

By using such aqueous solution of a strong acid it is possible to enable the reaction to occur at a convenient rate without the use of elevated reaction temperature. The temperature at which the present process is conducted also depends on the concentration of the solution of hydrogen peroxide or a source thereof used. For example, if a very concentrated solution of hydrogen peroxide is used (e.g., 70%), the reaction is preferably conducted around 20°C. If a less concentrated solution of hydrogen peroxide is used (e.g., 36%), the reaction is preferably conducted at room temperature, e.g., 25°C or higher. For convenience, coupled with safety considerations, the reaction temperature is maintained in many embodiments in the range that is from 0°C to 40°C.

The process of the present invention allows to form not only peracid-containing aqueous compositions being raw material aqueous compositions but also, fully formulated aqueous detergent compositions, i.e., compositions incorporating further ingredients commonly used in the detergent field.

Accordingly, the process of forming said peracid may further comprise a step where at least one ingredient, other than water, hydrogen peroxide or a water-soluble source thereof and peracid precursor is provided.

The additional ingredient provided is preferably selected from the group consisting of surfactants, soil suspending agent, builders, chelants, bleach activators, radical scavengers, pigments, enzymes, dye transfer inhibitors, solvents, buffering agents, suds suppressing agents, photobleaching agents, dyes, perfumes and the like, and mixtures thereof. Depending on the intended end use of the aqueous compositions according to the process of the present invention, different combinations of these optional ingredients may be provided in the process herein.

Aqueous compositions comprising the precursor for the particular peracid

The present invention also encompasses aqueous compositions comprising a peracid precursor as defined hereinbefore, hydrogen peroxide or a water-soluble source thereof and optionally an additional ingredient as defined herein above.

Typically, said aqueous compositions comprise from 0.1 % to 40% by weight of the total composition of said peracid precursor, or mixtures thereof, preferably from 0.5% to 30%, and more preferably from 1% to 20% and from 0.1% to

40% by weight of the total composition of hydrogen peroxide or a water-soluble source thereof, preferably from 0.5% to 30% and more preferably from 1% to 20%.

These aqueous compositions according to the present invention may be used as laundry detergent, as laundry pretreaters, i.e. compositions which are dispensed and left to act onto fabrics before they are washed, or as laundry additives to be used together with detergents to boost their performance. These compositions may also be particularly suitable as dishwashing compositions to be used either in the dishwashing machines or by hand, or as carpet cleaners to be used either by direct application onto the carpets or in carpet cleaning machines, or as toilet bowl cleaners or as hard surface cleaners or as denture cleaners.

Optionals

The following optional ingredients may be added in the compositions according to the present invention. Accordingly, the compositions according to the present invention may comprise up to 50% by weight of the total composition of a surfactant or mixtures thereof, preferably from 0.01% to 30% and more preferably from 0.1% to 25%. Surfactants for use herein are well known in the art and include anionic, nonionic, amphoteric, zwitterionic and cationic surfactants and mixtures thereof. The surfactants suitable for use herein are compatible with hydrogen peroxide and sources thereof and peracids herein. They also contribute to the cleaning performance of a composition herein.

Particularly suitable anionic surfactants to be used herein include water soluble salts or acids of the formula $ROSO_3M$ wherein R is preferably a C_6-C_{24} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_{10}-C_{20} alkyl component, more preferably a C_{12}-C_{18} alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like).

Other suitable anionic surfactants to be used herein include alkyl-diphenylether-sulphonates and alkyl-carboxylates. Other anionic surfactants can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_9-C_{20} linear alkylbenzenesulfonates, C_8-C_{22} primary or secondary alkanesulfonates, C_8-C_{24} olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C_8-C_{24} alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl ester sulfonates such as $C_{14\text{-}16}$ methyl ester sulfonates; acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6-C_{14} diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_kCH_2COO\text{-}M^+$ wherein R is a C_8-C_{22} alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

Preferred anionic surfactants for use in the compositions herein are the alkyl benzene sulfonates, alkyl sulfates, alkyl alkoxylated sulfates, and mixtures thereof.

Suitable nonionic surfactants to be used herein are fatty alcohol ethoxylates and/or propoxylates which are commercially available with a variety of fatty alcohol chain lengths and a variety of ethoxylation degrees. Indeed, the HLB values of such alkoxylated nonionic surfactants depend essentially on the chain length of the fatty alcohol, the nature of the alkoxylation and the degree of alkoxylation. Surfactant catalogues are available which list a number of surfactants, including nonionics, together with their respective HLB values.

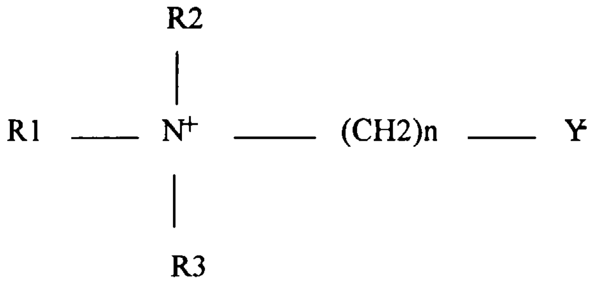
Suitable chemical processes for preparing the nonionic surfactants for use herein include condensation of corresponding alcohols with alkylene oxide, in the desired proportions. Such processes are well known to the man skilled in the art and have been extensively described in the art. As an alternative, a great variety of alkoxylated alcohols suitable for use herein is commercially available from various suppliers.

