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(54) **Dentifrices containing xanthan gum**

(57) Dentifrice contains polyoxyethylene - polyoxypropylene block copolymer nonionic surface active agent and xanthan gelling agent to provide high foaming, and also contains a liquid humectant vehicle. Foam and mouth feel is improved with poly (ethylene oxide). Poly (ethylene oxide) and siliceous polishing material produce flocculated polishing material which reduces stain formation without raising dentin abrasion. Maltitol is a desirable humectant and provides clarity to dentifrices containing complex alkali metal aluminosilicate polishing agent.

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SPECIFICATION

Dentifrices

The present invention relates to dentifrices and in particular to foaming dentifrices especially dentifrices in which the surface active agent employed is nonionic in nature.

Foam is a desirable characteristic of dentifrices since it spreads the dentifrice throughout the oral cavity during toothbrushing, thereby aiding in bringing the dentifrice into contact with tooth surfaces and providing a characteristic mouth feel.

Foam, particularly full-bodied foam, is generally achieved by the use of an anionic surface active agent. Other surface active agents, and particularly non-ionic surface active agents, typically do not foam as well as the anionic surface active agents. Of the many anionic surface active agents only a few have been used commercially in dentifrices; the most commonly used one being sodium lauryl sulphate.

Anionic surface active agents may cause some mild side effects which some users may find somewhat undesirable. For example some users may experience temporary moderate irritation in the oral cavity, mild bitterness, sloughing of some oral mucosa or an unpleasant flavour reaction when drinking or eating citrus shortly after brushing their teeth, when a dentifrice containing an anionic surface active agent is used.

Although it has been known that surface active properties could be provided to a dentifrice by a nonionic surface active agent, such an agent has not been commonly used since foaming is lost, unless the nonionic has been supplemented with an anionic surface agent.

The present invention aims to provide a dentifrice which is readily extrudible from a toothpaste tube, which contains a nonionic surface active agent and which by use of a particular binding agent achieves improved foaming compared with formulations not containing the binding agent.

The dentifrice of the present invention has the advantages that it is sweet without requiring the presence of a sweetening additive, has less tendency to cause irritation and less tendency to cause users to experience sloughing of oral mucosa or have an adverse citrus flavour reaction after use of the dentifrice.

In accordance with certain of its aspects, this invention relates to a dentifrice comprising about 20-80% by weight of a liquid humectant vehicle, about 0.5-7% by weight of xanthan gum, and about 1-10% by weight of surface active agent which is a nonionic polyoxyethylene - polyoxypropylene block copolymer surface active agent. Preferably up to about 5% by weight of resinous poly (ethylene oxide) is also present.

The nonionic surface active agent employed in the present invention is a block copolymer containing polyoxyethylene and polyoxypropylene. Such block copolymers are available from Wyandotte Chemicals Corporation under the trademark "Pluronic" (Registered Trade Mark). They may be liquids, pastes or solids and are generally chemically defined in terms of the molecular weight of the polyoxypropylene hydrophobic moiety and the percent by weight of the polyoxyethylene hydrophilic moiety. The following block copolymers are available from Wyandotte:

This print takes account of replacement documents later filed to enable the application to comply with the formal requirements of the Patents Rules 1978.

PLURONIC NUMBER	*PHYSICAL CHARACTER*	*HYDROPHIL (polyoxyethylene)*	*MOL. WT. HYDROPHOBE (polyoxypropylene)*
L 121	LIQUID	10	4000
L 101	LIQUID	10	3250
L 81	LIQUID	10	2250
L 61	LIQUID	10	1750
L 31	LIQUID	10	950
L 122	LIQUID	20	4000
L 92	LIQUID	20	2750
L 72	LIQUID	20	2050
L 52	LIQUID	20	1750
L 42	LIQUID	20	1200
P 123	PASTE	30	4000
P 103	PASTE	30	3250
L 63	LIQUID	30	1750
L 43	LIQUID	30	1200
P 104	PASTE	40	3250
P 94	PASTE	40	2750
P 84	PASTE	40	2250
L 64	LIQUID	40	1750
L 44	LIQUID	40	1200
P 105	PASTE	50	3250
P 85	PASTE	50	2250
P 75	PASTE	50	2050
P 65	PASTE	50	1750
L 35	LIQUID	50	950
F 127	SOLID	70	4000
F 87	SOLID	70	2250
F 77	SOLID	70	2050
F 108	SOLID	80	3250
F 98	SOLID	80	2750
F 88	SOLID	80	2250
F 68	SOLID	80	1750
F 38	SOLID	80	950

The preferred nonionic block copolymers are solid (or flake) materials and the most preferred are Pluronic 108 (80% polyoxyethylene: 3250 molecular weight polyxoypropylene) and F 87 (70% polyoxyethylene: 2250 molecular weight polyoxypropylene). The nonionic surface active agent is employed in the dentifrice in an amount of about 1-10% by weight, preferably about 2-5% and most preferably about 3%.

