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(54) Cleaning compositions

(57) A dual container delivery system comprises a first container containing a first aqueous solution comprising a peracid or a source thereof. A second container contains a second aqueous solution comprising a halide. Delivery means is provided for delivering the first and second solutions to a surface such that the peracid and halide react just before or upon impacting the surface to produce a cleaning composition comprising a hypohalite bleach.

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Description

Field of the Invention

[0001] The present invention relates to liquid cleaning systems providing a halogen bleach, for example for use as household cleaning products.

Background to the Invention

[0002] It is well known to use hypochlorite bleaches in household hard surface cleaning compositions, for example as kitchen surface cleaners typically containing 0.1-1.5% by weight of sodium hypochlorite at a pH of approximately 11.5-13.0, or at higher levels, e.g. up to 3% by weight of hypochlorite for mould removal. However, there remains a need to produce hypohalite bleaching compositions giving the same high standards of cleaning (and hygiene) performance as these standard sodium hypochlorite household cleaning products but with better sensory, safety and environmental properties.

[0003] The present invention solves this problem by use of a halogen bleach which is formed *in situ* at the point of delivery, by reaction of a peracid or source thereof and a halide or source thereof.

[0004] GB-A-2 187 748 describes solid mixtures of peroxomonosulphate and halides for use in fabric bleaches. JP-A-60 233200 discloses combinations of peroxomonosulphate, and optionally percarbonate, with inorganic chloride salts for use in laundry washing. The systems are said to work most efficiently in the pH range 2.5 - 8.0.

[0005] Organic peracid/halide systems for the generation of hypohalites are new. However, several hydrogen peroxide/'activator'/halide systems have been disclosed for use in laundry bleaching. For example, EP-A-168 253 discloses combinations of a halide salt with an aromatic diol (or its hydrolysable ester) for *in situ* production of hypohalites on reaction with peroxomonosulphate or peroxomonophosphate (which are described as sources of hydrogen peroxide). The diol is oxidised to a hydroquinone which catalyses the formation of low levels (< 60 ppm) of hypohalite. The system is claimed to be active in the pH range 9.0-10.5 and the powdered formulations are claimed as low temperature dye-safe laundry bleaches.

Definition of the Invention

[0006] The present invention now provides a dual container delivery system comprising a first container containing a first aqueous solution comprising of a peracid or a source thereof, a second container containing a second aqueous solution comprising a halide and delivery means for delivering the first and second solutions to a surface such that the peracid and halide react just before or upon impacting the surface to produce a cleaning composition comprising a hypohalite bleach.

[0007] Systems according to the invention are applicable for use in a range of products where relatively high concentrations of hypochlorite bleach are currently required to achieve acceptable cleaning and hygiene performance. Specific product types include mould removers, wc and kitchen cleaners.

Detailed Description of the Invention

[0008] Preferred forms of the first and second containers, the delivery means and the first and second aqueous solutions, will now be described in more detail.

The Containers

[0009] The first and second aqueous solutions need to be kept in different containers so that their components do not react until use. This could be achieved by providing them in respective separate containers. The consumer could then apply each to the surface, either sequentially or simultaneously to allow the reaction to form the hypobromite to occur on the surface.

[0010] However, it is more convenient to provide the products in a dual-compartment container in which the aqueous solutions are stored in separate compartments. The delivery means then allows them to be delivered to the surface so that the reaction to form the hypohalite occurs or is initiated as they are exiting the delivery means and/or in mid-air as they are directed to the surface and/or on the surface itself. Preferably, they are delivered to be mixed in approximately equal volumes, i.e. typically from 0.5 : 1 v/v to 1 : 0.5 v/v.

[0011] A particularly preferred delivery means, especially for non-thickened systems, is a trigger spray head. In the case of a dual compartment system, this will preferably have two siphon tubes, respectively leading into each compartment and either a single nozzle with a mixing chamber or two separate nozzles substantially adjacent to each other. If desired, a dispensing nozzle or nozzles configured to promote foaming may be used.

[0012] For thickened systems a pouring dual compartment packaging form is generally preferred.

The Solutions

[0013] The first aqueous solution contains a peracid or peracid source.

[0014] Generally speaking, peroxides can be classed as organic or inorganic peroxides.
Peracids are a subset of peroxides. The organic peracids may be used as the free peracid or a salt thereof, the salts being peracid precursors which readily yield the free peracid. An example of an inorganic peracid or peracid salt is peroxomonosulphate (oxane).