Accordingly, suitable nonionic surfactants for use herein are Dobanol ^{R} 91-2.5 (HLB=8.1; R is a mixture of C9 and C_{11} alkyl chains, n is 2.5 and m is 0), or Lutensol ^{R} TO3 (HLB=8; R is a C_{13} alkyl chains, n is 3 and m is 0), or Lutensol ^{R} AO3 (HLB=8; R is a mixture of C_{13} and C_{15} alkyl chains, n is 3 and m is 0), or Tergitol ^{R} 25L3 (HLB= 7.7; R is in the range of C_{12} to C_{15} alkyl chain length, n is 3 and m is 0), or Dobanol ^{R} 23-3 (HLB=8.1; R is a mixture of C_{12} and C_{13} alkyl chains, n is 3 and m is 0), or Dobanol ^{R} 23-2 (HLB=6.2; R is a mixture of C_{12} and C_{13} alkyl chains, n is 2 and m is

0), or Dobanol ^{R} 45-7 (HLB=11.6; R is a mixture of C_{14} and C_{15} alkyl chains, n is 7 and m is 0) Dobanol ^{R} 23-6.5 (HLB=11.9; R is a mixture of C_{12} and C_{13} alkyl chains, n is 6.5 and m is 0), or Dobanol ^{R} 25-7 (HLB=12; R is a mixture of C_{12} and C_{15} alkyl chains, n is 7 and m is 0), or Dobanol ^{R} 91-5 (HLB=11.6; R is a mixture of C_9 and C_{11} alkyl chains, n is 5 and m is 0), or Dobanol ^{R} 91-6 (HLB=12.5 ; R is a mixture of C_9 and C_{11} alkyl chains, n is 6 and m is 0), or Dobanol ^{R} 91-8 (HLB=13.7 ; R is a mixture of C_9 and C_{11} alkyl chains, n is 8 and m is 0), Dobanol ^{R} 91-10 (HLB=14.2 ; R is a mixture of C_9 to C_{11} alkyl chains, n is 10 and m is 0), or mixtures thereof. Preferred herein are Dobanol ^{R} 91-2.5 , or Lutensol ^{R} TO3, or Lutensol ^{R} AO3, or Tergitol ^{R} 25L3, or Dobanol ^{R} 23-3, or Dobanol ^{R} 23-2, or mixtures thereof. These Dobanol^{R} surfactants are commercially available from SHELL. These Lutensol^{R} surfactants are commercially available from BASF and these Tergitol ^{R} surfactants are commercially available from UNION CARBIDE.

Other nonionic surfactants include fatty acid C_6-C_{24} alkanolamides, C_6-C_{20} polyethylglycol ethers, polyethylene glycol with molecular weight 1000 to 80000 and glucose amides and alkyl pyrrolidones.

Suitable amphoteric surfactants to be used herein include betaine and sulphobetaine surfactants, derivatives thereof or mixtures thereof. Suitable betaine and sulphobetaine surfactants to be used herein are the betaine/sulphobetaine and betaine-like detergents wherein the molecule contains both basic and acidic groups which form an inner salt giving the molecule both cationic and anionic hydrophilic groups over a broad range of pH values. Some common examples of these detergents are described in U.S. Pat. Nos. 2,082,275, 2,702,279 and 2,255,082, incorporated herein by reference. Preferred betaine and sulphobetaine surfactants herein are according to the formula



$$R1 - \overset{\displaystyle R2}{\underset{\displaystyle R3}{N^{+}}} - (CH2)n - Y^{-}$$

wherein R1 is an alkyl radical containing from about 1 to about 24 carbon atoms, preferably from 8 to 18, and more preferably from 12 to 14, wherein R2 and R3 contain from 1 to 3 carbon atoms, and preferably 1 carbon atom, wherein n is an integer from 1 to 10, preferably from 1 to 6 and more preferably is 1, Y is selected from the group consisting of carboxyl and sulfonyl radicals and wherein the sum of R1, R2 and R3 radicals is from 14 to 24 carbon atoms, or mixtures thereof.

Examples of particularly suitable betaine surfactants include C12-C18 alkyl dimethyl betaine such as coconutbetaine and C10-C16 alkyl dimethyl betaine such as laurylbetaine. Coconutbetaine is commercially available from Seppic under the trade name of Amonyl 265®. Laurylbetaine is commercially available from Albright & Wilson under the trade name Empigen BB/L®.

