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(54) Title: EFFERVESCENT BLEACH COMPOSITIONS (57) Abstract The invention relates to solid, effervescent bleach compositions comprising: (i) a bleach activator; (ii) an oxygen effervescence generator comprising a persulphate salt and a perborate salt, wherein the weight ratio of the persulphate salt to the perborate salt is in the range from about 0.8:1 to about 5:1; and (iii) a carbon dioxide effervescence generator comprising a bicarbonate salt and an acid; wherein the weight ratio of the perborate salt to the bicarbonate salt is in the range from about 2:1 to about 20:1. The compositions provide excellent de-stain activity with improved effervescence and/or tablet disintegration. They are especially suitable in tablet form as denture cleansers.		

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EFFERVESCENT BLEACH COMPOSITIONS

Technical Field

The present invention relates to solid, effervescent bleach compositions. In particular, the invention relates to solid, effervescent bleach compositions which can be incorporated into compressed form, such as denture cleanser tablets and the like, to deliver enhanced bleach and/or de-stain activity together with excellent cleansing performance, physical characteristics, and in-use performance characteristics.

Background

Effervescent tablets and powders for cleansing dentures and the like are well known in the art. The aim of a denture cleanser product is to clean the denture as fully and as quickly as possible and especially to remove the accumulation of plaque, mucilaginous and bacterial deposits which collect while the denture is being worn. To wear a denture which has not been completely cleaned of plaque and bacterial deposits is not only unhygienic but can also within a short space of time result in a detrimental effect on the mucous membrane. Moreover bacterial deposits can lead to so-called bacterial corrosion of the plastics material used to produce the denture with consequent colour change and malodour formation.

Denture cleansers are usually used by being dissolved in a glass of warm water. To be effective, it is necessary for the tablet or powder to dissolve rapidly. This is particularly true of the compressed tablet form. Effervescence, generated as the tablet dissolves, assists in tablet break-up and the foam generated also helps signal efficacy to the consumer. Preferably then, denture cleanser tablets effervesce rapidly, produce a sustained foam and, importantly, deliver excellent bleaching and/or de-stain performance.

GB-A-1,052,796 discloses compositions, providing improved oxygen effervescence, which comprise potassium monopersulphate, an additional water-soluble peroxygen compound and an alkaline compound in amount sufficient to give a solution pH of at least 7.

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EP-A-253,772 discloses denture cleansing compositions comprising from 20 to 60% by weight of a monopersulphate salt, a bleach activator, an anhydrous alkali metal perborate and/or an alkali metal or alkaline earth perborate monohydrate.

WO-A-94/26246 describes a denture cleansing tablet comprising visually discrete
5 agglomerated particles of an organic acid bleach precursor dispersed in a water-soluble or dispersible matrix comprising an inorganic persalt bleaching agent and a solid base material which, in the presence of water, releases carbon dioxide or oxygen with effervescence. In highly preferred compositions therein, the solid base material incorporates both a (bi)carbonate/acid effervescent couple and a perborate/persulphate
10 oxygen effervescence generator.

Despite the foregoing, there remains a need for improved compositions which can combine excellent de-stain activity with improved effervescence and/or tablet disintegration.

Accordingly, it is an object of this invention to provide a solid, effervescent bleach
15 composition having improved bleaching and/or de-stain activity.

It is a further object of this invention to provide a solid, effervescent bleach composition which delivers rapid initial effervescence and generates a foam which is sustained over time.

It is yet a further object of this invention to provide a solid, effervescent bleach
20 composition which can be produced economically in compressed tablet form.

Summary Of The Invention

The invention provides a solid, effervescent bleach composition comprising:

- (i) a bleach activator; and
- (ii) an oxygen effervescence generator comprising a persulphate salt and a perborate
25 salt, wherein the weight ratio of the persulphate salt to the perborate salt is in the range from about 0.8:1 to about 5:1; and
- (iii) a carbon dioxide effervescence generator comprising a bicarbonate salt and an acid;

wherein the weight ratio of the perborate salt to the bicarbonate salt is in the range from
30 about 2:1 to about 20:1.

The compositions provide excellent de-stain activity with improved effervescence and/or tablet disintegration. They are especially suitable in tablet form as denture cleansers.

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All percentages and ratios herein are by weight of the composition, unless otherwise indicated.

Detailed Description of the Invention

5 The solid, effervescent, bleach compositions of the invention can be in tablet, granular or powder form, although tablet-form compositions are highly preferred herein. Compositions in tablet form can be single or multiple layered tablets.

The compositions comprise a bleach activator, an oxygen effervescence generator, and a carbon dioxide effervescence generator as essential components and can additionally comprise several optional components. Each of these will now be described in turn.

10 Bleach activator

A first essential ingredient of the compositions of the present invention is a bleach activator which is an organic peracid precursor, which in general terms can be defined as a compound having a titre of at least 1.5ml of 0.1N sodium thiosulphate in the following peracid formation test.

15 A test solution is prepared by dissolving the following materials in 1000 mls distilled water:

sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$)	2.5g
sodium perborate ($\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$) having 10.4% available oxygen	0.615g
sodium dodecylbenzene sulphonate	0.5g

20 To this solution at 60°C an amount of activator is added such that for each atom of available oxygen present one molecular equivalent of activator is introduced.

