(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 915 150 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
12.05.1999 Bulletin 1999/19

(51) Int. Cl.^{6}: **C11D 3/39**, D06L 3/02

(21) Application number: **97870172.0**

(22) Date of filing: **31.10.1997**

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV RO SI

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

(72) Inventors:
- **Scialla, Stefano, (NMN)**
  00128 Rome (IT)
- **Spadoni, Luca, (NMN)**
  00149 Rome (IT)
- **Masotti, Valentina, (NMN)**
  40033 Casalecchio di Reno (BO) (IT)

(74) Representative:
Engisch, Gautier et al
BVBA Procter & Gamble Europe SPRL,
Temselaan 100
1853 Strombeek-Bever (BE)

(54) Processes of soaking fabrics with a liquid aqueous persulfate salt-containing composition

(57) The present invention relates to a process of bleaching a fabric which comprises the steps of :

- diluting in an aqueous bath a liquid aqueous composition in its neat form, having a pH below 7 and comprising a persulfate salt,
- contacting said fabric with said aqueous bath comprising said liquid composition, and subsequently rinsing said fabric with water. This bleaching process delivers effective bleaching performance and effective overall stain removal performance while being particularly safe to the fabrics and fabric colours

Printed by Xerox (UK) Business Services
2.16.7/3.6

Description

Technical Field

[0001] The present invention relates to the bleaching of fabrics with liquid aqueous persulfate-containing bleaching compositions having a pH below 7.

Background of the invention

[0002] Liquid aqueous bleaching compositions suitable for laundry applications are well known in the art. It is also known that liquid bleaching compositions relying on hypochlorite as the bleaching agent can be preferred over oxygen bleaches like hydrogen peroxide, mainly for performance reasons, especially at lower temperatures.

[0003] However, there are some limitations to the convenience of hypochlorite beaches. In particular, it is well known from consumers that hypochlorite bleaching may cause yellowing and/or damage of the fabrics which are being bleached. This holds particularly true for synthetic fabrics and indeed there is a standing prejudice against using hypochlorite bleaches on synthetic fibers, as evidenced by warnings on labels of commercially available hypochlorite bleaches. Also, a variety of fabrics made of or containing synthetic fibers are labeled by their manufacturers as non-bleachable. Also another drawback associated to liquid aqueous hypochlorite-based bleaching compositions is that undesirable typical chlorine odor may be perceived by the consumer during and after use, e.g., on the hands of the user or fabrics that have been bleached with such compositions.

[0004] Colour and fabric damage can be minimised by using milder oxygen bleaches such as hydrogen peroxide. However, the bleaching characteristics of such peroxygen bleaches are much less desirable than those of the harsh halogen bleaching agents. Therefore liquid aqueous peroxygen bleach-containing compositions have been developed containing activators, i.e., compounds which enhance peroxygen bleaching performance. Such activated hydrogen peroxide-containing compositions are, for example, exemplified in EP-598 170. However, consumers are still not fully satisfactory when bleaching fabrics with such compositions and are looking for improved overall stain removal performance on a variety of stains including greasy stains and enzymatic stains as well as further improved bleaching performance when bleaching fabrics.

[0005] It is therefore an object of the present invention to address the issues mentioned above, namely those of providing improved overall stain removal performance on a wide range of stains as well as improved bleaching performance when bleaching fabrics. More particularly, it is an object of the present invention to provide effective overall stain removal and effective bleaching performance while being safe to the fabrics bleached and to colours.

[0006] We have found that these issues are efficiently addressed when soiled (coloured) fabrics are bleached with an acidic liquid aqueous composition (pH<7) containing a persulfate salt. Indeed, it has been found that when the process of bleaching fabrics according to the present invention includes the steps of diluting in an aqueous bath an acidic liquid aqueous composition comprising a persulfate salt, and of contacting said fabrics with said aqueous bath comprising said composition and subsequently rinsing said fabrics with water, improved overall stain removal performance and improved bleaching performance is delivered, as compared to the same bleaching process where the same acidic liquid aqueous composition but based, for example, on activated (e.g. acetyl triethyl citrate) hydrogen peroxide as the bleaching agents at the same total level of bleaching agents instead of persulfate salt, is used.

[0007] Advantageously, the bleaching processes herein starting from the liquid aqueous persulfate-containing compositions as described herein, provide effective bleaching performance and effective stain removal performance even under short soaking time conditions, typically below 30 minutes, more preferably below 10 minutes and most preferably below 5 minutes. Furthermore, the bleaching processes herein starting from the liquid persulfate-containing compositions as described herein, provide effective bleaching performance and effective stain removal performance even under soaking conditions where the aqueous bath is made of cold water, typically down to 4°C (preferably below 40°C and most preferably from 10°C to 30°C). Thus, the present invention provides a process of bleaching fabrics that best needs the today consumers needs, i.e. a process of bleaching fabrics that provides effective bleaching and stain removal performance in reduced time periods and/or by using cold water. Actually, an advantage of the process of bleaching a fabric herein is that the acidic liquid aqueous persulphate-containing composition herein is effective since the first instants of its dilution in the aqueous bath. This is because it quickly dissolves in the aqueous bath.

[0008] Advantageously, it has been found that these improved bleaching performance and improved overall stain removal performance are provided with the processes according to the present invention even for acidic liquid aqueous persulfate-containing compositions having undergone long storage time before their use according to the processes herein.

[0009] In a preferred aspect of the process of bleaching fabrics according to the present invention the acidic liquid aqueous composition used preferably comprises on top of the persulfate salt, a bleach activator being an aldehyde and/or ketone and/or halide activator compound, for further improved bleaching performance and improved stain removal performance.

[0010] Advantageously, the laundry bleaching operations according to the present invention are safe to the fabrics perse and/or fabrics colours. Indeed, it has been surprisingly been found that when formulating a persulfate salt and optionally an activator compound as described herein after, in a liquid aqueous composition having a pH below 7, the safety (both fabric safety and colour safety) delivered to the fabrics bleached therewith according to the process of the present invention is improved as compared to formulating the same ingredients in a granular composition.

[0011] Finally, the process of bleaching fabrics according to the present invention has the advantage of being odour free on hands if a hand bleaching operation is carried out and/or on the fabrics so bleached.

Summary of the invention

[0012] The present invention encompasses a process of bleaching a fabric which comprises the steps of :

- diluting in an aqueous bath a liquid aqueous composition in its neat form, having a pH below 7 and comprising a persulfate salt,
- contacting said fabric with said aqueous bath comprising said liquid composition, and subsequently rinsing said fabric with water.

[0013] In its broadest aspect, the present invention encompasses the use of a liquid aqueous bleaching composition having a pH below 7 and comprising a persulfate salt and optionally a bleach activator being an aldehyde, ketone and/or halide activator compound for the bleaching of fabrics, for reducing the loss of tensile strength in said fabrics. Furthermore, the present invention encompasses the use of a liquid aqueous bleaching composition having a pH below 7 and comprising a persulfate salt and optionally a bleach activator being an aldehyde, ketone and/or halide activator compound for the bleaching of coloured fabrics, for reducing the colour damage to said fabrics.

Detailed Description

The process of bleaching fabrics:

[0014] The present invention encompasses a process of bleaching fabrics as described herein after.

[0015] By "fabrics", it is to he understood any types of fabrics including for example clothes, curtains, drapes, bed linens, bath linens, table cloths, sleeping bags, tents, upholstered furniture and the like.

[0016] The process of bleaching fabrics herein is suitable for both natural fabrics and synthetic fabrics. By "natural" fabrics, it is meant fabrics made of cotton, viscose, linene, silk and/or wood. By "synthetic" fabrics, it is meant those made of synthetic fibers like polymeric fibers (polyamide, polyester, lycra® and elasthan®), and those made of both natural and synthetic fibers.

[0017] The process of bleaching fabrics according to the present invention comprises the steps of:

- diluting in an aqueous bath a liquid aqueous composition in its neat form, having a pH below 7 and comprising a persulfate salt,

- contacting said fabrics with said aqueous bath comprising said liquid composition,

- and subsequently rinsing said fabrics with water.

