**PCT** WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C11D 1/04, 1/82, 3/39, 3/395

A1

(11) International Publication Number: **WO 98/20091**

(43) International Publication Date: 14 May 1998 (14.05.98)

(21) International Application Number: PCT/US97/19952

(22) International Filing Date: 30 October 1997 (30.10.97)

(30) Priority Data:
9622844.0 1 November 1996 (01.11.96) GB

(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)*: THURLBY, Owen [GB/GB]; 24 Flemish Fields, Chertsey, Surrey KT16 8EQ (GB).

(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).

(81) Designated States: CA, CZ, HU, JP, TR, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
*With international search report.*

(54) Title: CLEANSING COMPOSITIONS

(57) Abstract

The invention relates to granular, denture cleansing compositions comprising an inorganic persalt bleaching agent, a silicone oil and a foam–forming surfactant selected from anionic surfactants, amphoteric surfactants and mixtures thereof, wherein the silicone oil and the foam–foaming surfactant are in discrete granules. The compositions provide excellent de–stain activity with improved effervescence and/or tablet disintegration. They are especially suitable in tablet form as denture cleansers.

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **AL** | Albania | **ES** | Spain | **LS** | Lesotho | **SI** | Slovenia |
| **AM** | Armenia | **FI** | Finland | **LT** | Lithuania | **SK** | Slovakia |
| **AT** | Austria | **FR** | France | **LU** | Luxembourg | **SN** | Senegal |
| **AU** | Australia | **GA** | Gabon | **LV** | Latvia | **SZ** | Swaziland |
| **AZ** | Azerbaijan | **GB** | United Kingdom | **MC** | Monaco | **TD** | Chad |
| **BA** | Bosnia and Herzegovina | **GE** | Georgia | **MD** | Republic of Moldova | **TG** | Togo |
| **BB** | Barbados | **GH** | Ghana | **MG** | Madagascar | **TJ** | Tajikistan |
| **BE** | Belgium | **GN** | Guinea | **MK** | The former Yugoslav Republic of Macedonia | **TM** | Turkmenistan |
| **BF** | Burkina Faso | **GR** | Greece | | | **TR** | Turkey |
| **BG** | Bulgaria | **HU** | Hungary | **ML** | Mali | **TT** | Trinidad and Tobago |
| **BJ** | Benin | **IE** | Ireland | **MN** | Mongolia | **UA** | Ukraine |
| **BR** | Brazil | **IL** | Israel | **MR** | Mauritania | **UG** | Uganda |
| **BY** | Belarus | **IS** | Iceland | **MW** | Malawi | **US** | United States of America |
| **CA** | Canada | **IT** | Italy | **MX** | Mexico | **UZ** | Uzbekistan |
| **CF** | Central African Republic | **JP** | Japan | **NE** | Niger | **VN** | Viet Nam |
| **CG** | Congo | **KE** | Kenya | **NL** | Netherlands | **YU** | Yugoslavia |
| **CH** | Switzerland | **KG** | Kyrgyzstan | **NO** | Norway | **ZW** | Zimbabwe |
| **CI** | Côte d'Ivoire | **KP** | Democratic People's Republic of Korea | **NZ** | New Zealand | | |
| **CM** | Cameroon | | | **PL** | Poland | | |
| **CN** | China | **KR** | Republic of Korea | **PT** | Portugal | | |
| **CU** | Cuba | **KZ** | Kazakstan | **RO** | Romania | | |
| **CZ** | Czech Republic | **LC** | Saint Lucia | **RU** | Russian Federation | | |
| **DE** | Germany | **LI** | Liechtenstein | **SD** | Sudan | | |
| **DK** | Denmark | **LK** | Sri Lanka | **SE** | Sweden | | |
| **EE** | Estonia | **LR** | Liberia | **SG** | Singapore | | |

# CLEANSING COMPOSITIONS

## Technical Field

The present invention relates to granular denture cleansing compositions. In particular, the invention relates to granular, cleansing compositions, suitable for cleaning teeth or dentures which can be incorporated into compressed form, such as denture cleanser tablets and the like, to deliver enhanced plaque prevention benefits together with excellent cleansing performance and in-use performance characteristics.