Other suitable amphoteric surfactants to be used herein include amine oxides having the following formula $R_1R_2R_3NO$ wherein each of R1, R2 and R3 is independently a saturated substituted or unsubstituted, linear or branched alkyl groups of from 1 to 30 carbon atoms, preferably of from 6 to 30 carbon atoms, more preferably of from 10 to 20 carbon atoms, and most preferably of from 8 to 18 carbon atoms. Preferred amine oxides for use herein are for instance natural blend C8-C10 amine oxides as well as C12-C16 amine oxides commercially available from Hoechst. Suitable short chain amine oxides to be used according to the present invention are amine oxides having the following formula $R_1R_2R_3NO$ wherein R1 is a C6 to C10 alkyl group, preferably a C8 to C10 alkyl group and wherein R2 and R3 are independently substituted or unsubstituted, linear or branched alkyl groups of from 1 to 4 carbon atoms, preferably of from 1 to 3 carbon atoms, and more preferably are methyl groups. R1 may be a saturated linear or branched alkyl group. Preferred short chain amine oxides for use herein are for instance natural blend C8-C10 amine oxides available from Hoechst.

Suitable cationic surfactants to be used herein include derivatives of quaternary ammonium, phosphonium, imidazolium and sulfonium compounds. Preferred cationic surfactants for use herein are quaternary ammonium compounds wherein one or two of the hydrocarbon groups linked to nitrogen are a saturated, linear or branched alkyl group of 6 to 30 carbon atoms, preferably of 10 to 25 carbon atoms, and more preferably of 12 to 20 carbon atoms, and wherein the other hydrocarbon groups (i.e. three when one hydrocarbon group is a long chain hydrocarbon group as mentioned hereinbefore or two when two hydrocarbon groups are long chain hydrocarbon groups as mentioned hereinbefore) linked to the nitrogen are independently substituted or unsubstituted, linear or branched, alkyl chain of from 1 to 4 carbon atoms, preferably of from 1 to 3 carbon atoms, and more preferably are methyl groups. The counterion used in said quaternary ammonium compounds are selected from the group of methyl sulfate, or methylsulfonate, and the like.

Particularly preferred cationic surfactants to be used herein are trimethyl quaternary ammonium compounds like myristyl trimethylsulfate, cetyl trimethylsulfate and/or tallow trimethylsulfate. Such trimethyl quaternary ammonium compounds are commercially available from Hoechst, or from Albright & Wilson under the trade name EMPIGEN CM®.

Suitable zwitterionic surfactants contain both cationic and anionic hydrophilic groups on the same molecule at a relatively wide range of pH's. The typical cationic group is a quaternary ammonium group, although other positively charged groups like phosphonium, imidazolium and sulfonium groups can be used. The typical anionic hydrophilic groups are carboxylates and sulfonates, although other groups like sulfates, phosphonates, and the like can be used. A generic formula for some preferred zwitterionic surfactants is

$$R_1\text{-}N^{+}(R_2)(R_3)R_4X^{-}$$

wherein R_1 is a hydrophobic group; R_2 and R_3 are each C_1-C_4 alkyl, hydroxy alkyl or other substituted alkyl group which can also be joined to form ring structures with the N; R_4 is a moiety joining the cationic nitrogen atom to the hydrophilic group and is typically an alkylene, hydroxy alkylene, or polyalkoxy group containing from 1 to 4 carbon atoms; and X is the hydrophilic group which is preferably a carboxylate or sulfonate group. Preferred hydrophobic groups R_1 are alkyl groups containing from 8 to 22, preferably less than 18, more preferably less than 16 carbon atoms. The hydrophobic group can contain unsaturation and/or substituents and/or linking groups such as aryl groups, amido groups, ester groups and the like. In general, the simple alkyl groups are preferred for cost and stability reasons.

Other specific zwitterionic surfactants have the generic formulas:

$$R_1\text{-}C(O)\text{-}N(R_2)\text{-}(C(R_3)_2)_n\text{-}N(R_2)_2^{(+)}\text{-}(C(R_3)_2)_n\text{-}SO_3^{(-)}$$

or

$$R_1\text{-}C(O)\text{-}N(R_2)\text{-}(C(R_3)_2)_n\text{-}N(R_2)_2^{(+)}\text{-}(C(R_3)_2)_n\text{-}COO^{(-)}$$

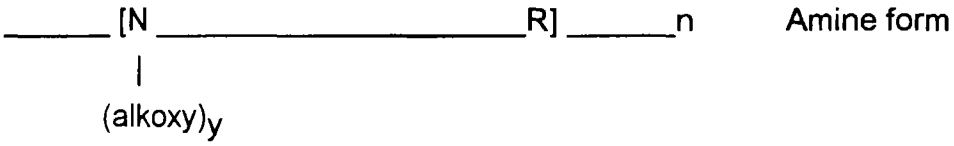
wherein each R_1 is a hydrocarbon, e.g. an alkyl group containing from 8 up to 20, preferably up to 18, more preferably up to 16 carbon atoms, each R_2 is either a hydrogen (when attached to the amido nitrogen), short chain alkyl or substituted alkyl containing from one to 4 carbon atoms, preferably groups selected from the group consisting of methyl, ethyl, propyl, hydroxy substituted ethyl or propyl and mixtures thereof, preferably methyl, each R_3 is selected from the group consisting of hydrogen and hydroxy groups and each n is a number from 1 to 4, preferably from 2 to 3, more preferably 3, with no more than one hydroxy group in any $(C(R_3)_2)$ moiety. The R_1 groups can be branched and/or unsaturated. The R_2 groups can also be connected to form ring structures. A surfactant of this type is a C_{10}-C_{14} fatty acylamidopropylene(hydroxypropylene)sulfobetaine that is available from the Sherex Company under the trade name "Varion CAS sulfobetaine"®.