[0018] By "diluting in an aqueous bath a liquid composition in its neat form", it is meant herein that the liquid compositions per se as described herein, are diluted typically with water to form an aqueous bath to which the fabrics to be bleached will be contacted before being rinsed.

[0019] In the process of bleaching fabrics of the present invention, the fabrics are left into contact with the aqueous bath (in the so-called "soaking step") for a period of time sufficient to bleach the fabrics. This period of time typically ranges from 1 minute to 24 hours, preferably from 3 minutes to 12 hours and more preferably from 4 minutes to 6 hours. Advantageously, the process of bleaching according to the present invention provides effective bleaching performance and effective stain removal performance even upon shorter soaking time, typically below 1 hour, preferably below 20 minutes and more preferably from 4 minutes to 15 minutes.

[0020] The dilution level that the liquid aqueous composition as described herein, undergoes in the process of the bleaching fabrics herein is a dilution of the composition into water of up to 500 times its weight, preferably from 5 to 200 times and more preferably from 10 to 80 times. Such dilution may occur for instance in hand laundry applications as well as by the other means such as in washing machine.

[0021] Although, the temperature of the bleaching process does have an influence on the stain removal performance and/or bleaching performance of the liquid aqueous persulfate-containing compositions used herein, effective stain removal performance and/or bleaching performance are provided even at low temperatures typically down to 4°C. More particularly, these benefits are observed not only at low temperatures but also under short soaking periods, typically below 20 minutes. It is also understood that by increasing the temperature the bleaching process can be accelerated, i.e. the time required to bleach a given soiled fabric is reduced. Typically, the aqueous baths occurring in the bleaching processes according to the present invention where the persulfate bleaching compositions as described herein are diluted have a temperature of from 4°C to 60°C, preferably from 10°C to 50°C and most preferably from 15°C to 30°C.

[0022] Surprisingly, the process of bleaching fabrics according to the present invention provides improved bleaching performance and improved overall stain removal performance, as compared to the same process where the bleaching composition used is a liquid aqueous composition based on activated hydrogen peroxide at the same total level of bleaching agents. Also these benefits are obtained with the process of bleaching fabrics according to the present invention with short soaking time in both cold or hot aqueous baths.

[0023] Indeed, effective bleaching performance is provided on a variety of bleachable soils, from hydrophobic to hydrophilic soils on both hydrophilic and hydrophobic fabrics. Effective bleaching performance herein also includes effective whiteness.

[0024] Advantageously, the present invention provides not only effective bleaching performance but also overall effective stain removal performance on various types of stains including greasy stains (e.g., lipstick, tomato, make-up) and/or enzymatic stains (e.g. blood, choco pudding).

[0025] If said fabrics are to be washed, i.e., with a conventional laundry detergent composition comprising at least one surface active agent, said washing may be conducted together with the bleaching of said fabrics by contacting said fabrics at the same time with the liquid aqueous bleaching composition as described herein and a laundry detergent composition, or said washing may be conducted before or after that said fabrics have been bleached. Accordingly, the process according to the present invention allows to bleach fabrics and optionally to wash fabrics with a detergent composition comprising at least one surface active agent before the step of contacting said fabrics with said aqueous bath comprising the liquid aqueous composition and/or in the step where said fabrics are contacted with said aqueous bath and/or after the step where said fabrics are contacted with said aqueous bath and before the rinsing step and/or after the rinsing step.

[0026] In a preferred embodiment herein the fabrics are preferably washed in a separate step from the bleaching step to get optimum bleaching and stain removal performance. Indeed, conducting the bleaching and washing with a detergent composition in the same step may cause chemical interaction between the persulfate salt coming from the liquid aqueous composition and the conventional detergent ingredients typically present in a conventional detergent composition, i.e. enzymes, surfactants and the like and thus may reduce the bleaching performance and/or overall stain removal performance.

[0027] In a highly preferred embodiment of the present invention, it is preferred to perform the bleaching process herein after said fabrics have been first washed with a conventional laundry detergent composition. Indeed, it has been observed that bleaching said fabrics with the compositions according to the present invention after to washing them with a detergent composition provides superior bleaching and stain removal performance with less energy and detergent than if said fabrics are bleached first then washed.

[0028] Indeed, it is speculated that when a fabric is washed with a conventional detergent composition residual alkalinity is left on the fabrics even when the fabrics is subsequently rinsed with water. Such alkaline residuality on the fabrics are believed to further boost the bleaching performance and stain removal performance of the acidic liquid aqueous persulfate-compositions as described herein when they are contacted to the fabrics in their diluted form.

[0029] It has further been found that reduced colour damage (i.e., colour change and/or decoloration) and reduced tensile strength loss are observed when bleaching the fabrics according to the present invention with a liquid aqueous composition comprising a persulfate salt and optionally a bleach activator compound.

[0030] The reduced tensile strength loss and reduced colour damage are observed even if the composition is left to soak with the acidic liquid aqueous composition as described herein after, upon prolonged periods of time before rinsing the fabrics, e.g. 24 hours. Actually, formulating the persulfate salt and optionally a bleach activator in a liquid aqueous composition having a pH below 7, prevents the decomposition (oxidation) of dyes generally present on the surface of coloured fabrics such as bleach sensitive dyes and/or metallized dyes including copper-formazan dyes and/or metal-azo dyes, when the fabrics are bleached therewith according to the process herein.

[0031] A typical issue associated to for example granular persulphate-containing compositions known in the art (see for example US 3822114) is the fabric and colour damage associated to residual persulphate that dissolves slowly in the aqueous bath obtained by diluting such a composition with water. When a slow-dissolving granular persulphate-containing composition is used to prepare an aqueous bath (soaking bath), the absence of agitation that typically occurs in hand washing soaking can cause prolonged contact between the persulphate in a granular form and the fabrics. Thus an advantage of the present invention is that the fast dissolution of the liquid aqueous composition as used herein reduces the fabric and colour damage typically associated to the use of granular persulphate-containing compositions.

[0032] The tensile strength in a fabric may be measured by stretching said fabric until it breaks. The force needed to break the fabric is the "Ultimate Tensile Stress" and may be measured with a stress-strain INSTRON ® machine available from INSTRON. The loss of tensile strength is the difference between the tensile strength of a fabric taken as a reference, e.g. a fabric which has not been bleached, and the tensile strength of the same fabric after having been bleached with a composition of the present invention. A tensile strength loss of zero means that no fabric damage is observed.

[0033] The colour safety can be evaluated visually by comparing side by side fabrics soaked with a composition of the present invention and a reference composition. Differences and graduations in colour can be visually assessed and ranked according to Panel Score Units (PSU) using any suitable scale. PSU data can be handled statistically using conventional techniques. Alternatively, various types of optical apparatus and procedures can be used to assess the improvement in colour safety afforded by the present invention. For example when evaluating colour safety on fabrics measurements with Hunterlab colour Quest 45/0 apparatus can be used.

[0034] An advantage of the persulfate-containing compositions suitable for use in the process of bleaching fabrics according to the present invention is that they are physically and chemically stable upon prolonged periods of storage.

[0035] Chemical stability of these compositions may be evaluated by measuring the concentration of available oxygen at given storage time after having manufactured the compositions. By "chemically stable", it is meant herein that the compositions used herein comprising a persulfate salt or mixtures thereof and optionally an activator compound do not undergo more than 15% AvO loss, in one month at 25°C and preferably not more than 10%.

[0036] Available oxygen (AvO) loss of a persulfate containing composition 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).

[0037] By "physically stable" it is meant herein that no phase separation occurs in the acidic liquid aqueous persulfate-containing compositions used herein for a period of 7 days at 50°C.

The liquid aqueous compositions used in the process of bleaching fabrics

[0038] The liquid persulfate-containing compositions for use in the process of bleaching fabrics according to the present invention are liquid compositions as opposed to a solid or a gas. As used herein "liquid" includes "pasty" compositions. These liquid compositions herein are aqueous compositions. These liquid compositions according to the present invention have a pH below 7, preferably from 0.1 to 6, more preferably from 0.5 to 4, even more preferably from 1 to 3 and most preferably from 1 to 2. Formulating these compositions in the acidic pH range is critical to the chemical stability of these compositions upon prolonged periods of storage before their use in the process of bleaching fabrics according to the present invention.