## Background

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 first necessary for the tablet or powder to dissolve rapidly. This is particularly true of the compressed tablet form. Effervescence, which can be generated as the tablet dissolves, assists in tablet break-up and the foam generated also helps signal efficacy to the consumer. Surfactants in the formulation enhance foam generation and cleaning. It is further desirable to deposit an agent on the teeth or dentures which prevents further plaque build-up. Many silicones are suitable for this purpose as described, for example, in WO 96/19563 and WO 96/19191. However the silicones can also act as foam suppressors. Moreover, the presence of a surfactant can also inhibit the silicone deposition and make compressed tablets slow to dissolve.

Accordingly, it is an object of this invention to provide a granular, denture cleansing composition which can prevent plaque build-up yet have a good foaming action.

It is a further object of this invention to provide a granular, denture cleansing composition which can be processed into compressed tablet form and still dissolve rapidly in solution.

## Summary Of The Invention

The invention provides a granular, denture cleansing composition comprising an inorganic persalt bleaching agent, a silicone oil and from 0.55 to 3.8% of a foam-forming surfactant selected from anionic surfactants, nonionic surfactants, amphoteric surfactants and mixtures thereof, wherein the silicone oil and the foam-forming surfactant are in discrete, separate granules.

The granular compositions have high foaming activity and help prevent plaque build-up on dentures or teeth. The granules are free-flowing and dissolve rapidly, even when processed into compressed tablet form.

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

## Detailed Description of the Invention

The granular, denture cleansing 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 an inorganic persalt bleaching agent, a silicone oil and from 0.55 to 3.8% of a foam-forming surfactant selected from anionic surfactants, nonionic surfactants, amphoteric surfactants and mixtures thereof, as essential components and can additionally comprise several optional components. Each of these will now be described in turn.

### Persalt bleaching agent

A first essential ingredient of the compositions of the present invention is a persalt bleaching agent. The bleaching agent can be selected from any of the well-known bleaching agents known for use in denture cleansers such as the alkali metal and ammonium persulfates, perborates, percarbonates and perphosphates and the alkali metal and alkaline earth metal peroxides. Examples of suitable bleaching agents include potassium, ammonium, sodium and lithium persulfates and perborate mono- and tetrahydrates, sodium pyrophosphate peroxyhydrate and magnesium, calcium, strontium and zinc peroxides. Of these, however, the alkali metal persulfates, perborates and mixtures thereof are preferred for use herein, highly preferred being the alkali metal perborates. Indeed, it is a feature of the invention that the tablet compositions herein will provide excellent antimicrobial activity even in the absence of alkali metal persulfates.

The amount of bleaching agent in the total composition is generally from about 5% to about 70%, preferably from about 20% to about 60%. Preferred compositions comprise both a persulphate salt and a perborate salt. The persulphate salt and perborate salt can be in any ratio but it has been found that better foaming is achieved with 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 cleansing compositions.

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 have an active oxygen content of about 4.5%. The level of persulphate salt is suitably from about 5% to about 60%, preferably from about 20% to about 50%, more preferably from about 35% to about 45% 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 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.

Silicone oils

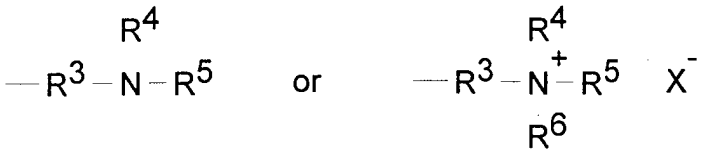
A second essential ingredient of the powder is a silicone oil. By "silicone oil" herein is meant a polymer with a silicon or siloxane backbone that is insoluble in or immiscible with water at 25°C and is liquid at 25°C; or mixtures therof. Suitable classes of silicone oils include, but are not limited to, dimethicones, dimethiconols, dimethicone copolyols and aminoalkylsilicones.