The binding or gelling agent system of xanthan or xanthan and resinous poly (ethylene oxide) cooperates with the nonionic surface active agent to provide stable full-bodied foaming (even though the only surface active agent present is nonionic) and desirable mouth feel characteristics to the dentifrice. Xanthan gum, in the concenrations described, permits a stable full-bodied foam. Moreover, in accordance with a further aspect of this invention, the mouth feel characteristics can be modified as described by the addition of resinous poly (ethylene oxide). The dentifrice has desirable viscosity to permit its extrusion from a dentifrice tube in the form of a ribbon.

Resinous poly (ethylene oxide) has been disclosed as a dentifrice gelling or binding agent in U.S. Patent 2,991,229 to Ivison. Its presence smooths the texture of the dentifrice.

The poly (ethylene oxides) employed in this invention are solid, colourless, water-soluble resins. They appear to form homogeneous systems in water in all proportions, although the relatively higher molecular weight ethylene oxide polymers merely swell on the addition of small amounts of water. On the addition of greater amounts of water, the polymers pass into solution. The water solutions are viscous, the viscosity increasing both with the concentration of the polymer in the solution and the reduced viscosity of the polymer. The ethylene oxide polymers employed in this invention show little change in melting point with increased "reduced viscosity" (an indication of increased molecular weight) and the melting point, as measured by change in stiffness with temperature, was found to be about 65° ± 2°C throughout the range of "reduced viscosities" of from about 1.0 to about 10, and greater. These polymers, upon X-ray examination, disclose a crystalline

structure similar to that exhibited by polyethylene. The crystallization temperature, as determined from measuring the break in the cooling curve, is about 55°C.

To facilitate understanding of the present invention, various terms will be defined. At the outset it should be noted that the work "poly (ethylene oxide)" as used throughout the specification and claims refers to ethylene oxide polymers which have a "reduced viscosity" in acetonitrile of at least 0.5. Preferred are those with a "reduced viscosity" in the range 0.5 to 75.

Unless otherwise stated, the term "reduced viscosity", as used herein, means a value obtained by dividing the specific viscosity by the concentration of the ethylene oxide polymer in the solution, the concentration being measured in grams of polymer per 100 millilitres of solvent at a given temperature, and is regarded as a measure of molecular weight. The specific viscosity is obtained by dividing the difference between the viscosity of the solution and the viscosity of the solvent by the viscosity of the solvent. The "reduced viscosities" herein referred to are measured at a concentration of 0.2 gram of poly (ethylene oxide) in 100 millilitres of acetonitrile at 30°C (unless stated otherwise).

Granular poly (ethylene oxide) results from the suspension polymerization of an agitated reaction mixture comprising ethylene oxide in contact with a polymerization catalyst therefor and in the presence of an inert organic diluent, e.g. heptane, in which ethylene oxide is soluble and the resulting poly (ethylene oxide) is insoluble. Granular poly (ethylene oxide) thus produced is obtained in a finely-divided solid particulate state and resembles finely-divided sand in particle size. Unlike granular poly (ethylene oxide) resulting from the suspension polymerization process, the bulk and solution polymerization processes yield a polymer which is substantially a homogeneous mass either conforming to the shape of the reaction vessel or, after driving off the organic medium, for example, by mechanical extrusion, e.g. Marshall Mill (under vacuum and at slightly elevated temperatures), resembles layers or sheets. This polymer subsequently can be reduced in particle size, for example, by dicing or the like.

The term "granular" refers to the particle size of the ethylene oxide polymers prepared by suspension polymerization. A granular product is one which is in a free-flowing state and comprises particles averaging less than 5 mesh in size (i.e. at least 50% by weight pass 5 mesh) (U.S. Standard Sieve Size which has openings 4 mm across). When present, the poly (ethylene oxide) comprises up to about 5% e.g. 0.05 or 0.1 to 5% by weight of the dentifrice, preferably about 0.1-1.5%.

Xanthan gum is a fermentation product prepared by action of the bacteria of the genus *Xanthomonas* upon carbohydrates. Four species of *Xanthomonas*, viz *X. campetris, X. phaseoli, X. malvocearum,* and *X. carotae* are reported in the literature to the most efficient gum producers. Although the exact chemical structure has not been determined, it is generally accepted to be a heteropolysaccharide with a molecular weight of several million. It contains D-glucose, D-mannose, and D-glucuronic acid in molar ratio of 2.8:3:2.0. The molecule contains 4.7% acetyl and about 3% pyruvate. The proposed chemical structural configuration can be found in McNeeley and Kang, Industrial Gums, ed. R. L. Whistler, CH XXI, 2nd Edition, New York, 1973. The procedure for growing, isolating and purifying the xanthan gum is found in Manufacturing Chemist, May 1960, pages 206-208 (including mentioned at page 208 of potential use of gums therein described for formulating toothpastes).

Use of special grades of xanthan gum, such as described in U.S Patent No. 4,263,399 are within the scope of this invention. A grade described in U.S. Patent No. 4,263,399 is a xanthan gum in which up to about 1.6% of the carboxyl groups are bound to calcium and the remaining carboxyl groups are bound to sodium, potassium, a mixture of sodium and potassium or other non-calcium cations.