The mixture obtained by addition of the activator is vigorously stirred and maintained at 60°C. After 5 minutes from addition, a 100 ml portion of the solution is withdrawn and immediately pipetted onto a mixture of 250 g cracked ice and 15 ml glacial acetic acid. Potassium iodide (0.4 g) is then added and the liberated iodine is immediately titrated
25 with 0.1 N sodium thiosulphate with starch as indicator until the first disappearance of the blue colour. The amount of sodium thiosulphate solution used in ml is the titre of the bleach activator.

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The organic peracid precursors are typically compounds containing one or more acyl groups, which are susceptible to perhydrolysis. The preferred activators are those of the N-acyl or O-acyl compound type containing a acyl radical R-CO wherein R is a hydrocarbon or substituted hydrocarbon group having preferably from about 1 to about 20 carbon atoms. Examples of suitable peracid precursors include:

- 1) Acyl organoamides of the formula $RCONR_1R_2$, where RCO is carboxylic acyl radical, R_1 is an acyl radical and R_2 is an organic radical, as disclosed in US-A-3,117,148. Examples of compounds falling under this group include:
 - a) N,N - diacetylaniline and N-acetylphthalimide;
 - 10 b) N-acylhydantoins, such as
N,N' -diacetyl-5,5-dimethylhydantoin;
 - c) Polyacylated alkylene diamines, such as
N,N,N,N' -tetraacetylenediamine (TAED) and the corresponding
15 hexamethylenediamine (TAHD) derivatives, as disclosed in GB-A-907,356, GB-A-907,357 and GB-A-907,358;
 - d) Acylated glycolurils, such as tetraacetyl glycoluril, as disclosed in GB-A-1,246,338, GB-A-1,246,339 and GB-A-1,247,429.
- 2) Acylated sulphonamides, such as N-methyl-N-benzoyl-menthane sulphonamide and N-phenyl-N-acetyl menthane sulphonamide, as disclosed in GB-A-20 3,183,266.
- 3) Carboxylic esters as disclosed in GB-A-836,988, GB-A-963,135 and GB-A-1,147,871. Examples of compounds of this type include phenyl acetate, sodium acetoxy benzene sulphonate, trichloroethylacetate, sorbitol hexaacetate, fructose pentaacetate, p-nitrobenzaldehyde diacetate, isopropenyl acetate, acetyl aceto
25 hydroxamic acid, and acetyl salicylic acid. Other examples are esters of a phenol or substituted phenol with an alpha-chlorinated lower aliphatic carboxylic acid, such as chloroacetylphenol and chloroacetylsalicylic acid, as disclosed in US-A-3,130,165.
- 4) Carboxylic esters having the general form $Ac\ L$ wherein Ac is the acyl moiety of an organic carboxylic acid comprising an optionally substituted, linear or
30 branched C_6-C_{20} alkyl or alkenyl moiety or a C_6-C_{20} alkyl-substituted aryl moiety and L is a leaving group, the conjugate acid of which has a pKa in the

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range from 4 to 13, for example oxybenzenesulphonate or oxybenzoate. Preferred compounds of this type are those wherein:

- 5 a) Ac is R_3 -CO and R_3 is a linear or branched alkyl group containing from 6 to 20, preferably 6 to 12, more preferably 7 to 9 carbon atoms and wherein the longest linear alkyl chain extending from and including the carbonyl carbon contains from 5 to 18, preferably 5 to 10 carbon atoms, R_3 optionally being substituted (preferably alpha to the carbonyl moiety) by Cl, Br, OCH₃ or OC₂H₅. Examples of this class of material include sodium 3,5,5-trimethylhexanoyloxybenzene sulphonate, sodium 3,5,5-trimethylhexanoyloxybenzoate, sodium 2-ethylhexanoyloxybenzene-sulphonate, sodium nonanoyl oxybenzene sulphonate and sodium octanoyl oxybenzenesulphonate, the acyloxy group in each instance preferably being p-substituted;
- 10 b) Ac has the formula $R_3(AO)_mXA$ wherein R_3 is a linear or branched alkyl or alkylaryl group containing from 6 to 20, preferably from 6 to 15 carbon atoms in the alkyl moiety, R_5 being optionally substituted by Cl, Br, OCH₃, or OC₂H₅, AO is oxyethylene or oxypropylene, m is from 0 to 100, X is O, NR₄ or CO-NR₄, and A is CO, CO-CO, R₆-CO, CO-R₆-CO, or CO-NR₄-R₆-CO wherein R₄ is C₁-C₄ alkyl and R₆ is alkylene, alkenylene, arylene or alkarylene containing from 1 to 8 carbon atoms in the alkylene or alkenylene moiety. Bleach activator compounds of this type include carbonic acid derivatives of the formula $R_3(AO)_mOCOL$, succinic acid derivatives of the formula $R_3OCO(CH_2)_2COL$, glycolic acid derivatives of the formula R_3OCH_2COL , hydroxypropionic acid derivatives of the formula $R_3OCH_2CH_2COL$, oxalic acid derivatives of the formula $R_3OCOCOL$, maleic and fumaric acid derivatives of the formula $R_3OCOCH=CHCOL$, acyl aminocaproic acid derivatives of the formula $R_3CONR_1(CH_2)_6COL$, acyl glycine derivatives of the formula $R_3CONR_1CH_2COL$, and amino-6-oxocaproic acid derivatives of the formula $R_3N(R_1)CO(CH_2)_4COL$. In the above, m is preferably from 0 to 10, and R_3 is preferably C₆-C₁₂, more preferably C₆-C₁₀ alkyl when m is zero and C₉-C₁₅ when m is non-zero. The leaving group L is as defined above.
- 30 5) Acyl-cyanurates, such as triacetyl- or tribenzoylcyanurates, as disclosed in US Patent No. 3,332,882.

