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

(11) **EP 1 799 804 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
05.08.2009 Bulletin 2009/32

(21) Application number: **05758388.2**

(22) Date of filing: **23.06.2005**

(51) Int Cl.:
C11D 3/395 *(2006.01)*

(86) International application number:
PCT/EP2005/006877

(87) International publication number:
WO 2006/010421 (02.02.2006 Gazette 2006/05)

(54) AQUEOUS LIQUID BLEACH COMPOSITIONS

WÄSSRIG-FLÜSSIGE BLEICHMITTEL

COMPOSITION DE BLANCHIMENT AQUEUSE

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU MC NL PL PT RO SE SI SK TR

(30) Priority: **27.07.2004 EP 04254469**
13.10.2004 EP 04256300

(43) Date of publication of application:
27.06.2007 Bulletin 2007/26

(73) Proprietors:
- **Unilever N.V.**
  3013 AL Rotterdam (NL)
  Designated Contracting States:
  AT BE BG CH CZ DE DK EE ES FI FR GR HU IS IT LI LT LU MC NL PL PT RO SE SI SK TR
- **Unilever PLC**
  London
  EC4Y 0DY (GB)
  Designated Contracting States:
  CY GB IE

(72) Inventors:
- **JAMIESON, Andrew S.,**
  Unilever R & D Port Sunlight
  Bebington,
  Merseyside CH63 3JW (GB)
- **JONES, Martin V.,**
  Unilever R & D Port Sunlight
  Bebington,
  Merseyside CH63 3JW (GB)
- **O'KEEFFE, Joanne C.,**
  Unilever R & D Port Sunlight
  Bebington,
  Merseyside CH63 3JW (GB)
- **THOMPSON, Katherine, M.**
  Unilever R & D Port Sunlight
  Bebington, Merseyside CH63 3JW (GB)
- **THORNTHWAITE, David, W.**
  Unilever R & D Port Sunlight
  Bebington,
  Merseyside CH63 3JW (GB)

(74) Representative: **Rosen Jacobson, Frans Lucas M. et al**
Unilever Patent Group
Olivier van Noortlaan 120
3133 AT Vlaardingen (NL)

(56) References cited:
EP-A- 0 165 676
US-A- 2 263 948
US-A- 3 054 753
US-A- 3 749 672

EP 1 799 804 B1

Description

Technical field

[0001] The present invention relates to aqueous liquid bleach compositions and to a method for disinfecting hard surfaces using the liquid bleach compositions.

Background and prior art

[0002] Aqueous liquid hypochlorite bleach compositions are well known in the art. On the one hand they are used for bleaching of and stain removal from laundry, on the other hand they are used for cleaning and disinfecting hard surfaces such as kitchen surfaces, floors, bathrooms and in particular toilets. To increase the contact time between the bleach and a surface, particularly an inclined or vertical surface the bleach compositions often have a relatively high viscosity and such compositions are generally known as "thick bleach".

[0003] Hypochlorite bleach compositions are generally strongly alkaline, typically pH 10 or higher. At acidic pH hypochlorite bleach decomposes, forming chlorine gas. For certain applications this has been considered to be an undesirable limitation and alternative "active chlorine" bleaching agents have been used for various applications. They generally belong to the group of N-chloro compounds such as mono-, di- and trichloro-isocyanurate, mono- and dichloro-sulphamic acid, N-chlorohydantoins, N-chloro-succinimide, N-chlorophthalimide, N-chloro-p.toluene-sulphonamide (Chloramine T), N-chloroimidodisulphate, N-chloromelamine, N-chloroglycoluracil and the like. The parent NH compounds generally react with chlorine gas under formation of the N-chloro compound and are thus said to stabilize hypochlorite at low pH by scavenging the chlorine formed through decomposition of the hypochlorite. In fact no stabilization takes place because although one active chlorine compound (hypochlorite) is substituted by another (the N-chloro compound), the bleaching power of the N-chloro compound is generally inferior to the bleaching power of hypochlorite and therefore the bleaching power of the total mixture is inferior to that of an equivalent amount of fresh hypochlorite alone.

