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(54) Stable compositions with persulfate salts.

(57) Stable highly acidic aqueous compositions are disclosed which comprise a nonionic surfactant or mixtures thereof and a persulfate salt or mixtures thereof to be used for treating hard surfaces. Preferably, emulsions of nonionic surfactants comprising a persulfate salt or mixtures thereof are disclosed.

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Technical field

The present invention relates to cleaning and bleaching compositions. Preferably, the cleaning and bleaching compositions according to the present invention are aqueous compositions comprising nonionic surfactants and persulfate salts. Said compositions are particularly suitable for the cleaning and bleaching of hard surfaces.

Background

A great variety of bleaching and cleaning compositions have been described in the art. It is also well known that it is desirable to use persulfate salts as a bleaching agent. For example, European Patent Application EP-A-0 373 613 discloses the preparation of a specific monopersulfate derivative, i.e. pyridine-3-percarboxylic acid monopersulfate useful as bleaching agent in detergent formulations.

However, persulfate salts have the drawback that they decompose in aqueous detergent compositions due to the presence of metal impurities which catalyze the decomposition of said persulfate salts and ingredients present in the compositions that can be oxidized by persulfate. Thus persulfate salts in aqueous detergent compositions tend to be chemically unstable. It is therefore an object of the present invention to provide compositions comprising persulfate salts which are chemically stable.

It is another object of the present invention to provide aqueous cleaning compositions comprising persulfate salts which are efficient on various surfaces to clean various soils and stains.

The present invention meets the above objects in proposing highly acidic aqueous compositions comprising nonionic surfactants and a persulfate salt. Preferably, the present invention encompasses highly acidic aqueous emulsions of nonionic surfactants, which further comprise a persulfate salt. It has been found that the storage stability of persulfate salts in the compositions of the present invention is improved compared to compositions without any nonionic surfactants.

Aqueous emulsions of a nonionic surfactant system have been disclosed in the art for instance in European Patent EP-B-0 092 932. Said patent discloses nonionic emulsions comprising hydrogen peroxide and an emulsified organic phase comprising a specific enol ester bleach activator. Such emulsions allow to keep the hydrogen peroxyde separate from the bleach activator. Persulfate salts are not disclosed.

As a further advantage it has unexpectedly been found that the highly acidic compositions of the present invention comprising nonionic surfactants and a persulfate salt, find a preferred application in the cleaning of toilet bowls.

Indeed, once a composition according to the present invention has been applied onto the top of the inclined surface of a toilet bowl, said composition slowly reaches the water, is diluted and thereby becomes less acidic, i.e. from about pH 1 to about pH 2. The compositions according to the present invention have enhanced cleaning performance in their dilute form, compared to their neat form. Thus it has been unexpectedly found that this "pH jump" effect allows to formulate compositions which are stable upon storage (acidic pH) and effective in cleaning (pH jumped). Additionally, the compositions of the present invention exhibit outstanding soil solubilization and soil discolouration properties when used diluted. Particularly on soil discolouration the performance of the compositions of the present invention is better than similar compositions comprising only hydrogen peroxide.

Summary of the invention

The present invention is a stable aqueous cleaning and bleaching composition comprising a nonionic surfactant or mixtures thereof, said aqueous composition further comprising a persulfate salt or mixtures thereof and said composition being formulated at a pH of from 0 to 4.

Preferred herein is a stable aqueous cleaning and bleaching composition in the form of an emulsion comprising at least two nonionic surfactants, said aqueous composition further comprising a persulfate salt or mixtures thereof and said composition having a pH of from 0 to 4.

The present invention also encompasses a process of treating surfaces wherein a composition according to the present invention is used in its diluted form.

The present invention also encompasses a process for the manufacture of said composition.

Detailed description of the invention

The compositions according to the present invention are highly acidic aqueous compositions comprising a nonionic surfactant or mixtures thereof and a persulfate salt or mixtures thereof. Preferred herein are highly

acidic aqueous emulsions of nonionic surfactants, which further comprise a persulfate salt or mixtures thereof.

The compositions according to the present invention are stable. By "stable" it is meant herein that a composition comprising a persulfate salt or mixtures thereof does not undergo more than 20 % persulfate loss, in one month at 25°C. Persulfate concentration can be measured by titration with potassium permanganate after reduction with a solution containing ammonium ferrous sulphate. Said stability test method is well known in the art and is reported,for example, on the technical information sheet of Curox^R commercially available from Interox.Alternatively persulfate concentration can also be measured using a chromatography method described in the literature for peracids (F. Di Furia et al., Gas-liquid Chromatography Method for Determination of Peracids, Analyst, Vol 113, May 1988, p 793-795).