[0039] The pH of these compositions may be adjusted by any acidifying or alkalinising agents known to those skilled in the art. Examples of acidifying agents are organic acids such as citric acid and inorganic acids such as sulphuric acid, sulphonic acid and/or methanesulphonic acid. Examples of alkalinising agents are sodium hydroxide, potassium hydroxide and/or sodium carbonate.

Persulfate salt

[0040] As an essential element the liquid aqueous compositions for use in the process of bleaching fabrics according to the present invention comprise a persulfate salt or a mixture thereof.

[0041] Suitable persulfate salts include any alkali metal persulfate salt including sodium persulfate salts and/or potassium persulfate salts. Preferred persulfate salt to be used herein is the monopersulfate salt. Examples of monopersulfate salts commercially available are those commercialised by Interox under the trade name Curox®, by Degussa under the trade name Caroat® or by DuPont under the trade name Oxone®. It is to understand herein that when the commercially available Curox® , Caroat® and/or Oxone® are used, the % weights of persulfate salts mentioned herein, refer to the total weight of said Curox® , Caroat® and/or Oxone® . The active concentration is approximately 1/2 of the total weight. Other persulfate salts such as dipersulfate salts commercially available among others from Peroxide Chemie GMBH can be used in the compositions according to the present invention. Another suitable persulphate salt is ammonium persulphate.

[0042] Typically, the liquid compositions for use in the process of bleaching fabrics according to the present invention comprise from 0.01% to 50% by weight of the total composition of the persulfate salt or mixtures thereof, preferably from

0.5% to 20%, more preferably from 1% to 15% and most preferably from 2% to 10%.

Optional ingredients:

[0043] The liquid aqueous persulfate-containing compositions used in the process of bleaching fabrics according to the present invention may comprise a variety of optional ingredients such as bleach activator compounds, surfactants, chelating agents, radical scavengers, antioxidants, other stabilisers, builders, soil suspenders, polymeric soil release agents, catalysts, dye transfer agents, solvents, suds controlling agents, brighteners, perfumes, pigments, dyes and the like.

Bleach activators:

[0044] Suitable bleach activators for use in these liquid persulfate-containing compositions include aldehyde activator compounds, ketone activator compounds, halide activator compounds and a mixture thereof.

[0045] By "aldehyde", it is meant herein any compound which contains at least one carbonyl group and has two hydrogen atoms or carbon atom and a hydrogen atom attached directly to at least one of the carbonyl carbon atoms.

[0046] By "ketone", it is meant herein any compound which contains at least one carbonyl group and has two carbon atoms attached directly to at least one of the carbonyl carbon atoms.

[0047] These compounds can be aliphatic or aromatic substituted or unsubstituted, saturated or unsaturated, or acyclic, carbocyclic or heterocyclic.

[0048] By "halide", it is meant chloride, bromide and/or iodide.

[0049] By "activator", it is meant herein ketone, aldehyde and halide compounds and mixtures thereof that react with persulfate salt to form an activated bleaching specie, i.e. a dioxirane (when the activator compound is ketone or aldehyde) or a hypohalogenite (when the activator compound is a halide). These activation mechanisms are known in the art and are for example described in US 3822114.

[0050] Advantageously, when the liquid aqueous compositions used in the process of bleaching fabrics herein further comprise such a bleach activator, the bleaching performance and overall stain removal performance is further improved. It is the activated species, i.e. dioxirane and hypohalogenite, which are thought to greatly enhance the bleaching in the present invention over persulfate alone or over other activated bleaching system, e.g. hydrogen peroxide and acetyl triethyl citrate. These activation mechanisms mainly occur upon dilution of the compositions herein with water and are emphased with the pH jump in the neutral to alkaline pH range (i.e. around 6 and higher) associated to this dilution. It is at those pHs that more dioxiranes and/or hypohalogenites are generated thereby outstandingly improving the bleaching performance of the process of bleaching fabrics herein.

[0051] Suitable aldehyde activator compounds for use herein include chloral-hydrate, acetaldehyde, butyraldehyde, benzaldehyde, and/or 4-trimethylammonio benzaldehyde methyl sulfate. Particularly preferred aldehyde activator compounds for use herein are acetaldehyde, butyraldehyde and/or, benzaldehyde and most preferred is acetaldehyde. Aldehyde activator compounds are in general less preferred than the ketone activators compounds as they may be oxidised during prolonged storage periods.

[0052] For example acetaldehyde may be commercially available from Aldrich.

[0053] Suitable aliphatic ketone activator compounds for use herein include acetacetone, 2,3-hexanedione, trimethylammonio acetone nitrate, 5-diethylbenzylammonio 2-pentanone nitrate, 5-diethylmethylammonio 2-pentanone nitrate, methyl pyruvate, diethyl keto malonate, 3-hydroxy-2-butanone, acetol, hexachloracetone, 2,5-hexanedione, phenylacetone, ethyl levulinate, 3-hydroxy-2-pentanone, acetone, 3-penten-2-one, methyl ethyl ketone, 4-hydroxy-3-methyl-2-butanone, 3-pentanone, and/or 2-heptanone.

[0054] For example acetacetone may be commercially available from Aldrich under its chemical name.

[0055] Suitable aromatic ketone activator compounds for use herein include hydroxyquinoline, 4-acetyl-1-methylpyridinium nitrate, di-2-pyridyl ketone N-oxide, 2-acetylquinoxaline, 2-acetyl-3-methylquinoxaline oxaline, di-2- pyridyl ketone, 6-acetyl-1,2,4-trimethyl quinolinium nitrate, 8-hydroxyquinoline N-oxide, methyl phenyl glyoxalate, N-methyl-p-morpholinio acetophenone methyl sulfate, 3-acetyl pyridine N-oxide, p-nitroacetophenone, m-nitroacetophenone, sodium p-acetyl benzene sulfonate, p-acetylbenzonitrile, 3,5-dinitroacetophenone, 4-trimethylammonioacetophenone nitrate, 4-methoxy-3-nitroacetophenone, p-chloroacetophenone, p-diacetylbenzene, N-methyl-p-morpholinio acetophenone nitrate, phenacyltriphenylphosphonium nitrate, 2-acetyl pyridine, 2-acetyl pyridine N-oxide, 3-acetyl pyridine, 4-acetyl pyridine, 4-acetyl pyridine N-oxide, 2,6- diacetyl pyridine, 3-acetyl pyridine N-oxide, and/or triacetylbenzene.

[0056] Suitable cyclic ketone activator compounds for use herein include cyclohexanone, 2-methylcyclohexanone, 2,6-dimethyl cyclohexanone, 3-methyl cyclohexanone, 4-ethyl cyclohexanone, 4-t-butyl cyclohexanone, 4,4-dimethyl cyclohexanone, methyl 4-oxo-cyclohexanone carboxylate, sodium 4-oxo-cyclohexanone carboxylate, 2-trimethylammoniocyclohexanone nitrate, 4-trimethylammonio cyclohexanone nitrate, 3 oxo-cyclohexyl acetic acid, cycloheptanone, 1,4-cyclohexadione, dehydrochloric acid, tropinone methonitrate, N-methyl-3-oxoquinuclidinium nitrate, cyclooctanone and/or cyclopentanone.

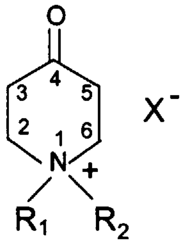
[0057] For example cyclohexanone may be commercially available from Aldrich under its chemical name.

[0058] Suitable heterocyclic ketone activator compounds for use herein include, 2,2,6,6-tetramethyl-4-piperidone hydrate, 1-methyl-4-piperidone N-oxide, N-carbethoxy 4-piperidone, tetrahydrothiopyran-4-one methonitrate, tetrahydrothiopyran-4-one S,S- dioxide, tetrahydrothiopyran-3-one,S,S,-dioxide, and/or 4-oxacyclohexanone.