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

Suitable aminoalkylsilicones are selected from noncyclic, hydrophobic aminoalkyl-silicones having a formula comprising two basic units:

1) $(R^1)_m(R)_nSiO_{(4-m-n)/2}$ wherein m+n is 1, 2 or 3; n is 1, 2 or 3; m is 0,1,2; and
2) $(R^1)_a(R^2)_bSiO_{(4-a-b)/2}$ wherein a+b is 1, 2, or 3, and a and b are integers,

wherein $R^1$ and $R^2$ are independently selected from H ,alkyl and alkenyl of about 1 to about 10 carbons optionally substituted with fluoro or cyano groups, hydroxy, alkoxy, and acetoxy, for example, wherein $R^1$ and $R^2$ are independently selected from methyl, ethyl, phenyl, vinyl, trifluoropropyl and cyanopropyl, and R is



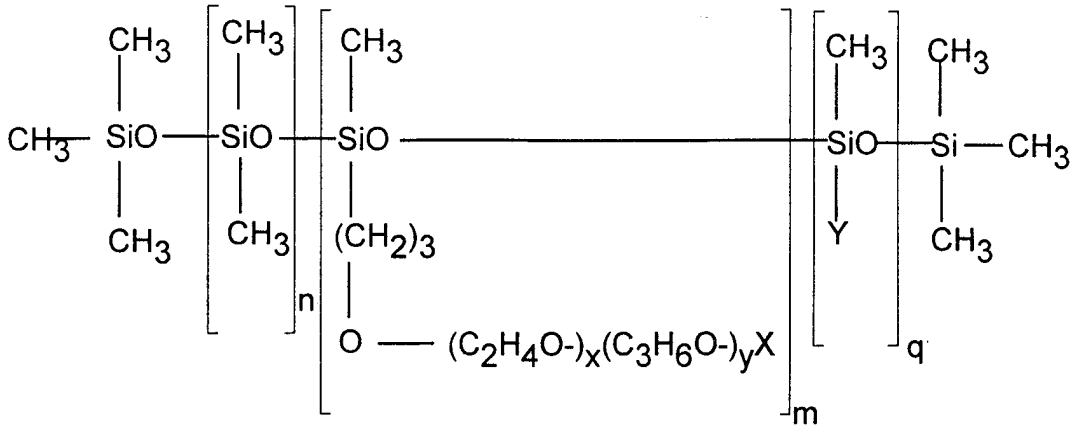
wherein $R^3$ is a divalent alkylene of about 1-20, preferably about 3-5 carbon atoms optionally substituted or interrupted by O atoms, $R^4$, $R^5$ and $R^6$ which may be the same or different are selected from H, alkyl of about 1-20, preferably about 1-10, more preferably about 1-4 carbons optionally substituted or interrupted by N and/or O atoms, and $X^-$ is a monovalent anion such as halide, hydroxide, and tosylate, said aminoalkylsilicone including from about 0.1-2%, preferably from about 0.5-2% of unit (1) on a repeating unit basis.

Preferred aminoalkylsilicones comprise amodimethicones. Amodimethicones are polydimethylsiloxane polymers containing aminoalkyl groups. The aminoalkyl groups may be present either pendant or at one or more ends of the polydimethylsiloxane chain. Preferred are aminoalkylsilicones in which aminoalkyl moiety R is selected from $(CH_2)_3NH_2$, $(CH_2)_3NHCH_2CH_2NH_2$, $(CH_2)_3N(CH_2CH_2OH)_2$, $(CH_2)_3NH_3^+X^-$, and $(CH_2)_3N(CH_3)_2(C_{18}H_{37})^+X^-$, and especially from $(CH_2)_3NH_2$ and $(CH_2)_3NHCH_2CH_2NH_2$. Also preferred are aminoalkyl silicones having an average molecular weight of about 5,000 and above, preferably from about 5000 to about 100,000, more preferably from about 5000 to about 30,000.