Any soil suspending polycarboxylate polymer known to those skilled in the art can be used in the compositions according to the present invention such as homo- or co-polymeric polycarboxylic acids or their salts including polyacrylates and copolymers of maleic anhydride or/and acrylic acid and the like. Indeed, such soil suspending polycarboxylate polymers can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein of monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates to be used herein can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued march 7, 1967.

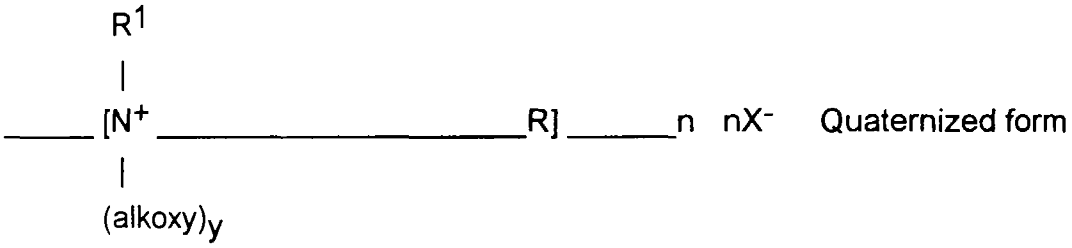
Acrylic/maleic-based copolymers may also be used as a preferred soil suspending polycarboxylic polymer. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982. Particularly preferred is a copolymer of maleic / acrylic acid with an average molecular weight of about 70,000. Such copolymers are commercially available from BASF under the trade name SOKALAN CP5.

Any soil suspending polyamine polymer known to those skilled in the art may also be used herein. Particularly suitable polyamine polymers for use herein are polymers having polyalkoxymoiety are alkoxylated polyamines. Such materials can conveniently be represented as molecules of the empirical structures with repeating units:



$$\underset{(\text{alkoxy})_y}{\underset{|}{[\text{N}}}\text{———}\text{R}]\text{—}_n \quad \text{Amine form}$$

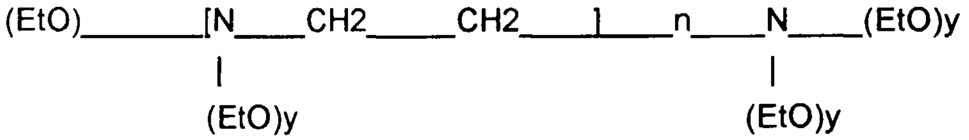
and



$$\underset{(\text{alkoxy})_y}{\underset{|}{\overset{\overset{R^1}{|}}{[\text{N}^+}}}\text{———}\text{R}]\text{—}_n \; nX^- \quad \text{Quaternized form}$$

wherein R is a hydrocarbyl group, usually of 2-6 carbon atoms; R^1 may be a C_1-C_{20} hydrocarbon; the alkoxy groups are ethoxy, propoxy, and the like, and y is 2-30, most preferably from 10-20; n is an integer of at least 2, preferably from 2-20, most preferably 3-5; and X^- is an anion such as halide or methylsulfate, resulting from the quaternization reaction.

The most highly preferred polyamines for use herein are the so-called ethoxylated polyethylene amines, i.e., the polymerized reaction product of ethylene oxide with ethyleneimine, having the general formula:



$$(\text{EtO})\text{—}\underset{(\text{EtO})y}{\underset{|}{[\text{N}}}\text{—CH2—CH2—}]\text{—}n\text{—}\underset{(\text{EtO})y}{\underset{|}{\text{N}}}\text{—}(\text{EtO})y$$

when y = 2-30. Particularly preferred for use herein is an ethoxylated polyethylene amine, in particular ethoxylated tetraethylenepentamine, and quaternized ethoxylated hexamethylene diamine.

The compositions according to the present invention may comprise up to 10% by weight of the total composition of a soil suspending polycarboxylate polymer and/or polyamine polymer, preferably from 0.01% to 5% and more preferably from 0.1% to 1%.

Suitable chelating agents to be used in the compositions according to the present invention include any chelating agent known to those skilled in the art. Suitable chelating agents include for example phosphonate chelating agents, polyfunctionally-substituted aromatic chelating agents, amino carboxylate chelating agents, other chelating agents like ethylene diamine N,N'- disuccinic acid and mixtures thereof.

Suitable phosphonate cheating agents to be used herein may include ethydronic acid, alkali metal ethane 1-hydroxy diphosphonates as well as amino phosphonate compounds, including amino alkylene poly (alkylene phosphonate), alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates, and diethylene triamine penta methylene phosphonates. The phosphonate compounds may be present either in their acid form or as salts of different cations on some or all of their acid functionalities. Preferred phosphonate chelating agents to be used herein are diethylene triamine penta methylene phosphonates (DETPMP). Such phosphonate cheating agents are commercially available from Monsanto under the trade name DEQUEST®.