[0059] All of the above-described aldehyde and ketone examples are all either commercially available or can obviously be synthesized by the skilled artisan having before him the teaching of the prior art Gardini et al., *J. Chem. Soc.(C),* (1970) page 929 and Lyle et al., *J. Org. Chem., Vol. 24* (March, 1959), page 342 are examples of such art and are hereby incorporated herein by reference. Also a method for the synthesis of oxopiperidinium compounds is described in "S.E. Denmark, D.C. Forbes, D.S. Hays, J.S. De Pue and R.G. Wilde, J.Org. Chem. 1995, 60, 1391-1407".

[0060] Particularly preferred bleach activators for use herein are the ketone activator compounds and highly preferred are the ketones activator compounds bearing a positive charge.

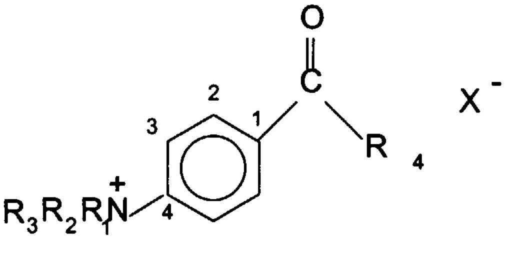
[0061] Particularly suitable ketone activator compounds bearing a positive charge are for example oxopiperidinium salts having the following formula:



wherein the carbonyl group >C=O, can be either at the 2, 3 or at the 4 position of the oxopiperidinium; R1 and R2 are each independently a substituted or unsubstituted hydrocarbon chain having from 1 to 20 carbon atoms, preferably a substituted or unsubstituted alkyl or alkenyl or alkinyl group containing from 1 to 20 carbon atoms, preferably from 1 to 12 carbon atoms, or a substituted or unsubstituted aryl group containing from 6 to 10 atoms, or a C1-C20 alkyl aryl group wherein the aryl group contains from 6 to 10 carbon atoms; X^- can be any negative ion, e.g., triflate, tosilate, mesilate, nitrate, more preferred is triflate, mesilate, tosilate and most preferred is triflate and the oxopiperidinium ring can be mono or polysubstituted at the 2,3,5, or 6 positions by one or more substituents as defined for R1 or R2 above or a halogen atom.

[0062] Examples of oxopiperidinium salts particularly suitable for use herein include 1,1-dimethyl-3-oxopiperidinium nitrate, 1,1-dimethyl-4-oxopiperidinium triflate, 1,1-dimethyl-3-oxopiperidinium triflate, 1,1-dimethyl-4-oxopiperidinium nitrate, 1-benzyl-4-piperidone methonitrate, 1-t-butyl-1-methyl-4-oxopiperidinium nitrate, 1-(4-dodecylbenzyl) 1-methyl-4 oxopiperidinium chloride, 3-(N-methyl-4 oxopiperidinium)-propane sulfonate, 1-allyl-1-methyl-4- oxopiperidinium chloride, 1-methyl-1-(1-naphthyl-methyl)-4- oxopiperidinium chloride, 1-methyl-1-pentamethylbenzyl-4-oxopiperidinium chloride, N,N'-dimethyl-N,N'-phenylene dimethylene -bis(4- oxopiperidinlum nitrate), 1-benzyl-1-methyl-4-oxopiperidinium triflate, 1-benzyl-1-methyl-3-oxopiperidinium triflate, 1-benzyl-1-methyl-4-oxopiperidinium nitrate, 1-dodecyl-1-methyl-4-oxopiperidinium nitrate, 1-octyl-1-methyl-4-oxopiperidinium nitrate, 1-nonyl-1-methyl-4-oxopiperidinium nitrate or a mixture thereof.

[0063] Other suitable ketone activator compounds bearing a positive charge suitable for use herein are for example the ammonium acetophenone salts according to the following formula:



wherein the ammonium group can be either at the 2 , at the 3 position or at the 4 position ; R1, R2 and R3 are each independently a substituted or unsubstituted hydrocarbon group having from 1 to 20 carbon atoms, preferably a substituted or unsubstituted alkyl, or alkenyl or alkinyl group containing from 1 to 20 carbon atoms, preferably from 1 to 12 carbon atoms, or a substituted or unsubstituted aryl group containing from 6 to 10 atoms or a C1-C20 alkyl aryl group wherein the aryl group contains from 6 to 10 carbon atoms; R4 is a substituted or nonsubstituted halogenate alkyl group having from 1 to 20 carbon atoms, preferably from 1 to 12 carbon atoms and more preferably is methyl, or trifluoromethyl or trichloromethyl or tribromomethyl, ;X^- can be any negative ion, e.g., triflate, tosilate, mesilate, or nitrate and the benzenic ring can be substituted at the 2, 3 and/or 4 positions by one or more substituents as defined for R1 , R2 or R3 as described above or a halogen atom.

[0064] Examples of such ammonium acetophenone salts for use herein include 4-trimethylammonium acetophenone nitrate, 2-trimethylammoniumacetophenone nitrate, 4-triethylammoniumacetophenone mesilate, 3-trimethylammoniumacetophenone mesilate, trihalogenatedmethylphenyl ketone like trifluoromethylphenylketone, trichloromethylphenylketone, tribromomethylphenylketone or a mixture thereof.

[0065] Suitable halide activator compounds for use herein include chloride, bromide, iodide and mixtures thereof. Particularly preferred halide activator compounds for use herein is an alkali metal of chloride. For example sodium chloride may be commercially available from Aldrich under its chemical name.

[0066] Typically, the compositions herein comprise up to 10% by weight of the total composition of said ketone, aldehyde and/or halide activator compound, preferably from 0.05% to 5%, more preferably from 0.1% to 2% and most preferably from 0.2% to 1.5%.

Surfactants:

[0067] The liquid persulfate-containing compositions suitable for use in the process of bleaching fabrics herein may comprise a surfactant or a mixture thereof including nonionic surfactants, anionic surfactants, cationic surfactants, zwitterionic surfactants and/or amphoteric surfactants. Typically these surfactants do not contain functional groups that can be oxidised by the persulphate salt, or that can substantially hydrolize at a low pH.

[0068] Typically, the compositions according to the present invention may comprise from 0.01% to 50% by weight of the total composition of a surfactant or a mixture thereof, preferably from 0.1% to 30 % and more preferably from 0.2% to 10%.

[0069] Suitable anionic surfactants for use in the compositions herein include water-soluble salts or acids of the formula $ROSO_3M$ wherein R preferably is a C_{10}-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). Typically, alkyl chains of C_{12}-$_{16}$ are preferred for lower wash temperatures (e.g., below about 50°C) and C_{16}-$_{18}$ alkyl chains are preferred for higher wash temperatures (e.g., above about 50°C).

[0070] Other suitable anionic surfactants for use herein are water-soluble salts or acids of the formula $RO(A)_mSO_3M$ wherein R is an unsubstituted C_{10}-C_{24} alkyl or hydroxyalkyl group having a C_{10}-C_{24} alkyl component, preferably a C_{12}-C_{20} alkyl or hydroxyalkyl, more preferably C_{12}-C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperdinium and cations derived from alkanolamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C_{12}-C_{18} alkyl polyethoxylate (1.0) sulfate, C_{12}-$C_{18}E(1.0)M$), C_{12}-C_{18} alkyl polyethoxylate (2.25) sulfate, C_{12}-$C_{18}E(2.25)M$), C_{12}-C_{18} alkyl polyethoxylate (3.0) sulfate C_{12}-$C_{18}E(3.0)$, and C_{12}-C_{18} alkyl polyethoxylate (4.0) sulfate C_{12}-$C_{18}E(4.0)M$), wherein M is conveniently selected from sodium and potassium.

[0071] Other particularly suitable anionic surfactants for use herein are alkyl sulphonates including water-soluble salts or acids of the formula RSO_3M wherein R is a C_6-C_{22} linear or branched, saturated or unsaturated alkyl group, preferably a C_{12}-C_{18} alkyl group and more preferably a C_{14}-C_{16} alkyl group, 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).

[0072] Suitable alkyl aryl sulphonates for use herein include water- soluble salts or acids of the formula RSO_3M wherein R is an aryl, preferably a benzyl, substituted by a C_6-C_{22} linear or branched saturated or unsaturated alkyl group, preferably a C_{12}-C_{18} alkyl group and more preferably a C_{14}-C_{16} alkyl group, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium, calcium, magnesium etc) or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quatemary 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).

