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(54) Hard surface cleaning compositions

(57) The invention concerns cationic nitriles and their use as bleach activator compounds in hard surface cleaning compositions comprising a peroxygen bleach compound. The cationic nitriles have the general formula:

$$R_2$$
 R_1 -- N^{\oplus} -- CH_2 -- CN X^{\oplus}
 R_3

wherein R_1 is an alkyl group of 3-10 carbon atoms, a phenyl-substituted alkyl group with a total of 7-12 carbon atoms, or a (alkyl-substituted) phenyl group of 6-10 carbon atoms, R_2 and R_3 are independently methyl or ethyl groups and X^{\odot} is a counterion.

The hard surface cleaning compositions are preferably aqueous liquids, comprising hydrogen peroxide as the peroxygen bleach compound.

Description

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Field of the invention

[0001] The invention relates to hard surface cleaning compositions comprising a peroxygen bleach compound and a cationic nitrile. The invention particularly relates to liquid hard surface cleaning compositions.

Background of the invention

10 [0002] In household and fabric cleaning and in other cleaning areas there is a need for agents which bleach unsightly stains on substrates such as surfaces or fabric, which help removing soil from such substrates and which disinfects them. Common agents for this purpose are those which contain active chlorine, the most common being sodium hypochlorite, which is widely used in cleaning compositions to decolourise soils or stains, remove mould stains, assist in cleaning through reaction with soils and kill microorganisms.

[0003] A problem which is associated with said compositions is that hypochlorite has an unpleasant odour and, when accidentally mixed with an acidic product, can liberate toxic amounts of chlorine gas. Therefore, there is a need for alternative bleaching agents.

[0004] Other bleaching agents are known, particularly many kinds of peroxygen bleaching compounds such as peroxides and peracids and their salts. However, the bleaching power of peroxygen bleaching compounds as such generally falls short of that of hypochlorite and therefore they are often used in conjunction with oxygen transfer or bleach activator agents. Such agents generally operate by reacting with the peroxygen compound to form an oxidative bleaching species which subsequently reacts with the substrate to be bleached, cleaned or disinfected.

[0005] Like hypochlorite, peroxygen bleaching compounds are most effective at alkaline pH, particularly at pH 9 and above.

[0006] Recently, various cationic nitriles, which contain the structural unit below, have been reported to act as bleach activator agents.

-- N
$$^{\oplus}$$
-- CH $_2$ -- CN X $⊝$

[0007] Typical examples of such compounds are disclosed in EP-A-0 303 520, EP-A-0 458 396 and EP-A-0 464 880 in which the organic groups attached to the positive nitrogen are alkyl groups. In WO 98/23532, WO 98/23533, WO94/40661 is the positive nitrogen part of a heterocyclic ring and in EP-A-0 790 244 part of a heterocyclic or carbocyclic ring. In EP-A-0 897 974 the general formula comprises a large group of organic substituents on the positive nitrogen, but N-methylmorpholiniumacetonitrile methosulphate is the only compound actually disclosed.

[0008] These cationic nitriles have been disclosed to lead to good bleaching in combination with a peroxygen compound and particularly with hydrogen peroxide or precursors thereof. Without being bound by theory, the bleaching is believed to take place by a reactive peroxy species formed in situ by oxidation of the cationic nitrile by the peroxygen compound.

[0009] Although the cationic nitriles have been generally described as being useful in a large variety of cleaning products for laundry, hard surfaces, toilet bowl, machine dishwash and even dental applications, the practical examples described have so far been limited to application in laundry cleaning for most of them. Due to the general instability of these compounds at high pH, at which bleaching results are expected to be best, the compounds have been described mostly for use in solid compositions or for separate addition to an alkaline wash liquor. The use in cleaning compositions packaged in dual compartment containers has been mentioned in passing for some heterocyclic cationic nitriles in WO 98/23533.

[0010] There is, however, still a need for better peroxygen bleach systems for a variety of cleaning purposes and particularly for hard surface cleaning and the systems actually disclosed in the prior art are not completely satisfactory.

50 Brief description of the invention

[0011] It has now been found that certain group of aliphatic and araliphatic cationic nitriles in combination with a peroxygen compound are substantially superior to the cationic nitriles descibed in the art so far for cleaning hard surfaces. Thus, the cationic nitriles according to the invention are able to provide comparableor even better cleaning at lower concentrations.

[0012] It is therefore an object of the present invention to provide bleaching and cleaning compositions which comprise a peroxygen bleach compound and an aliphatic or araliphatic cationic nitrile bleach activator compound which give superior bleaching and cleaning.

[0013] It is another object of the invention to provide bleaching and cleaning compositions comprising a peroxygen bleach compound and an aliphatic or araliphatic cationic nitril bleach activator which can be used at the pH at which the combination of bleach and bleach activator is effective.

[0014] It is a further object of the invention to provide a process for hard surface cleaning comprising the step of applying to the hard surface a cleaning composition comprising a peroxygen bleach compound and an aliphatic or araliphatic cationic nitrile bleach activator compound

Hereinafter the phrases 'clean' and 'cleaning' will also comprise 'bleach' and 'bleaching'

Detailed description of the invention

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[0015] All amounts mentioned are in percent by weight based on the total composition unless specifically mentioned otherwise.