[0015] Simple organic peracids such as peracetic or performic acid may be used but these are less preferred on grounds of their unpleasant odour. Other suitable organic peracids include the peroxocarboxylic acids and peroxyimidic acids such as monoperoxyphthalic acid (commercially available as the magnesium salt), phthalimidoperhexanoic acid, diperoxydodecanedioic acid, sulphoperbenzoic acid (commercially available as the potassium salt) and isobutylperoxytephthalimide (BIPTA).

[0016] Persalts and addition compounds such as urea peroxide are chosen for their ability to release hydrogen peroxide in aqueous solution. These normally require presence of a bleach activator within the composition, either in the first or second aqueous solution. Suitable inorganic persalts include the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate. The weight ratio of the inorganic persalt to bleach activator will usually be from 20:1 to 1:2, preferably from 5:1 to 1:1.

[0017] Preferred bleach activators are peroxycarboxylic acid precursors, more especially peracetic acid precursors and pemoanoic acid precursors. Especially preferred bleach activators suitable for use in the present invention are N, N,N',N',-tetracetyl ethylenediamine (TAED) and sodium noanoyloxybenzene sulphonate (SNOBS). The quaternary ammonium and phosphonium bleach precursors disclosed in US-A-4 751 015 and US-A-4 818 426 and EP-A-402 971A, and the cationic bleach precursors disclosed in EP-A-284 292 and EP-A-303 520A may also be used.

[0018] The halide may be a simple halide salt such as those of the alkali or alkaline earth metals. Chlorides and bromides are preferred. It is also possible to use any compatible species such as cationics, which have a halide counterion.

[0019] The peracid or peracid source is preferably present at about from 0.01% to 5% by weight, more preferably from 0.1% to 2% by weight of the first aqueous solution. The halide is preferably present at about from 0.01% to 5%, more preferably from 0.1% to 2% by weight of the second aqueous solution. The pH of the product when the two solutions are mixed is preferably from 7 to 13, more preferably from 8 to 11. The weight ratio of the peracid or its precursor to the halide is typically from 0.5 : 1 to 100: 1.

[0020] The peracid (or source thereof) and halide solutions are stored separately using dual-compartmentalised packaging and react together on mixing during application onto the surface. The resulting mixed formulations give efficient bleaching from generation of relatively low levels of the hypohalite so formed. In a typical embodiment, the peracid is maintained at an acidic pH (< 7) in order to minimise decomposition while the halide is present in alkaline solution whose pH is adjusted to a value such that on mixing the final pH of the formulation is optimised for the specific usage scenario. An alternative embodiment is to maintain a mixture of a peracid precursor and hydrogen peroxide at acidic pH and mix with alkaline halide. It is important that the mixing process be carefully controlled so that the pH of the final mixed solution is constrained not to fall below a value of 7.

Surfactants

[0021] The composition according to the invention optionally may comprise detergent actives (surfactants). These may be chosen from a wide range of anionic, nonionic, cationic, amphoteric or zwitterionic surfactants well known in the art.

[0022] Suitable anionic surfactants are e.g. water-soluble salts, particularly alkali metal, alkaline earth metal and ammonium salts, of organic sulphate esters and sulphonic acids having in the molecular structure a C_8-C_{22} alkyl radical or a C_{10}-C_{22} alkaryl radical. Examples of such anionic surfactants are alcohol sulphate salts, especially those obtained from the fatty alcohols derived from the glycerides of tallow or coconut oil; alkyl-benzene sulphonates such as those having a C_9-C_{11} radical. Examples of such anionic detergents are alcohol sulphate alkyl group attached to the benzene ring; secondary alkanesulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the fatty alcohols derived from tallow and coconut oil; sodium fatty acid monoglyceride sulphates, especially those derived from coconut fatty acids; salts of 1-6 EO ethoxylated fatty alcohol sulphates; salts of 1-8 EO ethoxylated alkylphenol sulphates in which the alkyl radicals contain 4-14 C-atoms; the reaction product of fatty acids esterified with isethionic acid and neutralised with sodium hydroxide.

[0023] The preferred water-soluble synthetic anionic surfactants are the alkyl benzene sulphonates, the olefin sulphonates, the alkyl sulphates, and the higher fatty acid monoglyceride sulphates and fatty acid soaps.