Aminoalkyl silicone compounds suitable for use herein are well known. Methods of preparing aminoalkylsilicones are given in, for example, US-A-2,930,809.

Examples of amodimethicones include OSI's Magnasoft fluid. These polymers comprise aminoalkyl groups affixed to a predominantly polydimethylsiloxane structure. The typical structure of Magnasoft's aminoalkyl group-containing units is -$OSi(Me)C_3H_6NHCH_2CH_2NH_2$.

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

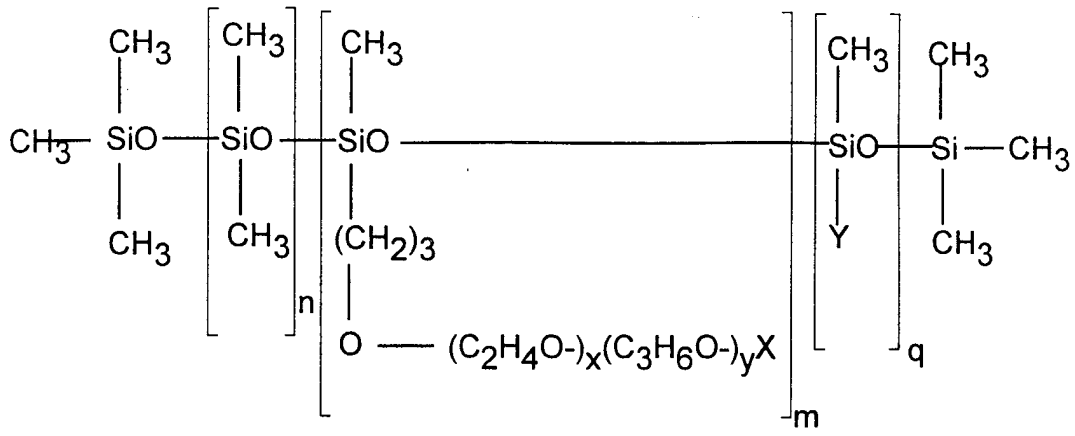


wherein X is selected from hydrogen, alkyl, alkoxy and acyl groups having from about 1 to about 16 carbon atoms, Y is selected from alkyl and alkoxy groups having from about 8 to about 22 carbon atoms, n is from 0 to about 200, m is from about 1 to about 40, q is from about 1 to about 100, the molecular weight of the residue $(C_2H_4O\text{-})_x(C_3H_6O\text{-})_yX$ 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.

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.

A desirable additional ingredient of the denture cleansing 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 $CH_3$, 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 $(C_2H_4O\text{-})_x(C_3H_6O\text{-})_yX$ 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.

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, gum arabic, gum tragacanth, gum acacia, carrageenans, cellulose derivatives and 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 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 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 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. 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 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 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% 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-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 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 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 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 flavor 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, lavendar oil, mustard oil, pine oil, pine needle oil, rosemary oil, thyme oil, cinnamon leaf oil, and mixtures 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 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 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 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.

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 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.

Foam-forming surfactant

A third essential feature of the present invention is a foam-forming surfactant selected from anionic surfactants, nonionic surfactants, amphoteric surfactants and mixtures thereof. The phrase 'foam-forming surfactant' as used herein excludes silicone surfactants as described hereinbefore. The foam-forming surfactant used in the denture cleansing compositions of the invention can be selected from the many available that are compatible with the other ingredients of the composition, both in the dry state and in solution.