The xanthan gelling agent is present in an amount of about 0.5-7% by weight of the dentifrice, preferably about 1.5-3%.

Since the surface active agent used in the present invention is nonionic in nature, the moderate bitterness generally contributed by an anionic surface active agent is not experienced by users. Accordingly, sweetening agents which are often added to dentifrices at least in part to overcome the bitterness, are less needed in the dentifrice of this invention in comparison with prior art practice. Indeed, sufficient satisfactory sweetness can be readily provided by the low sweetening character of many humectants which are commonly employed in dentifrice compositions. Such humectants are part of the liquid phase of the dentifrice, typically together with water. Typical humectants include sorbitol (as 70% aqueous solution), glycerine, maltitol, xylitol, polyethylene glycol 400 and polyethylene glycol 600. The liquid phase comprises about 20-80% by weight of the dentifrice, preferably about 30-60%, with water (if present) typically being in amount up to about 60% and humectant typically being about 20-60%. It is noted that maltitol is disclosed as a dentifrice ingredient in Japanese Patent Publications 73/10241 and 65/15120.

The liquid vehicle and gelling agent and other components of the dentifrice are proportioned to form a cream or gel mass of desired consistency which is extrudible from an aerosol or pump container or a collapsible tube (for example aluminium, lead or plastic).

The dentifrice typically contains a dentally acceptable polishing agent which is generally substantially water-insoluble and of the type commonly employed in dental creams.

Representative polishing agents include, for example, dicalcium phosphate, tricalcium phosphate, insoluble sodium metaphosphate, aluminium hydroxide including hydrated alumina, calcined alumina, colloidal silica, magnesium carbonate, calcium carbonate, calcium pyrophosphate, and bentonite, including suitable mixtures thereof. When employed, it is preferred to use the water-insoluble phosphate salts as the polishing agent and more particularly insoluble sodium metaphosphate and/or

a calcium phosphate such as dicalcium phosphate dihydrate in dental creams. When visually clear gels or opacified gels are employed, a polishing agent consisting of colloidal silica, such as those sold under the trademark Syloid as Syloid 72 and Syloid 74 or under the trademark Santocel as Santocel 100 and synthetic alkali metal aluminosilicate complexes or silica containing combined alumina may be particularly useful. When employed, the polishing agent content is generally in amounts from about 15 to 75% by weight in a dental cream and about 5 to 50% by weight in a clear or opacified gel.

A further aspect of invention is a dentifrice containing a siliceous polishing material, such as those mentioned in the foregoing paragraph and poly (ethylene oxide) as earlier described.

Based upon prior art considerations, as disclosed in U.S Patent 3,020,230 to Smith, wherein silica material is stated to coagulate or flocculate in the presence of resinous poly (ethylene oxide) in order to precipitate it from a liquid suspension, one skilled in the dentifrice art would not have been led to use silica materials in a dentifrice containing resinous poly (ethylene oxide). Indeed, in U.S. Patent 2,991,229 to Ivison, polishing agents or abrasives disclosed in a toothpaste containing poly (ethylene oxide) were "tricalcium phosphate, dicalcium phosphate and calcium carbonate and the like"; but not silica materials.

It is an advantage of this aspect of the present invention that a dentifrice is provided with improved stain removal which has acceptable cosmetic rheology and dentin abrasion characteristics.

It is a further advantage that desirable foaming is achieved with inclusion of polyoxyethylene - polyoxypropylene block copolymer and xanthan in the dentifrice.

According to this aspect of the present invention a dentifrice comprises about 20-80% by weight of a liquid humectant vehicle, about 5-50% by weight of a siliceous polishing material and about 0.05-5% by weight of a resinous poly (ethylene oxide), the said dentifrice containing flocculated particles of the said siliceous polishing agent in the presence of the said poly (ethylene oxide).

As mentioned above, with particular regard to a clear or opacified gel, the proportion of the siliceous polishing agent content is in the range from 5% to 50% by weight of the dentifrice, preferably from 10% to 30% such as from 10% to 25%. One such polishing agent is a complex alkali metal aluminosilicate having a refractive index of from 1.44 to 1.47 and containing at least 70% silica, up to 10% alumina, such as about 0.1-10%, e.g. about 0.1-3%, preferably up to about 20% of moisture, such as about 0.5-10%; and up to about 10% of alkali metal oxide. Typically this material has a particle size in the range of up to about 40 microns, preferably 1 to 4 microns. The preferred moisture content is from 5% to 20% measured by ignition at 1000°C and the typical content of alkali metal is from 5% to 10%.