[0004] US 3,749,672 describes the stabilization of hypochlorite solutions between pH 4 and 11 by adding an NH compound suitable for conversion to the corresponding NCl derivative. A list of all likely and a lot of less likely candidate NH compounds is given, but all examples focus on the use of sulphamic acid.

[0005] EP 119560 describes hypochlorite solutions of pH>11 stabilized by the addition of an NH compound in a ClO^- : NH molar ratio of ≤ 1. Again a large number of possible NH candidate compounds are listed, but only sulphamic acid is exemplified.

[0006] US 3,054,753 describes detergent powders comprising solid inorganic active chlorine sources such as chlorinated sodium phosphate or lithium hypochlorite and an organic sulphonamide as a stabilizing agent for the active chlorine compound. Likewise, EP 165676 describes solid hypochlorite containing detergent powders that are stabilized and brought into solid form by the addition of anhydrous builders, particularly sodium phosphates, and p.toluenesulphonamide. N-chloro-p.toluene-sulphonamide itself is described as being an inefficient source of active chlorine and providing little bleach activity. The detergent powders described in both these documents are typical laundry detergents in which sodium phosphate and sodium carbonate builders are the predominant materials in the composition.

[0007] WO 9821308 describes acidic bleaching compositions obtained by mixing an acidic solution of a chlorine deactivating compound (NH compound) with an alkaline hypochlorite solution immediately before use. The chlorine deactivating compound is further specified to be sulphamic acid.

[0008] WO 0100029 describes antimicrobial solutions that are called "stabilized hypochlorite" solutions, but which are essentially solutions of N-chloro- and N-dichlorosulphamate and a so-called "dopant" selected from a dialkylhydantoin, an aryl-sulphonamide, a succinimide and a glycoluracil.

[0009] WO 9627651 and 9627652 describe bleach compositions giving reduced skin malodour and comprising an active chlorine bleach such as hypochlorite and an NH compound. The compositions are said to be particularly useful to prevent the hands of the user which are in prolonged contact with the composition from acquiring the well-known bleached-skin malodour.

[0010] Although active chlorine compounds and particularly hypochlorite are known to be powerful disinfectants, after treatment of a substrate with the chlorine compound the disinfectant activity is normally short-lived. Thus, after a surface has been treated with hypochlorite it can quickly become microbially recontaminated again. This is particularly true if the surface is afterwards rinsed with water, because rinsing will wash away any traces of hypochlorite left on the surface.

[0011] There is a need for methods for oxidative cleaning/bleaching of a surface that provide powerful initial disinfectancy as well as give sufficient residual antimicrobial activity on a surface to prevent bacterial regrowth for extended periods of time. Also, compositions suitable for use in such methods should be sufficiently stable to be manufactured, shipped and stored without appreciable loss of active chlorine.

Summary of the invention

[0012] It has now been found that treatment of hard surfaces with a liquid composition comprising a combination of hypochlorite and one or more specific N-chloro compounds and a surfactant provides thorough oxidative cleaning and removal of stains while at the same time not only initially disinfecting the surface, but providing antimicrobial activity on the cleaned surface for an extended period of time, even after repeated rinsing. The selected N-chloro compounds provide compositions that are stable and can be stored for long periods without appreciable loss of active chlorine.

[0013] Thus, the invention provides a method for providing antimicrobial activity on hard surfaces involving treatment of the surface with a liquid bleaching composition comprising hypochlorite and one or more specific N-chloro compounds, and a surfactant.

[0014] Furthermore, the invention specifically provides a method of cleaning and disinfecting toilet surfaces, particularly toilet bowls, comprising applying to the surface a liquid bleaching composition comprising hypochlorite and one or more specific N-chloro compounds, and a surfactant.

[0015] Also, the invention provides stable liquid bleaching compositions suitable for use in the methods described above.

Detailed description of the invention

[0016] All percentages mentioned herein are by weight unless specified otherwise.

[0017] Accordingly, the invention provides a method for providing lasting antimicrobial activity on a substrate as well as an aqueous liquid bleaching composition suitable for use in that method. The method comprises treating the substrate with a composition comprises a hypochlorite salt and an N-chloro compound chosen from N-chloro-arylsulphonamides and N-chloro-imidodisulphate salt and the composition comprises a surfactant the composition having pH above 7. The method may be used on any substrate including textiles, but is particularly useful for application on hard surfaces.