Polyfunctionally-substituted aromatic chelating agents may also be useful in the compositions herein. See U.S. patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy -3,5-disulfobenzene.

A preferred biodegradable chelating agent for use herein is ethylene diamine N,N'- disuccinic acid, or alkali metal, or alkaline earth, ammonium or substitutes ammonium salts thereof or mixtures thereof. Ethylenediamine N,N'- disuccinic acids, especially the (S,S) isomer have been extensively described in US patent 4, 704, 233, November 3, 1987. to Hartman and Perkins. Ethylenediamine N,N'- disuccinic acid is, for instance, commercially available under the tradename ssEDDS® from Palmer Research Laboratories.

Suitable amino carboxylate chelants to be used herein include ethylene diamine tetra acetates, diethylene triamine pentaacetates, diethylene triamine pentaacetate (DTPA), N-hydroxyethylethylenediamine triacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexaacetates, ethanoldiglycines, propylene diamine tetracetic acid (PDTA) and methyl glycine di-acetic acid (MGDA), both in their acid form, or in their alkali metal, ammonium, and substituted ammonium salt forms. Particularly suitable amino carboxylate to be used herein is diethylene triamine penta acetic acid (DTPA).

The compositions according to the present invention may comprise up to 5% by weight of the total composition of a chelating agent or mixtures thereof, preferably from 0.01% to 3% and more preferably from 0.05% to 1.5%.

The compositions according to the present invention may further comprise a radical scavenger, or mixtures thereof, as an optional ingredient. Suitable radical scavengers for use herein include the well-known substituted mono and di hydroxy benzenes and their analogs, alkyl and aryl carboxylates and mixtures thereof. Preferred such radical scavengers for use herein include di-tert-butyl hydroxy toluene (BHT), hydroquinone, di-tert-butyl hydroquinone, mono-tert-butyl hydroquinone, tert-butyl-hydroxy anysole, benzoic acid, toluic acid, catechol, t-butyl catechol, benzylamine, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane, n-propyl-gallate or mixtures thereof and highly preferred is di-tert-butyl hydroxy toluene. Radical scavengers when used, are typically present herein in amounts ranging from 0.001% to 2% by weight of the total composition and preferably from 0.001% to 0.5% by weight.

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein. Suitable builders for use herein include citric acid, preferably in the form of a water-soluble salt, derivatives of succinic acid of the formula $R\_CH(COOH)CH_2(COOH)$ wherein R is C_{10-20} alkyl or alkenyl, preferably C_{12-16}, or wherein R can be substituted with hydroxyl, sulpho sulphoxyl or sulphone substituents. Specific examples include lauryl succinate, myristyl succinate, palmityl succinate, 2-dodecenylsuccinate, 2-tetradecenyl succinate. Succinate builders are preferably used in the form of their water-soluble salts, including sodium, potassium, ammonium and alkanolammonium salts.

Other suitable builders are oxodisuccinates and mixtures of tartrate monosuccinic and tartrate disuccinic acid such as described in US 4,663,071.

Further suitable builders for use herein are fatty acid builders including saturated or unsaturated C_{10-18} fatty acids, as well as the corresponding soaps. Preferred saturated species have from 12 to 16 carbon atoms in the alkyl chain. The preferred unsaturated fatty acid is oleic acid.

The compositions according to the present invention may comprise up to 20% by weight of the total composition of a builder or mixtures thereof, preferably from 5% to 10% and more preferably from 0.01% to 5%.

In one embodiment, the aqueous compositions of the present invention comprising a peracid of the formula H000C-Ra-Y wherein Ra is a linear or branched alkyl or aryl group of 1 to 30 carbon atoms, and Y is SO_3^-, $N(Rb)_3^+$ or $HO(CH2CH2O)_n$, wherein Rb is a linear or branched alkyl or aryl group of from 1 to 8 carbon atoms, and n is an integer of 1 to 40, or mixtures thereof may further comprise as an optional ingredient, hydrogen peroxide or a water-soluble source thereof or mixtures thereof, up to a level of 40%, preferably from 0.1% to 10%.

Suitable sources of hydrogen peroxide to be used herein are any source of hydrogen peroxide known to those skilled in the art including percarbonates, perborates, peroxides/hydroperoxides, persilicates, persulphates and mixtures thereof.

Suitable organic and inorganic peroxides/hydroperoxides for use herein include diacyl and dialkyl peroxides/hydroperoxides such as dibenzoyl peroxide, t-butyl hydroperoxide, dilauroyl peroxide, dicumyl peroxide and mixtures thereof.

Suitable preformed peroxyacids for use herein include diperoxydodecandioic acid DPDA, magnesium perphthalatic acid, perlauric acid, perbenzoic acid, diperoxyazelaic acid and mixtures thereof.

The compositions according to the present invention may be aqueous compositions formulated in the form of an emulsion. In this embodiment said peracid and/or precursor thereof is emulsified by means of a surfactant system of at least two different surfactants, i.e., at least a hydrophobic surfactant having an HLB below 11 and at least one hydrophilic surfactant having an HLB above 11. Indeed, said two different surfactants in order to form emulsions which are stable must have different HLB values (hydrophilic lipophilic balance), and preferably the difference in value of the HLBs of said two surfactants is at least 1, preferably at least 3.