[0016] The cationic nitriles, which the invention provides, have the general formula:

$$R_2$$
 R_1 -- N^{\oplus} -- CH_2 -- CN X^{\ominus}
 R_3

wherein R_1 is an alkyl group of 3-10 carbon atoms, a phenyl-substituted alkyl group with a total of 7-12 carbon atoms, or a (alkyl-substituted) phenyl group of 6-10 carbon atoms, R_2 and R_3 are independently methyl or ethyl groups and X^{\odot} is a counterion.

[0017] Preferably, if R_1 is an alkyl group it is linear and most preferably has 3-6 carbon atoms. If R_1 is a phenyl-substituted alkyl group it preferably has the structure R_4 - C_6H_4 - $(CH_2)_n$ - wherein R_4 is hydrogen, methyl or ethyl, most preferably hydrogen, and n is 1-4. Preferably R_2 and R_3 are methyl.

[0018] Suitable counterions X[©] are anions derived from inorganic or organic acids and include e.g.: chloride, bromide, sulphate, tosylate, methosulphate and surfactant anions such as decribed in EP-A-0 464 880. Counterions of unquestionable peroxide stability, such as tosylate and methosulphate, are particularly preferred.

[0019] The invention provides hard surface cleaning compositions comprising one or more of the cationic nitriles above and a peroxygen bleach compound.

[0020] The cationic nitriles are preferably present in the cleaning compositions in an amount of 0.01-10%, more preferably 0.05-5%, most preferably at least 0.1%

[0021] The peroxygen bleach compound may be any peroxide or peroxide generating system known in the art such as dihydrocarbon peroxides, diacyl peroxides, hydrocarbon hydroperoxides, organic and inorganic peracids and persalts and in particular hydrogen peroxide.

[0022] Preferred peroxygen bleach compounds are hydrogen peroxide, peracetic acid, PAP and alkali metal or alkaline earth metal monoperoxosulphate salts. Hydrogen peroxide is particularly suitable. The amount of peroxygen compound is preferably chosen such that the composition will contain 0.1-10% active oxygen, more preferably 0.5-5%, most preferably at least 1%.

[0023] The molar ratio between peroxygen compound and cationic nitrile is preferably between 100:1 and 1:5, more preferably between 50:1 and 1:1, most preferably above 3:1, or even 10:1.

[0024] The compositions according to the invention are suitable for a wide variety of cleaning operations, including cleaning of laundry, carpets and other fabric material. They are particularly suitable for cleaning hard surfaces. They may be provided as solids e.g. as a powder as granules or in tablet form. To the extend that a peroxygen compound is available as a stable solid it can be incorporated in these solid compositions. Stable solid peroxygen compounds such as perborate and percarbonate are well known in the art of laundry detergents. The solid compositions are dissolved in water to produce a cleaning solution ready for use.

[0025] However, for hard surface cleaning it is most convenient when the compositions according to the invention are liquids, preferably aqueous liquids. Such compositions clean most effectively if they have a pH of 6 or above, preferably 6.5 or above, more preferably between 7 and 12.

[0026] The compositions according to the invention preferably comprise one or more detergent surfactants chosen from anionic, cationic, nonionic, zwitterionic or amphoteric surfactants well known in the art.

[0027] Suitable anionic surfactants which may be combined with the amines according to the invention are water-soluble salts of organic sulphuric acid esters and sulphonic acids having in the molecular structure an alkyl group containing 8-22 C atoms or an alkylaryl group containing 6-20 C atoms in the alkyl part.

[0028] Examples of such anionic surfactants are the water soluble salts of:

- long chain (i.e. 8-22 C-atom) alcohol sulphates (hereinafter referred to as PAS), especially those obtained by sulphating the fatty alcohols produced by reducing the glycerides of tallow or coconut oil;
- alkylbenzene-sulphonates, such as those in which the alkyl group contains from 6 to 20 carbon atoms;
 - secondary alkanesulphonates.

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[0029] Also suitable are the salts of:

- 10 alkylglyceryl ether sulphates, especially of the ethers of fatty alcohols derived from tallow and coconut oil;
 - fatty acid monoglyceride sulphates;
 - sulphates of ethoxylated aliphatic alcohols containing 1-8 ethyleneoxy groups;
 - alkylphenol ethyleneoxy-ether sulphates with from 1 to 8 ethyleneoxy units per molecule and in which the alkyl groups contain from 4 to 14 carbon atoms;
- 15 the reaction product of fatty acids esterified with isethionic acid and neutralised with alkali.

[0030] Suitable nonionic surfactants can be broadly described as compounds produced by the condensation of simple alkylene oxides, which are hydrophilic in nature, with an organic hydrophobic compound which may be aliphatic or alkylaromatic in nature. The length of the hydrophilic or polyoxyalkylene chain which is attached to any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired balance between hydrophilic and hydrophobic elements. This enables the choice of nonionic surfactants with the right HLB.

[0031] Particular examples include the condensation products of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut alcohol ethylene oxide condensates having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol; condensates of alkylphenols having C6-C15 alkyl groups with 5 to 25 moles of ethylene oxide per mole of alkylphenol; condensates of the reaction product of ethylenediamine and propylene oxide with ethylene oxide, the condensates containing from 40 to 80% of ethyleneoxy groups by weight and having a molecular weight of from 5,000 to 11,000.