[0024] A special class of anionic surfactants which may be used in the cleaning compositions according to the invention are hydrotropes which are known in the art specifically for their thickening or liquid structuring capabilities. Well known examples of such compounds are the alkali metal salts of toluene-, xylene- and cumene-sulphonic acid.

[0025] Suitable nonionic surfactants can be broadly described as compounds produced by the condensation of alkylene oxide groups, 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 radical which is attached to any particular hydrophobic group can be readily adjusted to yield a water-soluble or water dispersible compound having the desired balance between hydrophilic and hydrophobic elements.

[0026] Particular examples include the condensation product of straight chain or branched chain aliphatic alcohols having 8-22 C-atoms with ethylene oxide, such as coconut oil fatty alcohol/ethylene oxide condensates having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol; condensates of alkylphenols whose alkyl group contains 6-16 C-atoms with 2 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. Other examples are: tertiary amine oxides of general structure RRRNO, where one R is a C_8-C_{22} alkyl group (preferably C_8-C_{18}) and the other Rs are each C_1-C_5 (preferably C_1-C_3) alkyl or hydroxyalkyl groups, for instance dimethyldodecylamine oxide; tertiary phosphine oxides of structure RRRPO, where one R is a C_8-C_{22} alkyl group (preferably C_8-C_{18}) and the other Rs are each C_1-C_5 (preferably C_1-C_3) alkyl or hydroxyalkyl groups, for instance dimethyl-dodecylphosphine oxide; dialkyl sulphoxides of structure RRSO where one R is a C_{10}-C_{18} alkyl group and the other is methyl or ethyl, for instance methyltetradecyl sulphoxide; fatty acid alkylolamides; alkylene oxide condensates of fatty acid alkylolamides and alkyl mercaptans. Amine oxides are especially preferred because they blend very well with inorganic electrolytes and show good stability to hypochlorite bleach.

[0027] Suitable amphoteric surfactants are derivatives of aliphatic secondary and tertiary amines containing a C_8-C_{18} alkyl group 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-hydroxydodecyl-N-methyl taurate.

[0028] Suitable cationic surfactants are quaternary ammonium salts having at least one C_8-C_{22} aliphatic or alkylaromatic group, e.g. dodecyl-trimethylammonium bromide or chloride, cetyltrimethyl-ammonium bromide or chloride, didecyl-dimethyl-ammonium bromide or chloride, octyl-benzyldimethyl-ammonium bromide or chloride, dodecyl- benzyldimethyl-ammonium bromide or chloride and (higher alkyl)- benzyldimethyl-ammonium bromide or chloride. Many quaternary ammonium salts have antimicrobial properties and their use in cleaning compositions according to the invention leads to products having exceptionally effective disinfection properties against a wide range of micro-organisms. They are used in the cleaning compositions according to the invention in an amount of 0-10%, preferably 0.1-8%, more preferably 0.5-6%

[0029] Suitable zwitterionic surfactants are derivatives of aliphatic quaternary ammonium, sulphonium and phosphonium compounds having a C_8-C_{18} aliphatic group 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-methylsulphonium)-propane-1-sulphonate betaine and 3-(cetylmethyl-phosphonium)-ethane-sulphonate betaine.

[0030] Further examples of suitable surfactants are 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 Birch.

[0031] Detergent surfactants often play an important role in thickening systems. Apart from that they are preferably added also for their wetting properties on hard surfaces and for their cleaning properties. Thus, preferably surfactants are present even if a non-surfactant thickening system is used. If not required for thickening, the total surfactants content is preferably between 0.1 and 20%, more preferably between 0.5 and 10%, most preferably at most 7%. If part of the thickening system the minimum total amount of surfactant will be at least 0.5%, preferably at least 1%.

[0032] Electrolytes, particularly inorganic salts, are part of many thickening systems. Suitable salts are alkali metal carbonates, sulphates and halogenides. Electrolytes are used in an amount of 0-20%, preferably 0-15%, more preferably 0-10%.

[0033] Many thickening systems have been used in thickened 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. Many thickening systems comprise as one of their components tertiary amine oxides containing one long alkyl chain e.g. having 8-22 C atoms and two shorter alkyl chains e.g. having 1-5 C-atoms, often in combination with an anionic surfactant.

[0034] 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.