Generally, the polishing agent has a loose bulk density of up to 0.2 g/cc, such as from 0.07 to 0.12 g/cc. Another suitable type of polishing agent is porous amorphous silicic anhydride having an average particle size preferably below 20 microns and above 1 micron, a surface area of at least 200 m^2/g, preferably at least 300 m^2/g, and a bulk density of at least 0.15 g/cm^3, preferably at least 0.30 g/cm^3, such as a dehydrated silica hydrogel (i.e. a xerogel), preferably of the well known regular density or intermediate density type. Examples of such amorphous silicic anhydride polishing agents are "Syloid 63", "Syloid 72", and "Syloid 74" (SYLOID is a Registered Trade Mark) which are described in "The Davison Family of Syloid Silicas" published by their manufacturer, Grace, Davison Chemical Company. "Santocel 100" of Monsanto (SANTOCEL is a Registered Trade Mark), is also a suitable dental abrasive. "Syloid 72" has an average particle size of about 4 microns, a surface area of about 340 m^2/g, and a bulk density of about 1.77 g/cm^3. For "Syloid 63" the corresponding figures are about 9 microns, about 675 m^2/g and about 0.4 g/cm^3. A grade of "Santocel 100" has a surface area of about 239 m^2/g and a bulk density of about 0.24 g/cm^3. These amorphous silicic anhydrides may be used singly or in mixtures.

As mentioned above, the poly (ethylene oxide) comprises about 0.05-5% by weight of the dentifrice, preferably about 0.1-1.5%.

In the dentifrice, the siliceous polishing agent flocculates *in situ* in the presence of the poly (ethylene oxide). The flocculated particles typically may agglomerate with each other and have apparent particles sizes up to about 250 microns or more, typically about 44 to 177 microns; in other words, the flocculated particles typically pass through a screen of U.S. Sieve No. 80 (which has openings 177 microns across) and are retained on a screen of U.S. Sieve No. 325 (which has openings of 44 microns across).

In spite of the presence of the flocculated particles the dentifrice is readily formulated to have a desirable appearance and rheological texture without undue "lumpy" appearance or "gritty" feel.

The liquid vehicle of the dentifrice of this aspect of the invention may be as indicated above and the components of the dentifrice are again proportioned to form a cream of gel mass of desired consistency which is extrudible from an aerosol or pump container or a collapsible tube (for example aluminium, lead or plastic).

In addition to the resinous poly (ethylene oxide), further gelling or binding agent such as sodium carboxymethyl cellulose, Irish moss, or xanthan gum may be present in amount of about 0.5-7%. Xanthan gum is preferred. The total amount of gelling or binding agent in the dentifrice can be about 0.1-12% by weight.

The dentifrice of this aspect of the invention may contain an anionic, nonionic, cationic or amphoteric surface active agent to achieve increased prophylactic action, assist in achieving thorough and complete dispersion of the compositions of this aspect of the present invention in the oral cavity and to render the compositions more cosmetically acceptable.

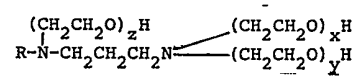
A preferred surface active agent is the nonionic block copolymer containing polyoxyethylene and polyoxypropylene as described above.

Other nonionic surface active agents which may

be employed include condensates of sorbitan monostearate with approximately 20 moles of ethylene oxide. Amphoteric agents include quaternized imidazole derivatives which are available under the trademark "Miranol" (Registered Trade Mark) such as Miranol C_2M.

Suitable types of anionic detergents are water-soluble salts of higher fatty acid monoglyceride monosulphates, such as the sodium salt of the monosulphated monoglyceride of hydrogenated coconut oil fatty acids, higher alkyl sulphates, such as sodium lauryl sulphate, alkyl aryl sulphonates, such as sodium dodecyl benzene sulphonate, olefin sulphonates, such as sodium olefin sulphonate in which the olefin group contains 12-21 carbon atoms, higher alkyl sulphoacetates, higher fatty acid esters of 1,2-dihydroxy propane sulphonate, and the substantially saturated higher aliphatic acyl amides of lower aliphatic amino carboxylic acid compounds, such as those having 12-16 carbons in the fatty acid, alkyl or acyl radicals. Examples of the last mentioned amides are N-lauroyl sarcosine and the sodium, potassium, and ethanolamine salts of N-lauroyl, N-myristoyl or N-palmitoyl sarcosine, which could be substantially free from soap or similar higher fatty acid material which tends to substantially reduce the effect of these compounds. The use of these sarcosine compounds in dentifrice compositions of the present invention is particularly advantageous since these materials exhibit a prolonged and marked effect in the inhibition of acid formation in the oral cavity due to carbohydrates breakdown in addition to exerting some reduction in the solubility of tooth enamel in acid solution.

Cationic surface active germicides and antibacterial compounds such as di-isobutylphenoxyethoxyethyl 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



where 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-acitve materials in the present dentifrice.

Another aspect of invention is dentifrice wherein the humectant present is maltitol and the polishing material is complex alkali metal aluminosilicate. Such dentifrice is visually clear.