[0018] The hypochlorite salt is generally an alkali metal or alkaline earthmetal salt although other salts may be used. The K, Na and Ca salts are preferred and the latter two particularly preferred. The compositions used for the purposes of the invention generally comprise 0.01-10% NaClO or an equivalent amount of other hypochlorite salt, which is equivalent to 0.0014-1.4 mol/l of hypochlorite ion. Preferably the hypochlorite ion content is 0.005-1.0 mol/l, more preferably at least 0.01 mol/l.

[0019] The compositions according to, and used for the purposes of the invention generally comprise 0.00001-0.5 mol/l of the N-chloro compound, preferably at least 0.00002 mol/l or even 0.00005 mol/l, more preferably 0.0001-0.2 mol/l, most preferably at most 0.1 mol/l. The molar ratio between hypochlorite ion and N-chloro compound is usefully kept between 15000:1 and 1:1, preferably at most 5000:1. Even more useful ratios are between 200:1 and 1:1, more preferably at most 100:1, even more preferably between 100:1 and 2:1, most preferably between 50:1 and 5:1.

[0020] Among the N-chloro-arylsulphonamides the benzene- and p.toluene-sulphonamide and N-chloro-saccharine (or the N-chloro compound derived therefrom) are preferred, the N-chloro-benzenesulphonamide and p.toluene-sulphonamide are more preferred. P.toluene-sulphonamide is especially preferred and is commercially available as its Na salt as Chloramine T. The N-Chloro compounds can be added to the composition as such or they can be made in situ by adding the corresponding NH compound to the hypochlorite solution. In order to have complete control over the amount of N-chloro compound present in the composition and not to consume part of the hypochlorite it is preferred to add the N-chloro compound as such.

[0021] For long-term stability the compositions used for the purposes of the invention need to be alkaline, i.e. have pH above 7. Preferably the pH is kept at or above 8 or even 9. At the pH of the compositions according to the invention the N-chloro compounds may primarily be present as their salts, which are preferably alkalimetal or alkaline earthmetal salts.

[0022] The method according to the invention involves treating the surface either with a dilute composition within the range described above, i.e. a composition in which the hypochlorite and the N-chloro compound are present in concentrations in the lower parts of the ranges described above, or with a concentrated composition i.e. a composition in which the components are present in the higher parts of the concentration ranges. The dilute compositions can be conveniently made by the consumer by proper dilution of a concentrated composition. Such concentrated compositions preferably have a hypochlorite concentration of 0.1-1.0 mol/l, an N-Cl compound concentration of 0.01-0.5 mol/l, more preferably 0.02-0.2 mol/l) and a pH of at least 9 and can conveniently be diluted 10-100 fold.

[0023] The concentrated compositions according to the invention are generally not suitable to come in contact with the skin and therefore should be diluted before being applied to a surface manually (e.g. with a wipe or cloth or other implement). Alternatively, and in preferred embodiments of the invention, compositions according to the invention, either dilute or concentrated, are applied to the surface to be treated without coming in contact with the skin of the user and are left in contact with that surface for a sufficiently long time to oxidatively clean and disinfect that surface, whereafter the surface may be rinsed if desired. Generally, contact times of 1 minute are sufficient for initial disinfectancy, with

contact times of at least 5 minutes being used to obtain long term disinfectancy, preferably at least 15 minutes, more preferably at least 30 minutes. One example of such embodiment involves applying a composition according to the invention with a spraying device such as a trigger spray or similar, as well known in the art of hard surface cleaning. Another embodiment of the invention involves applying to the surface to be treated a squirt of concentrated solution straight from the container in which it is provided.