An advantage associated with such aqueous emulsions is that their stability is further improved as compared to aqueous compositions not formulated in the form of an emulsion, i.e., the decomposition rate of said peracid is further reduced during storage.

The compositions according to the present invention in the form of an emulsion comprise from 1% to 50% by weight of the total composition of said hydrophilic and hydrophobic surfactants, preferably from 2% to 40% and more preferably from 3% to 30%. Said compositions according to the present invention in the form of an emulsion comprise at least from 0.1 % by weight of the total composition of said hydrophobic surfactant, preferably at least 1% and more preferably at least 2% and at least from 0.1 % by weight of the total composition of said hydrophilic surfactant, preferably at least 1% and more preferably at least 2%.

Preferred to be used in the emulsions of the present invention are the hydrophobic nonionic surfactants and hydrophilic nonionic surfactants. Said hydrophobic nonionic surfactants to be used herein have an HLB below 11, preferably below 10, more preferably below 8 and said hydrophilic surfactants have an HLB above 11, preferably above 12, more preferably above 13.

Suitable nonionic surfactants for use herein include alkoxylated fatty alcohols preferably, fatty alcohol ethoxylates and/or propoxylates. Indeed, a great variety of such alkoxylated fatty alcohols are commercially available which have very different HLB values (hydrophilic lipophilic balance). The HLB values of such alkoxylated nonionic surfactants depend essentially on the chain length of the fatty alcohol, the nature of the alkoxylation and the degree of alkoxylation. Hydrophilic nonionic surfactants tend to have a high degree of alkoxylation and a short chain fatty alcohol, while hydrophobic surfactants tend to have a low degree of alkoxylation and a long chain fatty alcohol. Surfactants catalogs are available which list a number of surfactants including nonionics, together with their respective HLB values.

Suitable chemical processes for preparing the nonionic surfactants for use herein include condensation of corresponding alcohols with alkylene oxide, in the desired proportions. Such processes are well known to the man skilled in the art and have been extensively described in the art. As an alternative, a great variety of alkoxylated alcohols suitable for use herein is commercially available from various suppliers. Examples of adequate nonionic surfactant systems would comprise a hydrophobic nonionic surfactant with for instance an HLB of 6, such as a Dobanol ^{R} 23-2 and a hydrophilic nonionic surfactant with for instance an HLB of 15, such as a Dobanol ^{R} 91-10. Another suitable nonionic surfactant system comprises a Dobanol ^{R} 23-6.5 (HLB about 12) and a Dobanol ^{R} 23 (HLB below 6).

Apart from hydrophobic and hydrophilic surfactants being nonionic surfactants any other types of surfactants known in the art and able to form emulsions may be used according to the present invention.

Other suitable hydrophilic surfactants to be used in the present invention may be anionic surfactants in particular sulfonate and sulfate surfactants. The like anionic surfactants are well-known in the art and have found wide application in commercial detergents. These anionic surfactants include the C8-C22 alkyl benzene sulfonates (LAS), the C8-C22 alkyl sulfates (AS), unsaturated sulfates such as oleyl sulfate, the C10-C18 alkyl alkoxy sulfates (AES) and the C10-C18 alkyl alkoxy carboxylates. The neutralizing cation for the anionic synthetic sulfonates and/or sulfates is represented by conventional cations which are widely used in detergent technology such as sodium, potassium or alkanolammonium.

The emulsions herein may further comprise other surfactants which should however not significantly alter the weighted average HLB value of the overall composition.

The present invention will be further illustrated by the following examples.

Examples

The compositions hereinafter are according to the present invention and contain the following ingredients in the following proportions (% by weight):

Compositions % weight	I	II	III	IV	V
$HOOOC\text{-}(CH_2)_5\text{-}SO_3\text{-}$	4	--	--	--	1
$HOOOC\text{-}(CH_2)_7N(CH_3)_3^+$	--	2	--	--	--
$HOOOC\text{-}(CH_2)_3\text{-}(OCH_2CH_2)_3\text{-}OH$	--	--	1	--	--
$HOOOC\text{-}(CH_2)_9\text{-}(OCH_2CH_2)_{10}OH$	--	--	1	2.5	1
$HOOOC\text{-}(CH_2)_{15}\text{-}(OCH_2CH_2)_3\text{-}OH$	--	--	--	0.5	1
H2O2	4	--	4	--	4
DTPA	0.1	--	0.1	--	0.1
BHT	0.05	0.05	0.05	0.05	0.05
Water and minors	-------------------up to 100%--------------				
DTPA is diethylene triamine pentaacetate. BHT is di-tert-butyl hydroxy toluene					

All these compositions are chemically stable upon prolonged storage periods, e.g., after one month of storage at ambient temperature (about 20°C) no more than 30% of available oxygen loss occurs.

Also, these compositions provide excellent cleaning performance even without the presence of a surfactant, as well as excellent bleaching performance on different types of stains.