In recent years, visually clear dentifrices have been developed which contain a dental cleaning or polishing agent. Such dental cleaning or polishing agents generally have been siliceous in nature with refractive indices of about 1.44-1.47. Use of such materials has permitted preparation of dentifrices in which the refractive index of the liquid vehicle matches that of the siliceous polishing agent. This has been typically accomplished using glycerin and/or sorbitol as humectants in the iiquid vehicle, since glycerin has a refractive index of 1.473 and sorbitol (70% water solution) of 1.460. However, since water has a refractive index of 1.333, only a very little formula water (i.e. separate from that associated with other components such as sorbitol) could be used without substantially reducing the refractive index and causing dimunition in or loss of clarity.

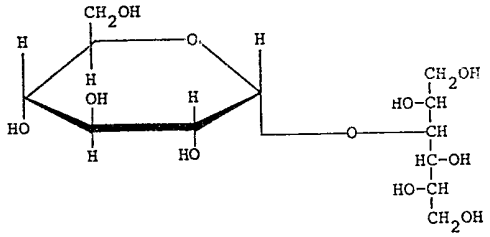
Efforts have been made to develop visually clear dentifrices in which less glycerin and/or sorbitol need be used. For instance: (1) in the U.S. Patent 3,842,167 to Block et al maltodextrin was added as a non-humectant component of the liquid phase to reduce the amount of glycerin and/or sorbitol needed; (2) in U.S Patent 3,927,202 to Harvey et al various phosphate non-siliceous polishing agents were used which permitted modification of the refractive index range of the liquid vehicle; in U.S. Patent 4,007,260 to Kim a silica polishing agent having a refractive index of about 1.410 to 1.440 was used.

It is an advantage of this aspect of the invention that a visually clear dentifrice is provided in which a liquid vehicle is present which comprises a humectant having a refractive index of about 1.48 (e.g. about 1.4750 to about 1.4849) and water.

It is a further advantage that increased free water can be used above that previously used in visually clear dentifrices containing an alkali metal aluminosilicate polishing agent having a refractive index of about 1.44 to about 1.47 and a humectant having a refractive index of about 1.48. The amount of water is not so high as to result in undesirable drying of the dentifrice due to substantial evaporation of water, particularly in view of the presence of maltitol.

In accordance with this aspect of the present invention a visually clear dentifrice contains a vehicle comprising about 0.5-10% by weight of a solid portion of gelling agent and about 50-94.5% by weight of a liquid portion comprising (a) a humectant wherein maltitol of refractive index of about 1.48 is present as the sole or major non-water component of the said liquid vehicle and (b) water in amount to provide a refractive index to the said liquid vehicle of between about 1.44 and about 1.47, the said visually clear dentifrice also containing about 5-50% by weight of a complex alkali metal aluminosilicate polishing agent having a refractive index between about 1.44 to about 1.47.

The liquid portion of the vehicle comprises about 50-94.5% by weight of the visually clear dentifrice, preferably about 55-80%. It contains a humectant which is all or a major amount (i.e. above about 50%) of maltitol. Maltitol is essentially a glycosyl sorbitol, i.e. 4 - D - α - D - glycopyranosyl - D - glucitol, having the structural formula:



It is prepared by hydrogenation of maltose. In substantially pure form it is a glassy solid. It readily dissolves in minor amounts of water and its solutions containing at least about 73% of maltitol and up to about 27% of water are observed to have refractive indices of about 1.48 (i.e. about 1.4750 to 1.4849). When incorporated into a dentifrice together with separately added water of refractive index of about 1.333, the liquid vehicle can be adjusted to provide a refractive index of about 1.44 to about 1.48. Typically, about 5-25% by weight of water can produce such a refractive index, with the lower amounts of water producing a higher refractive index (e.g. about 1.47) and the higher amounts of water (e.g. about 15-23%) producing a lower refractive index (e.g. near 1.44). Preferably, the refractive index of the liquid vehicle is about 1.44 to 1.47 and can be attained with about 5-10% by weight of formula water. The water portion of the dentifrice refers to water which is separately added to that water which is used to dissolve humectant.

Maltitol need not be pure in the sense of being the sugar alcohol derivative of pure maltose. Commercial maltitol consists of maltitol with minor amounts of the sugar alcohols derived from maltotriose, maltotetrose, and related low molecular weight maltodextrin portions of corn syrup and with very small amounts of D-sorbitol. Thus a commercial "hydrogenated starch hydrolysate" made from high maltose content corn syrup would also be useful in the practice of this invention.

Maltitol has been recommended for dentifrice use, albeit not as a principal humectant for visually clear dentifrices containing a polishing agent.

In this regard reference may had to "Caries Research", Vol. 14, Issue 2, (1980) pages 67-74, Rundegren et al (maltitol observed not to contribute to demineralization); "Shigaku", Vol. 60, Issue 6 (1973), pages 760-765, matsuo (maltitol observed not to be fermented by Streptococcus salivarious, S.); "Acta Odont. Scand", Vol 37, Issue 2, (1979) pages 103-115, Birkhed et al and "Caries Research", Vol. 12, Issue 3 (1978), pages 128-136, Birkhed (observations made on plaque) "Acta Odont. Scand, Vol. 35, Issue 5 (1977), pages 257-263, Edwardsson et al (observations made on oral bacteria); Japanese Patent Publication 73 10241 of Sunstar (describing maltitol as a mouthwash component). Further, maltitol may be a component of a variant of sorbitol known as "non-crystallizing sorbitol", which may be used as a dentifrice humectant. However, the substantial content of sorbitol in non-crystallizing sorbitol is such that a refractive index of about 1.48 is not achieved, thereby reducing ones ability to vary the water-humectant vehicle formulation as compared to the degree of variation which the present invention makes possible. It is also noted that fatty acid esters of maltitol and other sugar alcohols are disclosed as dentifrice taste components in British Patent Specification 2,038,182 of Lion Dentrifrice Company.