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- 6) Optionally substituted anhydrides of benzoic or phthalic acid, for example, benzoic anhydride, m-chlorobenzoic anhydride and phthalic anhydride.

Of all the above, preferred are organic peracid precursors of types 1(c) and 4(a). TAED is particularly preferred.

- 5 The level of bleach activator by weight of the total composition is preferably from about 0.1% to about 10%, more preferably from about 0.5% to about 5%.

Oxygen Effervescence Generator

- 10 The oxygen effervescence generator comprises a persulphate salt and a perborate salt, in a weight ratio of from about 0.8:1 to about 5:1, preferably from about 1.5:1 to about 4:1, more preferably from about 2:1 to about 3.5:1. Both of these ingredients are effective bleaches which contribute to the stain removal activity of the present invention. The bleach compositions thus comprise three active bleach / de-stain components: the bleach activator, a persulphate salt and a perborate salt. Stain removal is impaired if any one of these is missing.

- 15 Suitable sources of the persulphate salt are the alkali metal and ammonium persulphates. Preferred is potassium monopersulphate or a mixed salt thereof. Particularly preferred are the commercially available mixed salts such as Caroat®, marketed by Degussa, and Oxone®, marketed by E I du Pont de Nemours Co. and which are a 2:1:1 mixture of potassium monopersulphate, potassium sulphate and potassium bisulphate and which
20 have an active oxygen content of about 4.5%. The level of persulphate salt is suitably from about 20% to about 60%, preferably from about 35% to about 55%, more preferably from about 40% to about 50% by weight of the composition.

- Suitable perborate salts are the alkali metal perborates, particularly sodium perborate. Sodium perborate is preferably used as the monohydrate or anhydrous form, although
25 the tetrahydrate can also be used. Especially preferred is the monohydrate or mixtures of the monohydrate and anhydrous forms of sodium perborate. Suitably the ratio of anhydrous to monohydrate is from 0:100 to about 30:70. The total level of perborate salt is generally from about 6% to about 30%, preferably from about 10% to about 25%, more preferably from about 12% to about 18% by weight of the composition.

30 Carbon Dioxide Effervescence Generator

A third essential feature of the present invention is a carbon dioxide effervescence generator comprising a bicarbonate salt and an acid. The carbon dioxide effervescence generator is useful for providing rapid, initial effervescence when the composition is

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first added to water which will usually be about neutral pH but may be slightly acidic. The initial effervescence is valuable for dispersing the solid composition in water and assisting its dissolution by providing turbulence. Preferred bicarbonate salts are the rapidly soluble alkali metal bicarbonates, such as sodium bicarbonate, potassium bicarbonate and mixtures thereof, especially sodium bicarbonate. The bicarbonate salt is provided in admixture with at least one non-toxic, physiologically-acceptable organic or inorganic acid, such as tartaric, fumaric, citric, malic, maleic, gluconic, succinic, salicylic, adipic or sulphamic acid, sodium fumarate, sodium or potassium acid phosphates, betaine hydrochloride or mixtures thereof. Of these, sulphamic acid is preferred.

In preferred denture cleansing compositions in tablet form, the carbon dioxide effervescence generator takes the form of a solid premix comprising sodium bicarbonate and sulphamic acid, which in the presence of water releases carbon dioxide with effervescence. The premix can comprise further additives and excipients such as sodium carbonate and dye. Whilst sodium carbonate can itself provide carbon dioxide effervescence, since it is not as soluble as the bicarbonate it is less valuable in this respect.

It has further been found that whilst it is valuable to have the bicarbonate salt present, too much carbon dioxide can lead to early foam collapse. For this reason the proportion of bicarbonate is limited to well below that of the perborate salt so that oxygen effervescence predominates once the composition has started to fully dissolve. The weight ratio of the perborate salt to the bicarbonate salt is in the range of from about 2:1 to about 20:1, preferably from about 2.5:1 to about 10:1, more preferably from about 3:1 to about 5:1.

The bicarbonate salt generally comprises from about 1% to about 10%, preferably from about 3% to about 7%, more preferably from about 4% to about 6% of the total composition. The acid component generally comprises from about 2% to about 10%, preferably from about 3% to about 6% of the total composition.

