ASTRINGENT DENTIFRICE

The present invention relates to a dentifrice containing a water-soluble zinc salt which provides an astringent effect on oral mucosa and periodontal tissue during toothbrushing, and a gelling agent and optionally an alkali metal monofluorophosphate. Each of the components is compatible and substantially non-reactive with a hydrous silica gel polishing agent.

The astringent effectiveness of zinc ions provided by water-soluble zinc salts to promote and improve oral hygiene has long been known. Nevertheless, there have been limits on the practical use of zinc in dentifrice compositions since zinc ions can readily react with typical dentifrice components causing substantial loss of availability of zinc ions.

Likewise, the monofluorophosphate ion has long been known to promote oral hygiene and reduce caries formation by release of fluoride, but its effectiveness too has been reduced by incompatibility with some dentifrice components, such as water-soluble zinc compounds.

Nonionic gelling agents such as hydroxyethyl cellulose have been preferably used in dentifrices when a water-soluble zinc salt is employed. However, when alkali metal carboxymethyl cellulose has been employed in the presence of zinc ions, reaction occurs removing zinc ions, leading to possible gel

breakdown and phase separation. In U.S. Patent 3,728,446, to Roberts et al, the in situ reaction between zinc ions and alkali metal carboxymethyl cellulose to form visible particles is described.

Furthermore, gel-type dentifrices providing zinc astringency have been limited due to the incompatibility of zinc ions with various siliceous polishing agents. Such siliceous polishing agents as silica xerogel having an average particle size between about 2 and 20 microns and generally a surface area of at least about 300 m^2/gm, typically about 300-370 m^2/gm, or about 600-800 m^2/gm, which are described in U.S. Patent No. 3,538,230 to Pader et al, undergo in situ reaction with zinc ion so that much of the theoretically available zinc is lost by physio-chemical means such as absorption.

Similar compatibility problems would occur when water-soluble zinc salt is present together with other dentifrice salt polishing agents, particularly calcium salts such as dicalcium phosphate or calcium carbonate. In fact it has been believed that it would be difficult to employ a water-soluble zinc salt and maintain a high level of availability of zinc ions in such conventional dentifrices.

Compatibility is also a problem when an alkali metal monofluorophosphate is employed with such siliceous polishing agent in a dentifrice containing a water-soluble zinc salt.

It has therefore been difficult to prepare dentifrices containing a siliceous polishing agent and

amounts of zinc ions with or without alkali metal monofluorophosphate or alkali metal carboxymethyl cellulose or both, which remain effective in providing the astringent properties of zinc and the anti-caries properties of fluoride. In particular, gel-type dentifrices providing both zinc astringency with or without a fluoride anti-caries effect have not been satisfatorily available due to the incompatibility of zinc ion with monofluorphosphate and with alkali metal carboxymethyl cellulose in the presence of various siliceous polishing agents.

In the present invention, use is made of a precipitated, amorphous silica gel which has been described in British Published Patent Application No. 2038303 A to Feig et al and in U.S. Patent No. 4,528,181 granted 9 July 1985. In U.S. Patent No. 4,528,181 a dentifrice containing the precipitated, amorphous silica gel is described in which a dual source of fluoride containing sodium fluoride and sodium monofluorophosphate and a source of calcium is stabilized by an alkali metal phytate to improve fluoride retention.

Such precipitated, amorphous silica gel material is available from Grace GmbH as product such as Syloblanc (Registered Trade Mark) 81, Syloblanc 81C and Syloblanc 82. It is distinct from the types of xerogel which have been sold by W.R. Grace and Co. under the trade mark Syloid and which are particularly described in U.S. Patent 3,538,230 to Pader et al. Indeed, although some products sold by

Grace GmbH under the trade mark Syloblanc were formerly or are still available under the trade mark Syloid, none of Syloblanc 81, Syloblanc 81C or Syloblanc 82 has ever been available under the trade mark Syloid. It is particularly noteworthy that the grades of the silica gel employed in the present invention are less abrasive as the surface area increases whereas the grades of silica xerogel which are described in U S. patent 3,538,230 are generally more abrasive as their surface area increases.

In view of the low compatibility of most polishing agents with zinc including those polishing agents of U.S. patent No. 3,538,230, it was quite unexpected that a particular siliceous polishing material would not have such a problem and that further, in the presence of such polishing agent, the reaction between zinc ions and alkali metal carboxymethyl cellulose is substantially reduced. Furthermore, it was unexpected, that in the presence of these particular siliceous polishing materials and zinc ions. alkali metal monofluorophosphate remains stable and compatible to provide fluoride. Nevertheless, in accordance with the present invention it has been found that retention of high levels of astringency from zinc ions is attained when such particular siliceous polishing material is employed, or monofluorphosphate is employed to give high levels of fluoride ions which are also retained.

It is an advantage of the present invention that an astringent dentifrice containing zinc ions is

provided, which may effectively contain monofluorophosphate or an alkali metal carboxymethyl cellulose gelling agent or both.

