

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: C11D 7/06, 7/54, 17/04, 17/08, 7/32	A1	(11) International Publication Number: WO 97/20913 (43) International Publication Date: 12 June 1997 (12.06.97)
(21) International Application Number: PCT/US96/19404 (22) International Filing Date: 6 December 1996 (06.12.96) (30) Priority Data: 95870126.0 7 December 1995 (07.12.95) EP (34) Countries for which the regional or international application was filed: BE et al. (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): PETRI, Marco [IT/IT]; Via Ai Boschi, 70, I-21021 Angera Varese (IT). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: REDUCED RESPIRATORY IRRITATION SPRAY BLEACHING COMPOSITIONS ✓ (57) Abstract In a first embodiment, the present invention encompasses a composition comprising a halogen bleach and an organic or inorganic derived -NH₂ compound, said composition being packaged in a spray type dispenser. In a second embodiment, the present invention encompasses a method for cleaning hard surfaces, said method comprising contacting by spraying a surface in need of cleaning with a cleaning composition. In a third embodiment, the present invention encompasses the use of an organic or inorganic derived -NH₂ compound in a composition comprising a halogen bleach, to reduce irritation of the respiratory system when said composition is sprayed.		

REDUCED RESPIRATORY IRRITATION SPRAY BLEACHING COMPOSITIONS

Field of the Invention

The present invention relates to a sprayable bleaching composition packaged in a container adapted to produce a spray. The present invention is primarily but not exclusively applicable to the treatment of hard surfaces.

Background of the Invention

Halogen bleaches, in particular hypochlorite, are known to be some of the most effective hygiene agents, especially at low concentrations, and are available in commercial quantities at acceptable cost. Halogen bleaches provide a hygiene benefit against a wide range of microbes including bacteria, moulds, yeast and fungi.

Cleaning compositions have traditionally been delivered to surfaces by use of a carrier such as a cloth or sponge onto which the composition is poured or which is dipped into a solution of the composition. This mode of application results in some wastage of the product due to absorption onto the cloth or sponge.

More recently, liquid products have been provided in a package adapted to produce a fine spray (aerosol) or jet of the product to facilitate delivery to a surface. Typical spray heads comprise a single, relatively small, aperture to which product is fed by pump means operated by a trigger mechanism. The deciding factors in determining whether a particular spray head will produce a mist or a jet include product properties, spray aperture geometry and spray pressure.

Known problems with sprays are the formation of airborne droplets which irritate the respiratory system of the user, either as a direct result of spraying a fine mist or due to the impact of a jet on a hard surface. Consequently, in the instructions for use of certain products, especially those

containing relatively high levels of halogen bleaches, the user is recommended not to spray the product directly onto a surface but rather to spray onto a cloth for subsequent application onto the surface. Use of a cloth or sponge in this manner detracts from the convenience of using a spray.

It is thus an object of the present invention to provide a sprayable composition comprising a halogen bleach, which does not present the above mentioned problem of the irritation of the respiratory system of the user, due to inhalation of airborne droplets.

Various solutions to this problem have been proposed in the art. For instance, J62/28600 proposes the use of specific solvents; WO94/24259 proposes the use of surfactants in combination with a specific design of the spray head of the package; EP 594 314 proposes the control viscosity by means of a selected surfactant in order to reduce the bleach odor, including in cases when airborne droplets are created while dispensing. Finally, WO95/07957 proposes the use of thickeners to control the size of irritant particles which are generated upon use of a sprayer.

We have now found that the above object could be met by formulating a sprayable liquid composition which comprises a halogen bleach and which further comprises an effective amount of an organic or inorganic derived $-NH_2$ compound. Without wishing to be based by theory, it is believed that the derived $-NH_2$ compound does not prevent a formation or inhalation of airborne droplets, but that it reduces or eliminates the irritation that they cause.

Compositions comprising a halogen bleach and an inorganic derived $-NH_2$ compound have already been described in the art, but not in the context of a sprayable composition, see for instance Japanese Kokai 63-108099, EP 119 560, BE 749 728, US 2,438,781, US 3,749,672, GB 2,078,522, EP 362 178, US 3,749,672.