Suitable anionic surfactants include alkyl sulphates, such as sodium lauryl sulphate, alkyl ether sulphates, alkyl aryl sulphonates such as sodium doddecyl benzene sulphonate (SDBS), alkyl sarcosinates, and alkyl sulphosuccinates. A highly preferred anionic surface active agent is sodium lauryl sulphoacetate, commercially available as Lathanol® powder. It has also been found that the use of a surfactant mixture, comprising a primary surfactant and an additional co-surfactant, can boost foaming and reduce the total surfactant level. Suitably the total amount of foam-forming surfactant comprises from about 0.55% to about 3.8%, preferably from about 0.7% to about 3%, more preferably from about 0.9% to about 2% by weight of the composition; suitable levels of co-surfactant are from about 0.1% to about 1%, preferably from about 0.2% to about about 0.5% by weight of the composition. If the total level of foam-forming surfactant is too high then the compositions, especially tabletted compositions, can become slow to dissolve. If the level is too low then foaming is impaired.

Suitable non-ionic and ampholytic surface active agents include, for example, condensation products of alkylene oxides such as ethylene or propylene oxide with fatty alcohols, phenols, fatty amines or fatty acid alkanolamides, the fatty acid alkanolamides themselves, esters of long-chained ($C_8$-$C_{22}$) 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.

An important feature of the compositions of the present invention is that the silicone oil and the foam-forming surfactant are in discrete, separate granules. By 'discrete, separate granules' is meant that the foam-forming surfactant is incorporated into a distinctly separate granule from the silicone oil. It has been found that keeping foam-forming surfactant physically separate from the silicone oil helps prevent the surfactant interfering with the silicone deposition process. One method of achieving this is to form a spray-dried powder comprising the silicone oil, as described above and to either prepare a separate granular premix comprising the foam-forming surfactant, or to include the foam-forming surfactant with the excipients in the final mixing process prior to tabletting. It has been found that when the foam-forming surfactant is included with the excipients it can have a binding effect and eliminate or substantially reduce the need for additional binders such as polyethylene glycols which can have the effect of slowing down tablet disintegration.

Optional components

Denture cleansing compositions of the invention can be supplemented by other usual components of such formulations, especially additional effervescence generators, bleach actiavtors, 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 pyrogenic silicas, etc. The free moisture content of the final composition is desirably less than about 1% and especially less than about 0.5%.

The perborate salt / persulphate salt combinations described above give rise to oxygen effervescence. In preferred embodiments an additional, carbon dioxide effervescence generator comprising a bicarbonate salt and an acid is included. The carbon dioxide effervescence generator is useful for providing rapid, initial effervescence when the composition is 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 can 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 preferably 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, where both are used, is suitably 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.

Where used, the bicarbonate salt generally comprises from about 1% to about 20%, preferably from about 3% to about 10%, more preferably from about 4% to about 6% of the total composition. The acid component generally comprises from about 2% to about 15%, preferably from about 3% to about 10% of the total composition.

An especially preferred additional component of the present invention is a bleach activator. A preferred bleach activator is an organic peroxyacid 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.

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

| | |
|---|---|
| sodium pyrophosphate ($Na_4P_2O_7.10H_2O$) | 2.5g |
| sodium perborate ($NaBO_2.H_2O_2.3H_2O$) having 10.4% available oxygen | 0.615g |
| sodium dodecylbenzene sulphonate | 0.5g |

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 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 denture cleansing activator.

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;

   b) N-acylhydantoins, such as

      N,N' -diacetyl-5,5-dimethylhydantoin;

   c) Polyacylated alkylene diamines, such as

      N,N,N'N' -tetraacetylethylenediamine (TAED) and the corresponding hexamethylenediamine (TAHD) derivatives, as disclosed in GB-A-907,356, GB-A-907,357 and GB-A-907,358;

   d) Acylated glycolurils, such as tetraacetylglycoluril, 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-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 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 formal Ac L wherein Ac is the acyl moiety of an organic carboxylic acid comprising an optionally substituted, linear or 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 range from 4 to 13, for example oxybenzenesulphonate or oxybenzoate. Preferred compounds of this type are those wherein:

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 $OC_2H_5$. Examples of this class of material include sodium 3,5,5-trimethylhexanoyloxybenzene sulphonate, sodium 3,5,5-trimethyl-hexanoyloxybenzoate, sodium 2-ethylhexanoyloxybenzenesulphonate, sodium nonanoyl oxybenzene sulphonate and sodium octanoyl oxybenzenesulphonate, the acyloxy group in each instance preferably being p-substituted;

