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(54) Household cleaning products

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

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Description

Field of the Invention

[0001] The present invention relates to liquid household cleaning products containing a halogen bleach source.

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 provide a household cleaning composition based on a hypohalogen compound which can exert bleaching and/or bactericidal action faster than the conventional hypochlorite kind of product. Thereby, the amount of hypohalogen compound can be reduced, for improved safety and lower acrid smell, etc.

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

[0004] The state of the art is replete with disclosures of solid bromide/hypochlorite precursors. For example, GB-A-2 161 827 describes use of dual-compartment solid compositions containing an N-chloro hypochlorite precursor and a solid bromide salt for wc cleaning. The formulations are said to be suitable for rim or cistern block systems and rely on dissolution of the solid compounds in flush water followed by mixing to produce hypobromite *in situ.* EP-A-423 014, US-A-5 108 641, EP-A-395 186 and US-A-5 076 952 relate to very similar dual-component solid compositions for machine dish washer applications. US-A-3 575 865 describes production of hypobromous acid from an organic N-chloro hypochlorite precursor and brominated trisodium phosphate in scouring powder formulations. JP-A-01210499 and JP-A-03064399 relate to the use of solid compositions comprising dichloroisocyanuric acid together with bromide salts and alkali (preferably sodium metasilicate) as efficient safe bleaches for household cleaning/disinfection.

[0005] Regarding liquid compositions, *per se,* there are far fewer patents in this area. WO-A-97/34827 discloses a method of producing stabilised liquid hypobromite formulations for hard surface cleaning whereby hypochlorite is reacted with a bromide salt and then an organic amine/alkali 'stabilising' mixture. WO 97/43392 discloses a method of producing liquid hypobromite formulations for hard surface cleaning manufactured by reacting a hypochlorite with an amine (e.g. sulphamate) at pH <11 and then mixed with bromide salt before raising the pH to a value in the range 11-14.

[0006] JP-A-59168099 discloses preparation of low odour, high efficiency, bathroom tile cleaning compositions prepared on mixing liquid hypochlorite and bromide compositions. Packaging or delivery methods are not specified. JP-A-06009998 describes use of hypobromite bleach, claiming the use of a partitioned container to separate incompatible surfactants and bleaching components until the time of use. The method of hypobromite generation is not specified and separation of reactive components, e.g. bromide and oxidant are not mentioned. JP-A-059045399 discloses use of low levels of hypobromite generated from hypochlorite/bromide for cleaning contact lenses. JP-A-63075100 relates to use of liquid bromide/hypochlorite formulations as drain cleaners but does not specify the method of delivery. WO-A-97/34827 describes use of liquid hypochlorite - bromide derived hypobromite in anti-fouling solutions for industrial or institutional cleaning/disinfection and laundry bleaching. The solution is stabilised by addition of an alkali metal sulphamate salt which arguably may form an equilibrium with the corresponding N-brominated sulphamate species. SU-A-1325062 describes the disinfection/cleaning of milk processing equipment by mixing liquid hypochlorite and bromide solutions.

[0007] The present invention differs from known systems in that it provides for the delivery of the hypochlorite/bromide mixtures at the point of use, unlike the disclosures of WO-A-97/34827 & WO-A-97/43392 which relate to preparation of stabilised hypbromite solutions, the reactive species is formed during product application and the formulations do not include use amine compounds as 'stabilisers'.

Definition of the Invention

[0008] The present invention now provides a dual container delivery system comprising a first container containing a first aqueous solution comprising of a hypochlorite or a source thereof, a second container containing a second aqueous solution comprising a bromide or a source thereof and delivery means for delivering the first and second solutions to a surface such that the hypochlorite and bromide react just before or upon impacting the surface to produce a cleaning composition comprising a hypobromite bleach.

[0009] 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

[0010] 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

[0011] 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.

[0012] 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 hypobromide occurs or is initiated as they are exiting the delivery means and/or in midair 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.

[0013] 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.

[0014] For thickened systems a pouring dual compartment packaging form is generally preferred.

The solutions

[0015] The hypochlorite source may be a simple hypochlorite salt such as those of the alkali or alkaline earth metals or a compound which produces hypochlorite on hydrolysis, such as organic N-chloro compounds. The bromide source may be a simple bromide salt such as those of the alkali or alkaline earth metals, or a compound which undergoes transformation in solution to yield the bromide anion.

[0016] The hypochlorite or hypochlorite source is preferably present at about from 0.01% to 10% by weight, more preferably from 0.1% to 2% by weight of the first aqueous solution. The bromide or bromide source is preferably present at about from 0.01% to 10%, 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 8 to 13, more preferably from 9 to 13. The weight ratio of the hypochlorite or its precursor to the bromide or its precursor is typically from 0.5 : 1 to 100 : 1.