[0024] The invention particularly provides a method for cleaning and disinfecting toilet surfaces comprising applying to the surface a composition as described above. In a preferred embodiment, wherein the toilet surface to be treated is the toilet bowl, a concentrated composition as described above is applied directly from the container to the bowl, either above the water table to the surface of the bowl e.g. under the rim, or to the water in the bowl, without coming in contact with the skin of the user. Particularly suitable containers for that purpose are well known in the art. Typically for such containers the longitudinal axis of the dispensing opening in the cap makes an angle of generally less than 90° (preferably 10-80°) with the longitudinal axis of the container to enable easy application of the composition under the rim of the toilet bowl. An example of such a bottle is depicted in the UK Industrial Design registration no. 1057823. Applying the concentrated composition to the water in the bowl will generate a dilute solution according to the invention.

[0025] As outlined above, treating a surface with a bleaching composition according to the invention not only oxidatively cleans and disinfects that surface, but also provides extended antimicrobial activity on that surface such that regrowth of micro-organisms is prevented for many hours after the treatment is completed, particularly if the composition is left to dry out on the surface. This antimicrobial activity remains even after repeated rinsing of the surface, in spite of the fact that the active chlorine compounds in the composition are soluble in water and would be expected to be rinsed away.

[0026] The compositions according to the invention can optionally contain other components known in the art to be useful in bleach compositions. Particularly useful among these optional components are those which provide increased viscosity to the aqueous solutions. Viscous bleaching compositions known in the art as "thick bleach" are particularly useful for treating inclined and vertical surfaces, such as toilet bowls, because they can be applied to such surfaces and left there. The high viscosity causes the composition to slowly flow down the surface, thus providing prolonged contact time between the composition and the surface, leading to improved cleaning and disinfection, and without any manual intervention. Typically such bleaching compositions have a viscosity of 50-5000 mPa.s, preferably 100-2000 mPas.s, more preferably 200-1000 mPas.s (measured with a Haake RT20 Rotovisco rheometer fitted with a coaxial cylinder sensor DIN 53018 (Z41 rotor and Z43 measuring cylinder), using a 3 mm gap. Flow curves obtained at 25° C over the shear rate range 0.1 to 1000 s^{-1})

[0027] Components to increase viscosity of bleaching compositions are well known in the art. They may be chosen from polymeric thickening agents comprising natural or synthetic polymers, with the proviso that the polymers should be stable in active chlorine bleach environment. Such polymers have e.g. been described in EP 636689. They may also be chosen from thickening clays or thickening silica's known in the art. Particularly useful thickening systems are provided by suitable structuring surfactants. Many organic sulphate or sulphonate surfactants are known in the art to be suitable for this purpose, particularly in combination with nonionic or amine oxide surfactants. A very useful thickening system is formed by the combination of amine oxide surfactants and fatty acids. The amine oxides are preferably chosen from C8-C20 alkyl-dimethylamine oxide, preferably in an amount of 0.1-5%, and the fatty acids from C8-C20 fatty acids, preferably in an amount of 0.1-3%.

[0028] Other optional components include antioxidants, radical scavengers, chelating agents for metals prone to induce or accelerate hypochlorite decomposition (such as silicates or periodates), hydrotropes and anticorrosion agents. Solid abrasives may be added as well. On the other hand inorganic phosphate builders have no useful role to play in compositions according to the invention. Thus, they are preferably present in only minor amounts (less than 0.1%, preferably less than 0.01%), if at all. Most preferably they are completely absent. Likewise, large amounts of carbonate builders are preferably not used either, although small amounts of alkalimetal carbonate ($\leq$ 5%, preferably $\leq$ 1%) may be used as alkalising/buffering agent to set the desired pH.

[0029] Further hypochlorite-stable surfactants are added to improve cleaning properties, specifically anionic, nonionic, amphoteric and zwitterionic surfactants. Examples of suitable surfactants are given in the well-known textbooks: "Surface Active Agents" Vol.1, by Schwartz & Perry, Interscience 1949; "Surface Active Agents" Vol.2 by Schwartz, Perry & Berch, Interscience 1958; the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company; "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981. Total surfactant content in the compositions will normally be at most 10%, preferably at most 5%.

[0030] Thus, the aqueous liquid bleach compositions according to the invention contain at least one surfactant, either added for improved cleaning only, or as part of a thickening system thereby also providing the improved cleaning.