In accordance with certain of its aspects, the present invention relates to an astringent dentifrice comprising about 20-90% by weight of liquid vehicle comprising water in amount of at least about 3% by weight of the said dentifrice, about 0.05-5% by weight of a gelling agent and about 10-50% by weight of a polishing agent comprising a synthetic precipitated, amorphous silica gel having an average particle size of 1 to 30 microns and

a) a surface area of 1 to 600 m^2/g,

b) a pore volume of 0.05 to 0.5 cm^3/g,

c) a product of surface area (in m^2/g) by pore volume (in cm^3/g) less than or equal to 240,

d) a calculated pore diameter of 1.5 to 2.5 nm (10^{-9} metres), and

e) a water content of less than 25% by weight;

and up to about 5% of a water-soluble zinc salt which provides at least about 50 ppm of zinc ions to said dentifrice. Furthermore, the said dentifrice may contain an alkali metal carboxymethyl cellulose as the gelling agent and may contain in addition an alkali metal monofluorophosphate in an amount to provide about 0.01-1% fluoride.

As indicated above, the synthetic precipitated silica is of the type described in British Published Patent Application 2038303 and U.S. Patent No. 4,528,181. Specific grades of the silica material described therein are suitable for use in the practice of the present invention. Further, specific grades which are particularly preferred are describd in an October 1980 trade publication of Grace GmbH of Norderstadt, Germany, as Syloblanc 81 and Syloblanc 82 and as having the following typical physical and chemical characteristics.

	SYLOBLANC 81	SYLOBLANC 82
Average particle size (according to Coulter) microns	4	7
Wet screen residue % (42 microns)	0.02	0.02
pH (5% suspension in water)	3	6
Surface area (B.E.T.) m^2/g	400	480
Loss on drying %	7	4
SiO_2 content (on ignited substance) %	96	99
Refractive index	1.46	1.46

In a variation of Syloblanc 81 available as Syloblanc 81C, the pH (5% suspension in water) is about 6-8.

Syloblanc 81 and 81C, in particular, are highly effective in polishing dental surfaces. Syloblanc 82 is lower in polishing effect, but can be used by consumers desiring such reduced effect. Likewise, grades of the silica material may be proportioned in

mixtures to produced appropriate polishing characteristics. It is noteworthy that the dentifrices are compatible in unlined aluminium dentifrice tubes even in the absence of phytate salt, which is necessary in the invention described in U.S. Patent No. 4,528,181. The precipitated amorphous silica gel is employed in amount of about 10-50% by weight, typically about 10-40% in a gel dentifrice.

Aqueous slurries of the silica material (e.g. about 5 to 20% slurries) typically have a pH of about 2 to 9. Since the dentifrice composition of the present invention preferably has a pH (measured in 10% aqueous slurry) of at least about 5.5, e.g. about 5.5-7.5, the pH of the dentifrice may be adjusted with an appropriate material such as sodium hydroxide.

The water-soluble zinc salt is present in the dentifrice in an amount of up to about 5% by weight, preferably from above 0.01 to 3% and most preferably from about 0.1 to 2%. Water-soluble zinc salts useful in the present invention are soluble in water to the extent of at least about 10% by weight, preferably at least 20%. There is provided at least about 50 ppm of zinc ions to the dentifrice, preferably at least about 750 ppm and most preferably at least about 1000 ppm of zinc ions. Suitable zinc salts include zinc sulphate, zinc chloride, zinc bromide, zinc iodide, zinc nitrate and zinc acetate. In the case of the zinc chloride, 0.01% by weight provides about 50 ppm of zinc ions and 0.2% by weight provides about 1000 ppm of zinc ions. 0.48% by

weight of zinc sulphate heptahydrate provides about 1000 ppm of zinc ions. In addition, zinc oxide, a sparingly soluble (below 0.0005%) zinc compound may also be added to prevent a lowering of the pH in the product. This acts as a buffer system and improves pH stability and compatibility in unlined aluminium tubes. It may be present in an amount of about 0.005%-0.5% by weight.

The dentifrice comprises a liquid vehicle containing preferably about 3-60% by weight of water, typically mixed with at least one humectant. The liquid phase comprises about 20-90% by weight of the dentifrice and is generally about 25-80% liquid, typically with about 3-50% by weight, preferably 3-10% of water in a substantially clear gel dentifrice or gel dentifrice which would be substantially clear except for the presence of an opacifying agent, such as titanium dioxide, and about 11-50% of water in a hazy to opaque gel dentifrice with about 10-90% by weight, preferably about 15-80%, of humectant. Typical humectants include glycerine, sorbitol (e.g. 70% solution), maltitol, polyethylene glycol of molecular weight of about 400-600, propylene glycol and mixtures thereof.