Summary of the Invention

In a first embodiment, the present invention encompasses a composition comprising a halogen bleach and an organic or inorganic derived $-NH_2$ compound, said composition being packaged in a spray type dispenser.

In a second embodiment, the present invention encompasses a method for cleaning hard surfaces, said method comprising contacting by spraying a surface in need of cleaning with said composition.

In a third embodiment, the present invention encompasses the use of an organic or inorganic derived $-NH_2$ compound in a composition comprising a halogen bleach, to reduce irritation of the respiratory system when said composition is sprayed.

Detailed Description of the Invention

The present invention provides compositions comprising the following ingredients.

The bleach

The present invention comprises halogen bleaching agents that are oxidative bleaches and subsequently lead to the formation of positive halide ion. Common among these types of bleaches are the alkaline metal and alkaline earth metal hypochlorites, hypobromites and hypoiodites although other bleaches that are organic based sources of halide, such as chloroisocyanurate, are also applicable. Preferred bleach has the formula $M(OX)_y$ where : M is a member selected from the group consisting of sodium, potassium, magnesium, calcium, and mixtures thereof; O is an oxygen atom; X is a member selected from the group consisting of chlorine, bromine, iodine, and mixtures thereof; and y is 1 or 2 depending on the charge of M. The preferred embodiment of the invention will effectively contain hypochlorite or hypochlorite and hypobromite.

The preferred hypohalite bleaches that comprise the present invention are sodium hypochlorite, potassium hypochlorite, calcium hypochlorite, magnesium hypochlorite, sodium hypobromite, potassium hypobromite, calcium hypobromite, magnesium hypobromite, sodium hypoiodite and potassium hypoiodite, more preferably sodium hypochlorite, potassium hypochlorite, calcium hypochlorite, magnesium hypochlorite, most preferably sodium hypochlorite. A preferred organic-based bleach is chloroisocyanurate, however any organic halide that produces active halide ion is suitable for use in the present invention.

The compositions of the present invention preferably comprise bleach which is present at a level from about 0.01% to about 10%, preferably about 0.01% to about 2%, more preferably from about 0.1% to about 2%, most preferably from about 0.5% to about 2% by weight.

The $-NH_2$ compound

The compositions of the invention further comprise an organic and inorganic derived $-NH_2$ compound, or mixtures thereof, which are effective in reducing or eliminating the irritation of the respiratory system of the user, caused by inhalation of airborne droplets of said composition. Examples of such compounds are sulphamic acid, sulphamide, p-toluenesulphonamide,

imidodisulphonamide, benzenesulphonamide, melamine, cyanamide, alkyl sulfonamides, and mixtures thereof. At pH levels of the present invention, which are greater than 11, the above mentioned compounds may be de-protonated, that is they may be in the form of a salt and therefore due to expediency, ease of synthesis or preparation, or due to formulation practices the salt form of any or all of the above mentioned compounds will suffice.

Although any suitable cation will suffice for the purposes of the present invention, sodium, potassium, lithium, magnesium, calcium, and mixtures thereof are preferred.

The present invention comprises said $-NH_2$ compounds in amounts such that the mole ratio of hypohalite bleach to malodor control agent is from about 10:1 to about 1:10, preferably from about 5:1 to about 1:2, more preferably from about 3:1 to about 1:2.

The spray-type dispenser

According to the present invention, the compositions herein are packaged in a spray-type dispenser. By spray-type dispenser, it is meant herein a dispenser which is able to dispense the composition it contains in the form of an array of fine airborne liquid droplets. Such dispensers generate droplets of different sizes, and it is the smallest fraction which creates the irritancy issue referred to in the background discussion hereinabove.

Suitable spray-type dispensers to be used according to the present invention include aerosols as well as manually operated foam trigger-type dispensers sold for example by Specialty Packaging Products, Inc. or Continental Sprayers, Inc.