[0031] Colourants, dyes and pigments may be added to impart a desired colour to the compositions and perfumes to give the compositions a desired odour, particularly to overcome the hypochlorite odour which many people do not appreciate. The components should be chosen to be bleach-stable, as is well known in the art.

[0032] As outlined above, the compositions according to the invention are alkaline and sufficient alkali, preferably alkalimetal hydroxide, should be present to ensure this. The compositions could also usefully contain buffer to ensure

long term pH stability. Alkalimetal carbonates/bicarbonates and silicates are particularly useful for that purpose.

[0033] The compositions are preferably clear aqueous liquids.

[0034] In a particularly useful and preferred embodiment the invention provides products for cleaning toilet bowls comprising an oblong container having a dispensing opening of which the longitudinal axis makes an angle of at least 5°, but less than 90° (preferably 10-80°) with the longitudinal axis of the container, the container containing a concentrated aqueous liquid bleaching composition as described above and having a viscosity of 50-5000 mPa.s

Examples

[0035] Aqueous liquid bleaching compositions were prepared according to the formulations 1-3 (amounts in %):

	1	2	3
Na hypochlorite	4.80	4.80	4.80
Chloramine T trihydrate	1.00	0.75	1.00
Empigen OD *	1.75	2.10	1.16
Lauric acid	0.30	0.35	0.60
Perfume	0.06	0.06	0.06
Alkaline Na silicate	0.05	0.05	0.05

All examples contain sufficient NaOH to pH 12.5
All examples contain demineralised water to 100%
*) C_{10}-C_{18} alkyl-dimethylamine oxide marketed by Huntsman

Comparative tests:

[0036] The stability of Formulation 3 above and of compositions comprising hypochlorite and various other N-chloro compounds was tested. For the other N-chloro compounds or their NH precursors 1% of each compound was added instead of Chloramine T to a formulation according to Formulation 3. Some of the tested materials immediately reacted with the hypochlorite, evolving heat and in some cases effervescing or giving a colour change or precipitate. No assays of available chlorine were carried out on these unstable mixtures. For samples that were of higher stability the residual available chlorine content, expressed as a percentage of the initial available chlorine content, was assessed after 7 days storage in the dark at ambient temperature. The results are presented in Table 1. From the table it can be seen that only the first three N-chloro compounds, which are compounds according to the invention, are sufficiently stable and thus have a negligible or small effect on the amount of available chlorine, whereas the other N-chloro compounds decompose and thereby consume an appreciable amount of hypochlorite.

Table 1 (X = not assayed, for the reasons stated)

N-chloro compound or precursor	**% residual available Cl_2**
None	100
N-chloro-p-toluene-sulfonamide, Na salt (Chloramine-T)	100
Tri-sodium imidodisulfate	99
N-chloro-saccharine	92%
Sulfamic acid	X (exothermic; effervesced)
Methylsulfamic acid	51
Cyclohexylsulfamic acid, Na salt	41
Dichloroisocyanuric acid, Na salt (NaDCCA)	X (exothermic; effervesced)
N-chloro-succinamide	X (exothermic; effervesced; white precipitate)
Indoline-2-carboxylic acid	X (dark brown precipitate)
1,3-dichloro-5,5-dimethyl hydantoin	X (exothermic; effervesced)

(continued)

N-chloro compound or precursor	% residual available Cl_2
Sarcosine	X (exothermic; effervesced)
Iminodiacetic acid, Na salt	X (exothermic; effervesced, white precipitate)
Melamine	3
Glycoluracil	4

[0037] The residual available chlorine present was analysed iodometrically, using the following procedure:
A known weight of the test solution (w) was placed in an iodine flask. The sample was diluted with approximately 20 ml distilled water. 10 g of 5% potassium iodide solution was added followed by 10 ml of 0.5 M sulphuric acid. The flask was stoppered and swirled to mix the contents before placing in the dark for 5 minutes, until the brown colour of the evolved iodine had fully developed. The liberated iodine was titrated against 0.1 M sodium thiosulphate solution until the solution became colourless, with addition of soluble starch indicator near the end point to increase accuracy.