The dentifrice also contains a gelling or binding agent such as a solid vehicle agent, although this may be in small amount, since the synthetic, precipitated silica can effect a thickening or gelling of the dentifrice into a creamy or pasty consistency. Alkali metal carboxymethyl cellulose is preferred in accordance with one aspect of the

present invention, but other gelling or binding agents that may be present include hydroxyethyl cellulose, hydroxpropyl cellulose, xanthan, Irish moss, iota-carrageenan, gum tragacanth, polyvinyl pyrrolidone, starch and mixtures thereof. Such gelling agents are used in an amount of about 0.05%-5% by weight, typically about 0.05-2% and preferably about 0.1-1.5%. Particularly desirable is the use of sodium carboxymethyl cellulose.

Alkali metal monofluorophosphates, such as sodium, and potassium monofluorophosphates are compatible in the dentifrice. Sodium monofluorophosphate is especially preferred. In the past, when it has been attempted to formulate a dentifrice with liquid vehicle, gelling agent, polishing agent, zinc salt and sodium monofluorphosphate, substantial levels of zinc ions and fluoride ions have been lost by insolubilisation. Unexpectedly, when the polishing agent is the defined synthetic, precipitated, amosphous silica gel, high levels of fluoride ions and substantial retention of zinc ions are attained. Such high levels of fluoride retention are not attained when a simple fluoride such as sodium fluoride is employed.

Sodium monofluorophosphate, Na_2PO_3F, as commercially available, may vary considerably in purity. It may be used in any suitable purity provided that any impurities do not substantially adversely affect the desired properties. In general, the purity is desirably at least 80%, and preferably

at least 90% by weight of sodium monofluorophosphate with the balance being primarily impurities or by-products of manufacture such as sodium fluoride and water-soluble sodium phosphate salt. Expressed in another way, the sodium monofluorophosphate employed should have a total fluoride content of above 12%, preferably 12.7%, a content of not more than 1.5%, preferably not more than 1.2%, of free sodium fluoride; and a sodium monofluorophosphate content of at least 12%; preferably at least 12.1% all calculated as fluoride. Alkali metal monofluorophosphate is present in amount to provide fluoride in an amount of about 0.01-1% by weight, preferably about 0.1%. Thus, sodium monofluorophosphate can be present in amount of about 0.076-7.6%, preferably 0.76%, which corresponds to about 100-10000 ppm of fluoride, preferably about 1000 ppm.

Any suitable surface active or detersive material may be included in the dentifrice compositions. Such compatible materials are desirable to provide additional detersive foaming and antibacterial properties depending upon the specific type of surface active material and are selected accordingly. These detergents are usually water-soluble compounds, and may be anionic, nonionic, amphoteric or cationic in structure. It is usually preferred to use water-soluble non-soap or synthetic organic detergents. Suitable detersive materials are known and include, for example, the water-soluble salts of higher fatty acid and monoglyceride monosul-

phate detergents (e.g. sodium coconut fatty acid monoglyceride monosulphate), higher alkyl sulphate (e.g. sodium lauryl sulphate), alkyl aryl sulphonate (e.g. sodium dodecyl benzene sulphonate, higher fatty acid esters of 1,2-dihydroxy propane sulphonate) and the like.

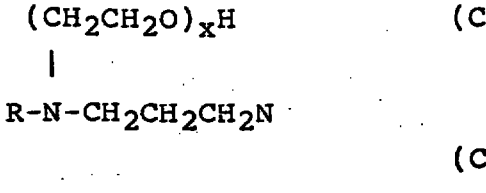
Further surface active agents include the substantially saturated higher aliphatic acyl amides of lower aliphatic amino carboxylic acid compounds, such as those having 12 to 16 carbons in the acyl radical. The amino acid portion is derived generally from the lower aliphatic saturated monoaminocarboxylic acid compounds. Suitable compounds are the fatty acid amides of glycine, sarcosine, alanine, 3-amino-propanoic acid and valine having about 12 to 16 carbons in the acid group. It is preferred to use the N-lauroyl, myristoyl and palmitoyl sarcoside compounds, however, for optimum effects.

The amide compounds may be employed in the form of the free acid or preferably as the water-soluble salts thereof, such as the alkali metal, ammonium, amine and alkylolamine salts. Specific examples thereof are the sodium and potassium N-lauroyl, myristoyl and palmitoyl sarcosides, ammonium and ethanolamine N-lauroyl glycide and alanine. For convenience herein, reference to "amino carboxylic acid compound", "sarcoside" and the like refers to such compounds having a free carboxylic group or the water-soluble carboxylate salts.

Such materials are utilized in pure or

substantially pure form. They should be as free as practicable from soap or similar higher fatty acid materials which tend to reduce the activity of these compounds. In usual practice, the amount of such higher fatty acid material is less than 15% by weight of the amide and insufficient to adversely affect it, and preferably less than about 10% of the said amide material.