[0073] The alkylsulfonates and alkyl aryl sulphonates for use herein include primary and secondary alkylsulfonates and primary and secondary alkyl aryl sulphonates. By "secondary C6-C22 alkyl or C6-C22 alkyl aryl sulphonates", it is meant herein that in the formula as defined above, the SO3M or aryl-SO3M group is linked to a carbon atom of the alkyl chain being placed between two other carbons of the said alkyl chain (secondary carbon atom).

[0074] For example C14-C16 alkyl sulphonate salt is commercially available under the name Hostapur ® SAS from Hoechst and C8-alkylsulphonate sodium salt is commercially available under the name Witconate NAS 8® from Witco SA. An example of commercially available alkyl aryl sulphonate is Lauryl aryl sulphonate from Su.Ma. Particularly preferred alkyl aryl sulphonates are alkyl benzene sulphonates commercially available under trade name Nansa® available from Albright&Wilson.

[0075] Other anionic surfactants useful for detersive purposes can also be used herein. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, 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_{14-16} 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), 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).

[0076] Other particularly suitable anionic surfactants for use herein are alkyl carboxylates and alkyl alkoxycarboxylates having from 4 to 24 carbon atoms in the alkyl chain, preferably from 8 to 18 and more preferably from 8 to 16, wherein the alkoxy is propoxy and/or ethoxy and preferably is ethoxy at an alkoxylation degree of from 0.5 to 20, preferably from 5 to 15. Preferred alkylalkoxycarboxylate for use herein is sodium laureth 11 carboxylate (i.e., $RO(C_2H_4O)_{10}$-CN_2COONa, with R= C12-C14) commercially available under the name Akyposoft® 100NV from Kao Chemical Gbmh.

[0077] Suitable amphoteric surfactants for use herein include amine oxides having the following formula R_1 R_2R_3NO wherein each of R1, R2 and R3 is independently a saturated substituted or unsubstituted, linear or branched hydrocarbon chains of from 1 to 30 carbon atoms. Preferred amine oxide surfactants to be used according to the present invention are amine oxides having the following formula R_1 R_2R_3NO wherein R1 is an hydrocarbon chain comprising from 1 to 30 carbon atoms, preferably from 6 to 20, more preferably from 8 to 16, most preferably from 8 to 12, and wherein R2 and R3 are independently substituted or unsubstituted, linear or branched hydrocarbon chains comprising from 1 to 4 carbon atoms, preferably from 1 to 3 carbon atoms, and more preferably are methyl groups. R1 may be a saturated substituted or unsubstituted linear or branched hydrocarbon chain. Suitable 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.

[0078] Suitable zwitterionic surfactants for use herein contain both a cationic hydrophilic group, i.e., a quaternary ammonium group, and anionic hydrophilic group on the same molecule at a relatively wide range of pH's. 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 the zwitterionic surfactants to be used herein is:

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

wherein R_1 is a hydrophobic group; R_2 is hydrogen, C_1-C_6 alkyl, hydroxy alkyl or other substituted C_1-C_6 alkyl group; R_3 is C_1-C_6 alkyl, hydroxy alkyl or other substituted C_1-C_6 alkyl group which can also be joined to R_2 to form ring structures with the N, or a C_1-C_6 carboxylic acid group or a C_1-C_6 sulfonate group; 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 10 carbon atoms; and X is the hydrophilic group which is a carboxylate or sulfonate group.

[0079] Preferred hydrophobic groups R_1 are aliphatic or aromatic, saturated or unsaturated, substituted or unsubstituted hydrocarbon chains that can contain linking groups such as amido groups, ester groups. More preferred R_1 is an alkyl group containing from 1 to 24 carbon atoms, preferably from 8 to 18, and more preferably from 10 to 16. These simple alkyl groups are preferred for cost and stability reasons. However, the hydrophobic group R_1 can also be an amido radical of the formula R_a-C(O)-NH-$(C(R_b)_2)_m$, wherein R_a is an aliphatic or aromatic, saturated or unsaturated, substituted or unsubstituted hydrocarbon chain, preferably an alkyl group containing from 8 up to 20 carbon atoms, preferably up to 18, more preferably up to 16, R_b is selected from the group consisting of hydrogen and hydroxy groups, and m is from 1 to 4, preferably from 2 to 3, more preferably 3, with no more than one hydroxy group in any $(C(R_b)_2)$ moiety.

[0080] Preferred R_2 is hydrogen, or a C_1-C_3 alkyl and more preferably methyl. Preferred R_3 is a C_1-C_4 carboxylic acid group or C1-C4 sulfonate group, or a C_1-C_3 alkyl and more preferably methyl. Preferred R_4 is $(CH2)_n$ wherein n is an integer from 1 to 10, preferably from 1 to 6, more preferably is from 1 to 3.

[0081] Some common examples of betaine/sulphobetaine are described in U.S. Pat. Nos. 2,082,275, 2,702,279 and 2,255,082, incorporated herein by reference.

[0082] Examples of particularly suitable alkyldimethyl betaines include coconut-dimethyl betaine, lauryl dimethyl betaine, decyl dimethyl betaine, 2-(N-decyl-N, N-dimethyl-ammonia)acetate, 2-(N-coco N, N-dimethylammonio) acetate, myristyl dimethyl betaine, palmityl dimethyl betaine, cetyl dimethyl betaine, stearyl dimethyl betaine. For example Coconut dimethyl betaine is commercially available from Seppic under the trade name of Amonyl 265®. Lauryl betaine is commercially available from Albright & Wilson under the trade name Empigen BB/L®.

[0083] Examples of amidobetaines include cocoamidoethylbetaine, cocoamidopropyl betaine or C10-C14 fatty acylamidopropylene(hydropropylene)sulfobetaine. For example C10-C14 fatty acylamidopropylene(hydropropylene)sulfobetaine is commercially available from Sherex Company under the trade name "Varion CAS® sulfobetaine".

[0084] A further example of betaine is Lauryl-immino-dipropionate commercially available from Rhone-Poulenc under the trade name Mirataine H2C-HA ®.

[0085] Suitable cationic surfactants for use 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. Preferred quaternary ammonium compounds suitable for use herein are non-chloride/non halogen quaternary ammonium compounds. The counterion used in said quaternary ammonium compounds are compatible with any persulfate salt and are selected from the group of methyl sulfate, or methylsulfonate, and the like.

[0086] Particularly preferred for use in the compositions of the present invention 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®.

[0087] Amongst the nonionic surfactants, alkoxylated nonionic surfactants and especially ethoxylated nonionic surfactants are suitable for use herein. Particularly preferred nonionic surfactants for use herein are the capped alkoxylated nonionic surfactants as they have improved stability to the persulfate salts.

[0088] Suitable capped alkoxylated nonionic surfactants for use herein are according to the formula:

$$R_1(O\text{-}CH_2\text{-}CH_2)_n\text{-}(OR_2)_m\text{-}O\text{-}R_3$$

wherein R_1 is a C_8-C_{24} linear or branched alkyl or alkenyl group, aryl group, alkaryl group, preferably R_1 is a C_8-C_{18} alkyl or alkenyl group, more preferably a C_{10}-C_{15} alkyl or alkenyl group, even more preferably a C_{10}-C_{15} alkyl group;

wherein R_2 is a C_1 -C_{10} linear or branched alkyl group, preferably a C_2-C_{10} linear or branched alkyl group;

wherein R_3 is a C_1-C_{10} alkyl or alkenyl group, preferably a C_1-C_5 alkyl group, more preferably methyl;

and wherein n and m are integers independently ranging in the range of from 1 to 20, preferably from 1 to 10, more preferably from 1 to 5; or mixtures thereof.

[0089] These surfactants are commercially available from BASF under the trade name Plurafac®, from HOECHST under the trade name Genapol® or from ICI under the trade name Symperonic®. Preferred capped nonionic alkoxylated surfactants of the above formula are those commercially available under the tradename Genapol® L 2.5 NR from Hoechst, and Plurafac® from BASF.