[0035] Other suitable thickening systems comprise polymeric substances which in solution thicken in response to an increase in pH or electrolyte concentration. Examples thereof are polymers of acrylic acid known for their thickening properties such as those sold under the trademark "Acusol".

[0036] In the case of the dual container systems of the present invention, the final composition may be thickened if desired, preferably by a multi-component thickening system of which the components are divided over at least two partial compositions, such that on mixing of the partial compositions on delivery to the surface to be cleaned the combination of the components of the thickening system causes the final composition to thicken. This will improve the composition's ability to cling to a non-horizontal surface and prevent it from draining off before proper cleaning is obtained. Usefully the viscosity of the final composition after dispensing is at least 50 mPa.s, more preferably at least 100 mPa.s. On the other hand the viscosity is preferably not more than 1000 mPa.s.

[0037] A large number of multicomponent thickening systems is known in the art. For them to be suitable for the cleaning compositions according to the invention, preferably at least one component should be storage stable in the same partial composition as the hypochlorite bleach. The total thickening system should be sufficiently stable in the final composition to enable it to thicken and remain on the surface for long enough to perform its cleaning action.

[0038] 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.

[0039] Surfactants which are storage stable in combination with the peracid or peracid precursor may be combined with the peracid/precursor in the same (first) partial composition. Surfactants which do not have such stability should be made part of the other (second) partial composition.

[0040] 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 di-succinate and oxydisuccinate.

Other Optional Components

[0041] The mixed composition on the surface may also contain polymers and other formulation components such as a perfume, colourant and foam control agents. Some or all of these additional components can be stored separately from the peracid or peracid source, i.e. together in the second solution with the halide or halide source, allowing use of formulation ingredients that do not have long term stability in strong oxidising agents and are therefore not used in conventional single compartment hypochlorite bleach formulations. The peracid/peracid source, i.e. the first solution, may also include a transition metal sequestering agent in order to minimise decomposition.

Examples

A. FORMULATIONS

Example 1

[0042] A typical non-limiting formulation suitable for delivery from a dual-compartment pack is as follows:

Partial composition A: potassium peroxomonosulphate - 2.0%, pH adjusted to 2.0.
Partial composition B: sodium chloride - 0.38%, sodium hydroxide - 0.32% (pH 12.8).

[0043] Solutions A & B when dispensed from a suitable dual-compartment and mixed in equal proportions will produce a reaction mixture containing:

1.0% potassium peroxomonosulphate
0.16% sodium chloride
at a pH of 8.0.

Example 2

[0044] Another typical non-limiting formulation suitable for delivery from a dual-compartment pack is as follows:

Partial composition A: magnesium monoperoxyphthalate - 1.6%, 0.02% Dequest 2041 pH adjusted to 2.0.

Partial composition B: sodium bromide - 0.68%, sodium hydroxide - 0.32%.

[0045] Solutions A & B when dispensed from a suitable dual-compartment and mixed in equal proportions will produce a reaction mixture containing:

0.8% magnesium monoperoxyphthalate
0.34% sodium bromide
at a pH of 8.0.

Example 3a and 3b

[0046] Example 3a is the composition of a halide/peracid mould remover or kitchen cleaner formulation suitable for delivery from dual-compartment spray pack. Compositions A & B were stable over extended periods (> 2 weeks). Example 3b gives the composition of the mixed formulation (A + B) on delivery from the dual-compartment pack onto the surface.

[0047] Example 3a partial compositions for a bromide/peroxomonosulphate mould remover or kitchen cleaner before mixing.

Chemical Name	% active level
Partial Composition A:	
Potassium peroxomonosulphate	2.0
Water	to 100%
Partial Composition B:	
Sodium xylene sulphonate	1.20
Decyl-dimethyl amine oxide	0.40
Sodium laurate (soap)	0.20
Sodium hydroxide	0.32
Sodium bromide	0.68
Water	to 100%

[0048] Example 3b: Typical formulation of a prototype bromide/peroxomonosulphate mould remover or kitchen cleaner on delivery.

Chemical Name	% active level in formulation as delivered from pack
Sodium xylene sulphonate	0.60
Sodium hydroxide	0.16
Potassium peroxomonosulphate	1.00
Decyl-dimethyl amine oxide	0.20
Sodium laurate (soap)	0.10
Sodium bromide	0.34
Water	to 100%
The mixed formulation had a pH of 8.0	

[0049] Further, if desired, viscous products suitable for providing 'cling' to vertical surfaces, such as wc bowls, are prepared by use of suitable surfactants or thickening agents. These are added to partial compositions A & B such that the partial compositions are non-viscous during storage but develop viscosity on mixing, during delivery from the pack.