Other particularly suitable surface-active materials include nonionic agents such as condensates of sorbitan monostearate with approximately 20 moles of ethylene oxide, condensates of ethylene oxide with propylene oxide, condensates of propylene glycol ("Pluronic" (Registered Trade Mark) materials) and amphoteric agents such as long chain (alkyl) amide-alkylene-alkalated amine derivatives, which are available under the trademark "Miranol" C_2M. Cationic surface active germicides and antibacterial compounds such as diisobutylphenoxyethoxyethyl dimethyl benzyl ammonium chloride, benzyl dimethyl stearyl ammonium chloride, tertiary amines having one fatty alkyl group (of from 12-18 carbon atoms) and two (poly) oxyethylene groups attached to the nitrogen (typically containing a total of from about 2 to 50 ethanoxy groups per molecule) and salts thereof with acids, and compounds of the structure



wherein R represents a fatty alkyl group containing from about 12 to 18 carbon atoms, and x, y and z total 3 or higher, as well as salts thereof with mineral or organic acids, may also be used. It is preferred to use from about 0.05 to 5% by weight of the foregoing surface-active materials in the oral preparation of the present invention.

Various other materials may be incorporated in the dental creams of the present invention. Examples thereof are opacifiers, preservatives, stabilizers, silicones, chlorophyll compounds and ammoniated materials such as urea, diammonium phosphate and mixtures thereof. These adjuvants are incorporated in the compositions of the present invention in amounts which do not substantially adversely affect the desired properties and characteristics and are suitably selected and used in conventional amounts.

For some purposes it may be desirable to include antibacterial agents in the compositions of the present invention. Typical antibacterial agents (which may be used in amounts of about 0.01% to about 5%, preferably about 0.05 to about 1.0%, by weight of the dentifrice composition) include cetyl pyridinium chloride, and benzethonium chloride as well as.

N^1-4 (chlorobenzyl) -N^5- (2,4-dichlorobenzyl) biguanide,

p-chlorophenyl biguanide,

4-chlorobenzhydryl biguanide;

4-chlorobenzhydrylguanylurea;

N-3-lauroxypropyl-N^5-p-chlorobenzylbiguanide;

1,6-di-p-chlorophenylbiguanidohexane;

1-(lauryldimethylammonium)-8-(p-chlorobenzyldimethylammonium) 5,6-dichloro-2-guanidinobenzimidazole;

N^1-p-chlorophenyl-N^5-laurylbiguanide;

5-amino-1,3-bis (2-ethylhexyl)-5-methylhexahydropyrimidine;

and their non-toxic addition salts.

Any suitable flavouring or sweetening materials may be employed in formulating a flavour for the compositions of the present invention. Examples of suitable flavouring constituents include the flavouring oils, e g. oils of spearmint, peppermint, wintergreen, sassafras, clove, sage, eucalyptus, marjoram, cinnamon, lemon and orange, as well as methyl salicylate. Suitable sweetening agents include sucrose, lactose, maltose, sorbitol, sodium cyclamate, sodium saccharine, dipeptides of U.S. Patent 3,939,261 and oxathiazin salts of U.S. Patent 3,932,606. Suitable flavour and sweetening agents may together comprise from about 0.01 to 5% or more of the composition.

The dentifrice is packaged in a container from which it can be readily extruded such as a pressure differential or mechanically operated dental cream dispenser or a lined or unlined aluminium tube or wax lined lead tube or plastic tube, which may be laminated with aluminium. The rheological properties are highly desirable when a mechanically operated dispensing container of the type described in British

Patent Application 2,070,695A, published 9th September, 1981, is employed. This dispensing container comprises a dispensing mouthpiece, a tension member, a central rod, a piston and operating hand control.

A pressure differential dispensing container may be of the aerosol or vacuum type. Suitable pressure differential dispensers include those comprising a collapsible product-containing bag being disposed within a rigid container which contains a propellant fluid. In such dispensing containers, operation of the valve permits release of the product only, the propellant fluid being separated from the product by the fluid impermeable bag. Dispensers of this type are described in U.S. Patents 3,828,977 and 3,838,796. These are the so-called Sepro dispensers. So-called Exxel and Enviro Spray containers also utilize pressure.

Still another type dispenser is the barrier piston container described in U.S. 4,171,757. Such container includes a valve, a product-containing compartment and an essentially fluid-tight barrier piston which separates the propellant fluid from the contained product (the so-called Diamond container).

The dentifrice is typically prepared by forming a premix of the gelling agent with the liquid vehicle components, e.g. water and humectant, which may also contain additional ingredients such as the monofluorophosphate and/or sweetener, and blending therewith the synthetic precipitated silica gel and zinc salt.

Additional employed ingredients may then be added.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples. All amounts are by weight unless otherwise indicated.

EXAMPLES 1A to 1G

The following opacified gel dentifrices having the compositions given in Table 1 are prepared and placed in unlined aluminium tubes:

TABLE 1

EXAMPLE	PARTS 1A	1B
Ingredients		
Glycerine	25.000	25.000
Sorbitol (70%)	47.050	43.830
Xanthan	0.260	0.260
Sodium saccharin	0.170	0.170
Titanium dioxide	1.000	1.000
Water	3.000	3.000
Zinc sulphate heptahydrate	0.480	0.480
Precipitated amorphous silica gel(1)	20.000	-
Silica xerogel(2)	-	17.000
Silica aerogel(3)	-	6.500
Sodium hydroxide (40%)	0.280	-
Sodium lauryl sulphate	1.760	1.760
Flavour	1.000	1.000
pH (20% slurry)	5.9	6.1

Notes on Table 1

(1) Syloblanc 81 available from Grace G.m.b.H.;

(2) Syloid AL1 available from Grace G.m.b.H.;

(3) Syloid 244 thickener available from W.R. Grace & Co.