If desired, the liquid vehicle of the visually clear dentifrice of the present invention may be a minor amount (i.e. less than about 50%) of a humectant in addition to maltitol or even a non-humectant liquid vehicle component such as maltodextrin. Humectants such as indicated earlier, for instance glycerine, sorbitol (typically 70% solution of sorbitol), polyethylene glycol 400, polyethylene glycol 600, and the like may be used. Preferably, maltitol comprises above about 50% by weight of the non-water portion of the liquid vehicle, preferably about 65-100%. Maltitol is typically provided in about 73-85% solution and is available from suppliers including Aldrich Chemical Company, Merck and Co. Inc., Imperial Chemicals Industries, Pfizer Inc., Lonza, Roquette Freres, and Hayashibara Chemical Laboratories.

The solid portion of the vehicle is a gelling agent, such as indicated earlier, for instance the natural and synthetic gums and gum-like materials, such as Irish Moss, alkali metal (e.g. sodium) carboxymethyl cellulose and xanthan as well as gum tragacanth, hydroxymethyl carboxymethyl cellulose, polyvinyl pyrrolidone, starch, guar gum, sodium alginate, hydrophilic colloidal carboxyvinyl polymers, such as those sold under the trademark Carbopol (Registered Trade Mark) 934 and 940 and synthetic inorganic silicated clays such as those sold under the trademark LAPONITE (Registered Trade Mark) CP and LAPONITE SP. These grades of LAPONITE have the formula $(Si_8Mg_{5.1}Li_{0.6}H_{7.6}O_{24})^{0.6-}Na^{0.6+}$. The solid portion of the vehicle is typically present in amount up to about 10% by weight of the dentifrice and preferably about 0.25-5% by weight. When employed, grades of LAPONITE are typically used in amounts of about 1-5% by weight.

The complex alkali metal aluminosilicate salt is as described above. It is typically alkaline in nature, typically a sodium salt, and effectively promotes oral hygiene. It is an amorphous powder which further has the property that when incorporated in the vehicle the particles thereof become substantially invisible.

The amount of alumina in the aluminosilicate is typically about 0.1-3% by weight and preferably about 1%. Desirably the refractive index of the aluminosilicate is within about 0.005 units, typically within about 0.001 of that of the liquid vehicle.

As mentioned, the polishing agent typically comprises about 5-50% by weight of the dentifrice formulation, preferably about 10-30% by weight.

The complex alkali metal aluminosilicate salt appears to contain interbonded silica and alumina having Al–O–Si bonds as described by Temele "Chemistry of the Surface and the Activity of Alumina-Silica Cracking Catalyst", Discussions of the Faraday Society, No. 8, Pages 270-279 (1950) and particularly at page 273, Figure 1, curve 3, wherein the interaction between silica and aluminium ions is potentiometrically detected. Further literature describing this type of complex includes Milliken et al, "The Chemical Characteristics and Structures of

Cracking Catalysts", Discussion of the Faraday Society, No. 8, pages 279-290 (1950) and particularly the sentence bridging pages 284-285. These complexes clearly differ from silica gel as is described by Plank et al. "Differences Between Silica and Silica-Alumina Gels I. Factors Affecting the Porous Structure of These Gels," Journal of Colloid Science, 2, pages 399-412 (1947) and Plank, "Differences Between Silica and Silica-Alumina Gels II. A Proposed Mechanism for the Gelation and Syneresis of These Gels," Journal of Colloid Science 2, pages 413-427, (1947) in which formation of the Al–O–Si bond is described at pages 419-422. The aluminosilicate may be described as silica containing combined alumina.

As above mentioned, maltitol was disclosed for use in dentifrices in Japanese Patent Publications 115120/65 (Patent No. 461,281) and 73/10241. In the former, siliceous polishing agent is not disclosed; in the latter silici anhydride is mentioned as a polishing agent. However, it has been found that when silici anhydride, such as colloidal silica xerogel available from Grace Davison as SYLOID (Registered Trade Mark) 74 is employed in a visually clear dentifrice containing maltitol, the dentifrice quickly becomes dull in appearance and dries when exposed to air to become a hardened opacified product. When the complex aluminosilicate of the present invention is employed the dentifrice substantially retains its desirable clear appearance and rheology.