Optional components

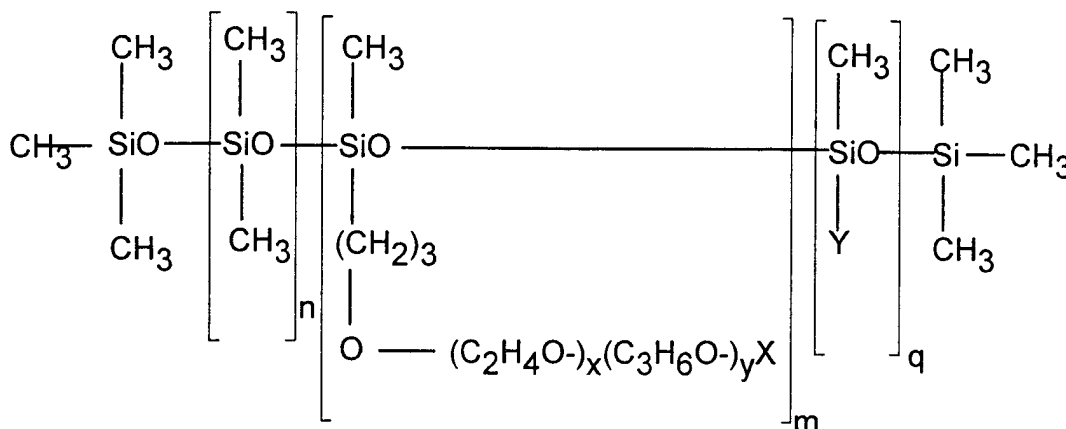
Denture cleansing compositions of the invention can be supplemented by other usual components of such formulations, especially surfactants, desiccants, chelating agents, enzymes, flavours, physiological cooling agents, antimicrobial compounds, dyestuffs, sweeteners, tablet binders and fillers, foam stabilisers such as the fatty acid sugar esters, preservatives, lubricants such as talc, magnesium stearate, finely divided amorphous

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pyrogenic silicas, etc. The free moisture content of the final composition is desirably less than about 1% and especially less than about 0.5%.

A highly preferred optional component is a dimethicone copolyol or aminoalkylsilicone antiplaque agent such as those described in WO 96/19563 and WO 96/19554.

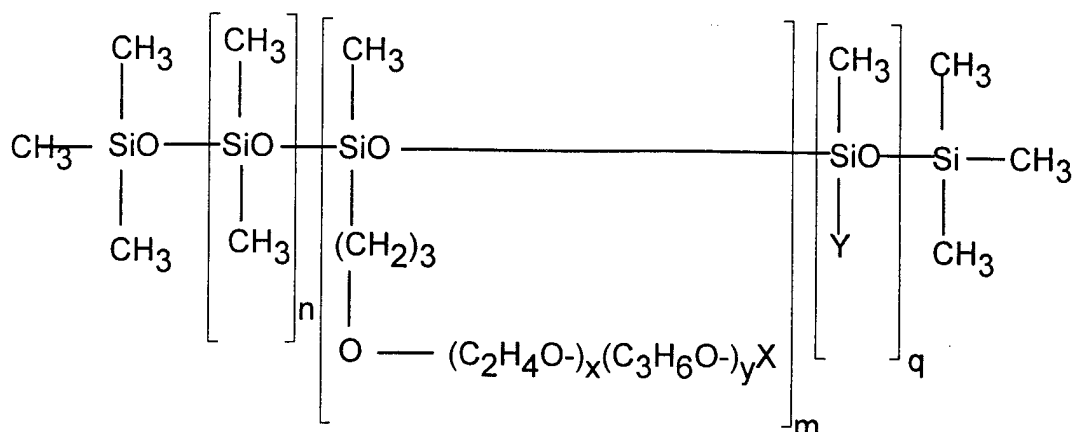
- 5 Preferred for use herein are alkyl or alkoxy dimethicone copolyols having the formula (I):



- wherein X is selected from hydrogen, alkyl, alkoxy and acyl groups having from about 1 to about 16 carbon atoms, Y is selected from alkyl and alkoxy groups having from about 8 to about 22 carbon atoms, n is from 0 to about 200, m is from about 1 to about 40, q is from about 1 to about 100, the molecular weight of the residue $(\text{C}_2\text{H}_4\text{O})_x(\text{C}_3\text{H}_6\text{O})_y\text{X}$ is from about 50 to about 2000, preferably from about 250 to about 1000 and x and y are such that the weight ratio of oxyethylene:oxypropylene is from 100:0 to 0:100, preferably from 100:0 to about 20:80.
- 15 In preferred embodiments, the dimethicone copolyol is selected from C_{12} to C_{20} alkyl dimethicone copolyols and mixtures thereof. Highly preferred is cetyl dimethicone copolyol marketed under the Trade Name Abil EM90.

- The silicone antiplaque agent is generally present in a level of from about 0.1% to about 5%, preferably from about 0.2% to about 3%, more preferably from about 0.3% to about 1.5% by weight.
- 20

A desirable additional ingredient of the effervescent, bleach compositions of the invention is a silicone surfactant having the general formula (I)



wherein X is selected from hydrogen, alkyl, alkoxy and acyl groups having from about 1 to about 16 carbon atoms, Y is CH₃, q is 0, n is from about 1 to about 100, m is from about 1 to about 40, the molecular weight of the residue (C₂H₄O)_x(C₃H₆O)_yX is from about 50 to about 2000, and x and y are such that the weight ratio of oxyethylene:oxypropylene is from about 100:0 to about 0:100.