The theoretical amount of soluble zinc ions in each gel dentifrice is 1000 ppm or 0.100%.

The dentifrice of Example 1A does not require the presence of thickener material to provide desirable gel character. Its consistency is about equivalent to that of the dentifrice of Example 1B.

Each dentifrice is aged at room temperature and at 43°C. Both retain generally equivalent desirable consistencies. The percentage amounts of available soluble zinc ions in each dentifrice on aging was determined and is given in Table 2 below:

TABLE 2

% Zn^{+2}-Room Temperature

				43°C		
		1	3	2	1	3
EXAMPLE	Initial	Month	Months	Weeks	Month	Months
1A	0.084	0.080	0.050	0.091	0.070	0.050
1B	0.054	0.042	0.005	0.049	0.048	0.005

The dentifrice of Example 1A containing Syloblanc 81 retains superior levels of soluble zinc ions compared to the otherwise generally equivalent dentifrice of Example 1B containing Syloblanc AL1.

Similar superior levels of retention of soluble zinc ions are attained when the Syloblanc 81 of the

dentifrice of Example 1A is replaced with Syloblanc 82 (Example 1C) and with a 1:1 mixture of Syloblanc 81 and 82 (Example 1D), in each case, with the levels of sodium hydroxide reduced or omitted, any omitted sodium hydroxide being replaced by an additional weight of sorbitol (70%).

Likewise, superior retention levels of soluble zinc ions are attained when Syloblanc 81 is replaced with Syloblanc 81C (Example 1E), with sodium hydroxide omitted and its amount added to sorbitol (70%) (i.e. sodium hydroxide zero %, sorbitol 47.33%).

EXAMPLES 1F and 1G

0.25 parts of zinc oxide are incorporated into each of the dentifrices of Examples 1A and 1B, in place of corresponding amounts of sorbitol, thereby stabilizing the pH during aging and improving the compatibility of the compositions with unlined aluminium tubes for prolonged periods.

EXAMPLES 2A to 2G

The following opacified gel dentifrices having the compositions set out in Table 3 are prepared and placed in unlined aluminium tubes:

TABLE 3

	PARTS	
EXAMPLES	2A	2B
Ingredients		
Glycerine	25.000	25.000
Sorbitol (70%)	47.050	43.550
Sodium carboxymethyl cellulose	0.260	0.260
Sodium saccharin	0.170	0.170

TABLE 3 (continued)

EXAMPLES	PARTS 2A	2B
Ingredients		
Titanium dioxide	1.000	1.000
Water	3.000	3.000
Zinc sulphate heptahydrate	0.480	0.480
Precipitated amorphous silica gel(1)	20.000	-
Silica xerogel(2)	-	17.000
Silica aerogel(3)	-	6.500
Sodium hydroxide (40%)	0.280	0.280
Sodium lauryl sulphate	1.760	1.760
Flavour	1.000	1.000
pH (20% slurry)	5.9	6.1

Notes on Table 3

(1), (2) and (3) - see notes (1), (2) and (3) on Table 1.

The theoretical amount of soluble zinc ions in each gel dentifrice is 1000 ppm or 0.100%.

The dentifrice of Example 2A does not require the presence of thickener material to provide desirable gel character initially.

Each dentifrice is aged at room temperature and at 43°C. Both generally retain equivalent desirable consistencies. The percentage amounts of available soluble zinc ions in each dentifrice on aging was determined and is given in Table 4 below:

TABLE 4

Example	% Zn^{+2}-Room Temperature			43°C		
	Initial	1 Month	3 Months	2 Weeks	1 Month	3 Months
2A	0.080	0.079	0.050	0.082	0.069	0.050
2B	0.052	0.039	0.002	0.050	0.060	0.002

The dentifrice of Example 2A containing Syloblanc 81 retains gel character and superior levels of soluble zinc ions compared to the otherwise generally equivalent dentifrice of Example 2B containing Syloblanc 63. When the conventional 7 MXF grade of sodium carboxymethyl cellulose is employed there is phase separation and breakdown in the presence of Syloid 63 polishing agent which does not occur as much when Syloblanc 81 is employed.

It is noted that the two-week and one-month evaluation levels of the dentifrice of Example 2B at 43°C reflect routine experimental variations.

Similar superior levels of retention of soluble zinc ions are attained when Syloblanc 81 of the dentifrice of Example 2A is replaced with Syloblanc 82 (Example 2C) and with a 1:1 mixture of Syloblanc 81 and 82 (Example 2D), in each, with levels of sodium hydroxide reduced, or omitted, any omitted sodium hydroxide being replaced by an additional weight of sorbitol (70%).