B. CLEANING APPRAISAL DATA

[0050] Examples showing the enhanced cleaning efficacy of the halide 'activated' peracid solutions will now be described.

Example 4

[0051] Cultures of hyphal *Cladosporium cladosporioides* were prepared on agar jelly. Warm water was used to dissolve the jelly and separate it from the mould hyphae, which were then autoclaved. A little distilled water was added to the hyphae which were crushed to a 'paste' using a pestle and mortar. The 'paste' consisted of a mixture of fine particles of hyphal cell wall together with a dark black mould ink. Once prepared, the mould paste was stable to storage for several weeks at 5°C.

[0052] A small amount of the 'mould paste' was applied to the surface of a porous ceramic tile and a small amount of distilled water added. This mixture was evenly spread across and rubbed into the surface of the tile using a flexible plastic spatula. Additional mould paste or water was added to ease the soiling process as necessary. The final appearance of the soiled tile was a uniform dark grey. The tiles were left to dry overnight in the dark and then large tiles were then cut into smaller test pieces using a standard 'tile cutter'.

[0053] Small circular pieces of single ply tissue paper were cut to a convenient size and placed on the surface of the 'mould tile' test pieces, such that the edges of the test pieces remained uncovered. A fixed quantity of the test solution was allowed to drop onto the surface of the tissue and allowed to soak into the tile. The test solution only contacted that area of the tile that was originally covered by the tissue paper, thus preserving a background of untreated 'mould paste' around the periphery of the test piece about 1 cm^3 of bleach liquor was required to cover a circular area around 3 cm in diameter). The test solution was allowed to remain in contact with the soil for a fixed contact time, i.e. about 3 minutes or 20 minutes, after which the test piece was immersed in 1.0M sodium thiosulphate solution for 10 minutes (to quench the reaction and prevent further bleaching). The test pieces were then immersed in distilled water for 10 minutes before rinsing with further distilled water and air drying.

[0054] Test pieces were assessed for the level of mould bleaching by an expert panel, using a integer scale running from 0 (no decolorisation) to 6 (complete bleaching). Panel test data for each system were collated and analysed statistically to provide mean scores for each test system. Each test (bleaching) system was tested using at least 3 replicate tiles.

[0055] Test data comparing halide 'activated' peracids with the same peracids alone and with sodium hypochlorite are shown in Table 1. Data sets 1 & 2 were obtained from different batches of soiled tiles.

[0056] The data shows that by addition of low levels of halide, it is possible to increase the bleaching performance of peracids to parity with that obtained from a typical commercial mould remover formulation which contains 2.0 - 3.0% sodium hypochlorite at a pH of c.a. 13.0.

[0057] Addition of bromide 'activates' peracid under all pH conditions, but the effects are more evident at the lower pH. Chloride is a less active activator than bromide but still provides significant enhancements in performance after a period of standing time.

Table 1:

Bleaching of autoclaved 'mould paste' on porous ceramic tile by various hypochlorite containing systems (ambient temperature, 3 minutes contact time)

	Mean Score	
System	0% NaBr	0.34% NaBr
3.0% sodium hypochlorite, pH 13.0	4.8	- - -
1.0% potassium peroxomonosulphate, pH 8.0	0.3	4.5
1.0% potassium peroxomonosulphate, pH 10.0	0.6	3.0
0.8% magnesium monoperoxyphthalate, pH 8.0	0.1	2.6
0.8% magnesium monoperoxyphthalate, pH 10.0	0.1	1.6

Table 1: (continued)

Bleaching of autoclaved 'mould paste' on porous ceramic tile by various hypochlorite containing systems (ambient temperature, 3 minutes contact time)			
	Mean Score		
System	0% NaCl	0.19% NaCl	0.19% NaCl (after 1 hour)
1.0% potassium peroxomonosulphate, pH 8.0	0.8	1.5	3.2
1.0% potassium peroxomonosulphate, pH 10.0	0.8	0.8	3.3

Example 5: Application as a Kitchen Cleaner

[0058] A length of pre-stained cotton cloth was cut into square swatches (2 cm x 2 cm). Four replicate cloths were placed in the bottom of a clean glass beaker and covered with the cleaning liquor at room temperature. After a contact time of 2 to 5 minutes has elapsed, the cloths were removed from the cleaning solution using tweezers and immediately immersed in distilled water. The cloths were stirred in the water, and washing procedure repeated twice more using fresh water each time. Washed cloths were then pressed between two filter papers to remove excess water and left in the dark to dry.