Process for forming a peracid according to the present invention:

A peracid having the formula HOOOC-(CH2)9-(CH2CH2O)3-OH was obtained by carrying out the following method.

Preparation of the precursor of said peracid:

10-hydroxydecanoic acid commercially available from Aldrich was reacted with methyl alcohol used in excess, before undergoing an ethoxylation at a temperature of 120°C to 140°c in presence of ethylen oxide. Then the resulting compound was submitted to an ester hydrolysis reaction in alkaline water media to obtain the peracid precursor of the formula HO-(CH2CH2O)3-(CH2)9-COOOH.

Preparation of the peracid perse:

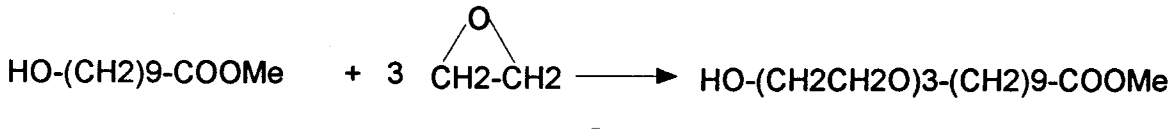
0.02 moles of the precursor of the formula HO-(CH2CH2O)3-(CH2)9-COOOH was solubilized in 18 grs of a concentrated aqueous solution of sulfuric acid (95% by weight). Then said solution was contacted under stirring with a concentrated solution of hydrogen peroxide (70% by weight) that was added drop by drop up to 100% excess with respect to the precursor of the formula HO-(CH2CH2O)3-(CH2)9-COOOH. After the addition of said concentrated solution of hydrogen peroxide, the reaction mixture was stirred at room temperature (about 20-25°C) for 50 minutes. Thereafter the resulting composition was diluted with water to get the desired concentration of peracid in the end product. In this dilution stage other optional ingredients may be added as chelants, surfactants, radical scavengers and the like.

According to the present invention the following reactions occur to prepare a peracid having the formula HOOOC-(CH2)9-(CH2CH2O)3-OH:

1. Protection of the carboxylic group

$$HO\text{-}(CH2)9\text{-}COOH + MeOH \rightarrow HO\text{-}(CH2)9\text{-}COOMe$$

2. Ethoxylation at 120°C-140°C



3. Ester hydrolysis

$$\mathrm{HO\text{-}(CH2CH2O)3\text{-}(CH2)9\text{-}COOMe} \xrightarrow{OH^-} \mathrm{HO\text{-}(CH2CH2O)3\text{-}(CH2)9\text{-}COOH}$$

4. Peracid formation

$$\mathrm{HO\text{-}(CH2CH2O)3\text{-}(CH2)9\text{-}COOH + H2O2} \rightarrow \mathrm{HO\text{-}(CH2CH2O)3\text{-}(CH2)9\text{-}COOOH}$$

Claims

1. An aqueous composition comprising from 0.1% to 40% by weight of the total composition of a peracid of the formula H000C-Ra-Y wherein Ra is a linear or branched alkyl or aryl group of 1 to 30 carbon atoms, and Y is SO_3^-, $N(Rb)_3^+$ or $HO(CH2CH2O)_n$, wherein Rb is a linear or branched alkyl or aryl group of from 1 to 8 carbon atoms, n is an integer of 1 to 40, or mixtures thereof.

2. A composition according to claim 1 wherein Ra is a linear or branched alkyl or aryl group of 1 to 20 carbon atoms, preferably from 2 to 18, preferably 4 to 16, Rb is linear or branched alkyl or aryl group of from 1 to 6, preferably 2 to 4, and wherein n is an integer of 2 to 20, preferably 2 to 12.

3. A composition according to any of the preceding claims wherein said peracid is

$HOOOC\text{-}(CH_2)_5\text{-}SO_3^-$,
$HOOOC\text{-}(CH_2)_7N(CH_3)_3^+$,
$HOOOC\text{-}(CH_2)_3\text{-}(OCH_2CH_2)_3\text{-}OH$,
$HOOOC\text{-}(CH_2)_9\text{-}(OCH_2CH_2)_{10}OH$,
$HOOOC\text{-}(CH_2)_{15}\text{-}(OCH_2CH_2)_3\text{-}OH$, or mixtures thereof.

4. A composition according to any of the preceding claims which comprises from 1% to 20% by weight of the total composition of said peracid or mixtures thereof, preferably from 1.5% to 18% and more preferably from 2% to 15%.

5. A composition according to any of the preceding claims which further comprises at least one optional ingredient selected from the group consisting of surfactants, hydrogen peroxide and a water-soluble source thereof, soil suspending agents, builders, chelants, bleach activators, radical scavengers, pigments, enzymes, dye transfer inhibitors, solvents, buffering agents, suds suppressing agents, photobleaching agents, dyes, perfumes and mixtures thereof.

6. A peracid suitable for use in the aqueous composition according to any of the claims 1 to 5, having the formula H000C-Ra-Y wherein Ra is a linear or branched alkyl or aryl group of 1 to 30 carbon atoms and Y is $HO(CH2CH2O)_n$, wherein n is an integer of 1 to 40.