[0017] The hypochlorite is preferably present in alkaline solution, in order to minimise decomposition, while the pH of the bromide solution is adjusted to a value such that on mixing the final pH of the formulation is optimised for the specific usage scenario. 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 8. However, higher pH values are preferred (see further below). Lower pH values could result in incomplete mixing and localised areas of very low pH with the consequent risk of generating toxic halogen gas.

Surfactants:

[0018] 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.

[0019] 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}. 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.

[0020] 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.

[0021] 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.

[0022] 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.

[0023] 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.

[0024] 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.

[0025] 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%

[0026] 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-methyl-sulphonium)-propane-1-sulphonate betaine and 3-(cetylmethyl-phosphonium)-ethane-sulphonate betaine.

[0027] 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.

[0028] 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%.

[0029] 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%.

[0030] 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.

[0031] 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.

[0032] 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".

[0033] 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.

[0034] 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.

[0035] 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.

[0036] Surfactants which are storage stable in combination with the hypochlorite bleach may be combined with the hypochlorite in the same partial composition. Surfactants which do not have such stability should be made part of the other partial composition.

[0037] 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.

Alkalinity

[0038] Preferably, the first (hypochlorite or hypochlorite precursor) aqueous solution also contains a source of alkalinity which keeps its pH at or above 11.0, not only during production of the product but also during storage. For the purposes of this invention a source of alkalinity is defined as a mixture of ingredients which is able to keep the pH at or above the required level.

[0039] Thus, preferably the pH of the first (hypochlorite or hypochlorite precursor) aqueous solution should be kept at or above 11, more preferably at or above 11.5, especially at or above 12. Preferably, the maximum pH is 13.5. Such alkali sources are known in the art and are generally made up of highly alkaline compounds such as alkali metal hydroxides and alkali metal salts of weak acids. Suitable sources of alkalinity comprise mixtures of alkali metal hydroxide and alkali metal silicate, particularly alkaline sodium silicate wherein the Na20/Si02 ratio is 1:1 or above, preferably 1.5:1 or above. A particularly suitable alkali source comprises 0.2-0.6% of NaOH and a suitable amount of alkaline Na silicate (e.g. 0.1-3%wt) to maintain the required pH.

Other Optional Components

[0040] The mixed composition on the surface may also contain surfactants, 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 hypochlorite, i.e. together with the bromide salt, allowing use of formulation ingredients that do not have long term stability in hypochlorite solution and are therefore not used in conventional single compartment hypochlorite bleach formulations.

Examples

Example 1

[0041] A typical non-limiting formulation suitable for delivery from a dual-compartment pack is as follows:

[0042] Partial composition A: sodium hypochlorite - 1.0%, pH adjusted to 12.0 (in order to minimise hypochlorite decomposition).

[0043] Partial composition B: sodium bromide - 0.8%, pH adjusted to a value of 12.0. Solutions A & B when dispensed from a suitable dual-compartment and mixed in equal proportions will produce a hypochlorite/bromide reaction mixture with a pH of 12.0.

Examples 2 & 3

[0044] Table 1 (a). shows the composition (Example 2) of a typical prototype bromide activated 'low' hypochlorite mould remover or kitchen cleaner formulation suitable for delivery from dual-compartment spray pack. Compositions A & B are stable over extended periods (> 1 month) and Table 1 (b) (Example 3) gives the composition of the mixed formulation on delivery from the dual-compartment pack onto the surface, based on a 1:1 v/v mixing.

Table 1(a):

Typical partial compositions for a bromide/hypochlorite mould remover or kitchen cleaner:	
Version 1	
Chemical Name	% active level in formulation
Partial Composition A:	
Sodium xylene Sulphonate	1.20
Sodium hydroxide	0.08
Sodium hypochlorite	1.00
Decyl-dimethyl amine oxide	0.40
Sodium laurate (soap)	0.20
Water	to 100%
Partial Composition B:	
Sodium hydroxide	0.10
Sodium bromide	0.80
Water	to 100%
Version 2	
Chemical Name	% active level in formulation
Partial Composition A:	
Sodium hydroxide	0.08
Sodium hypochlorite	1.00
Water	to 100%
Partial Composition B:	
Sodium hydroxide	0.10
Sodium bromide	0.80
Sodium xylene Sulphonate	1.20
Decyl-dimethyl amine oxide	0.40
Sodium laurate (soap)	0.20
Water	to 100%

[0045] Version (2) is identical to Version (1) except that the foaming surfactant system is in the bromide solution rather than the hypochlorite solution. Upon 1:1 v/v mixing, it yields the composition as listed in Table 1 (b).