The silicone surfactant, itself a dimethicone copolyol, assists in subsequent re-dispersion of the silicone antiplaque agent in aqueous media whilst still allowing the antiplaque agent to deposit onto surfaces such as teeth, gums or artificial dentures. In preferred embodiments, the silicone surfactant is selected from dimethicone copolyols having a HLB value in the range from about 8 to about 14, more preferably from about 9 to about 12, and mixtures thereof. A suitable example of such a material is that marketed under the Trade Name Silwet L7230. The silicone surfactant is generally present in a level of from about 0.1% to about 5%, preferably from about 0.2% to about 3%, more preferably from about 0.3% to about 1.5% by weight of the composition. In general, the level of the silicone surfactant should be chosen such that the ratio of silicone surfactant to the silicone antiplaque agent is from about 0.5:1 to about 5:1, more preferably from about 0.8:1 to about 3:1, most preferably from about 0.9:1 to about 2:1 by weight.

A preferred method of incorporating the silicone antiplaque agent and/or the silicone surfactant is via a spray-dried powder as will be described further below.

20 The powder includes a water-soluble carrier. By "water-soluble carrier" herein is meant any material which is has a solid at 25°C, is capable of being processed into granular form, is capable of being made into a clear or translucent aqueous solution at 25°C at a level of about 1% by weight of the solution, and is safe for use on human skin or mucosa. Suitable carriers include, but are not limited to, polyethylene glycols, starches, 25 gum arabic, gum tragacanth, gum acacia, carrageenans, cellulose derivatives and

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mixtures thereof. Preferably, the carrier is capable of being spray-dried into a free-flowing powder. In especially preferred embodiments the water-soluble carrier is a food-grade carrier selected from starches, gum arabic, gum tragacanth, gum acacia and mixtures thereof. A particularly preferred carrier is a modified starch available under
5 the tradename Capsul E from National Starch & Chemical of Manchester, UK. Optionally, the carrier can comprise a sugar alcohol or saccharide, such as sorbitol, mannitol or maltodextrin. Without being limited by theory, it is believed that the sugar alcohol or saccharide helps to form a film on the surface of the particle which improves the encapsulation of the oil by the powder particle. A preferred carrier consists of a
10 mixture of starch and sorbitol, preferably from about 2.5:1 to about 4:1, more especially about 3:1 by weight of the carrier. A mixture of gum acacia and maltodextrin in the ratio of from about 1:2 to about 2:1 can also suitably be used.

The water-soluble carrier is generally present in a level of from about 50% to about 99%, preferably from about 60% to about 90%, more preferably from about 65% to
15 about 90% by weight of the spray-dried powder.

The powders are generally in granular form, wherein the powder has a volume average particle size in the range from about 20 μm to about 500 μm , preferably from about 50 μm to about 250 μm , more preferably from about 80 μm to about 150 μm . The average particle size can be measured using standard sieve techniques well known in the art.
20 Alternatively, the average particle size can be measured using a commercial instrument such as the Malvern Mastersizer X available from Malvern Instruments Ltd. of Malvern, Worcs., UK,. The Mastersizer is preferably fitted with a MSX64 Dry Powder Feeder and a 300 mm lens for measuring particles in the range 1.2 to 600 microns.

The powders can be prepared by dispersing the silicone antiplaque agent and/or the
25 silicone surfactant in a aqueous solution of the water-soluble carrier and spray-drying the resultant dispersion. Whilst, the strength of the carrier solution is not critical, it will be understood that very dilute solutions will require considerable input of energy to dry. Suitably the aqueous solution of the carrier will comprise from about 25% to about 50%, more preferably from about 30% to about 45%, more especially from about 35%
30 to about 40% of the carrier by weight of the solution.

In order that the powder hereof has the desired properties, it is important to control the silicone droplet size within the dispersion. In general, the silicone should be present in the dispersion in the form of discrete droplets having a volume average droplet size in the range from about 0.5 μm to about 20 μm . Further, the ratio of the average spray-

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dried particle size to the average droplet size should be at least about 2.5:1. In preferred embodiments the ratio of the average spray-dried particle size to the average droplet size is at least about 4:1, preferably at least about 6:1, more preferably at least about 10:1. Smaller droplets, in relation to the final spray-dried powder particle size, serve to
5 improve the flow characteristics and further processability of the powder. The desired droplet size can be achieved by using shear mixing to form the dispersion and measured by using phase contrast photomicroscopy. A suitable procedure is to use, for example, a Nikon Labophot 2 at 400x magnification with fixed focal length and fitted with a graticule. It will be appreciated that a suitable number of observations need to be made
10 to reduce the sampling error. The precise number to be made will depend, for example, upon the droplet size distribution achieved. The dispersion is mixed, with adjustment of the shear rate if necessary, until the desired droplet size is attained.

The spray-dried silicone powders preferably also include a flavour or perfume oil. As used herein, the term 'flavour or perfume oil' means those flavour or perfume essences
15 and equivalent synthetic ingredients which are added to the powder for the principal purpose of modifying the taste and / or odour or other organoleptic sensations of the powder or the final product into which the powder is incorporated. It excludes silicone antiplaque agents and silicone surfactants as described above but includes lipophilic physiological cooling agents.