Organic surface-active agents may be used in the compositions of this aspect of the present invention to achieve increased prophylactic action, assist in achieving thorough and complete dispersion of the compositions of the present invention throughout the oral cavity, and render the compositions more cosmetically acceptable. The organic surface active material may be anionic, nonionic, ampholytic, or cationic in nature as indicated above, and it is desirable to employ as the surface active agent a detersive material which imparts to the composition detersive and foaming properties.

An alkali metal fluorine-providing compound may be employed in the dentifrices described herein. Suitable alkali metal fluorine-providing compounds includes sodium fluoride, stannous fluoride, stannous chlorofluoride, potassium stannous fluoride (SnF_2-KF), lithium fluoride, ammonium fluoride and complex fluorides, such as potassium fluorozirconate, sodium hexafluoro stannate and alkali metal monofluorophosphates. These compounds have a beneficial effect on the care and hygiene of the oral cavity, e.g. diminution of enamel solubility in acid and protection of the teeth against decay, and exhibit satisfactory retentions of soluble fluoride in dentifrices of the present invention. In particular, the level of retention of monofluorophosphate ion as fluoride with the alkali metal monofluorophosphates is quite high. The fluorine-containing compound is employed in an amount which provides an effective non-toxic amount of fluorine-containing ion to the dentifrice typically about 0.01-1% by weight preferably about 0.1% fluorine. Thus, sodium fluoride is typically employed in amount of about 0.02-2% by weight, preferably about 0.2%, and sodium monofluorophosphate, Na_2PO_3F, in amount of about 0.1-7.6% by weight, preferably about 0.76%.

The alkali metal monofluorophosphates which may be employed include sodium monofluorophosphate, lithium monofluorophosphate, potassium monofluorophosphate and ammonium monofluorophosphate. The preferred salt is sodium monofluorophosphate, Na_2PO_3F, which, 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 about 80%. For best results, it should be at least 85%, 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, water-soluble sodium phosphate salt, and the like. Expressed in another way, the sodium monofluorophosphate employed should have a total fluoride content of about 12%, preferably about 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 fluorine.

Other monofluorophosphate salts which may be used in the present invention include monofluoropolyphosphates such as $Na_4P_3O_9F$, $K_4P_3O_9F$, $(NH_4)_4P_3O_9F$, $Na_3KP_3O_9F$, $(NH_4)_3NaP_3O_9F$ and $Li_4P_3O_9F$.

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 including the flavouring oils, e.g., oils of spearmint, peppermint, wintergreen, sassafras, clove, sage, eucalyptus, marjoram, cinnamon, lemon and orange, as well as methylsalicylate. Suitable sweetening agents include, sucrose, lactose, maltose, sorbitol, sodium cyclamate, perillartine and saccharine. Suitably, falvour and sweetening agents may together comprise form about 0.01% to 5% or more of the compositions of the present invention. Chloroform may also be used. Sweetening agents are less necessary when no anionic surface active agent is present, since anionic surface active agents contribute slight bitterness to the dentifrice.

Antibacterial agents may be employed in the dentifrice of the present invention in an amount of about 0.01 to 5% by weight. Typical antibacterial agents include:

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

P-chlorophenyl biguanide;

4-chlorobenzhydryl biguanide;

4-chlorobenzhydrylguanylurea;

N - 3 - lauroxypropyl - N^5 - p - chlorobenzyl-biguanide;

1,6 - di - p - chlorophenylbiguanidohexane;

1,6 - bis (2 - ethylhexylbiguanido) hexane;

1 - (lauryldimethylammonium) - 8 - (p - chlorbenzyldimethylammonium) octane dichloride;

5,6 - dichloro - 2 - guanidobenzimidazole;

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

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

and their non-toxid acid addition salts.

Various other materials may be incorporated in the preparations of this invention. Examples thereof are colouring or whitening agents or dyestuffs, preservatives, silicones, chlorophyll compounds, ammoniated materials such as urea, diammonium-phosphate and mixtures thereof, and other constituents. Adjuvants may be incorporated in the compositions of the present invention in amounts which do not substantially adversely affect the properties and characteristics desired and are selected and used in proper amounts depending upon the particular type of preparation involved.

Synthetic finely divided pyrogenic silicas such as those sold under the trademarks CAB-O-SIL (Registered Trade Mark) M-5, SYLOID (Registered Trade Mark) 244, SYLOID 266 and AEROSIL (Registered Trade Mark) D-200 may also be employed in amounts of about 1-5% by weight to promote thickening or gelling of the described dentifrice.

The dentifrices should have a pH practicable for use. A moderately acid to alkaline pH is preferred.

The present 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 1 and 2

The following opacified gel dentifrices were prepared.

	EXAMPLES	
	1	*2*
Glycerine	10.0	10.0
Maltitol	15.0	15.0
Sodium aluminosilicate (silica combined with about 1% combined alumina) Zeo 49B (Huber)	18.0	18.0
PLURONIC 108 block copolymer	–	3.0
Sodium lauryl sulphate	1.0	–
Xanthan	2.0	2.0
POLYOX WSR 301	0.2	0.2
Sodium monofluorophosphate	0.76	0.76
Titanium dioxide	0.4	0.4
Low menthol flavour	–	0.5
Peppermint oil flavour	0.5	–
Sodium saccharin	0.2	–
Colour solution (1%)	0.05	0.05
Water	Q.S. to 100	Q.S. to 100

The silica with combined alumina indicated as Zeo 49 in the Examples was obtained from the J. M. Huber, Corp. of Havre de Grace, Maryland, as Zeo 49 (A or B).