[0038] A further series of N-chloro compounds or precursor thereof were assessed in the presence of sufficient hypochlorite to have 5% available Cl_2 and 0.9% sodium hydroxide giving a solution pH > 13, but without surfactants or other formulation components. Materials that are acidic, e.g. sulphamic acid, were first neutralised by mixing with the sodium hydroxide solution before addition of the sodium hypochlorite. The residual available chlorine contents of these samples were examined after various periods of storage in the dark and results of these stability tests, expressed as the percentage of the initial available chlorine content, are shown in Table 2. Most of these materials (sulfamic acid, NaDCCA, TCCA, uracil, taurine) underwent immediately reaction with the hypochlorite, evolving heat and effervescing. The residual available chlorine of some of these samples was examined within 30 minutes and found to be low (> 55% of the initial content).

Table 2 (X = not further assayed)

N-chloro compound or precursor	% residual available Cl_2			
	30 mins.	**3 days**	**9 days**	**35 days**
None	100	100	99	98
Sulfamic acid	53	26	24	18
DiCl-isocyanuric acid, Na salt (NaDCCA) (2%)	40	4	4	3
TriCl-isocyanuric acid (TCCA) (1%)	26	5	2	X
Uracil (1%)	40	5	X	X
Taurine (1%)	22	8	X	X
Chloramine-T (1%)	100	100	100	98
Tri-Na imido-disulfate (1%)	100	99	99	99

[0039] These assessments show that of the pre-formed N-chloro compounds, only Chloramine-T, maintains good stability in the presence of high levels of sodium hypochlorite, giving more than 90% residual available chlorine after 1 month at ambient temperature. Of the N-chloro precursors, only imidodisulfate also fulfils this criterion.

Hygiene score test

[0040] This test measures the ability of a composition to impart lasting and rinse-resistant disinfection of a surface. The test uses a high-throughput screening method to assess the hygienic properties of standard samples of 10μl of composition, dispensed in microtitre plate wells that have been left to dry (at 30°C overnight) and are thereafter subjected to a number of automatic rinses. Each test was done in 8 replicates. The rinses were done with an Ascent Wellwash™ plate washer with sterile water of standard hardness. After a set number of rinses the plates were dried at 30°C for 45 minutes and left to cool at 20°C for 15 minutes. Each well was thereafter incubated with 50μl of an aqueous suspension of *E.coli* ($0.5x10^8$ cfu) in 0.3% protein (BSA) soil and left in contact for 1h at 20°C. The wells were then washed by adding 100μl water of standard hardness and shaking for 10sec., whereafter the wash liquour and unattached cells were aspirated off.

Thereafter 270μl of tryptone soya broth growth medium was placed in each well and the plates were incubated for 24h at 37°C to allow remaining bacteria to re-grow. A test was classified as successful after the set number of rinses if at least 90% of the samples showed no regrowth. The highest number of rinses that lead to a successful test is taken as the "hygiene score".

[0041] Table 3 shows a comparison of the hygiene scores obtained for a simple 1% aqueous solution of Chloramine-T and two viscosity matched formulations: formulation 4 which is according to the invention and contains 1% Chloramine-T, and formulation 5 which does not contain Chloramine-T. The table shows that incorporation of Chloramine-T into a hypochlorite base significantly increases its rinse-resistant long-lasting hygiene.

	4	**5**
Na hypochlorite	4.80	4.80
Chloramine T trihydrate	1.00	0
Empigen OD *	2.00	2.00
Lauric acid	0.2	0.5
Perfume	0.06	0.06
Alkaline Na silicate	0.05	0.05
Both formulations contain sufficient NaOH to pH 12.5		
Both formulations contain demineralised water to 100%		
Viscosity (1-3 s^{-1}): 450 mPa.s for all		

Table 3

Formulation composition	**Hyg. * score:**
1% Chloramine-T	1
Formulation 4	6
Formulation 5	3

[0042] Hygiene score expressed as the number of rinses that a microtitre plate well remained bacteria-free.

[0043] The table clearly shows that Chloramine T itself is unable to provide disinfectancy which is able withstand a single rinse cycle. The disinfectant effect of hypochlorite lasts for 3 rinses, but the combination of both is still effective after 6 rinses.