The compositions according to the present invention are aqueous. Accordingly, the compositions according to the present invention comprise from 10% to 95% by weight of the total composition of water, preferably from 30% to 90%, most preferably from 60% to 85%. Deionized water is preferably used.

The compositions according to the present invention comprise as an essential element a persulfate salt or mixtures thereof. Preferably the compositions according to the present invention comprise from 0.1% to 30% by weight of the total composition of said persulfate salt or mixtures thereof, more preferably from 1% to 20%, most preferably from 2% to 10%. Preferred persulfate salt to be used herein is the monopersulfate salt. One example of monopersulfate salts commercially available are those commercialized by Interox under the trade name Curox^R. Other persulfate salts such as dipersulfate salts commercially available from Peroxide Chemie GMBH can be used in the compositions according to the present invention.

The compositions according to the present invention comprise as a further essential element a nonionic surfactant or mixtures thereof. Preferably the compositions according to the present invention comprise from 1% to 50% by weight of the total composition of said nonionic surfactant or mixtures thereof, more preferably from 4% to 30%, most preferably from 6% to 20%.

Suitable nonionic surfactants to be used herein are alkoxylated alcohol nonionic surfactants which can be readily made by condensation processes which are well known in the art. However, a great variety of such alkoxylated alcohols, especially ethoxylated and/or propoxylated alcohols is also conveniently commercially available. Surfactants catalogs are available which list a number of surfactants, including nonionics, together with their respective HLB values.

Accordingly, preferred alkoxylated alcohols for use herein are nonionic surfactants according to the formula RO(E)e(P)pH where R is a hydrocarbon chain of from 6 to 22 carbon atoms, E is ethylene oxide and P is propylene oxide, and e and p which represent the average degree of respectively ethoxylation and propoxylation, are of from 0 to 60.

A particularly suitable nonionic surfactant is for instance Dobanol^R 91-10 (R=C9-C11, e=10, p=0) which is commercially available from Shell.

The preferred compositions according to the present invention can be suitably prepared in the form of an emulsion of at least two nonionic surfactants. Said two nonionic surfactants must have different HLB values (hydrophilic lipophilic balance) in order to form emulsions which are stable, and preferably the difference in value of the HLBs of said two surfactants is of at least 1, preferably at least 3, more preferably of at least 6.5. By appropriately combining at least two of said nonionic surfactants with different HLBs, emulsions according to the present invention will be formed.

One of said nonionic surfactants used herein is a nonionic surfactant with an HLB above 11 (herein referred to as hydrophilic nonionic surfactant), whereas the other one is a nonionic surfactant with an HLB below 10 (herein referred to as hydrophobic nonionic surfactant).

A great variety of the alkoxylated fatty alcohols to be used herein have very different HLB values. 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.

In a preferred embodiment said hydrophobic and hydrophilic nonionic surfactants are alkoxylated alcohols according to the present invention where the R group is a hydrocarbon chain with only from 8 to 13 carbon atoms, preferably from 8 to 11. A particularly suitable system comprises a hydrophobic nonionic surfactant for instance a Dobanol^R 91-2.5 (R=C9-C11, e=2.5, p=0) and a hydrophilic nonionic surfactant for instance a Dobanol^R 91-10 (R=C9-C11, e=10, p=0). These Dobanol^R surfactants are commercially available from Shell.

The compositions according to the present invention may further comprise other nonionic surfactants which should however not significantly alter the weighted average HLB value of the overall composition.

Another essential feature of the compositions according to the present invention is their acidity. In order to obtain appropriate stability of the persulfate salts in the compositions according to the present invention, said compositions need to be formulated at a pH of from 0 to 4, preferably 0 to 3 and most preferably from 0

to 2. The pH of said compositions can be trimmed by appropriate organic or/and inorganic acids which physically stabilize the compositions and may build up viscosity. Said acids can be added typically from 1% to 20% by weight of the total composition. Examples of organic acids to be used alone or in combination with other organic or/and inorganic acids are citric acid, succinic acid, maleic acid, tartaric acid and the like. An example of inorganic acids to be used herein is sulfuric acid.

In one embodiment, the compositions of the present invention are free of hydrogen peroxide. Said compositions are particularly stable. In another embodiment, the compositions of the present invention further comprise from 0.5% to 20% by weight of the total composition of hydrogen peroxide, preferably from 2% to 15%, most preferably from 3% to 10%. Said compositions exhibit outstanding cleaning performances.