Likewise, superior retention levels of soluble zinc ions are attained when Syloblanc 81 is replaced with Syloblanc 81C (Example 2E), with sodium

hydroxide omitted and its amount added to sorbitol (70%) (i.e. sodium hydroxide zero %, sorbitol 47.33%).

EXAMPLES 2F and 2G

0.25 parts of zinc oxide are incorporated into each of dentifrices of Examples 2A and 2B, in place of corresponding amounts of sorbitol, thereby stabilizing the pH during aging and improving compatibility with unlined aluminium tubes for prolonged periods.

EXAMPLES 3A to 3I

The following opacified gel dentifrices having the compositions as set out in Table 5 below are prepared and placed in unlined aluminium tubes:

TABLE 5

EXAMPLES	PARTS 3A	3B
Ingredients		
Glycerine	25.000	25.000
Sorbitol (70%)	46.340	46.880
Sodium carboxymethyl cellulose	0.190	0.190
Sodium saccharin	0.170	0.170
Titanium dioxide	1.000	1.000
Water	3.000	3.000
Zinc sulphate heptahydrate	0.480	0.480
Sodium monofluorophosphate	0.760	-
Sodium fluoride	-	0.220
Precipitated amorphous silica gel(1)	20.000	20.000
Sodium hydroxide (40%)	0.300	0.300
Sodium lauryl sulphate	1.760	1.760
Flavour	1.000	1.000
pH (20% slurry)	6.0	5.9

Notes on Table 5

(1) - See note (1) on Table 1.

The theoretical amounts of soluble zinc ions and fluoride in each gel dentifrice is 1000 ppm or 0.100%, for each of the zinc ions and fluoride.

Each dentifrice is aged at room temperature and at 43°C. The percentage amounts of available soluble zinc ions and of fluoride in each dentifrice on aging at room temperature was determined and is given in Table 6 below:

TABLE 6

EXAMPLE	Initial	One Month
3A	0.66 Zn(4)	0.066 Zn
	0.096 F(5)	0.097 F
3B	0.070 Zn	0.051 Zn
	0.100 F(6)	0.048 F

Notes on Table 6

(4) - % Zn^{+2}

(5) - % Monofluorophosphate as fluoride

(6) - % Fluoride

The dentifrice of Example 3A containing sodium monofluorophosphate provides substantial retention of both zinc ions and fluoride compared to the dentifrice of Example 3B containing sodium fluoride. At 43°C, gas forms in the unlined aluminium tube containing the dentifrice of Example 3B, while the unlined aluminium tube containing the dentifrice of Example 3A remains stable.

Zinc ion and fluoride retention are low when the xerogel Syloid 63 (Examples 3C and 3D) available from W.R. Grace & Co. replaces Syloblanc 81.

Similar results to those determined with the

dentifrice of Example 3A are attained when potassium monofluorophosphate replaces sodium monofluorophosphate.

Similar superior levels of retention of soluble zinc ions and fluoride are attained when Syloblanc 81 of dentifrice A is replaced with Syloblanc 82 (Example 3E) and with a 1:1 mixture of Syloblanc 81 and 82 (Example 3F), in each, with the levels of sodium hydroxide reduced or omitted, any omitted sodium hydroxide being replaced by an additional weight of sorbitol (70%).

Likewise, superior retention levels of soluble zinc ions and fluoride are attained when Syloblanc 81 is replaced with Syloblanc 81C (Example 3G), with sodium hydroxide omitted and its amount added to sorbitol (70%) (i.e. sodium hydroxide zero %, sorbitol 46.64%).

EXAMPLES 3H AND 3I

0.25 parts of zinc oxide are incorporated into each of the dentifrices of Examples 3A and 3B, in place of corresponding amounts of sorbitol, thereby stabilizing the pH during aging and improving compatibility with unlined aluminium tubes for prolonged periods.

EXAMPLES 4A to 4D

The following stable visually clear gel dentifrices having the compositions set out in Table 7 below are prepared and placed in unlined aluminium tubes:

TABLE 7

EXAMPLE	PARTS 4A	4B	4C	4D
Ingredients				
Glycerine	25.000	25.000	25.000	25.000
Sorbitol (70%)	48.310	48.590	48.590	48.450
Xanthan	0.260	0.260	0.260	0.260
Sodium saccharin	0.170	0.170	0.170	0.170
Water	3.000	3.000	3.000	3.000
Zinc chloride	0.020	0.020	0.020	0.020
Syloblanc 81	20.000	-	-	10.000
Syloblanc 81C	-	20.000	-	-
Syloblanc 82	-	-	20.000	10.000
Sodium hydroxide (40%)	0.280	-	-	0.140
Sodium lauryl sulphate	1.760	1.760	1.760	1.760
Flavour	1.000	1.000	1.000	1.000
Blue colour solution	0.200	0.200	0.200	0.200

EXAMPLES 5A to 5D

The following stable visually clear gel dentifrices having the compositions set out in Table 8 below are prepared and placed in unlined aluminium tubes:

TABLE 8

EXAMPLE	PARTS 5A	5B	5C	5D
Ingredients				
Glycerine	25.000	25.000	25.000	25.000
Sorbitol (70%)	48.310	48.590	48.590	48.450
Sodium carboxymethyl cellulose	0.260	0.260	0.260	0.260

TABLE 8 (continued)

EXAMPLE	PARTS 5A	5B	5C	5D
Ingredients				
Sodium saccharin	0.170	0.170	0.170	0.170
Water	3.000	3.000	3.000	3.000
Zinc chloride	0.020	0.020	0.020	0.020
Syloblanc 81	20.000	-	-	10.000
Syloblanc 81C	-	20.000	-	-
Syloblanc 82	-	-	20.000	10.000
Sodium hydroxide (40%)	0.280	-	-	0.140
Sodium lauryl sulphate	1.760	1.760	1.760	1.760
Flavour	1.000	1.000	1.000	1.000
Blue colour solution (1%)	0.200	0.200	0.200	0.200

Similarly stability is attained when potassium carboxymethyl cellulose replaces sodium carboxymethyl cellulose.

EXAMPLES 6A to 6D

The following stable visually clear gel dentifrices having the compositions set out in Table 9 below are prepared and placed in unlined aluminium tubes:

TABLE 9

EXAMPLES	PARTS 6A	6B	6C	6D
Ingredients				
Glycerine	25.000	25.000	25.000	25.000
Sorbitol (70%)	47.550	47.830	47.830	47.690
Xanthan	0.260	0.260	0.260	0.260
Sodium saccharin	0.170	0.170	0.170	0.170

TABLE 9 (continued

EXAMPLES	PARTS 6A	6B	6C	6D
Ingredients				
Water	3.000	3.000	3.000	3.000
Sodium monofluoro-phosphate	0.760	0.760	0.760	0.760
Zinc chloride	0.020	0.020	0.020	0.020
Syloblanc 81	20.000	-	-	10.000
Syloblanc 81C	-	20.000	-	-
Syloblanc 82	-	-	20.000	10.000
Sodium hydroxide (40%)	0.280	-	-	0.140
Sodium lauryl sulphate	1.760	1.760	1.760	1.760
Flavour	1.000	1.000	1.000	1.000
Blue colour solution (1%)	0.200	0.200	0.200	0.200

EXAMPLES 7A to 7D

The following hazy and opaque gel dentifrices having the compositions set out in Table 10 below are prepared and packaged in mechanically operated dispensing containers:

TABLE 10

EXAMPLE	PARTS 7A	7B	7C	7D
Ingredients				
Glycerine	25.000	25.000	25.000	25.000
Sorbitol (70%)	24.970	24.870	24.870	24.870
Iota carrageenan	0.700	0.700	0.700	0.700
Sodium saccharin	0.170	0.170	0.170	0.170
Water	25.000	25.000	25.000	25.000
Zinc bromide dihydrate	0.400	-	-	-

TABLE 10 (continued)

EXAMPLE	PARTS 7A	7B	7C	7D
Ingredients				
Zinc iodide	-	0.500	-	-
Zinc nitrate hexa-hydrate	-	-	0.500	-
Zinc acetate dihydrate	-	-	-	0.500
Syloblanc 81C	21.000	21.000	21.000	21.000
Sodium lauryl sulphate	1.760	1.760	1.760	1.760
Flavour	1.000	1.000	1.000	1.000

EXAMPLES 8A to 8D

The following stable hazy and opaque gel dentifrices having the compositions set out in Table 11 below are prepared and placed in unlined aluminium tubes:

TABLE 11

EXAMPLES	PARTS 8A	8B	8C	8D
Ingredients				
Glycerine	25.000	25.000	25.000	25.000
Sorbitol (70%)	24.970	24.870	24.870	24.870
Sodium carboxymethyl cellulose	0.700	0.700	0.700	0.700
Sodium saccharin	0.170	0.170	0.170	0.170
Water	25.000	25.000	25.000	25.000
Zinc bromide dihydrate	0.400	-	-	-
Zinc iodide	-	0.500	-	-
Zinc nitrate hexa-hydrate	-	-	0.500	-
Zinc acetate di hydrate	-	-	-	0.500

TABLE 11 (continued)

EXAMPLES	PARTS 8A	8B	8C	8D
Syloblanc 81C	21.000	21.000	21.000	21.000
Sodium lauryl sulphate	1.760	1.760	1.760	1.760
Flavour	1.000	1.000	1.000	1.000

EXAMPLES 9A to 9D

The following stable hazy and opaque gel dentifrices having the compositions set out in Table 12 below are prepared and packaged in mechanically operated dispensing containers:

TABLE 12

EXAMPLES	PARTS 9A	9B	9C	9D
Ingredients				
Glycerine	25.000	25.000	25.000	25.000
Sorbitol (70%)	24.210	24.110	24.110	24.110
Iota carrageenan	0.700	0.700	0.700	0.700
Sodium saccharin	0.170	0.170	0.170	0.170
Water	25.000	25.000	25.000	25.000
Sodium monofluorophosphate	0.760	0.760	0.760	0.760
Zinc bromide dihydrate	0.400	-	-	-
Zinc iodide	-	0.500	-	-
Zinc nitrate hexahydrate	-	-	0.500	-
Zinc acetate dihydrate	-	-	-	0.500
Syloblanc 81C	21.000	21.000	21.000	21.000
Sodium lauryl sulphate	1.760	1.760	1.760	1.760
Flavour	1.000	1.000	1.000	1.000

In all the examples, sodium cyclamate may replace sodium saccharin.