Cheating agents:

[0090] The liquid aqueous persulfate-containing compositions suitable for use in the process of bleaching fabrics herein may comprise a chelating agent as a preferred optional ingredient. Suitable chelating agents may be any of those known to those skilled in the art such as the ones selected from the group comprising phosphonate chelating agents, amino carboxylate chelating agents, other carboxylate chelating agents, polyfunctionally-substituted aromatic chelating agents, ethylenediamine N,N'- disuccinic acids, or mixtures thereof.

[0091] The presence of chelating agents contribute to further enhance the chemical stability of the compositions. A cheating agent may be also desired in the compositions herein as it allows to increase the ionic strength of the compositions and thus their stain removal and bleaching performance on various surfaces.

[0092] Suitable phosphonate chelating agents for use herein may include alkali metal ethane 1-hydroxy diphosphonates (HEDP), alkylene poly (alkylene phosphonate), as well as amino phosphonate compounds, including amino aminotri(methylene phosphonic acid) (ATMP), nitrilo trimethylene phosphonates (NTP), ethylene diamine tetra methylene phosphonates, and diethylene triamine penta methylene phosphonates (DTPMP). 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 cheating agents to be used herein are diethylene triamine penta methylene phosphonate (DTPMP) and ethane 1-hydroxy diphosphonate (HEDP). Such phosphonate chelating agents are commercially available from Monsanto under the trade name DEQUEST®.

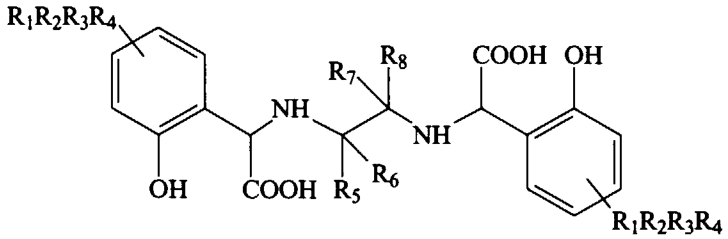
[0093] Polyfunctionally-substituted aromatic chelating agents may also be useful in the compositions herein. See U.S. patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy -3,5-disulfobenzene.

[0094] 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 acids is, for instance, commercially available under the tradename ssEDDS® from Palmer Research Laboratories.

[0095] Suitable amino carboxylates for use herein include ethylene diamine tetra acetates, diethylene triamine pentaacetates, diethylene triamine pentaacetate (DTPA),N- hydroxyethylethylenediamine triacetates, nitrilotri-acetates, ethylenediamine tetrapropionates, triethylenetetraaminehexa-acetates, ethanol-diglycines, propylene diamine tetracetic acid (PDTA) and methyl glycine diacetic acid (MGDA), both in their acid form, or in their alkali metal, ammonium, and substituted ammonium salt forms. Particularly suitable amino carboxylates to be used herein are diethylene triamine penta acetic acid, propylene diamine tetracetic acid (PDTA) which is, for instance, commercially available from BASF under the trade name Trilon FS® and methyl glycine di-acetic acid (MGDA).

[0096] Further carboxylate chelating agents for use herein include salicylic acid, aspartic acid, glutamic acid, glycine, malonic acid or mixtures thereof.

[0097] Another chelating agent for use herein is of the formula:



wherein R_1, R_2, R_3, and R_4 are independently selected from the group consisting of -H, alkyl, alkoxy, aryl, aryloxy, -Cl, -Br, $-NO_2$, -C(O)R', and $-SO_2R''$; wherein R' is selected from the group consisting of -H, -OH, alkyl, alkoxy, aryl, and aryloxy; R'' is selected from the group consisting of alkyl, alkoxy, aryl, and aryloxy; and R_5, R_6, R_7, and R_8 are independently selected from the group consisting of -H and alkyl.

[0098] Particularly preferred cheating agents to be used herein are amino aminotri(methylene phosphonic acid), di-ethylene-triamino-pentaacetic acid, diethylene triamine penta methylene phosphonate, 1-hydroxy ethane diphosphonate, ethylenediamine N, N'-disuccinic acid, and mixtures thereof.

[0099] Typically, the liquid aqueous persulfate-containing compositions suitable for use in the process of bleaching fabrics herein comprise up to 5% by weight of the total composition of a chelating agent, or mixtures thereof, preferably from 0.01% to 1.5% by weight and more preferably from 0.01% to 0.5%.

Radical scavengers:

[0100] The liquid aqueous persulfate-containing compositions suitable for use in the process of bleaching fabrics herein may comprise a radical scavenger or a mixture thereof. Suitable radical scavengers for use herein include the well-known substituted mono and dihydroxy 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. Such radical scavengers like N-propyl-gallate may be commercially available from Nipa Laboratories under the trade name Nipanox S1 ®. Radical scavengers when used, are typically present herein in amounts ranging from up to 10% by weight of the total composition and preferably from 0.001% to 0.5% by weight.

[0101] The presence of radical scavengers may contribute to the chemical stability of the bleaching compositions herein as well as to the safety profile of these compositions.

Test methods:

[0102] The bleaching performance may be evaluated by the following test methods on various type of bleachable stains.

[0103] A suitable test method for evaluating the bleaching performance on a soiled fabric under soaking conditions is the following: A composition according to the present invention is diluted with water typically at a dilution level of 1 to 100 ml/L, preferably 20 ml/L (composition :water), then the soiled fabrics are soaked in it for 20 minutes to 6 hours and then rinsed. Alternatively the bleaching composition can be used in a washing machine at a dilution level of typically at a dilution level of 1 to 100 ml/L (composition :water). In the washing machine the soiled fabrics are washed at a temperature of from 30° to 70°C for 10 to 100 minutes and then rinsed. The reference composition in this comparative test undergoes the same treatment. Soiled fabrics/swatches with for example tea, coffee and the like may be commercially available from E.M.C. Co. Inc..

[0104] The bleaching performance is then evaluated by comparing side by side the soiled fabrics treated with the composition used in the present invention with those treated with the reference, e.g., the same composition but comprising another bleaching system, e.g., hydrogen peroxide and acetyl triethyl citrate at equal bleaching agents total level. A visual grading may be used to assign difference in panel units (psu) in a range from 0 to 4.

[0105] For stain removal performance on various stains the same test method is followed but on enzymatic and greasy stains.

Examples

[0106] Following liquid aqueous persulfate compositions were made by mixing the listed ingredients in the listed proportions (weight % unless otherwise specified).

Compositions (% weight)	I	II	III	IV	V
Akyposoft 100 NV®	0.5	0.5	-	0.3	0.4
Curox®	3	2	4	4.3	5
Trifluoromethylphenylketone	0.5	-	-	0.3	-
Acetoacetone	-	0.4	-	-	0.4
HEDP	0.1	0.05	0.16	0.1	-
BHT	0.05	-	-	-	0.1
Propyl gallate	-	0.1	-	0.05	-

(continued)

Compositions (% weight)	I	II	III	IV	V
NaCl	-	-	0.1	0.5	-
NaBr	-	-	-	-	1.0
Water and minors	up to 100%				
Alkanizing agent up to pH	2	2.5	4	4	1.5

Compositions (% weight)	**VI**	**VII**	**VIII**	**IX**	**X**	**XI**
Akyposoft 100 NV®	0.5	0.5	0.5	0.2	0.2	-
Curox®	5	7	10	10	6	9.5
Acetylacetone	0.5	0.5	0.5	-	-	-
N,N dymethyl-4						
-oxopiperidinium nitrate	-	-	-	0.5	0.5	-
Propyl gallate	0.05	0.05	0.1	0.1	0.05	-
Water and minors	up to 100%					
pH	2	1.8	1.5	1.5	2	2

Compositions (% weight)	**XII**	**XIII**	**XIV**	**XV**	**XVI**	**XVII**
Akyposoft 100 NV®	0.5	0.5	0.5	0.2	0.2	0.2
Curox®	5	7	10	10	6	9.5
Cyclohexanone	0.5	-	0.5	0.5	-	-
N,N dymethyl-3	-	0.5	-	-	0.5	-
-oxopiperidinium nitrate						
Propyl gallate	0.05	0.05	0.1	0.1	0.05	0.1
Water and minors	up to 100%					
pH	2	1.8	1.5	1.5	2	2