[0032] Other examples are: alkylglycosides, which are condensation products of long chain aliphatic alcohols and saccharides; tertiary amine oxides of structure RRRN0, where one R is an alkyl group of 8 to 20 carbon atoms and the other R's are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, e.g. dimethyldodecylamine oxide; tertiary phosphine oxides of structure RRRP0, where one R is an alkyl group of 8 to 20 carbon atoms and the other R's are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyl-dodecylphosphine oxide; and dialkyl sulphoxides of structure RRS0 where one R is an alkyl group of from 10 to 18 carbon atoms and the other is methyl or ethyl, for instance methyltetradecyl sulphoxide; fatty acid alkylolamides; alkylene oxide condensates of fatty acid alkylolamides; alkyl mercaptans. Ethoxylated aliphatic alcohols are particularly preferred.

[0033] Suitable amphoteric surfactants are derivatives of aliphatic secondary and tertiary amines containing an alkyl group of 8 to 20 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance sodium 3-dodecylamino-propionate, sodium 3-dodecylaminopropane-sulphonate and sodium N-2-hydroxy-dodecyl-N-methyltaurate.

[0034] Suitable cationic surfactants are quaternary ammonium salts having one or two alkyl or aralkyl groups of from 8 to 20 carbon atoms and two or three small aliphatic (e.g. methyl) groups, for instance cetyltrimethyl ammonium bromide.

[0035] Suitable zwitterionic surfactants are derivatives of aliphatic quaternary ammonium, sulphonium and phosphonium compounds having an aliphatic group of from 8 to 18 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance 3-(N,N-dimethyl-N-hexadecylammonium)-propane-1-sulphonate betaine, 3-(dodecyl methyl-sulphonium)-propane-1-sulphonate betaine and 3-(cetylmethyl-phosphonium)-ethanesulphonate betaine.

[0036] Further examples of suitable surfactants are compounds commonly used as surface-active agents given in the well-known textbooks "Surface Active Agents", Volume I by Schwartz and Perry and "Surface Active Agents and Detergents", Volume II by Schwartz, Perry and Berch.

[0037] A surfactant system is preferably present in a total amount of between 0.1 and 20%, more preferably between 0.5 and 10%.

[0038] The composition according to the invention preferably also contains a sequestering agent to bind metal ions, particularly transition metal ions, which could otherwise destabilise the peroxygen compound. Suitable sequestering agents are e.g. ethylenediamine tetraacetate, amino-polyphosphonates (such as those in the DEQUEST™ range). Phosphates and a wide variety of other poly-functional organic acids and salts, can also optionally be employed. Preferred sequestering agents are selected from dipicolinic acid, ethylenediamine tetra acetic acid (EDTA) and its salts, hydroxyethylidene diphosphonic acid (Dequest 2010), ethylenediamine tetra(methylene-phosphonic acid) (Dequest

2040), diethylene-triamine penta(methylene-phosphonic acid) (Dequest 2060) and their salts. Sequestering agents are generally used in an amount of 0.01-5%, preferably 0.05-2%.

[0039] Apart from sequestering agents particularly suitable for binding transition metal ions, as mentioned above, the cleaning compositions according to the invention may also usefully contain a sequestering agent suitable for binding Ca ions. Suitable sequestering agents for this purpose are well known in the art and include compounds such as: alkali metal tripolyphosphate, pyrophosphate and ortho-phosphate, sodium nitrilotriacetic acid salt, sodium methylglycine-diacetic acid salt, alkali metal citrate, carboxymethyl malonate, carboxymethyloxysuccinate, tartrate, mono- and disuccinate and oxydisuccinate.

[0040] For certain cleaning applications it is most useful if the composition contains a thickening system which will improve the composition's ability to cling to a non-horizontal surface, thus imcreasing the contact time of the composition with the soiled surface. Many thickening systems are known from the art of thickening hypochlorite bleach compositions. Such systems often consist of two or more different detergent surfactants, or of one or more such surfactants in combination with an electrolyte such as an inorganic salt. Examples of such thickening systems are combinations of tertiary amine oxides containing one long alkyl chain e.g. having 8-22 Catoms and two shorter alkyl chains e.g. having 1-3 Catoms with anionic surfactants.

[0041] More examples of such thickening systems are described in EP-A-079697, EP-A-110544, EP-A-137551, EP-A-145084, EP-A-244611, EP-A-635568, WO95/08611, DE-A-19621048 and the literature cited in these patent applications.

[0042] Other suitable thickening systems comprise various polymeric substances such as natural and chemically modified polysaccharides and synthetic polymers such as those of acrylic acid or copolymers thereof with other monomers. Such synthetic polymers are e.g. sold under the trademarks: ACUSOL, CARBOPOL, POLYGEL, RHEOVIS, STRUCTURE and ALCOGUM.

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[0043] Another way to improve cling of the final composition to a non-horizontal surface is to cause it to foam on dispensing through the addition of a foaming surfactant to at least one partial composition and the use of an appropriate dispensing device such as foaming trigger sprays known in the art.

[0044] Many peroxygen compounds have limited stability in strongly alkaline solutions and are therefore stored preferably at mildly alkaline, neutral or acid pH. Hydrogen peroxide is reasonably stable up to pH 10.

[0045] To improve long term stability of the cleaning compositions it may be advisable to keep various ingredients of the composition apart until the moment of use. Thus, it may be preferred to keep the cationic nitrile separate from the peroxygen compound and/or from a pH adjusting compound which is present in the total composition to adjust the pH of the end product to the desired value suitable for adequate cleaning. A suitable arrangement for this is to provide separate "partial" compositions which together contain all the required ingredients of the total composition and which are mixed just before use.