These types of dispensers are disclosed, for instance, in US 4,701,311 to Dunnining et al. and US 4,646,973 and US 4,538,745 both to Focarracci. Particularly preferred to be used herein are spray-type dispensers such as T8900® and T8500® commercially available from Continental Spray International or T8100® commercially available from Canyon, Northern Ireland. In such a dispenser the liquid composition is divided in fine liquid droplets resulting in a spray that is directed onto the surface to be treated. Indeed, in such a spray-type dispenser the composition contained in the body of said dispenser is directed through the spray-type head via energy communicated to a pumping mechanism by the user as said user activates said pumping mechanism. More particularly, in said spray-type dispenser head the composition is forced against an obstacle, e.g. a grid or a cone or the like, thereby providing shocks to help atomise the liquid composition, i.e. to help the formation of liquid droplets.

Adjunct Materials

The compositions herein can optionally include one or more other detergent adjunct materials or other materials for assisting or enhancing cleaning performance, treatment of the surface to be cleaned, or to modify the aesthetics of the composition (e.g. perfumes, colorants, dyes, etc.). The following are illustrative examples of such adjunct materials but are not meant to be exclusive or limiting in scope.

Surfactant - The cleaning compositions contain from about 0.1% to about 95% by weight of a surfactant selected from the group consisting of anionic, nonionic, ampholytic and zwitterionic surface active agents. The surfactant is preferably present to the extent of from about 0.1% to 30% by weight of the composition.

Anionic surfactants can be broadly described as the water-soluble salts, particularly the alkali metal salts, of organic sulfonation reaction products having in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. (Included in the term alkyl is the alkyl portion of higher acyl radicals.) Important examples of the anionic synthetic detergents which can form the surfactant component of the compositions of the present invention are the sodium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈₋₁₈ carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, (the alkyl radical can be a straight or branched aliphatic chain); sodium alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid ester of the reaction product of one mole of a higher fatty alcohol (e.g. tallow or coconut alcohols) and about 1 to about 10 moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain from 8 to 12 carbon atoms; the reaction products of fatty acids are derived from coconut oil sodium or potassium salts of fatty acid amides of a methyl tauride in which the fatty acids, for example, are derived from coconut oil and sodium or potassium beta-acetoxy- or beta-acetamido-alkanesulfonates where the alkane has from 8 to 22 carbon atoms.

Additionally, secondary alkyl sulfates may be used by the formulator exclusively or in conjunction with other surfactant materials and the following identifies and illustrates the differences between sulfated surfactants and otherwise conventional alkyl sulfate surfactants. Non-limiting examples of such ingredients are as follows.

Conventional primary alkyl sulfates, such as those illustrated above, have the general formula $\text{ROSO}_3\text{-M}^+$ wherein R is typically a linear $\text{C}_8\text{-C}_{22}$ hydrocarbon group and M is a water solubilizing cation. Branched chain primary alkyl sulfate surfactants (i.e., branched-chain "PAS") having 8-20 carbon atoms are also known; see, for example, Eur. Pat. Appl. 439 316, Smith et al., filed January 21, 1991.

Conventional secondary alkyl sulfate surfactants are those materials which have the sulfate moiety distributed randomly along the hydrocarbon "backbone" of the molecule. Such materials may be depicted by the structure



wherein m and n are integers of 2 or greater and the sum of m+n is typically about 9 to 17, and M is a water-solubilizing cation.

In addition, the selected secondary (2,3) alkyl sulfate surfactants used herein may comprise structures of formulas I and II



I



II

for the 2-sulfate and 3-sulfate, respectively. Mixtures of the 2- and 3-sulfate can be used herein. In formulas I and II, x and (y+1) are, respectively, integers of at least about 6, and can range from about 7 to about 20, preferably from about 10 to about 16. M is a cation, such as an alkali metal, ammonium, alkanolammonium, triethanol-ammonium, and the like, can also be used.