Lipophilic flavorants suitable for use herein comprise one or more flavour components selected from wintergreen oil, oregano oil, bay leaf oil, peppermint oil, spearmint oil, clove oil, sage oil, sassafras oil, lemon oil, orange oil, anise oil, benzaldehyde, bitter almond oil, camphor, cedar leaf oil, marjoram oil, citronella oil, lavender oil, mustard oil, pine oil, pine needle oil, rosemary oil, thyme oil, cinnamon leaf oil, and mixtures
25 thereof.

Physiological cooling agents suitable for use herein include carboxamides, menthane esters and menthane ethers, and mixtures thereof. Examples of preferred cooling agents suitable for use herein include Takasago 10 [3-l-menthoxy propan-1,2-diol (MPD)], from Takasago International Corporation, and carboxamides such as those described in
30 US-A-4,136,163, January 23, 1979 to Watson et al., and US-A-4,230, 688, October 28, 1980 to Rawsell et al.

The amount of flavour or perfume oil employed is normally a matter of preference subject to such factors as flavour type, base type and strength desired. The level of flavour or perfume oil in the compositions of the invention is generally in the range

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from about 1% to about 15% by weight of the spray-dried powder. Preferably the flavour or perfume oil is incorporated by making an intimate premix of the silicone antiplaque agent and the flavour or perfume oil, along with the silicone surfactant, where used, and then forming a dispersion of the premix in the carrier solution as
5 described above.

It has been found that forming an intimate admixture of the flavour or perfume oil with the silicone antiplaque agent prior to dispersing the mixture in the aqueous carrier solution acts to reduce the droplet size of the dispersed oil and improve the flow characteristics and further processability of the powder.

10 It has further been found that the flavour or perfume oil being in intimate admixture with the silicone antiplaque agent acts to enhance the substantivity of the flavour or perfume oil to teeth and/or dentures, thereby providing enhanced and/or sustained organoleptic impact. In the same way, lipophilic antimicrobial compounds can advantageously be included along in the same manner as the flavour or perfume oil, to
15 provide enhanced and/or sustained antimicrobial efficacy. Suitable lipophilic antimicrobial compounds for use herein include thymol, menthol, triclosan, 4-hexylresorcinol, phenol, eucalyptol, benzoic acid, benzoyl peroxide, butyl paraben, methyl paraben, propyl paraben, salicylamides, and mixtures thereof.

Bleach compositions according to the invention can additionally include one or more
20 additional bleaching agents. Examples of suitable additional bleaching agents include sodium pyrophosphate peroxyhydrate and magnesium, calcium, strontium and zinc peroxides.

Tablet binders and fillers suitable for use herein include polyvinyl-pyrrolidone, poly (oxyethylene) of molecular weight 20,000 to 500,000, polyethyleneglycols of molecular
25 weight of from about 1000 to about 50,000, Carbowax having a molecular weight of from 4000 to 20,000, nonionic surfactants, fatty acids, sodium carboxymethyl cellulose, gelatin, fatty alcohols, clays, polymeric polycarboxylates, sodium carbonate, calcium carbonate, calcium hydroxide, magnesium oxide, magnesium hydroxide carbonate, sodium sulphate, proteins, cellulose ethers, cellulose esters, polyvinyl alcohol, alginic
30 acid esters, and triglycerides. Of the above, polyethyleneglycols, especially those having molecular weight of from about 1,000 to about 30,000, preferably from about 12,000 to about 30,000, and triglycerides are highly preferred.

The surface active agent used in the bleach compositions of the invention can be selected from the many available that are compatible with the other ingredients of the

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composition, both in the dry state and in solution. Such materials are believed to improve the effectiveness of the other ingredients of the composition by aiding their penetration into the interdental surfaces. Also, these materials aid in the removal of food debris attached to the teeth. Between 0.1 and 5 percent by weight of the dry
5 composition of a dry powder or granular anionic surface active agent, such as sodium lauryl sulphate, sodium N-lauroylsarcosinate, sodium lauryl sulphoacetate or dioctyl sodium sulphasuccinate or ricinoleyl sodium sulphasuccinate, can, for example, be included in the composition. A highly preferred anionic surface active agent is sodium lauryl sulphoacetate, commercially available as Lathanol® powder. Preferably the
10 surface active agent comprises between 0.5 and 4 percent of the composition, more preferably from 0.7% to 1.5% by weight.

Suitable cationic, non-ionic and ampholytic surface active agents include, for example, quaternary ammonium compounds such as cetyltrimethyl-ammonium bromide, condensation products of alkylene oxides such as ethylene or propylene oxide with fatty
15 alcohols, phenols, fatty amines or fatty acid alkanolamides, the fatty acid alkanolamides themselves, esters of long-chained (C₈-C₂₂) fatty acids with polyalcohols or sugars, for example glycerylmonostearate or saccharose monolaurate or sorbitolpolyoxyethylene-mono-or di-stearate, betaines, sulphobetaines or long-chain alkylaminocarboxylic acids.