[0046] Accordingly, the invention also provides liquid cleaning compositions consisting of at least two liquid partial compositions which are held separate from each other in a single container comprising at least two chambers or reservoirs or compartments (hereinafter referred to as 'chambers') wherein at least one partial composition comprises a peroxygen compound, at least one partial composition comprises a cationic nitrile and at least one partial composition comprises a pH adjusting compound which on mixing of the partial compositions is able to set the pH of the final composition to a desired value at which the combination of the cationic nitrile and the peroxygen compound are active. Each partial composition has a pH such that the components of that partial composition are adequately stable on storage.

[0047] Furthermore the invention provides liquid cleaning compositions obtained through mixing of the above mentioned liquid partial compositions. Also, the invention provides a container comprising two or more chambers holding the liquid partial compositions.

[0048] For the purposes of this invention a 'partial composition' is defined as a solution of a component, or a mixture of more, but not all, components of the final composition, which solution is held in a separate chamber of the container containing the total composition. Two or more partial compositions together make up the final composition according to this aspect of the invention.

[0049] A container suitable for holding the hard surface cleaning compositions according to this aspect of the invention has at least as many separate chambers as the number of partial compositions making up the total composition. Such container may have one outer wall embracing all chambers which are separated from each other by partion walls inside the container or, alternatively, it may be made up of a plurality of separate containers, equivalent to the chambers, which are held together by some external means, such as a connecting part of the walls or a sleeve surrounding them, in such a way that they can be held and handled as one container. A dispensing system is provided in that each chamber is provided with an outlet opening through which the partial composition is dispensed. These outlet openings may all lead to a separate mixing chamber in which the dispensed amounts of the partial compositions mix just before being applied to the substrate through a dispensing opening in the mixing chamber. Alternatively, the outlet openings may all lead to the outside of the container in such a way that the dispensed amounts of the partial compositions are all

applied simultaneously to the same area of the substrate so as to mix while being applied to the substrate or immediately after application onto the substrate. To this end the outlet openings will generally be positioned in close proximity to each other such that all partial compositions are poured, squirted or sprayed onto the same area of the substrate in one action. The outlet openings may be provided with a nozzle system designed to further improve the mixing of the partial components on leaving the container. Alternatively, the container may be provided with a multiple spray system able to either produce a single spray of a mixture of all the partial compositions or simultaneous sprays of each partial composition directed to the same area of a substrate whereafter the partial compositions mix on the substrate.

[0050] For practical reasons, such as ease of construction and handling, the container preferably comprises no more than two chambers each holding a partial composition which compositions together make up the final composition. This implies that for the same reasons the compositions according to this aspect of the invention are preferably made up of two partial compositions. Additionally the container may comprise a mixing chamber as outlined above.

[0051] The amounts of the partial compositions making up the final composition need not necessarily all be equal as long as care is taken that the concentration of each component in each of the partial compositions is chosen such that on mixing of the envisaged amounts of the partial compositions the right concentration of each component is present in the final composition. The volume of each chamber of the container is adapted to the amount of the partial composition contained in that chamber which is required to make up the total amount of the final composition. The total liquid volume of the final composition to be obtained from the container in general will be determined by the total volume of the container, excluding the volume of the mixing chamber, if present.

[0052] The dispensing or outlet openings or other dispensing means of the various chambers in the container are dimensioned such that one single dispensing action dispenses the right amounts of all partial compositions necessary to properly make up the final in which each component is present in the required concentration. The dispensing or spray system may be so dimensioned that the final composition is dispensed as a foam.

[0053] Although there is no theoretical limitation as to the size and shape of the containers, for practical purposes, such as ease of handling and dispensing, the containers will generally have a total volume of 0.1 - 2 liters, preferably at least 0.25 I, but preferably not more than 1.5 I. Also for practical purposes two-chamber containers preferably have chambers of about equal volume, holding about equal amounts of each of the two partial compositions.

[0054] Optionally cleaning compositions according to the invention may further comprise 1% or more of a solvent of the formula R_1 -O-(EO)_m-(PO)_n- R_2 , wherein

 R_1 and R_2 are independently C1-6 alkyl or H, but not both hydrogen, m and n are independently 0-5.

Suitable examples of such solvents are di-ethylene glycol mono-butyl ether, mono-ethylene glycol mono-butyl ether, propylene glycol butyl ether, isopropanol, ethanol, butanol and mixtures thereof.

Typically, the level of solvent in cleaning compositions is 1-10%.

[0055] Other minor components may be present in the compositions according to the invention, such as microbiocidally active compounds or components to improve their consumer appeal such as perfumes and dyes. Many other optional components customary in the art of cleaning compositions may be present as well.

[0056] The compositions according to the invention give excellent cleaning on a variety of soils, such as common kitchen soils, and are able to bleach the well known stains of black mould often occuring in damp spaces. Furthermore, at pH 6.5 or above the cationic nitriles according to the invention effectively boost the antimicrobial properties of peroxides, particularly hydrogen peroxide, thus giving the compositions according to the invention improved hygenic properties. For this purpose a peroxide/nitile ratio of between 2:1 and 1:5 is preferred. The combination is active against gram-negative as well as gram-positive bacteria.

[0057] The cleaning process according to the invention comprises the step of applying a cleaning composition as described above to the surface to be cleaned. If the composition is a solid it is to be converted previously into a solution in a suitable solvent, preferably water. Preferably the cleaning compositions are freshly prepared just before being applied to the surface. A conveniently procedure for this comprises the application of the composition from a multichamber container as described above.