7. A peracid precursor, suitable for forming a peracid according to claim 6, having the formula $HO\text{-}(CH2\text{-}CH2O)_n\text{-}Ra\text{-}CO\text{-}O\text{-}CO\text{-}Ra\text{-}(OCH2\text{-}CH2)_n\text{-}OH$ or $HO\text{-}(CH2\text{-}CH2O)_n\text{-}Ra\text{-}CO\text{-}OH$, wherein Ra is a linear or branched alkyl or aryl group of 1 to 30 carbon atoms, and wherein n is an integer of 1 to 40.

8. A peracid or peracid precursor according to claims 6 or 7 wherein Ra is a linear or branched alkyl or aryl group of 1 to 20 carbon atoms, preferably from 2 to 18, more preferably from 4 to 16, and wherein n is an integer from 2 to 20, preferably 2 to 12.

9. A process for forming a peracid according to claim 6, said process comprising the step of reacting in an aqueous medium the corresponding peracid precursor with hydrogen peroxide or a water-soluble source thereof.

10. A process according to claim 9, wherein at least 1.1 moles of hydrogen peroxide or a water-soluble source thereof per molar equivalent of the corresponding peracid precursor are reacted, preferably at least 1.5 and more preferably at least 2.

11. A process according to any of the preceding claims 9 to 10, wherein said peracid precursor is according to claim 7.

12. A process according to any of the claims 9 to 11 which further comprises a step where at least one additional ingredient, other than water, hydrogen peroxide or a water-soluble source thereof, and said peracid precursor is provided.

13. A process according to claim 12 wherein said additional ingredient is selected from the group consisting of surfactants, soil suspending agents, builders, chelants, bleach activators, radical scavengers, pigments, enzymes, dye transfer inhibitors, solvents, buffering agents, suds suppressing agents, photobleaching agents, dyes, perfumes and mixtures thereof.

14. An aqueous composition comprising hydrogen peroxide or a water-soluble source thereof and a peracid precursor according to claim 7.

15. A composition according to claim 14 wherein said composition comprises from 0.1% to 40% by weight of the total composition of hydrogen peroxide or a water-soluble source thereof, or mixtures thereof, preferably from 0.5% to 30% and more preferably from 1 to 20% and from 0.1% to 40% by weight of the total composition of said peracid precursor, or mixtures thereof, preferably from 0.5% to 30% and more preferably from 1% to 20%.

16. A composition according to any of the claims 14 or 15 which further comprises at least one optional ingredient selected from the group consisting of surfactants, soil suspending agents, builders, chelants, bleach activators, radical scavengers, pigments, enzymes, dye transfer inhibitors, solvents, buffering agents, suds suppressing agents, photobleaching agents, dyes, perfumes and mixtures thereof.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 20 2104

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.6)
X	US 3 414 593 A (P. ROBSON) * the whole document *	1,2,4,5	C11D3/39 C07C409/24 C07C409/40 C07C409/42
X	EP 0 124 968 A (INTEROX CHEMICALS LTD) * claims 10-15 *	1,2,4,5	
X	CHEMICAL ABSTRACTS, vol. 111, no. 20, 13 November 1989 Columbus, Ohio, US; abstract no. 176804, XP002023745 * abstract; RN: 123220-61-1 * & JP 01 056 797 A (KAO CORP)	1,4,5	
X	EP 0 316 809 A (AUSIMONT SRL) * page 4, lines 40-44; example 21, table 1: example 3; claims 1, 2, 4, 8, 18 *	1,2,4	
X	US 3 988 433 A (J.J. BENEDICT) * column 3, line 17 - column 10, line 55; examples II-I *	1,2,4,5	**TECHNICAL FIELDS SEARCHED (Int.Cl.6)**
A	EP 0 447 553 A (KAO CORP) * page 3, line 51 - page 4, line 48; page 6, line 22 - page 7, line 56; table 3, entries 1, 2; table 10, embodiment 4; table 11, embodiment 8; claims 1, 2, 4-10 *	1,2,4-16	C11D C07C
A	US 3 799 977 A (T.F. RUTLEDGE) * examples 3,6-8 *	7,8	

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	24 January 1997	Van Amsterdam, L

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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.6)
A	CHEMICAL ABSTRACTS, vol. 110, no. 22, 29 May 1989 Columbus, Ohio, US; abstract no. 193553, XP002023746 * abstract; RN: 120394-66-3, 70678-95-4 * & MAKROMOL. CHEM., RAPID COMMUN., vol. 10, no. 2, 1989, pages 63-67, ---	7,8	
A	CHEMICAL ABSTRACTS, vol. 121, no. 17, 24 October 1994 Columbus, Ohio, US; abstract no. 204836, XP002023747 * abstract; RN: 157978-19-3 * & JP 06 135 889 A (TOKUYAMA SODA KK) ---	7,8	
A	WO 91 18876 A (INTEROX CHEMICALS LTD) * claims 1-25 * ---	1,2,4,5	
A	WO 94 01399 A (UNILEVER PLC) * claims 1-8,10 * -----	1,2,4,5	TECHNICAL FIELDS SEARCHED (Int.Cl.6)

The present search report has been drawn up for all claims

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