Table 1(b):

Typical formulation of a prototype bromide/hypochlorite mould remover or kitchen cleaner on delivery	
Chemical Name	% active level in formulation on mixing
Sodium xylene sulphonate	0.60
Sodium hydroxide	0.09

Table 1(b): (continued)

Typical formulation of a prototype bromide/hypochlorite mould remover or kitchen cleaner on delivery	
Chemical Name	% active level in formulation on mixing
Sodium hypochlorite	0.5
Decyl-dimethyl amine oxide	0.20
Sodium laurate (soap)	0.10
Sodium bromide	0.40
Water	to 100%

[0046] The mixed formulation has a pH of 12.0.

[0047] Viscous products suitable for providing 'cling' to vertical surfaces, such as wc bowls, can be prepared by use of suitable surfactants or thickening agents. These are added to partial compositions A & B such that the partial compositions are preferably non-viscous during storage but develop viscosity on mixing, during delivery from the pack.

Cleaning appraisal data

[0048] Specific examples showing the enhanced cleaning efficacy of the bromide 'activated' hypochlorite solutions are described below.

Application as a Mould Remover :

Appraisal of mould bleaching using 'autoclaved' mould paste on porous ceramic tiles

[0049] Mould growth, like all natural processes, is somewhat variable and in order to provide a reproducible test methodology the following process was used to produce uniformly soiled test substrate.

[0050] Cultures of hyphal *Cladosporium cladosporoides* 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 can be stored for several weeks at 5°C.

[0051] 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 (if necessary, additional mould paste or water was added to ease the soiling process). 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'.

[0052] 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 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 (generally 1 cm^3 of bleach liquor is 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, generally 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. 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.

[0053] The test data comparing bromide 'activated' hypochlorite with hypochlorite alone are shown in Table 2. Data sets 1 & 2 were obtained from different batches of soiled tiles.

Table 2:

Bleaching of autoclaved 'mould paste' on porous ceramic tile by various hypochlorite containing systems (ambient temperature, 3 minutes contact time)						
	Mean score					
	zero 'standing time'			after 5 minutes 'standing time'		
Data set 1:						
System	0% NaBr	0.4% NaBr	0.8% NaBr	0% NaBr	0.4% NaBr	0.8% NaBr
3.0 % NaOCl, pH 13.0	4.8	—	—	5.3	—	—
0.5 % NaOCl, pH 13.0	1.3	1.2	—	2.1	4.8	—
1.0 % NaOCl, pH 13.0	3.2	—	3.5	3.2	—	4.2
Data set 2:						
System	0% NaBr	0.1% NaBr	0.2% NaBr	0% NaBr	0.1% NaBr	0.2% NaBr
3.0 % NaOCl, pH 12.0	5.5	—	—	5.5	—	—
0.5 % NaOCl, pH 12.0	2.7	3.9	5.1	2.2	4.7	5.4

[0054] The data shows that by addition of low levels of bromide salt, it is possible to increase the bleaching performance of 'low' levels of hypochlorite to parity with that obtained from a typical commercial mould remover formulation which contains 2.0 - 3.0% sodium hypochlorite at a pH of 12.5-13.0.

[0055] Addition of bromide 'activates' sodium hypochlorite under all pH conditions, but at pH 13.0 the improvement in bleaching only becomes evident after a few minutes standing time. Use of a slightly lower formulation pH (e.g. 12.0) gives instantaneous generation of hypobromite and allows use of lower levels of bromide.

Application as a Kitchen Cleaner :

Appraisal of bleaching of hydrophilic stains using tea stained cotton cloth

[0056] Tea stained cotton (BC-1) cloth is routinely used in the assessment of laundry bleaches. Here the method was adapted as an easy and readily reproducible indicator of the activity of bleaches against common hydrophilic household 'soils', e.g. tea, coffee, wine, fruit and vegetable stains.

[0057] A length of pre-stained BC-1 cotton cloth was cut into square swatches (2 cm x 2 cm). Four replicate cloths are placed in the bottom of a clean glass beaker and covered with the cleaning liquor at room temperature. After the required contact time (generally 2 or 5 minutes) had 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 the washing procedure was repeated twice more using fresh water each time. Washed cloths were then pressed between two filters to remove excess water and placed on fresh filter papers, in the dark, to dry.

[0058] Reflectance measurements were carried out on a Spectraflash 400 instrument. Δ R measurements were calculated using '40ptspec' software, using a portion of untreated cloth from the same BC-1 cloth batch as a standard. Results obtained from each of the four replicate test cloths were then statistically analysed to obtain mean Δ R values for each bleach system. The test data comparing bromide 'activated' hypochlorite with hypochlorite alone are shown in Table 3.

Table 3:

Bleaching of tea stained cotton cloth (BC-1) by various hypochlorite containing systems (ambient temperature, 1 minute contact time)		
	Mean Δ R (460 nm)	
System	without sodium bromide	with 0.0138% NaBr
1.0 % sodium hypochlorite, pH 13.0	10	—
0.1 % sodium hypochlorite, pH 13.0	2	9.5
1.0 % sodium hypochlorite, pH 11.0	26	—
0.1 % sodium hypochlorite, pH 11.0	13	21

[0059] The data shows that addition of low levels of bromide salt enhances the bleaching performance of 'low' levels of hypochlorite to parity with 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.