[0058] The compositions may be applied to the surface in any convenient way. They are preferably applied directly to the surface, such as by spraying, pouring or any similar operation, but they may also first be applied to a cleaning implement, such as a wipe, cloth or towel, whereafter the surface is cleaned with the implement.

Examples:

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[0059] Various cationic nitrile/hydrogen peroxide combinations were tested on their ability to remove a light model oily kitchen soil: 'curcumin/oil' on Decamel. The soil comprises sunflower oil and curcumin (the principal pigment in curry powder)

[0060] Decamel tiles $(7.5 \times 7.5 \text{ cm}^2 \text{ square})$ were cleaned using JifTM LAC and thoroughly rinsed using distilled water and dried before application of the soil. Care was taken not to contaminate the cleaned surface, especially by touch as otherwise red streaking occurs when the soil is applied.

[0061] The soil was prepared by adding 0.5 g of powdered curcumin pigment to 9.5 g of commercial sunflower oil and stirring the mixture for 5 minutes. 90g of absolute ethanol was then slowly added to the mixture and the resulting solution stirred for at least 10 minutes prior to application to the substrate.

[0062] The curcumin/oil/ethanol solution was sprayed onto the vertical Decamel tiles using a 'COBALT' gravity feed spray gun (ex. SIP, 500 ml pot capacity, 1.5 mm nozzle) attached to a compressor. Care was taken to ensure even soil coverage and it is important that the curcumin/oil solution was constantly swirled whilst in the spray gun 'cup', in order to maintain a homogeneous solution. The soiled tiles were allowed to stand for a minimum of 1 hour allowing evaporation of the ethanol solvent, producing a slightly tacky yellow coloured oil film. The colour of treated tiles fades over time (due to photobleaching) and soiled tiles were prepared on the same day as they were used.

[0063] A circular glass ring (diameter 5 cm) was placed over the centre of the soiled tile and 5 ml of the cleaning solution pipetted into the enclosed area. The glass template was pressed flat onto the tile surface for 30 seconds (preventing leakage of the cleaning solution) after which time the template was removed and the tile immediately rinsed under demineralised water and then allowed to dry for up to 30 minutes. At least two replicate soiled tiles were treated with each bleach system. The level of soil removal was visually assessed by trained panellists using a half integer scale ranging from 0 (no soil removal) to 5 (complete soil removal). The resulting data were statistically analysed to yield mean soil removal. The nitriles which were tested are mentioned in table I below. R_1-R_3 refer to the general formula above, except for compounds 4 and 5 which are cationic nitriles according to the prior art, mentioned in EP-A-0 464 880 and EP-A-0 897 974 respectively. In all cases the counter ion was R_1 - R_2 - R_3 - $R_$

Га		

	R ₁	R_2	R_3
1	2-phenylethyl	methyl	methyl
2	n-butyl	methyl	methyl
3	phenylmethyl	methyl	methyl
4*	methyl	methyl	methyl
5**	$R_1 + R_2 = morpl$	holinium	methyl

^{*} Cationic nitrile according to EP-A-0 464 880

[0064] The scores are given in Table II below. Small series of soiled tiles were produced and treated together, always including one duplicate set of tiles treated with only hydrogen peroxide as a reference. Due to the fact that soiling of the tiles is not completely reproducible between series, only results measured against the same reference may be compared (one row in the table). All test solutions contained 3% hydrogen peroxide. The cationic nitrile was always used in 1%. All test solutions had pH 10.5.

Table II

Reference cleaning	nitrile	cleaning	nitrile	cleaning
2.0	1	3.8		
2.2	2	3.7		
1.2	2	2.9	5	2.3
1.7	4	2.1		
1.3	3	3.4		

[0065] From table II it can be seen that the N-methyl-morpholinium nitrile from the prior art performed significantly less than the cationic nitrile 2 according to the invention. Also, whereas all cationic nitriles according to the invention performed much better than hydrogen peroxide alone, the nitrile 4 according to the prior art was only marginally better than hydrogen peroxide alone.

Claims

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1. Cationic nitriles according to the general formula:

^{**} Cationic nitrile according to EP-A-0 897 974

$$R_2$$
 R_1 -- N^{\oplus} -- CH_2 -- CN X^{\ominus}
 R_3

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wherein R_1 is an alkyl group of 3-10 carbon atoms, a phenyl-substituted alkyl group with a total of 7-12 carbon atoms, or a (alkyl-substituted) phenyl group of 6-10 carbon atoms, R_2 and R_3 are independently methyl or ethyl groups and X^{\odot} is a counterion.

- 2. Cationic nitriles according to claim 1 wherein if R₁ is an alkyl group it is linear and has 3-6 carbon atoms and if R₁ is a phenyl-substituted alkyl group it has the structure R₄-C₆H₄-(CH₂)_n- wherein R₄ is hydrogen, methyl or ethyl, most preferably hydrogen, and n is 1-4.
- **3.** Cationic nitriles according to claims 1 or 2 wherein X[⊖] is derived from an organic or inorganic acid.
- **4.** Hard surface cleaning compositions comprising a peroxy bleaching compound and a cationic nitrile, wherein the cationic nitrile has a structure according to the general formula:

$$R_2$$

$$R_1--N^{\oplus}--CH_2--CN X^{\ominus}$$

$$R_3$$

- wherein R_1 is an alkyl group of 3-10 carbon atoms, a phenyl-substituted alkyl group with a total of 7-12 carbon atoms, or a (alkyl-substituted) phenyl group of 6-10 carbon atoms, R_2 and R_3 are independently methyl or ethyl groups and X^{\odot} is a counterion.
- 5. Hard surface cleaning compositions according to claim 4 wherein if R₁ is an alkyl group it is linear and has 3-6 carbon atoms and if R₁ is a phenyl-substituted alkyl group it has the structure R₄-C₆H₄-(CH₂)_n- wherein R₄ is hydrogen, methyl or ethyl, most preferably hydrogen, and n is 1-4.
 - **6.** Hard surface cleaning compositions according to claims 4 or 5 wherein X[⊕] is derived from an organic or inorganic acid.
 - Hard surface cleaning compositions according to claims 4-6 wherein the peroxygen bleach compound is hydrogen peroxide.
- **8.** Hard surface cleaning compositions according to claims 4-7 wherein the molar ratio between peroxide compound and cationic nitrile is between 100:1 and 1:5.
 - **9.** Hard surface cleaning compositions according to claims 4-8 which are aqueous liquids having pH 6 or above.
- 10. Hard surface cleaning compositions according to claim 9 consisting of at least two liquid partial compositions which are held separate from each other in a single container comprising at least two chambers or reservoirs or compartments (hereinafter referred to as 'chambers') wherein at least one partial composition comprises a peroxygen compound, at least one partial composition comprises a cationic nitrile and at least one partial composition comprises a pH adjusting compound which on mixing of the partial compositions is able to set the pH of the final composition to a desired value at which the combination of the cationic nitrile and the peroxygen compound are active.
 - 11. Hard surface cleaning compositions obtained through mixing of the partial compositions according to claim 10.

	12.	Process for cleaning hard surfaces comprising the step of applying to the surface a cleaning composition according to any one of claims 4-11 in the form of a solution.
5	13.	Process according to claim 12 wherein the solution is freshly prepared just before being applied to the the surface.
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EUROPEAN SEARCH REPORT

Application Number EP 01 30 0059

	-	ERED TO BE RELEVANT		
Category	Citation of document with i of relevant pass	ndication, where appropriate, sages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CI.7)
D,X	EP 0 303 520 A (KAC 15 February 1989 (1 * examples 2,12 *	989-02-15)	1,3,4, 6-9	C11D3/39 C07C255/25
A	* production exampl * page 19, line 42 * page 11, line 15 * page 6, line 25 -	- line 45 * - line 25 *	2,5	
Υ	* claims 1-3,8,9 *		10,11,13	
X		heir quaternary	1-3	
X		ular Rearrangement to I-Dimethylphenylalanine	1-3	TECHNICAL FIELDS
	1969, pages 2130-2 page 2130: compound			SEARCHED (Int.Cl.7) C11D C07C
X	p-Methyl Substituen on Competition betw sommelet Rearrangem J. GEN. CHEM. USSR	ents" 90, pages 2277–2282,	1-3	
		-/		
	The present search report has	been drawn up for all claims		
	Place of search	Date of completion of the search		Examiner
	THE HAGUE	5 July 2001	Ney	s, P
X : part Y : part docu A : tech O : non	ATEGORY OF CITED DOCUMENTS icularly relevant if taken alone cularly relevant if combined with anotyment of the same category inological background—written disclosure mediate document	E : earlier patent de after the filing d. cher D : document cited L : document cited	ole underlying the incomment, but publicate in the application for other reasons	nvention shed on, or



EUROPEAN SEARCH REPORT

Application Number EP 01 30 0059

A-1-	Citation of document with in	dication, where appropriate,	Relevant	CLASSIFICATION OF THE
Category	of relevant pass		to claim	APPLICATION (Int.Cl.7)
X	SCHIEMENZ G.P.: "I Tetraphenyloborat-I Kernresonanzverschi Quartären Ammonium-I TETRAHEDRON, vol. 29, 1973, page * Table 1: compound	on als ebungsreagens bei Kationen" s 741-745, XP002168855	1,3	
X	the region of amine	Stevens and Sommelet nmonium salts ethyl group" s 1627-1630,	1-3	
X	PATENT ABSTRACTS OF vol. 013, no. 501 (0 10 November 1989 (19 -& JP 01 198700 A (19	C-652), 989-11-10) KAO CORP),	1-6,12	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
Υ	10 August 1989 (1989 * abstract * * Page 6: compound (•	10,11,13	
X Y	DE 197 40 669 A (CL) 18 March 1999 (1999- * claims 1,2,13 *		1-6	
A			7	
		-/		
	The present search report has b	een drawn up for all claims		
	Place of search	Date of completion of the search	_ 	Examiner
	THE HAGUE	5 July 2001	Ney	s, P
X : parti Y : parti docu A : tech O : non-	ATEGORY OF CITED DOCUMENTS cularly relevant if taken alone cularly relevant if combined with anoth ment of the same category nological background -written disclosure mediate document	E : earlier patent d after the filling d er D : document cited L : document cited	in the application for other reasons	shed on, or

EPO FORM 1503 03.82 (P04C01)