Compositions (% weight)	**XVIII**	**XIX**	**XX**	**XXI**	**XXII**	**XXIII**
Witconate NAS 8 (40% active)®	5	5	5	5	5	-

(continued)

Compositions (% weight)	XVIII	XIX	XX	XXI	XXII	XXIII
Curox®	9.5	9.5	9.5	9.5	9.5	9.5
N,N dymethyl-4 -oxopiperidinium triflate	0.5	1	0.1	0.5	0.5	-
HEDP	0.1	0.2	0.1	-	-	0.1
BHT	0.05	0.05	0.1	0.1	0.05	0.05
Water and minors	up to 100%					
pH	1.5	1.5	1.5	1.5	1.5	1.5

Compositions (% weight)	XXIV	XXV
Witconate NAS 8 (40% active)®	5	5
Curox®	9.5	9.5
Cycloheptanone	0.5	0.5
HEDP	-	0.1
BHT	-	0.05
Water and minors	up to 100%	
pH	1.5	1.5

Akyposoft 100 NV® is a C12-C14 alkyl ethoxycarboxylate (EO10) commercially available from Kao Chemicala Gmbh.
BHT is di-tert butyl hydroxy toluene.
HEDP is ethane 1-hydroxy diphosphonate commercially available from Monsanto under the serie Dequest®.
Cycloheptanone is commercially available from Aldrich.
Witconate NAS 8® is C8 alkyl sulphonate commercially available from Witco SA.
Curox® is a triple salt of potassium monopersulfate, potassium sulphate and potassium bisulphate commercially available from Interox.

The following processes of bleaching fabrics will illustrate the present invention:

Example 1

[0107] 100 ml of a liquid persulphate composition as exemplified above (compositions I to XXV) was diluted in 5L of water. Then soiled fabrics were contacted with the aqueous bath so obtained for 20 minutes before being rinsed with water.

Example 2

[0108] 200 ml of a liquid persulphate composition as exemplified above (compositions I to XXV) was diluted in 5L of water. Then soiled fabrics were contacted with the aqueous bath so obtained for 20 minutes before being rinsed with water for 20 minutes.

Example 3

[0109] 300 ml of a liquid persulphate composition as exemplified above (compositions I to XXV) was diluted in 5L of water. Then soiled fabrics were contacted with the aqueous bath so obtained for 20 minutes before being rinsed with water for 20 minutes.

Example 4

[0110] 100 ml of a liquid persulphate composition as exemplified above (compositions I to XXV) was diluted in 5L of water. Then soiled fabrics were contacted with the aqueous bath so obtained for 1 hour before being rinsed with water for 20 minutes.

Example 5

[0111] 100 ml of a liquid persulphate composition as exemplified above (compositions I to XXV) was diluted in 5L of water. Then soiled fabrics were contacted with the aqueous bath so obtained for 6 hours before being rinsed with water for 20 minutes.

Example 6

[0112] 100 ml of a liquid persulphate composition as exemplified above (compositions I to XXV) was diluted in 5L of water. Then soiled fabrics were contacted with the aqueous bath so obtained for 24 hours before being rinsed with water for 20 minutes.

Example 7

[0113] 100 ml of a liquid persulphate composition as exemplified above (compositions I to XXV) was diluted in 5L of water. Then soiled fabrics were contacted with the aqueous bath so obtained for 1 hour before being rinsed with water for 20 minutes. Finally the fabrics so bleached were contacting for 1 hour with 40g of Dash Futur® diluted in 5L of water and subsequently rinsed with water.

Example 8

[0114] 140 ml of Ariel a mano® were diluted with 5 liters of water. The soiled fabrics were contacted to the soaking solution so obtained for 1 hour and subsequently rinsed. Then 100 ml of a liquid persulphate composition as exemplified above (compositions I to XXV) was diluted in 5L of water. Then the fabrics were contacted with the aqueous bath so obtained for 1 hour before being rinsed with water for 20 minutes.

Example 9

[0115] 100 ml of a liquid persulfate-containing composition as exemplified above (compositions I to XXV) was diluted in 5L of water to obtain an aqueous bath to which the soiled fabrics were contacted for 20 minutes. The fabrics were then rinsed for 2 minutes than washed in a washing machine (e.g. San Giorgio 352 ZX®, main cycle) with 225g of Dash Futur®.

[0116] All the above processes provide excellent bleaching performance as well as effective stain removal performance when bleaching fabrics while being safe to the fabrics and the colours.

Claims

1. A process of bleaching a fabric which comprises the steps of :

   - diluting in an aqueous bath a liquid aqueous composition in its neat form, having a pH below 7 and comprising a persulfate salt,
   - contacting said fabric with said aqueous bath comprising said liquid composition, and subsequently rinsing said fabric with water.

2. A process according to claim 1 wherein the fabric is left to soak in said aqueous bath comprising said liquid aqueous composition for a period of time ranging from 1 minute to 24 hours, preferably from 3 minutes to 12 hours, more

preferably from 4 minutes to 6 hours and most preferably 4 minutes to 15 minutes.

3. A process according to any of the preceding claims wherein the composition is diluted with water at a dilution level up to 500 times its weight, preferably from 5 to 200 times and more preferably from 10 to 80 times.

4. A process according to any of the preceding claims wherein said fabric is washed with a laundry detergent composition comprising at least one surface active agent before the step of contacting said fabrics with said aqueous bath comprising said liquid aqueous composition and/or in the step where said fabrics are contacted with said aqueous bath and/or after the step where said fabrics are contacted with said aqueous bath and before the rinsing step and/or after the rinsing step.

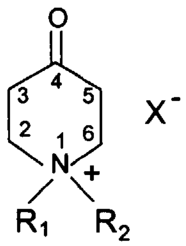
5. A process according to the preceding claims wherein said liquid aqueous composition comprises from 0.01% to 50% by weight of the total composition of a persulfate salt or mixtures thereof, preferably from 0.5% to 20%, more preferably from 1% to 15% and most preferably from 2% to 10%.

6. A process according to any of the preceding claims wherein in said liquid composition said persulfate salt is a monopersulfate salt, preferably sodium monopersulfate and/or potassium monopersulfate.

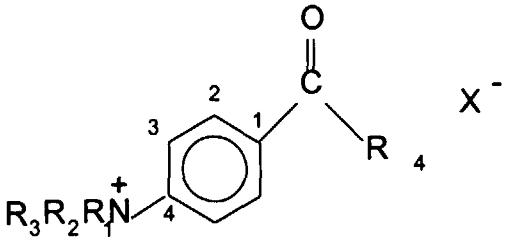
7. A process according to any of the preceding claims wherein said liquid composition further comprises up to 10% by weight of the total composition of a ketone, aldehyde and/or halide activator compound, preferably from 0.05% to 5%, more preferably from 0.1% to 2% and most preferably from 0.2% to 1.5%.