Hygiene Appraisal Data

[0060] Specific examples showing the enhanced bactericidal activity of the bromide 'activated' hypochlorite solutions are described below:

Application as a wc cleaner

Appraisal of hygiene performance using suspension test methodology

[0061] The bactericidal test was designed to reflect the European Suspension Test protocol (European Standard EN1276). The bacterial test suspension contain of between 1.5 and 5.0 x 10^8 cfu mL^{-1}. Testing was performed in the presence of an interfering substance (i.e. under conditions of high proteinaceous soil relevant to a wc product). A solution of 3% bovine albumin was prepared resulting in an in-test concentration of 0.3%. The test formulation was pre-diluted to the relevant concentration in sterile Water of Standard Hardness (24^0 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.

[0062] A volume of the interfering substance was pipetted into a sterile container and an equal volume of the bacterial test suspension was added and the contents of the tube are mixed. The bacteria and soil were allowed a contact time of 2 min ± 10 s. 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 disinfectancy contact time of either 5 min ± 10 s or 30 min ± 10 s. At the end of the contact time, an aliquot was removed and diluted 1:10 in to a sterile container containing a suitable chemical quenching solution. The contents were mixed thoroughly and left for a contact time of 5 min ± 1 min. The dilution process was repeated a further five times into a suitable diluent to produce a series of six dilutions of the disinfectancy stage ranging from 10^{-1} to 10^{-6}. Total viable counts were enumerated by a suitable method and the reduction in numbers of viable cells elicited by the test formulation were calculated.

[0063] The test data comparing the bactericidal efficacy of the bromide 'activated' hypochlorite with hypochlorite alone are shown in Table 4. Data are the mean of at least two replicate samples.

Table 4

Bactericidal activity of 'low hypochlorite' bleach solutions (5 minutes contact time)		
	Mean Log reduction in cell numbers (from log-8 suspension) 1:40 dilution	
Formulation	*E. coli*	*S. aureus*
1.0 % NaOCl, pH 13	2.8	0.6
1% NaOCl + 1.38% NaBr, pH 13	5.9	3.0

Table 4 (continued)

Bactericidal activity of 'low hypochlorite' bleach solutions (5 minutes contact time)		
	Mean Log reduction in cell numbers (from log-8 suspension) 1:40 dilution	
Formulation	*E. coli*	*S. aureus*
1% NaOCl + 0.69% NaBr, pH13	4.7	3.3
1% NaOCl + 0.345% NaBr, pH 13	3.4	2.9
0.5% NaOCl + 1.38% NaBr, pH13	3.2	0.6
	Mean Log reduction in cell numbers (from log-8 suspension) 1:20 dilution	
0.35 % NaOCl pH13	1.0	<0.1
0.35 % NaOCl + 0.48% NaBr, pH13	1.3	<0.1
0.35 % NaOCl, pH11	3.2	1.2
0.35% NaOCl + 0.48% NaBr, pH11	4.9	4.0

[0064] The data show that addition of a low level of a bromide salt substantially increases the microbicidal activity of low hypochlorite liquid bleach over a five-minute contact time. These effects may be accentuated by the use of a longer contact time such as 30 minutes, which may reflect more accurately the practical application of a thickened wc product.

[0065] The use of bleach solutions at lower initial pH values (e.g. 11.0) again gives improved performance particularity against Gram-positive bacteria. The technology is also applicable to thin liquid products suitable for delivery from pouring or spray packs such as General Purpose Cleaners or Floor Cleaners under variable soiling conditions.

Claims

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

4. A system according to any preceding claim, wherein the first aqueous solution contains from 0.01% to 10% by weight, preferably from 0.1% to 2% by weight of the hypochlorite or hypochlorite source.

5. A system according to any preceding claim, wherein the first aqueous solution contains a source of alkalinity to maintain its pH at or 11.0, preferably at or above 11.5, more preferably at or above 12.0 and preferably no more than 13.5.

6. A system according to any preceding claim, wherein the second aqueous solution contains from 0.01% to 10%, preferably from 0.1% to 2% by weight of the bromide or bromide source.

7. A system according to any preceding claim, wherein the pH of the composition resulting from mixing of the two aqueous solutions is from 8 to 13, preferably from 9 to 13.

8. A system according to any preceding claim, wherein the weight ratio of the hypochlorite or its precursor to the bromide or its precursor is from 0.5 : 1 to 100 : 1.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 30 9852

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 May 2000	Richards, M

CATEGORY OF CITED DOCUMENTS

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