Claims

1. Aqueous liquid bleaching compositions comprising sufficient of a hypochlorite salt to give 0.0014-1.4 mol/l of hypochlorite ion and an N-chloro compound and having pH above 7 **characterized in that** the N-chloro compound is chosen from N-chloro-aryl-sulphonamides, and N-chloro-imidodisulphate salt and the composition comprises at least one surfactant.

2. Aqueous liquid bleaching compositions according to claim 1 **characterized in that** they comprise 0.00001-0.5 mol/l of the N-chloro compound.

3. Aqueous liquid bleaching compositions according to claim 2 **characterized in that** they comprise at least 0.0001 mol/l of the N-chloro compound.

4. Aqueous liquid bleaching compositions according to claim 2 **characterized in that** the molar ratio of hypochlorite ion to N-chloro compound is between 15000:1 and 1:1.

5. Aqueous liquid bleaching compositions according to claim 4 **characterized in that** the molar ratio of hypochlorite ion to N-chloro compound is at most 200:1.

6. Aqueous liquid bleaching compositions according to claims 1-5 **characterized in that** the N-chloro compound is N-chloro-benzenesulphonamide or N-chloro-p.toluenesulphonamide or a salt of any of these.

7. Aqueous liquid bleaching compositions according to any one of claims 1-6 **characterized in that** they have a viscosity of 50-5000 mPas.s.

8. Aqueous liquid bleaching compositions according to claim 7 **characterized in that** they comprise a thickening system comprising C8-C20 alkyl-dimethyl amine oxide and C8-C20 fatty acid

9. A product for cleaning toilet bowls comprising an oblong container having a dispensing opening of which the longitudinal axis makes an angle of at least 5°, but less than 90° with the longitudinal axis of the container, the container containing a concentrated aqueous liquid bleaching composition as described in claim 7.

10. A method for disinfecting a hard surface comprising the step of treating said surface with the compositions of any one of claims 1-8.

11. A method according to claim 10, wherein the surface is a toilet surface.

Patentansprüche

1. Wässrige flüssige Bleichmittel, umfassend ausreichend eines Hypochlorit-Salzes, um 0,0014-1,4 mol/l Hypochlorition zu ergeben, und eine N-Chlor-Verbindung und einen pH von über 7 aufweisend, **dadurch gekennzeichnet, dass** die N-Chlor-Verbindung aus N-Chloraryl-sulfonamiden und N-Chlorimidodisulfat-Salz ausgewählt ist und das Mittel wenigstens ein Tensid umfasst.

2. Wässrige flüssige Bleichmittel gemäß Anspruch 1, **dadurch gekennzeichnet, dass** sie 0,00001-0,5 mol/l der N-Chlor-Verbindung umfassen.

3. Wässrige flüssige Bleichmittel gemäß Anspruch 2, **dadurch gekennzeichnet, dass** sie wenigstens 0,0001 mol/l der N-Chlor-Verbindung umfassen.

4. Wässrige flüssige Bleichmittel gemäß Anspruch 2, **dadurch gekennzeichnet, dass** das Molverhältnis von Hypochlorition zu N-Chlor-Verbindung zwischen 15000:1 und 1:1 liegt.

5. Wässrige flüssige Bleichmittel gemäß Anspruch 4, **dadurch gekennzeichnet, dass** das Molverhältnis von Hypochlorition zu N-Chlor-Verbindung höchstens 200:1 ist.

6. Wässrige flüssige Bleichmittel gemäß den Ansprüchen 1-5, **dadurch gekennzeichnet, dass** die N-Chlor-Verbindung N-Chlorbenzolsulfonamid oder N-Chlor-p-toluolsulfonamid oder ein Salz von einer dieser ist.

7. Wässrige flüssige Bleichmittel gemäß einem der Ansprüche 1-6, **dadurch gekennzeichnet, dass** sie eine Viskosität von 50-5000 mPas.s haben.

8. Wässrige flüssige Bleichmittel gemäß Anspruch 7, **dadurch gekennzeichnet, dass** sie ein Verdickungssystem umfassen, das C8-C20-Alkyldimethylaminoxid und C8-C20-Fettsäure umfasst.