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, $OCH_3$, or $OC_2H_5$, AO is oxyethylene or oxypropylene, m is from 0 to 100, X is O, $NR_4$ or CO-$NR_4$, and A is CO, CO-CO, $R_6$-CO, CO-$R_6$-CO, or CO-$NR_4$-$R_6$-CO wherein $R_4$ is $C_1$-$C_4$ alkyl and $R_6$ is alkylene, alkenylene, arylene or alkarylene containing from 1 to 8 carbon atoms in the alkylene or alkenylene moiety. Denture cleansing 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 R3 is preferably $C_6$-$C_{12}$, more preferably $C_6$-$C_{10}$ alkyl when m is zero and $C_9$-$C_{15}$ when m is non-zero. The leaving group L is as defined above.

5) Acyl-cyanurates, such as triacetyl- or tribenzoylcyanurates, as disclosed in US Patent No. 3,332,882.

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.

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%.

Denture cleansing compositions according to the invention can additionally include one or more 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 weight of from about 1000 to about 50,000, Carbowax having a molecular weight of from 4000 to 20,000, 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 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.

Chelating agents beneficially aid cleaning and denture cleansing stability by keeping metal ions, 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 tetracetic acid (EDTA) and salts thereof, and polyphosphonates and aminopolyphosphonates such as hydroxyethanediphosphonic acid, ethylenediamine tetramethylenephosphonic acid, diethylenetriaminepentamethylene-

phosphonic 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 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.

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. 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 mixture of components in a punch and dye rotary tabletting press at a pressure of about 2 $x10^5$ 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 |
| Lathanol® powder | - | - | 3.40 |
| TOTAL WHITE GRANULATE | 32.56 | 50.58 | 62.20 |
| **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 |
| **EXCIPIENTS** | | | |
| TAED | 3.08 | 2.33 | 1.75 |
| Sodium perborate monohydrate | 18.75 | 15.51 | 11.10 |
| Lathanol® powder | 0.55 | 0.97 | - |
| Sodium carbonate | 18.5 | 5.78 | 3.96 |
| Fumed silica | 0.39 | 0.58 | 0.62 |
| Hydrated silica | 0.29 | 0.31 | 0.33 |
| Beeson 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 | 20.33 |
| | 100 | 100 | 100 |

[1] Caroat®.

[2] Cetyl dimethicone copolyol from Goldschmidt.

[3] Dimethicone copolyol from Union Carbide, a silicone surfactant.

[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, cleansing and anti-bacterial activity together with excellent cohesion and other physical and in-use performance characteristics.

What is claimed is:

1. A granular, denture cleansing composition comprising an inorganic persalt bleaching agent, a silicone oil and from 0.55% to 3.8% of a foam-forming surfactant selected from anionic surfactants, nonionic surfactants, amphoteric surfactants and mixtures thereof, wherein the silicone oil and the foam-forming surfactant are in discrete, separate granules.

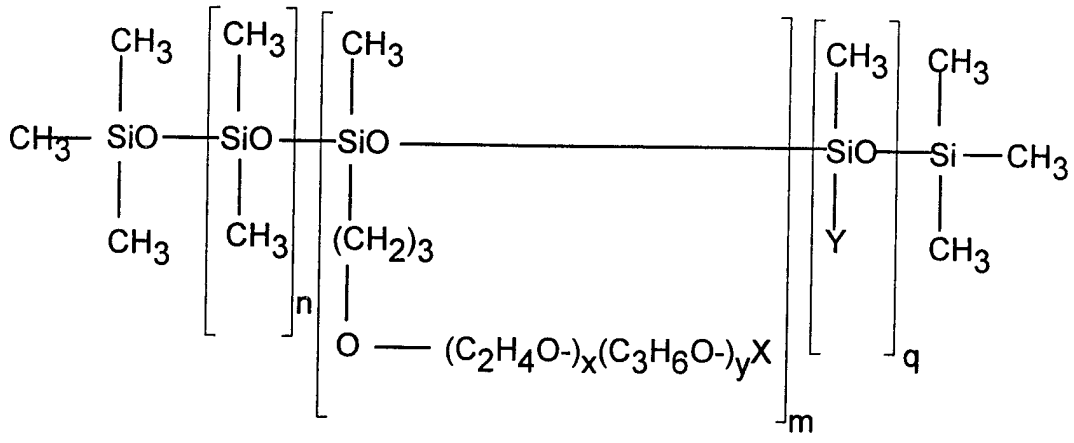
2. A denture cleansing composition according to Claim 1 wherein the foam-forming surfactant comprises an anionic surfactant.