Depending on the end use envisioned, the compositions according to the present invention may further comprise a variety of other ingredients including other surfactants of all types, organic or inorganic alkalis, perfumes, dyes, optical brighteners, builders, chelants, pigments, enzymes, dye transfer inhibitors, solvents, buffering agents, stabilizers and the like.

The present invention further encompasses a process of treating hard-surfaces wherein a composition as hereinbefore defined is used in its diluted form. By "in its diluted form" it is meant herein that the compositions according to the present invention may be diluted with water up to a pH of 6. Said dilution may occur either before, after or while said composition is applied to a hard-surface.

Compositions according to the present invention find a preferred application in the cleaning of hard-surfaces, particularly toilet bowls and bath tubs. In this field it is preferred to use a process of treating a hard-surface wherein a composition according to the present invention is diluted after or while it is applied to said surface. For example, said composition may be dispensed from a container onto said hard-surface, then diluted in water and left to act onto said surfaces, then removed by rinsing or flushing.

However, the compositions according to the present invention are also particularly suitable to be used for denture applications. In this field it is suitable to use a process of treating a hard-surface wherein a composition according to the present invention is either diluted before, after or while said composition is applied to said surface. For example said composition may be first diluted in water before it is applied to said denture or may be diluted in water which is already in contact with a denture.

As used in the foregoing paragraphs, the expression "treating" includes washing as the compositions according to the present invention comprise surfactants and bleaching as the compositions according to the present invention comprise persulfate salts.

The present invention further encompasses a process for the manufacture of the emulsions described herein. The process according to the present invention comprises at least three steps:

In the first step, a hydrophobic mixture is prepared which comprises said hydrophobic nonionic surfactant together with other hydrophobic ingredients which are to be formulated in the composition, such as metal chelants, perfumes, solvents, enzymes.

In the second step, a hydrophilic mixture is prepared which comprises at least said water, said hydrophilic nonionic surfactant and said persulfate salts. Said hydrophilic mixture optionally further comprises other hydrophilic ingredients which are to be formulated in the composition such as dyes, optical brighteners, builders, stabilizers, chelants, an organic acid or mixtures thereof, hydrogen peroxide and buffering agents. In this second step hydrogen peroxide if present is preferably added last, after said buffering agent has been added. The pH of said hydrophilic phase is adjusted to the desired value before the third step.

Naturally, said first and said second steps can be performed in any order, i.e. second step first is also suitable.

In the third step of the process according to the present invention, said hydrophobic mixture and said hydrophilic mixture are mixed together and stirred.

The present invention is further illustrated by the following examples.

Examples

Compositions are made which comprise the listed ingredients in the listed proportions (weight %).

Compositions :	#1	#2	#3
Dobanol@ 91-2.5	4.8%	1.2%	4.2%
Dobanol@ 91-10 (R=C9-C11, e=10, p=0)	1.2%	4.8%	1.8%
Curox^R *	2.0%	6.0%	6.0%
Citric acid	6.0%	6.0%	---
Perfume	0.5%	0.5%	0.5%
Water and minors	----up to 100%----		
Sulfuric acid up to pH	1	1	0.2

* Curox^R is one of the commercial names of monopersulfate salts

Compositions #1 ,#2 and #3 are representative of the compositions according to the present invention. Compositions #1 and #3 are emulsions of nonionic surfactants and composition #2 is a solution of nonionic surfactants, these compositions comprise a monopersulfate salt.

It has surprisingly been found that the compositions according to the present invention exhibit good stability. For example, composition #3 had virtually no persulfate loss after 3 weeks at 20°C.

Performance data

Compositions are made which comprise the listed ingredients in the listed proportions (weight %).

Compositions :	#1	#2
Dobanol@ 91-2.5	4.8%	4.8%
Dobanol@ 91-10 (R=C9-C11, e=10, p=0)	1.2%	1.2%
Curox^R *	6.00%	---
Hydrogen peroxide	6.00%	6.00%
citric acid	6.00%	6.00%
Water and minors up to	100%	100%
pH=1		

* Curox^R is one of the commercial names of monopersulfate salts

Composition #1 which is representative of the present invention was evaluated for its cleaning performance on artificial toilet soils, i.e. soil solubilization efficiency and soil discolouration efficiency. In this study composition #2 which is an emulsion comprising hydrogen peroxide, is taken as the reference. The evaluation (psu) used was a visual evaluation on a four points scale wherein "O" is attributed to the tested composition when no difference versus the reference is observed and wherein "4" is attributed when the tested composition is much better than the reference.