The aforementioned secondary alkyl sulfates are those prepared by the addition of H_2SO_4 to olefins. A typical synthesis using alpha olefins and sulfuric acid is disclosed in U.S. Pat. No. 3,234,258, Morris, issued February 8, 1966 or in U.S. Pat. No. 5,075,041, Lutz, issued December 24, 1991. The synthesis conducted in solvents which afford the secondary (2,3) alkyl sulfates on cooling, yields products which, when purified to remove the unreacted materials, randomly sulfated materials, unsulfated by-products such as C_{10} and higher alcohols, secondary olefin sulfonates, and the like, are typically 90+% pure mixtures of 2- and 3-sulfated materials (some sodium sulfate may be present) and are white, non tacky, apparently crystalline, solids. Some 2,3-disulfates may also be present, but generally comprise no more than 5% of the mixture of secondary (2,3) alkyl mono-sulfates. Such materials are available as under the name "DAN", e.g. "DAN 200" from Shell Oil Company.

Buffers - Buffers can be included in the formulations herein for a variety of purposes. One such purpose is to adjust the cleaning solution pH to optimize the hard surface cleaner composition effectiveness relative to a particular type of soil or stain. Buffers may be included to stabilize the

adjunct ingredients with respect to extended shelf life or for the purpose of maintaining compatibility between various aesthetic ingredients. The hard surface cleaner of the present invention optionally contains buffers to adjust the pH in a preferred range above 11. Non-limiting examples of such suitable buffers are potassium carbonate, sodium carbonate, and trisodium phosphate, however, the formulator is not restricted to these examples or combinations thereof.

Chelating Agents - The cleaning compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Examples of such compatible chelating agents are ethane-1-hydroxy-1, 1-diphosphonic acid (EDHP) and dipicolinic acid.

Perfumes - Perfumes are an important ingredient especially for the liquid composition embodiment. Perfume is usually used at levels of from 0% to 5%. In U.S. Pat.No. 4,246,129, Karcher, issued January 20, 1981 (incorporated herein by reference), certain perfume materials are disclosed which perform the added function reducing the solubility of anionic sulfonate and sulfate surfactants.

Other Adjunct Ingredients - As a preferred embodiment, the conventional adjunct ingredients employed herein can be selected from bleach stabilizers, pigments, color speckles, suds boosters, suds suppressors, anti-tarnish and/or anti-corrosion agents, soil-suspending agents, germicides, alkalinity sources, hydrotropes, anti-oxidants, clay soil removal/anti-redeposition agents, polymeric dispersing agents, etc.

Boosters - As a further optimal, but preferred ingredient, the present compositions comprise bleach boosters. Bleach boosters are those compounds that in an alkaline pH environment are capable of releasing a halide ion, undergoing an oxidation, a reduction or other disproportionation that otherwise yields an activated halide ion. Typically boosters containing bromine atoms and iodine atoms are used in the presence of chlorine atom based bleaches and iodine is used when bromine based bleaches are employed as the primary bleaching agent. Preferred bleach booster has the formula $M(X)_y$ where : a) M is a member selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, copper, zinc, and mixtures thereof; and b) X is the radical bromide, hypobromite, bromate, iodide, hypoiodite, and mixtures thereof; wherein y is 1 or 2.

While not wishing to be limited by theory, it is believed that the boosters have the effect, as in the case of hypochlorite based bleach, of converting the hypochlorite bleach into a more reactive and/or a more stable species, for example, hypobromite, thus providing for the full utility of the bleach formulated. Bleach boosters of the present invention may be added as a precursor which itself can be a bleach booster, for example, iodide ion is a suitable bleach booster according to the

present invention but, the ratio of hypohalite and iodide can be adjusted by the formulation to provide for the *in situ* formation of iodate, a preferable bleach booster. The boosters thus formed by oxidation/reduction or other disproportionations, for example, iodate, may be instead added directly.

The bleach boosters of the present invention are of the formula MX where M is a member selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, copper, and zinc while the X is halogen. The preferred bleach boosters are the sodium and potassium salts of bromine and iodine, more preferably sodium and potassium bromide and iodide.

The present invention comprises bleach boosters that are present such that the mole ratio of bleach to bleach booster is from about 1:0.1 to about 1:2, preferably from about 1:0.2 to about 1:1.

EXAMPLES

The following compositions are made by mixing the following ingredients in the listed proportions. The compositions are packaged in trigger-type spray dispensers which are available from Continental Spray International, models T8900® and T8500®.