8. A process according to claim 7 wherein said activator is an oxopiperidinium salt, an ammonium acetophenone salt, acetacetone, 2,3-hexanedione, trimethylammonio acetone nitrate, 5-diethylbenzylammonio 2-pentanone nitrate, 5-diethylmethylammonio 2-pentanone nitrate, methyl pyruvate, diethyl keto malonate, 3-hydroxy-2-butanone, acetol, hexachloracetone, 2,5- hexanedione, phenylacetone, ethyl levulinate, 3-hydroxy-2-pentanone, acetone, 3-penten-2-one, methyl ethyl ketone, 4-hydroxy-3-methyl-2-butanone, 3-pentanone, 2-heptanone, hydroxyquinoline, 4-acetyl-1-methylpyridinium nitrate, di-2-pyridyl ketone N-oxide, 2-acetylquinoxaline, 2-acetyl-3-methylquinoxaline oxaline, di-2-pyridyl ketone, 6-acetyl-1,2,4-trimethyl quinolinium nitrate, 8-hydroxyquinoline N-oxide, methyl phenyl glyoxalate, N-methyl-p-morpholinio acetophenone methyl sulfate, 3-acetyl pyridine N-oxide, p-nitroacetophenone, m-nitroacetophenone, sodium p-acetyl benzene sulfonate, p-acetylbenzonitrile, 3,5-dinitroacetophenone, 4-trimethylammonioacetophenone nitrate, 4-methoxy-3-nitroacetophenone, p-chloroacetophenone, p-diacetylbenzene, N-methyl-p-morpholinio acetophenone nitrate, phenacyltriphenylphosphonium nitrate, 2-acetyl pyridine, 2-acetyl pyridine N-oxide, 3-acetyl pyridine, 4-acetyl pyridine, 4-acetyl pyridine N-oxide, 2,6- diacetyl pyridine, 3-acetyl pyridine N-oxide, triacetylbenzene, cyclohexanone, 2-methylcyclohexanone, 2,6-dimethyl cyclohexanone, 3-methyl cyclohexanone, 4-ethyl cyclohexanone, 4-t-butyl cyclohexanone, 4,4-dimethyl cyclohexanone, methyl 4-oxo-cyclohexanone carboxylate, sodium 4-oxo-cyclohexanone carboxylate, 2-trimethylammoniocyclohexanone nitrate, 4-trimethylammonio cyclohexanone nitrate, 3 oxo-cyclohexyl acetic acid, cycloheptanone, 1,4-cyclohexadione, dehydrochloric acid, tropinone methonitrate, N-methyl-3-oxoquinuclidinium nitrate, cyclooctanone, cyclopentanone, 2,2,6,6-tetramethyl-4-piperidone hydrate, 1-methyl-4-piperidone N-oxide, N-carbethoxy 4-piperidone, tetrahydrothiopyran-4-one methonitrate, tetrahydrothiopyran-4-one S,S- dioxide, tetrahydrothiopyran-3-one,S,S,-dioxide, 4-oxacyclohexanone, or a mixture thereof.

9. A process according to any of the preceding claims 7 or 8 wherein in said liquid aqueous composition said bleach activator is an oxopiperidinium salt having the following formula:



wherein the carbonyl group >C=O, can be either at the 2, 3 or at the 4 position of the oxopiperidinium; R1 and R2 are each independently a substituted or unsubstituted hydrocarbon chain having from 1 to 20 carbon atoms, preferably a substituted or unsubstituted alkyl or alkenyl or alkinyl group containing from 1 to 20 carbon atoms, preferably from 1 to 12, or a substituted or unsubstituted aryl group containing from 6 to 10 atoms, or a C1-C20 alkyl aryl group wherein the aryl group contains from 6 to 10 carbon atoms; X^- can be any negative ion, e.g., triflate, tosilate, mesiltae, nitrate, more preferred is triflate, mesilate, tosilate and most preferred is triflate and the oxopiperidinium ring can be mono or polysubstituted at the 2,3,5, or 6 positions by one or more substituents as defined for R1 or R2 or a halogen atom and/or an ammonium acetophenone salt according to the following formula:



wherein the ammonium group can be either at the 2, at the 3 position or at the 4 position ; R1, R2 and R3 are each independently a substituted or unsubstituted hydrocarbon group having from 1 to 20 carbon atoms, preferably a substituted or unsubstituted alkyl, or alkenyl or alkinyl group containing from 1 to 20 carbon atoms, preferably from 1 to 12, or a substituted or unsubstituted aryl group containing from 6 to 10 atoms or a C1-C20 alkyl aryl group wherein the aryl group contains from 6 to 10 carbon atoms; R4 is an alkyl group having from 1 to 20 carbon atoms, preferably from *1* to *12* and more preferably is methyl, or trifluoromethyl, trichloromethyl or tribromomethyl; X^- can be any negative ion, e.g., triflate, tosilate, mesilate, or nitrate and the benzenic ring can be substituted at the 2, 3 and/or 4 positions by one or more substituents as defined for R1, R2 or R3 as described above or a halogen atom.

10. A process according to any of the preceding claims 7 to 9, wherein in said liquid aqueous composition said bleach activator is 1,1-dimethyl-3-oxopiperidinium nitrate, 1,1-dimethyl-4-oxopiperidinium triflate, 1,1-dimethyl-3-oxopiperidinium triflate, 1,1-dimethyl-4-oxopiperidinium nitrate, 1-benzyl-4-piperidone methonitrate, 1-t-butyl-1-methyl-4-oxopiperidinium nitrate, 1-(4-dodecylbenzyl) 1-methyl-4 oxopiperidinium chloride, 3-(N-methyl-4 oxopiperidinium)-propane sulfonate, 1-allyl-1-methyl-4-oxopiperidinium chloride, 1-methyl-1-(1-naphthyl-methyl)-4-oxopiperidinium chloride, 1-methyl-1-pentamethylbenzyl- 4-oxopiperidinium chloride, N,N'-dimethyl-N,N'-phenylene dimethylene - bis(4- oxopiperidinlum nitrate), 1-benzyl-1-methyl-4-oxopiperidinium triflate, 1-benzyl-1-methyl-3-oxopiperidinium triflate, 1-benzyl-1-methyl-4-oxopiperidinium nitrate, 1-dodecyl-1-methyl-4-oxopiperidinium nitrate, 1-octyl-1-methyl-4-oxopiperidinium nitrate, 1-nonyl-1-methyl-4-oxopiperidinium nitrate, 4-trimethylammonium acetophenone nitrate, 2-trimethylammoniumacetophenone nitrate, 4-triethylammoniumacetophenone mesilate, 3-trimethylammoniumacetophenone mesilate, trihalogenatedmethylphenyl ketone or a mixture thereof.

11. A process according to any of the preceding claims wherein said liquid composition has a pH in the range from 0.1 to 6, more preferably from 0.5 to 4, even more preferably from 1 to 3 and most preferably from 1 to 2.

12. A process according to any of the preceding claims wherein said liquid composition further comprises at least an optional ingredient selected from the group consisting of chelating agents, radical scavengers, builders, surfactants, antioxidants, stabilisers, soil suspenders, polymeric soil release agents, catalysts, dye transfer agents, solvents, suds controlling agents, brighteners, perfumes, dyes, pigments and mixtures thereof.

13. The use of a liquid aqueous bleaching composition having a pH below 7 and comprising a persulfate salt and optionally a bleach activator compound being an aldehyde, ketone and/or halide activator compound for the bleaching of fabrics, for reducing the loss of tensile strength in said fabrics.

14. The use of a liquid aqueous bleaching composition having a pH below 7 and comprising a persulfate salt and optionally a bleach activator compound being an aldehyde, ketone and/or halide activator compound for the bleaching of coloured fabrics, for reducing the colour damage to said fabrics.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 87 0172

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	EP 0 791 362 A (PROCTER & GAMBLE) * page 5, line 52 - page 6, line 57 * * page 11, line 15 - line 59 * * page 13, line 1 - line 3 * * claims 1-20 * ---	1-6,11, 12,14	C11D3/39 D06L3/02
X	US 3 556 711 A (STALTER NEIL J) * column 3, line 41 - line 44 * * column 4, line 33 - line 44 * * column 5, line 41 - line 62 * * claim 18 * ---	1-6,11, 14	
X	GB 2 022 641 A (COLGATE PALMOLIVE CO) * page 5, line 55 - page 6, line 8 * * page 13, line 14 - line 18 * * claims 1-13 * ---	1-6, 11-14	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	US 3 822 114 A (MONTGOMERY R) * claims 1-9 * * column 3, line 36 - line 43 * * column 13, line 65 - column 14, line 8 * ---	1-14	C11D
A	WO 97 24430 A (COLGATE PALMOLIVE CO) * claims 1-23 * * page 6, line 13 - line 20 * * page 8, line 27 - line 28 * ---	1-14	
A	WO 97 24429 A (COLGATE PALMOLIVE CO) * claims 1-17 * * page 12, line 7 - line 9 * ---	1-14	
A	US 4 006 092 A (JONES J PAUL) * claims 1-6 * --- -/--	1-14	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	3 April 1998	Richards, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 87 0172

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	US 5 512 206 A (STELTENKAMP ROBERT ET AL) * claims 1-8 * -----	1-14	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	3 April 1998	Richards, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)