Chelating agents beneficially aid cleaning and bleach stability by keeping metal ions,
20 such as calcium, magnesium, and heavy metal cations in solution. Examples of suitable chelating agents include sodium tripolyphosphate, sodium acid pyrophosphate, tetrasodium pyrophosphate, aminopoly-carboxylates such as nitrilotriacetic acid and ethylenediamine tetraacetic acid (EDTA) and salts thereof, and polyphosphonates and aminopolyphosphonates such as hydroxyethanediphosphonic acid, ethylenediamine
25 tetramethylenephosphonic acid, diethylenetriaminepentamethylenephosphonic acid and salts thereof. The chelating agent selected is not critical except that it must be compatible with the other ingredients of the denture cleanser when in the dry state and in aqueous solution. EDTA and its salts, especially the tetrasodium salt, are preferred. Advantageously, the chelating agent comprises between 0.1 and 20 percent by weight of
30 the composition and preferably between 0.5 and 5 percent. Phosphonic acid chelating agents, however, preferably comprise from about 0.1 to about 1 percent, preferably from about 0.1% to about 0.5% by weight of composition.

Enzymes suitable for use herein are exemplified by proteases, alkalases, amylases, lipases, dextranases, mutanases, glucanases etc.

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The following Examples further describe and demonstrate the preferred embodiments within the scope of the present invention.

EXAMPLES I TO III

The following are representative denture cleanser tablets according to the invention.

5 The percentages are by weight of the denture cleanser tablet.

In the following examples the blue and white granulates are made separately by roller compaction. The silicone-containing spray-dried powder is made as described hereinbefore. The two granulates, the spray-dried powder and the excipients are then mixed together in a planetary mixer and the tablets are made by compressing the
 10 mixture of components in a punch and dye rotary tableting press at a pressure of about 2×10^5 kPa.

	I	II	III
	%	%	%
WHITE GRANULATE			
Potassium monopersulphate salt ¹	25.54	42.66	50.40
Sodium carbonate	6.82	7.45	7.91
Tetrasodium EDTA	0.20	0.47	0.49
TOTAL WHITE GRANULATE	32.56	50.58	58.80
BLUE GRANULATE			
Sodium carbonate	3.02	0.78	0.82
Sulphamic acid	1.51	4.88	5.19
Sodium bicarbonate	2.2	4.67	1.1
Blue dye	0.11	0.21	0.33
TOTAL BLUE GRANULATE	6.84	10.54	7.44
SPRAY-DRIED POWDER			
Abil® EM 90 ²	1.5	1.13	0.41
Silwet® L7230 ³	5.33	1.4	0.15
Peppermint flavour oil	1.91	1.23	0.45
Capsul E ⁴	5.59	6.55	6.1
Sorbitol	0.6	2.18	0.92
Fumed Silica	0.66	0.13	2.00
TOTAL SPRAY-DRIED POWDER	15.59	12.62	10.03

.....CONTINUED

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	I	II	III
	%	%	%
EXCIPIENTS			
TAED	3.08	2.33	1.75
Sodium perborate monohydrate	18.75	15.51	11.10
Lathanol [®] powder	0.55	0.97	3.40
Sodium carbonate	18.5	5.78	3.96
Fumed silica	0.39	0.58	0.62
Hydrated silica	0.29	0.31	0.33
Boeson VP 60 ⁵	0.1	0.78	0.82
Spray-dried peppermint oil	3.35	0	1.75
TOTAL WHITE EXCIPIENTS	45.01	26.26	23.73
	100	100	100

1 Carolat[®].

2 Cetyl dimethicone copolyol from Goldschmidt.

3 Dimethicone copolyol from Union Carbide, a silicone surfactant.

5 4 Modified starch from National Starch & Chemical

5 Mixture of hardened triglycerides from soya oil, available from Ingelheim Boehringer

In Examples IV to VII above, the overall tablet weight is 3 g; diameter 25 mm.

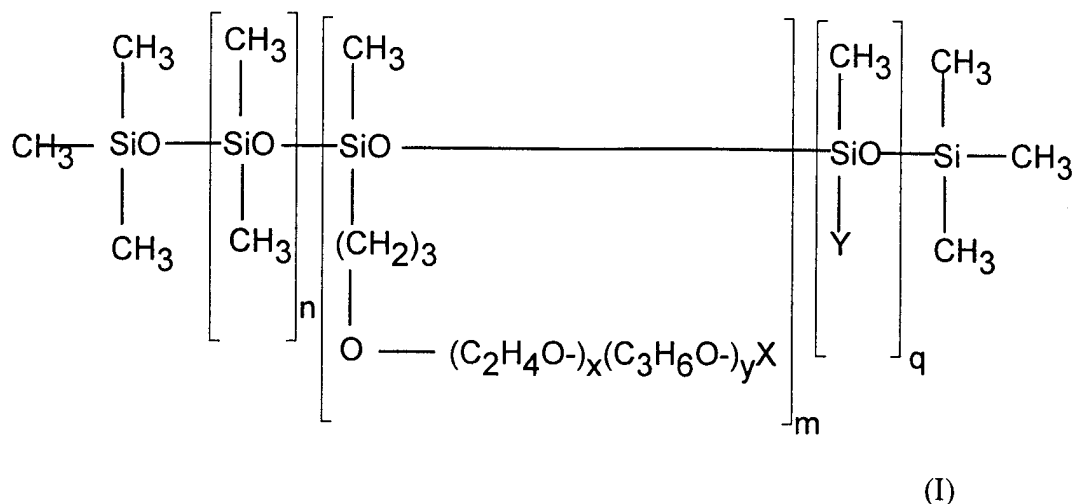
The denture cleansing tablets of Examples IV to VII display improved antiplaque,
 10 cleansing and anti-bacterial activity together with excellent cohesion and other physical
 and in-use performance characteristics.