Ingredients

Sodium Lauryl sulfate	2	1	-	4	4	0.5
Sodium Octyl sulfate	-	-	-	2	2	-
Lauryl dimethyl amineoxide	-	-	0.8	-	-	0.6
LAS	-	0.5	-	-	-	-
Silicate	-	-	0.2	0.1	0.1	-
Perfume	-	0.1	-	0.3	0.3	-
Caustic	2	3.2	2	3	3	2.2
Sulfamic acid	2.5	3.5	1.5	2.9	2.9	4.0
Sodium bromide	-	0.5	0.3	-	0.5	0.8
Hypochlorite	1.5	2.0	1.0	1.7	1.7	3.0
Water and minors	up to 100%					

Ingredients

Sodium Lauryl sulfate	0.8	-	0.5	-	-	0.9
Sodium Octyl sulfate	-	1.0	-	0.8	0.9	-
Lauryl dimethyl amineoxide	-	0.5	0.5	-	0.6	-
LAS	0.5	-	-	1.0	-	-
Silicate	-	0.1	-	-	0.2	0.1
Perfume	0.2	-	-	0.1	-	-
Caustic	1.0	0.9	0.8	1.1	0.8	1.0
Sulfamic acid	-	-	-	-	-	-
Sodium Bromide	-	0.4	-	-	-	0.2
Hypochlorite	1.0	1.5	1.0	1.3	1.6	2.0
p-toluenesulphonamide	2.2	2.5	-	-	-	-
benzenesulfonamide	-	-	1.0	1.6	-	-
Sodium sulfamate	-	-	-	-	2.5	3.0
Water and minors	up to 100%					

WHAT IS CLAIMED IS:

1. A liquid composition comprising a halogen bleach, and an organic or inorganic derived - NH_2 compound, said composition being packaged in a spray-type dispenser.
2. A composition according to claim 1 which has a pH greater than about 11.
3. A composition according to claims 1 and 2 wherein said bleach has the formula $\text{M}(\text{OX})_y$ where :
 - a) M is a member selected from the group consisting of sodium, potassium, magnesium, calcium, and mixtures thereof;
 - b) O is an oxygen atom; and
 - c) X is a member selected from the group consisting of chlorine, bromine, iodine, and mixtures thereof;wherein y is 1 or 2.
4. A composition according to the preceding claims, comprising from about 0.01% to about 10% by weight of said bleach.
5. A composition according to the preceding claims, which comprise a bleach booster which has the formula $\text{M}(\text{X})_y$ where :
 - a) M is a member selected from the group consisting of lithium, sodium, potassium, magnesium, calcium, copper, zinc, and mixtures thereof;and
 - b) X is a member selected from the group consisting of bromide, hypobromite, bromate, iodine, hypoiodite, iodate, and mixtures thereof;wherein y is 1 or 2.
6. A composition according to claim 5 wherein the molar ratio of bleach to bleach booster is from about 1:0.05 to about 1:4.



7. A composition according to the preceding claims wherein said -NH_2 compound is a member selected from the group consisting of sulphamic acid, sodium sulphamate, potassium sulphamate, sulfamide, p-toluenesulphonamide, imidodisulphonamide, benzenesulphonamide, melamine, cyanamide, alkyl sulfonamide, and mixtures thereof.
8. A composition according to the preceding claims which has a viscosity from 0.5 to 3000 centipoise at 22°C .
9. A composition according to the preceding claims wherein the molar ratio of bleach to said -NH_2 compound is from about 10:1 to about 1:10.
10. A composition according to claim 9 wherein the molar ratio of bleach to said -NH_2 compound is from about 5:1 to about 1:2.
11. A composition according to claim 10 wherein the molar ratio of bleach to said -NH_2 compound is from about 3:1 to about 1:2.
12. A composition according to the preceding claims which further comprises from 0.1% to 95% by weight of a deterative surfactant.
13. A method for cleaning hard surfaces, said method comprising contacting by spraying a surface in need of cleaning with a cleaning composition according to any of the preceding claims.
14. The use of an organic or inorganic derived -NH_2 compound in a composition comprising a halogen bleach, to reduce irritation of the respiratory system when said composition is sprayed.