[0059] Reflectance measurements were carried out on a Spectraflash 400 instrument. ΔR measurements were calculated using '40ptspec' software, using a portion of untreated cloth from the same cloth batch as a standard. Results obtained from each of the four replicate test cloths were then statistically analysed to obtain mean ΔR values for each bleach system. Test data comparing halide 'activated' peracids with those same peracids alone and with standard sodium hypochlorite are shown in Table 2.

Table 2:

Bleaching of tea stained cotton cloth (BC-1) by various bleaching systems (ambient temperature, 1 minute contact time)			
System	**Mean ΔR (460nm)**		
Data set 1:			
	0% NaBr	with 0.176% NaBr	
1.0% sodium hypochlorite, pH 13.0	10	- - -	
1.0% potassium peroxomonosulphate, pH 8.0	3.6	27.1	
1.0% potassium peroxomonosulphate, pH 10.0	4.4	24.4	
0.8% magnesium monoperoxyphthalate, pH 8.0	4.3	7.9	
Date set 2:			
	without NaCl	with 0.176% NaCl	
1.0% potassium peroxomonosulphate, pH 7.0	4.8	10.3	
1.0% potassium peroxomonosulphate, pH 8.0	4.8	10.1	
1.0% potassium peroxomonosulphate, pH 9.0	6.4	8.7	
2.0% potassium peroxomonosulphate, pH 7.0	4.8	12.6	
2.0% potassium peroxomonosulphate, pH 8.0	6.2	17.0	
2.0% potassium peroxomonosulphate, pH 9.0	8.0	16.0	
Data set 3:			
	0% NaBr	0.088% NaBr	0.352% NaBr
0.8% magnesium monoperoxyphthalate, pH 7.0	1.8	16.9	24.8
0.8% magnesium monoperoxyphthalate, pH 8.0	2.7	17.8	25.3

Table 2: (continued)

Bleaching of tea stained cotton cloth (BC-1) by various bleaching systems (ambient temperature, 1 minute contact time)			
System	**Mean ΔR (460nm)**		
Data set 3:			
	0% NaBr	0.088% NaBr	0.352% NaBr
0.8% magnesium monoperoxyphthalate, pH 9.0	1.3	15.6	25.6
0.8% magnesium monoperoxyphthalate, pH 10.0	1.6	14.7	24.5
0.8% magnesium monoperoxyphthalate, pH 11.0	0.2	8.7	19.7

[0060] The data in Table 2 show that addition of low levels of bromide or chloride salt enhances the bleaching performance of peracids to parity or greater than that obtained from a typical commercial hypochlorite based kitchen cleaner formulation containing c.a. 0.5% - 1.5% sodium hypochlorite at a pH of 11.0-13.0.

Example 6: Bactericidal Performance of Mixed Systems on Dilute Application

[0061] The test was designed to reflect the European Suspension Test protocol (European Standard EN1276). The bacterial test suspension contained between 1.5 and 5.0 x 10^8 cfu.mL^{-1}.

[0062] Testing was performed under conditions of heavy soil. A stock solution of 3% bovine albumin was prepared as an interfering substance. The test formulation was pre-diluted to the relevant concentration in sterile Water of Standard Hardness (24° French Hard). The presence of the bacterial test solution and interfering substance resulted in a further 1 : 1.25 dilution of the formulation in the test procedure.

[0063] *Test Procedure:* A volume of the interfering substance was pipetted into a sterile container and an equal volume of the bacterial test suspension was added and contents of the tube were mixed. The bacteria and soil were allowed a contact time of 2 min ± 10s. At the end of this contact time, a volume of the diluted formulation was added to produce an overall 1:10 dilution of both the bacterial test suspension and interfering substance and the contents of the tube were mixed again. The formulation was allowed a bactericidal contact time of 5 min ± 10s.