9. Ein Produkt zur Reinigung von Toilettenschüsseln, umfassend einen rechteckigen Behälter, der eine Abgabeöffnung hat, deren Längsachse einen Winkel von wenigstens 5°, aber weniger als 90° mit der Längsachse des Behälters bildet, wobei der Behälter ein konzentriertes wässriges flüssiges Bleichmittel, wie es in Anspruch 7 beschrieben ist, enthält.

10. Verfahren zum Desinfizieren einer harten Oberfläche, umfassend den Schritt des Behandelns der Oberfläche mit den Mitteln nach einem der Ansprüche 1-8.

11. Verfahren gemäß Anspruch 10, wobei die Oberfläche eine Toilettenoberfläche ist.

Revendications

1. Compositions de blanchiment liquides aqueuses comprenant une quantité suffisante de sel d'hypochlorite pour donner 0,0014-1,4 mol/l d'ion hypochlorite et un composé N-chloro et ayant un pH supérieur à 7, **caractérisées en ce que** le composé N-chloro est choisi parmi les N-chloro-aryl-sulfonamides, et le sel N-chloro-imidodisulfate et la composition comprend au moins un tensio-actif.

2. Compositions de blanchiment liquides aqueuses selon la revendication 1, **caractérisées en ce qu'**elles comprennent 0,00001-0,5 mol/l du composé N-chloro.

3. Compositions de blanchiment liquides aqueuses selon la revendication 2, **caractérisées en ce qu'**elles comprennent au moins 0,0001 mol/l du composé N-chloro.

4. Compositions de blanchiment liquides aqueuses selon la revendication 2, **caractérisées en ce que** le rapport molaire de l'ion hypochlorite au composé N-chloro est compris entre 15000:1 et 1:1.

5. Compositions de blanchiment liquides aqueuses selon la revendication 4, **caractérisées en ce que** le rapport molaire de l'ion hypochlorite au composé N-chloro est d'au plus 200:1.

6. Compositions de blanchiment liquides aqueuses selon les revendications 1 à 5, **caractérisées en ce que** le composé N-chloro est un N-chloro-benzènesulfonamide ou un N-chloro-p-toluènesulfonamide ou un sel de l'un quelconque de ceux-ci.

7. Compositions de blanchiment liquides aqueuses selon l'une quelconque des revendications 1 à 6, **caractérisées en ce qu'**elles présentent une viscosité de 50-5000 mPas.s.

8. Compositions de blanchiment liquides aqueuses selon la revendication 7, **caractérisée en ce qu'**elles comprennent un système épaississant comprenant un oxyde d'alkyle-diméthyl-amine en C8-C20 et un acide gras en C8-C20.

9. Produit pour nettoyer les cuvettes des toilettes comprenant un récipient oblong doté d'une ouverture de distribution dont l'axe longitudinal fait un angle d'au moins 5°, mais inférieur à 90° avec l'axe longitudinal du récipient, ledit récipient contenant une composition de blanchiment liquide aqueuse concentrée comme décrit dans la revendication 7.

10. Méthode de désinfection d'une surface dure comprenant l'étape consistant à traiter ladite surface avec les compositions selon l'une quelconque des revendications 1 à 8.

11. Méthode selon la revendication 10, dans laquelle la surface est une surface de toilettes.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 3749672 A **[0004]**
- EP 119560 A **[0005]**
- US 3054753 A **[0006]**
- EP 165676 A **[0006]**
- WO 9821308 A **[0007]**
- WO 0100029 A **[0008]**
- WO 9627651 A **[0009]**
- WO 9627652 A **[0009]**
- EP 636689 A **[0027]**

Non-patent literature cited in the description

- **Schwartz ; Perry.** Surface Active Agents. Interscience, 1949, vol. 1 **[0029]**
- **Schwartz ; Perry ; Berch.** Surface Active Agents. Interscience, 1958, vol. 2 **[0029]**
- McCutcheon's Emulsifiers and Detergents. Tenside-Taschenbuch. Carl Hauser Verlag, 1981 **[0029]**