EUROPEAN SEARCH REPORT

Application Number EP 01 30 0059

Category	Citation of document with indic	cation, where appropriate.	Relevant	CLASSIFICATION OF THE
Jategory	of relevant passag		to claim	APPLICATION (Int.CI.7)
X	the field of amines a compounds. CLXXX. The	e Stevens and Sommelet onium salts containing oup."		
D,Y	WO 98 23533 A (CLOROX	(CO)	10,11,13	
	4 June 1998 (1998-06-	-04)		
A	* claims 12-29 * * page 15, line 17	page 16, line 31 * 	1,4,12	
				TECHNICAL FIELDS SEARCHED (Int.CI.7)
			-	
			1	
	The present search report has bee			
	Place of search	Date of completion of the search	Nove	Examiner
	THE HAGUE	5 July 2001	Neys	
X : parti Y : parti docu	ATEGORY OF CITED DOCUMENTS cularly relevant if taken alone cularly relevant if combined with another iment of the same category nological background	T : theory or principl E : earlier patent do after the filing da D : document cited i L : document cited f	cument, but publis te n the application or other reasons	
O : non	-written disclosure mediate document	& : member of the sidocument		

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 01 30 0059

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

05-07-2001

03520	A	15-02-1989	JP SP JP	1242699 A 2017160 A 2538646 B 1045499 A 1953305 C 6078555 B 1069697 A 1963530 C 6089358 B 1068347 A 1905935 C 6029230 B 617686 B 2092088 A 3889165 D 3889165 T 451488 A 2063040 T 9105027 B 883581 A,B, 225815 A 233651 A 4915863 A	27-09-19 22-01-19 25-09-19 17-02-19 28-07-19 05-10-19 15-03-19 25-08-19 09-11-19 14-03-19 24-02-19 20-04-19 26-05-19 01-01-19 22-07-19 15-02-19 26-04-19 26-04-19 26-04-19 26-04-19 18-12-19
			JP JP JP JP JP AU DE DK SKR NZ US US	2538646 B 1045499 A 1953305 C 6078555 B 1069697 A 1963530 C 6089358 B 1068347 A 1905935 C 6029230 B 617686 B 2092088 A 3889165 D 3889165 T 451488 A 2063040 T 9105027 B 883581 A,B, 225815 A 233651 A 4915863 A	25-09-19 17-02-19 28-07-19 05-10-19 15-03-19 25-08-19 09-11-19 14-03-19 24-02-19 20-04-19 05-12-19 16-02-19 26-05-19 01-01-19 22-07-19 15-02-19 26-04-19 26-04-19 10-04-19 18-12-19
			JP JP JP JP JP AU DE DK SKR NO NZ US US	1045499 A 1953305 C 6078555 B 1069697 A 1963530 C 6089358 B 1068347 A 1905935 C 6029230 B 617686 B 2092088 A 3889165 D 3889165 T 451488 A 2063040 T 9105027 B 883581 A,B, 225815 A 233651 A 4915863 A	17-02-19 28-07-19 05-10-19 15-03-19 25-08-19 09-11-19 14-03-19 24-02-19 20-04-19 05-12-19 16-02-19 26-05-19 01-01-19 22-07-19 15-02-19 26-04-19 26-04-19 26-04-19 10-04-19
			JP JP JP JP JP AU DE DK SR NO NZ US US	1953305 C 6078555 B 1069697 A 1963530 C 6089358 B 1068347 A 1905935 C 6029230 B 617686 B 2092088 A 3889165 D 3889165 T 451488 A 2063040 T 9105027 B 883581 A,B, 225815 A 233651 A 4915863 A	28-07-19 05-10-19 15-03-19 25-08-19 09-11-19 14-03-19 24-02-19 05-12-19 16-02-19 26-05-19 04-08-19 15-02-19 01-01-19 22-07-19 15-02-19 26-04-19 26-04-19 10-04-19 18-12-19
			JP JP JP JP AU DE DK ES NO NZ US US	6078555 B 1069697 A 1963530 C 6089358 B 1068347 A 1905935 C 6029230 B 617686 B 2092088 A 3889165 D 3889165 T 451488 A 2063040 T 9105027 B 883581 A,B, 225815 A 233651 A 4915863 A	05-10-19 15-03-19 25-08-19 09-11-19 14-03-19 24-02-19 20-04-19 16-02-19 26-05-19 04-08-19 15-02-19 01-01-19 22-07-19 15-02-19 26-04-19 26-04-19 10-04-19
			JP JP JP JP AU DE DK ES KR NO NZ US US	1069697 A 1963530 C 6089358 B 1068347 A 1905935 C 6029230 B 617686 B 2092088 A 3889165 D 3889165 T 451488 A 2063040 T 9105027 B 883581 A,B, 225815 A 233651 A 4915863 A	15-03-19 25-08-19 09-11-19 14-03-19 24-02-19 20-04-19 05-12-19 16-02-19 26-05-19 01-01-19 22-07-19 15-02-19 26-04-19 26-04-19 10-04-19 18-12-19
			JP JP JP JP AU DE DK ES KR NO NZ US US	1069697 A 1963530 C 6089358 B 1068347 A 1905935 C 6029230 B 617686 B 2092088 A 3889165 D 3889165 T 451488 A 2063040 T 9105027 B 883581 A,B, 225815 A 233651 A 4915863 A	15-03-19 25-08-19 09-11-19 14-03-19 24-02-19 20-04-19 05-12-19 16-02-19 26-05-19 01-01-19 22-07-19 15-02-19 26-04-19 26-04-19 10-04-19 18-12-19