CLAIMS

1. An astringent dentifrice comprising about 20-90% by weight of liquid vehicle comprising water in amount of at least about 3% by weight of said dentifrice, about 0.05-5% by weight of a gelling agent and about 10-50% by weight of a polishing agent comprising a synthetic precipitated, amorphous silica gel having an average particle size of 1 to 30 microns and

a) a surface area of 1 to 600m^2/g,

b) a pore volume of 0.05 to 0.5 cm^3/g,

c) a product of surface area (in m^2/g) x pore volume (in cm^3/g) less than or equal to 240,

d) a calculated pore diameter of 1.5 to 2.5 nm, and

e) a water content of less than 25% by weight;

and with up to about 5% of a water-soluble zinc salt which provides at least about 50 ppm of zinc ions to the said dentifrice.

2. An astringent dentifrice as claimed in Claim 1 in which the said gelling agent is an alkali metal carboxymethyl cellulose gelling agent.

3. An astringent dentifrice as claimed in Claim 1 or Claim 2 which further contains an alkali metal monofluorophosphate in an amount which provides about 0.01-1% fluoride ions.

* C L M S *

4. An astringent dentifrice as claimed in any one of Claims 1 to 3 in which the said zinc salt is present in an amount of 0.01-3% by weight.

5. An astringent dentifrice as claimed in any one of Claims 1 to 4 in which the said zinc salt is zinc sulphate, zinc bromide, zinc iodide, zinc nitrate or zinc acetate or a mixture thereof.

6. An astringent dentifrice as claimed in Claim 5 in which the said zinc salt is zinc sulphate heptahydrate.

7. An astringent dentifrice as claimed in any one of Claims 1 to 5 in which the said zinc salt is or includes zinc chloride.

8. An astringent dentifrice as claimed in any one of Claims 1 to 7 in which the said water in the said liquid vehicle comprises about 3-10% by weight of the said dentifrice.

9. An astringent dentifrice as claimed in any one of Claims 1 to 8 in which the said synthetic amorphous silica gel comprises about 10-40% by weight of the said dentifrice.

10. An astringent dentifrice as claimed in any one of Claims 1 to 7 in which the said water in the said liquid vehicle comprises about 11-50% by weight of said dentifrice.

* C L M S *

11. An astringent dentifrice as claimed in any one of Claims 1 to 10 in which the said synthetic amorphous silica gel is at least one of the synthetic amorphous silica gels having the further characteristics of:

		a	b	c
Average particle size (according to Coulter)	microns	4	7	4
Wet screen residue (42 microns)	%	0.02	0.02	0.02
pH (5% suspension in water)		3	6	6-8
Surface area (B.E.T.)	m^2/g	7	4	7
Loss in drying	%	7	4	7
SiO_2 content (on ignited substance)		96	99	96
Refractive index		1.46	1.46	1.46

12. An astringent gel dentifrice as claimed in any one of Claims 1 to 11 in which the said gelling agent is sodium carboxymethyl cellulose.

13. An astringent dentifrice as claimed in any one of Claims 3 to 12 in which the said alkali metal monofluorophosphate is sodium monofluorophosphate.

14. An astringent dentifrice as claimed in Claim 3 and any one of Claims 4 to 13 when dependent on Claim 3 in which the said water-soluble zinc salt is present in an amount which provides about 1000 ppm



of zinc ions and said alkali metal monofluorophosphate is present in an amount which provides about 1000 ppm of fluoride.

15. An astringent dentifrice as claimed in Claim 14 in which the said zinc salt is zinc sulphate heptahydrate and the said alkali metal monofluorophosphate is sodium monofluorophosphate.

16. An astringent dentifrice as claimed in any one of Claims 1 to 15 in which the said dentifrice also contains about 0.005-0.5% by weight of zinc oxide.

17. An astringent dentifrice as claimed in Claim 1 substantially as specifically described herein with reference to any one of Examples 1A, 1C, 1D, 1E or 1F, or 2A, 2C, 2D, 2E or 2F, 3A, 3B, 3E, 3F, 3G, 3H or 3I, or 4A to 4D, 5A to 5D, 6A to 6D, 7A to 7D, 8A to 8D or 9A to 9D.

18. An astringent dentifrice as claimed in any one of Claims 1 to 17 in which the said dentifrice is packaged in an unlined aluminium tube.