[0064] At the end of the contact time an aliquot was removed and diluted 1 : 10 into a sterile container containing a suitable chemical quenching solution. The contents were mixed thoroughly and left for a contact time of 5 min ± 1 minute. The dilution process was repeated a further five times into a suitable diluent to produce a series of six dilutions of the bactericidal stage ranging from 10^{-1} to 10^{-6}.

[0065] Total viable counts were enumerated by a suitable method and the reduction in number of viable cells elicited by the test formulation was calculated. Table 3 shows the bactericidal activity of a halide "activated"peracid. The results were achieved after 1 : 40 dilution of the test formulation.

Table 3:

Biocidal activity of peracid/bromide formulations at pH 10 against *E. coli.*	
	Log Reduction (*E. coli*)*
2% Oxone	0.49
2% Oxone + 0.69% NaBr	3.45
2% Oxone + 0.345% NaBr	2.79

*Data are the mean of two replicate samples

[0066] The data in Table 3 show that the addition of low levels of a bromide salt gave enhanced bactericidal activity compared with the peracid alone.

Claims

1. A dual container delivery system comprising a first container containing a first aqueous solution comprising a peracid or a source thereof, a second container containing a second aqueous solution comprising a halide and delivery means for delivering the first and second solutions to a surface such that the peracid and halide react just before or upon impacting the surface to produce a cleaning composition comprising a hypohalite bleach.

2. A system according to claim 1, wherein the first and second containers respectively are in the form of first and second compartments of a dual-compartment container.

3. A system according to either preceding claim, wherein the delivery means is in the form of a trigger-spray head, or a pouring system.

4. A system according to any preceding claim, wherein the first aqueous solution contains from 0.01% to 5% by weight, preferably from 0.1% to 2% by weight of the peracid or peracid source.

5. A system according to any preceding claim, wherein the second aqueous solution contains from 0.01% to 5%, preferably from 0.1% to 2% by weight of the halide.

6. A system according to any preceding claim, wherein the pH of the composition resulting from mixing of the two aqueous solutions is from 7 to 13, preferably from 8 to 11.

7. A system according to any preceding claim, wherein the weight ratio of the peracid or its precursor to the halide is from 0.5 : 1 to 100 : 1.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 30 1725

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.7)
A	WO 98 33880 A (JOHNSON & SON INC S C) 6 August 1998 (1998-08-06) * claims 1-11 * ---	1-7	C11D3/39 C11D3/395 C11D3/02 C11D17/04
A	WO 97 31087 A (CLOROX CO) 28 August 1997 (1997-08-28) * claims 1-24 * ---	1-7	
D,A	GB 2 187 748 A (UNILEVER PLC) 16 September 1987 (1987-09-16) * claims 1-7 * ---	1-7	
D,A	EP 0 168 253 A (CLOROX CO) 15 January 1986 (1986-01-15) * claims 1-16 * ---	1-7	
A	DATABASE WPI Section Ch, Week 198611 Derwent Publications Ltd., London, GB; Class D25, AN 1986-071395 XP002068790 & JP 60 013897 A (LION CORP), 24 January 1985 (1985-01-24) * abstract * -----	1	**TECHNICAL FIELDS SEARCHED (Int.Cl.7)** C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	30 June 2000	Richards, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 00 30 1725

30-06-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9833880 A	06-08-1998	AU 6256098 A	25-08-1998
		ZA 9800935 A	06-08-1998
WO 9731087 A	28-08-1997	AU 1962997 A	10-09-1997
		BR 9702098 A	20-07-1999
		CA 2219126 A	28-08-1997
		EP 0827530 A	11-03-1998
		JP 11504384 T	20-04-1999
GB 2187748 A	16-09-1987	NONE	
EP 0168253 A	15-01-1986	US 4613332 A	23-09-1986
		AU 588813 B	28-09-1989
		AU 4421685 A	16-01-1986
		CA 1224902 A	04-08-1987
		DE 3573441 D	09-11-1989
		EG 17200 A	30-08-1990
		ES 545429 D	16-02-1987
		ES 8703515 A	01-05-1987
		ES 552820 D	16-04-1987
		ES 8705028 A	01-07-1987
		ES 552821 D	16-04-1987
		ES 8705029 A	01-07-1987
		MX 166434 B	07-01-1993
		TR 22707 A	13-04-1988
JP 60013897 A	24-01-1985	JP 1853089 C	21-06-1994
		JP 4029719 B	19-05-1992