Artificial toilet soil solubilization (psu) :

Neat form of #1 : 1
Diluted form of #1 : 2

Artificial toilet soil discolouration (psu) :

Neat form of #1 : 3
Diluted form of #1 : 3

The compositions of the present invention in the form of an emulsion exhibit outstanding cleaning performance by exploiting the pH jump that takes place upon product usage/dilution. Indeed, the cleaning performance of the composition #1 is enhanced when increasing the pH from 1 (neat product) to 2 (diluted product).

The above results surprisingly show that compositions according to the present invention provide significant benefits in toilet soils cleaning compared to hydrogen peroxide emulsions, both when used neat or diluted.

Claims

1. An aqueous composition comprising a nonionic surfactant or mixtures thereof and a persulfate salt or mixtures thereof **characterized in that** said composition is formulated at a pH of from 0 to 4.

2. A composition according to claim 1 comprising a hydrophilic and a hydrophobic nonionic surfactant whereby said composition is in the form of an emulsion.

3. A composition according to any of the preceding claims wherein said persulphate salt is a monopersulfate salt.

4. A composition according to any of the preceding claims wherein the level of said persulfate salt or mixtures thereof is from 0.1% to 30% by total weight of the composition, preferably from 1% to 20%, more preferably from 2% to 10%.

5. A composition according to any of the preceding claims which has a pH of from 0 to 3, preferably from 0 to 2.

6. A composition according to any of the preceding claims which comprises from 1% to 50% by weight of the total composition of said nonionic surfactant or mixtures thereof, more preferably from 4% to 30%, most preferably from 6% to 20%.

7. A composition according to any of the preceding claims wherein said nonionic surfactant is an alkoxylated alcohol of the formula RO(E)e(P)pH where R is a hydrocarbon chain of from 6 to 22 carbon atoms, E is ethylene oxide and P is propylene oxide, and e and p which represent the average degree of, respectively ethoxylation and propoxylation, are of from 0 to 60.

8. A composition according to any of the preceding claims wherein said composition is free of hydrogen peroxyde.

9. A composition according to any of claims 1 to 7 wherein said composition further comprises from 0.5% to 20% by weight of the total composition of hydrogen peroxide, preferably from 2% to 15%, most preferably from 3% to 10%.

10. A process of treating a hard-surface wherein a composition according to any of the preceding claims is used in its diluted form.

11. A process of treating a hard-surface according to claim 10 wherein said composition is diluted before it is applied to said surface.

12. A process of treating a hard-surface according to claim 11 wherein said hard-surface is a denture.

13. A process of treating a hard-surface according to claim 10 wherein said composition is diluted after or while it is applied to said surface.

14. A process of treating a hard-surface according to claim 13 wherein said hard-surface is a denture or a toilet bowl.

15. A process for the manufacture of an emulsion according to any of claims 2 to 9 wherein:
- a hydrophobic mixture is prepared which comprises at least said hydrophobic nonionic surfactant;
- a hydrophilic mixture is prepared which comprises at least water, said persulfate salt, said hydrophilic nonionic surfactant and an organic acid or mixtures thereof;
- said hydrophobic mixture and said hydrophilic mixture are mixed together.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 87 0198

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.5)
P,X	CA-A-2 062 006 (LUCIEN) 28 August 1993 * page 8, line 12 - line 14 * * page 10, line 3 - line 14 * * page 11, line 10 - line 13 * * page 11, line 20 - line 26; claims 1,4 *	1,3,5,6, 9,10	C11D3/39
X	EP-A-0 188 025 (UNILEVER N.V.) * claims 1-4,9 *	1,3-6,9	
X	EP-A-0 199 385 (UNILEVER N. V.) * claims 1-4,8 *	1,3-5,9	
P,A	DATABASE WPI Week 9332, Derwent Publications Ltd., London, GB; AN 93-253068 & JP-A-5 171 195 (LION CO.) 9 July 1993 * abstract *	1,4,6-9	
A	DATABASE WPI Week 8832, Derwent Publications Ltd., London, GB; AN 88-225107 & JP-A-63 161 089 (LION CO.) 4 July 1988 * abstract *	1,4,6-9	TECHNICAL FIELDS SEARCHED (Int.Cl.5) C11D
A	EP-A-0 271 189 (THE CLOROX COMPANY) * claim 1 *	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	15 February 1994	Van Bellingen, I

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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