3. A denture cleansing composition according to Claim 1 or Claim 2 wherein the foam-forming surfactant comprises sodium lauryl sulphoacetate.

4. A denture cleansing composition according to any of Claims 1 to 3 wherein the foam-forming surfactant comprises from 0.7% to 3%, preferably from 0.9% to 2% by weight of the composition.

5. A denture cleansing composition according to any of Claims 1 to 4 wherein the foam-forming surfactant is a surfactant mixture, comprising a primary surfactant and an additional co-surfactant.

6. A denture cleansing composition according to any of Claims 1 to 5 wherein the silicone oil is of the general formula (I):




(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 $(C_2H_4O\text{-})_x(C_3H_6O\text{-})_yX$ 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.

7. A denture cleansing composition according to Claim 6 wherein the silicone oil is cetyl dimethicone copolyol.

8. A denture cleansing composition according to any of Claims 6 or 7 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 $CH_3$, 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 $(C_2H_4O\text{-})_x(C_3H_6O\text{-})_yX$ 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.

9. A denture cleansing composition according to any of Claims 1 to 8 wherein the composition is in compressed tablet form.

10. A denture cleansing composition according to Claim 9 wherein the tablet comprises a spray-dried powder comprising the silicone oil, and a separate granular premix comprising the foam-forming surfactant.

11. A denture cleansing composition according to Claim 9 wherein the tablet comprises a spray-dried powder comprising the silicone oil, and tabletting excipients comprising the foam-forming surfactant.

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/19952

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :C11D 1/04, 1/82, 3/39, 3/395
US CL :510/116, 117, 375, 378, 446, 450

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. : 510/116, 117, 375, 378, 446, 450

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)

Please See Extra Sheet.

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | US 3,962,107 A (LEVIN ET AL) 08 June 1976 (08-06-76), see abstract; column 1, lines 5-20; column 2, lines 24-35; column 3, lines 1-55; column 5, lines 15-45. | 1-3 |
| X | US 4,155,868 A (KAPLAN ET AL) 22 May 1979 (22-05-79), see abstract; column 1, lines 45-60; column 2, lines 28-40; column 3, line 64 to column 4, line 20; column 5, lines 5-61; column 8, lines 30-69. | 1-3 |
| X | US 4,647,451 A (PIECHOTA, JR.) 03 March 1987 (03-03-87), see abstract; column 3, line 40 to column 4, line 40; column 5, line 25 to column 6, line 25. | 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 |
| "E" | 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) | "&" | 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<br>02 JANUARY 1998 | Date of mailing of the international search report<br>27 JAN 1998 |
| Name and mailing address of the ISA/US<br>Commissioner of Patents and Trademarks<br>Box PCT<br>Washington, D.C. 20231<br>Facsimile No. (703) 305-3230 | Authorized officer<br>GREGORY R. DEL COTTO<br>Telephone No. (703) 308-0661 |

Form PCT/ISA/210 (second sheet)(July 1992)★

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/19952

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

APS
search terms: sulphoacetate, sulfoacetate, perborate, percarbonate, tablet, solid, granule, grain, silicone oil, dimethicone, alkylaminosilicone, silicone

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/19952

**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.: 4-11
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.