			JP JP JP AU DE DK ES KR NO NZ US US	1963530 C 6089358 B 1068347 A 1905935 C 6029230 B 617686 B 2092088 A 3889165 D 3889165 T 451488 A 2063040 T 9105027 B 883581 A,B, 225815 A 233651 A 4915863 A 4978770 A	25-08-19 09-11-19 14-03-19 24-02-19 20-04-19 05-12-19 16-02-19 26-05-19 01-01-19 22-07-19 15-02-19 26-04-19 26-04-19 18-12-19
			JP JP JP AU DE DK ES KR NO NZ US US	6089358 B 1068347 A 1905935 C 6029230 B 617686 B 2092088 A 3889165 T 451488 A 2063040 T 9105027 B 883581 A,B, 225815 A 233651 A 4915863 A 4978770 A	09-11-19 14-03-19 24-02-19 20-04-19 05-12-19 16-02-19 26-05-19 01-01-19 22-07-19 15-02-19 26-04-19 26-04-19 10-04-19 18-12-19
			JP JP AU DE DK ES KR NO NZ US US	1068347 A 1905935 C 6029230 B 617686 B 2092088 A 3889165 D 3889165 T 451488 A 2063040 T 9105027 B 883581 A,B, 225815 A 233651 A 4915863 A	14-03-19 24-02-19 20-04-19 05-12-19 16-02-19 26-05-19 01-01-19 22-07-19 15-02-19 26-04-19 26-04-19 18-12-19
			JP JP AU DE DK ES KR NO NZ US US	1905935 C 6029230 B 617686 B 2092088 A 3889165 T 451488 A 2063040 T 9105027 B 883581 A,B, 225815 A 233651 A 4915863 A 4978770 A	24-02-19 20-04-19 05-12-19 16-02-19 26-05-19 04-08-19 15-02-19 22-07-19 15-02-19 26-04-19 26-04-19 18-12-19
			JP AU DE DE DK ES KR NO NZ US US	6029230 B 617686 B 2092088 A 3889165 D 3889165 T 451488 A 2063040 T 9105027 B 883581 A,B, 225815 A 233651 A 4915863 A 4978770 A	20-04-19 05-12-19 16-02-19 26-05-19 04-08-19 15-02-19 01-01-19 22-07-19 15-02-19 26-04-19 26-04-19 10-04-19 18-12-19
			AU DE DE DK ES KR NO NZ NZ US US	617686 B 2092088 A 3889165 D 3889165 T 451488 A 2063040 T 9105027 B 883581 A,B, 225815 A 233651 A 4915863 A	05-12-19 16-02-19 26-05-19 04-08-19 15-02-19 01-01-19 22-07-19 15-02-19 26-04-19 10-04-19 18-12-19
			AU DE DK ES KR NO NZ NZ US US	2092088 A 3889165 D 3889165 T 451488 A 2063040 T 9105027 B 883581 A,B, 225815 A 233651 A 4915863 A 4978770 A	16-02-19 26-05-19 04-08-19 15-02-19 01-01-19 22-07-19 15-02-19 26-04-19 10-04-19 18-12-19
			DE DK ES KR NO NZ NZ US US	3889165 D 3889165 T 451488 A 2063040 T 9105027 B 883581 A,B, 225815 A 233651 A 4915863 A 4978770 A	26-05-19 04-08-19 15-02-19 01-01-19 22-07-19 15-02-19 26-04-19 10-04-19 18-12-19
			DE DK ES KR NO NZ NZ US US	3889165 T 451488 A 2063040 T 9105027 B 883581 A,B, 225815 A 233651 A 4915863 A 4978770 A	04-08-19 15-02-19 01-01-19 22-07-19 15-02-19 26-04-19 10-04-19 18-12-19
			DK ES KR NO NZ NZ US US	451488 A 2063040 T 9105027 B 883581 A,B, 225815 A 233651 A 4915863 A 4978770 A	15-02-19 01-01-19 22-07-19 15-02-19 26-04-19 26-04-19 10-04-19 18-12-19
			ES KR NO NZ NZ US US	2063040 T 9105027 B 883581 A,B, 225815 A 233651 A 4915863 A 4978770 A	01-01-19 22-07-19 15-02-19 26-04-19 26-04-19 10-04-19 18-12-19
			KR NO NZ NZ US US	9105027 B 883581 A,B, 225815 A 233651 A 4915863 A 4978770 A	22-07-19 15-02-19 26-04-19 26-04-19 10-04-19 18-12-19
			NO NZ NZ US US	883581 A,B, 225815 A 233651 A 4915863 A 4978770 A	15-02-19 26-04-19 26-04-19 10-04-19 18-12-19
			NZ NZ US US	225815 A 233651 A 4915863 A 4978770 A	26-04-19 26-04-19 10-04-19 18-12-19
			NZ US US	233651 A 4915863 A 4978770 A	26-04-19 10-04-19 18-12-19
			US US	4915863 A 4978770 A	10-04-19 18-12-19
			US	4978770 A	18-12-19
					A1 12 16
			CN	1022929 B	01-12-19
.98700	Α	10-08-1989	JP	2551962 B	06-11-19
40669	Α	18-03-1999	AU	9741698 A	05-04-19
			BR	9812334 A	19-09-20
			CN	1270624 T	18-10-20
			WO	9914296 A	25-03-19
			EP	1017773 A	12-07-20
3533	Α	04-06-1998	US	6010994 A	04-01-20
			AU	5451098 A	22-06-19
			BR	9713460 A	28-03-20
			CN	1244174 A	09-02-20
					20-10-19
				6046150 A	04-04-20
				9710686 A	22-07-19
-				BR CN WO EP 3533 A 04-06-1998 US AU BR	BR 9812334 A CN 1270624 T W0 9914296 A EP 1017773 A 3533 A 04-06-1998 US 6010994 A AU 5451098 A BR 9713460 A CN 1244174 A EP 0950016 A US 6046150 A

FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82