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WHAT IS CLAIMED IS:

1. A solid, effervescent bleach composition comprising:
 - (i) a bleach activator; and
 - (ii) an oxygen effervescence generator comprising a persulphate salt and a perborate salt, wherein the weight ratio of the persulphate salt to the perborate salt is in the range from 0.8:1 to 5:1; and
 - (iii) a carbon dioxide effervescence generator comprising a bicarbonate salt and an acid;wherein the weight ratio of the perborate salt to the bicarbonate salt is in the range from 2:1 to 20:1.
2. A bleach composition according to Claim 1 wherein the level of bleach activator by weight of the total composition is from 0.1% to 10%, preferably from 0.5% to 5%.
3. A bleach composition according to Claim 1 or Claim 2 wherein the bleach activator is TAED.
4. A bleach composition according to any of Claims 1 to 3 wherein the persulphate salt is potassium monopersulphate or a mixed salt thereof, comprising from 20% to 60%, preferably from 35% to 55% by weight of the composition.
5. A bleach composition according to any of Claims 1 to 4 wherein the perborate salt is selected from sodium perborate monohydrate and mixtures of sodium perborate monohydrate with anhydrous sodium perborate.
6. A bleach composition according to any of Claims 1 to 5 wherein the perborate salt comprises from 6% to 30%, preferably from 10% to 25%, more preferably from 12% to 18% by weight of the composition.
7. A bleach composition according to any of Claims 1 to 6 wherein the weight ratio of the persulphate salt to the perborate salt is in the range from 1.5:1 to 4:1, preferably from 2:1 to 3.5:1.
8. A bleach composition according to any of Claims 1 to 7 wherein the bicarbonate salt comprises from about 1% to about 10%, preferably from about 3% to about 7% by weight of the composition.
9. A bleach composition according to any of Claims 1 to 8 wherein the weight ratio of the the perborate salt to the bicarbonate salt is in the range from 2.5:1 to 10:1, preferably from 3:1 to 5:1.

10. A bleach composition according to any of Claims 1 to 9 wherein the composition further comprises a silicone antiplaque agent of the general formula (I):



wherein X is selected from hydrogen, alkyl, alkoxy and acyl groups having from 1 to about 16 carbon atoms, Y is selected from alkyl and alkoxy groups having from about 8 to about 22 carbon atoms, n is from 0 to about 200, m is from about 1 to about 40, q is from about 1 to about 100, the molecular weight of the residue $(C_2H_4O)_x(C_3H_6O)_yX$ is from about 50 to about 2000, preferably from about 250 to about 1000 and x and y are such that the weight ratio of oxyethylene:oxypropylene is from 100:0 to 0:100, preferably from 100:0 to about 20:80.

11. A bleach composition according to Claim 10 wherein the silicone antiplaque agent is cetyl dimethicone copolyol.
12. A bleach composition according to any of Claims 10 or 11 further comprising a silicone surfactant of the general formula (I) wherein X is selected from hydrogen, alkyl, alkoxy and acyl groups having from 1 to about 16 carbon atoms, Y is CH₃, q is 0, n is from about 1 to about 100, m is from about 1 to about 40, the molecular weight of the residue (C₂H₄O)_x(C₃H₆O)_yX is from about 50 to about 2000, and x and y are such that the weight ratio of oxyethylene:oxypropylene is from 100:0 to 0:100, the silicone surfactant being in intimate admixture with the silicone antiplaque agent.
13. A bleach composition according to any of Claims 1 to 12 wherein the composition is in compressed tablet form.

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/US97/19954

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C11D 3/10, 3/39, 3/395, 7/54

US CL : 510/117, 376, 378; 252/186.3, 186.38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 510/117, 376, 378; 252/186.3, 186.38

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

search terms: taed, tetraacetyl ethylenediamine, persulfate, perborate, bicarbonate, granular, grains, solid, tablet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,009,804 A (CLAYTON ET AL) 23 April 1991 (23-04-91), see abstract; column 1, lines 1-10; column 5, line 3 to column 6, line 8; column 13, lines 30-60.	1-3
X	US 5,458,810 A (FREDJ ET AL) 17 October 1995 (17-10-95), see abstract; column 11, line 10 to column 13, line 30.	1-3
X	US 5,510,049 A (CONNOR ET AL) 23 April 1996 (23-04-96), see abstract; column 12, line 58 to column 13, line 25; column 15, line 62 to column 16, line 55.	1-3

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

31 DECEMBER 1997

Date of mailing of the international search report

29 JAN 1998

 Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

GREGORY R. DEL COTTO

Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JS97/19954

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-13
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.