The dentifrice of Example 1 with sodium lauryl sulphate had desirable foam character. The dentifrice of Example 2 also had very good stable full-bodied foam character even though no anionic surface active agent was employed. The foam remained throughout the oral cavity, with desirable mouth feel, when the dentifrice was brushed onto the teeth. Moreover, it had no bitter note even though low menthol flavour was present and no sweetener was added. The dentifrices had fine smooth texture and appearance, effectively removed stain and had acceptable dentin abrasion character. They contained flocculated particles of sodium aluminosilicate.

EXAMPLE 3

Similar desirable results were obtained when the xanthan of Example 2 was replaced with the low-calcium xanthan of Example 1 of U.S. Patent 4,263,399.

EXAMPLE 4

Similar foam and feel was attained when other block copolymers of polyoxyethylene and polyoxypropylene replace PLURONIC F-108, particularly PLURONIC F 87.

POLYOX WSR-301 is available from Union Carbide Corp. as granules of water soluble poly (ethylene oxide) resin having a molecular weight of about 4,000,000 and a Brookfield viscosity of 1650-3850 cps. (25°C, spindle 1, speed 2 rpm) when in water at 1% by weight.

EXAMPLES 5 to 10

Likewise, similar foam and feel was attained when other water-soluble poly (ethylene oxide) resins available from Union Carbide Corp. such as POLYOX WSR-N-10, WSR-N-80, WSR-N-750, WSR-N-3000, WSR-205 and WSR-1105 replaced POLYOX WSR-301, in different concentrations.

EXAMPLES 11 to 14

The following clear gel (Examples 11 and 12) and opacified gel (Examples 13 and 14) dentifrices were prepared:

EXAMPLE	*11*	*12*	*13*	*14*
Glycerine	10.0	–	10.0	–
Sorbitol	16.0	–	15.0	–
Maltitol (Active)	16.0	35.0	15.0	30.0
Sodium alumino-silicate silica with combined alumina) (1)	22.0	18.0	18.0	18.0
PLURONIC F-108	3.0	3.0	5.0	–
PLURONIC F-87	–	–	–	3.0
Xanthan	1.5	2.0	2.0	2.0
POLYOX WSR-301	0.2	0.2	0.2	0.2
Sodium mono-fluorophosphate	0.76	0.76	0.76	0.76
Titanium dioxide	–	–	0.4	0.4
Low menthol flavour	0.5	0.5	0.5	0.5
Colour solution (1%)	0.05	0.05	0.05	0.05
Water	Q.S. to 100	Q.S. to 100	Q.S. to 100	Q.S. to 100

Notes

(1) Zeo 49A was used for Examples 11 and 12; Zeo 49B for Examples 13 and 14.

The dentifrices of Examples 11 and 12 were clear and those of Examples 13 and 14 were opacified. They had smooth texture. All four had very good stable full-bodied foam, with that of the dentifrice of Example 13 being more full than with the dentifrices

of Examples 11 and 12. A higher amount of foam occurred with the dentifrice of Example 14. All foams provided desirable mouth feel throught the entire oral cavity during toothbrushing. There were no bitter notes. The dentifrices effectively removed stain and had acceptable dentin abrasion. They contained flocculated particles of sodium aluminosilicate.

EXAMPLES 15 to 19

The following dentifrices were prepared:

EXAMPLE	*15*	*16*	*17*	*18*	*19*
Maltitol (ACTIVE)	30.0	30.0	30.0	30.0	30.0
Sodium aluminosilicate (silica with combined alumina) Zeo 49B	12.0	12.0	12.0	18.0	15.0
Calcined alumina	5.0	5.0	5.0	5.0	2.0
PLURONIC F-108	3.0	3.0	3.0	3.0	3.0
Xanthan	2.0	2.0	2.0	1.7	2.0
POLYOX WSR-301	0.2	–	–	0.2	0.2
WSR-1105	–	0.2	–	–	–
WSR-N-750	–	–	1.0	–	–
Sodium monofluorophosphate	0.76	0.76	0.76	0.76	0.76
Titanium dioxide	0.4	0.4	0.4	0.4	0.4
Low menthol flavour	0.5	0.5	0.5	0.5	0.5
Water	Q.S. to 100	Q.S. to 100	Q.S. to 100	Q.S. to 100	Q.S. to 100

The dentifrices of Examples 15 to 19 provided high cleaning effectiveness and had good, stable, full-bodied foam. They had smooth textures, with the dentifrices of Examples 15, 18 and 19 containing POLYOX WSR-301 having the best texture. All foamed to provide desirable mouth feel throughout the entire oral cavity during toothbrushing. There were no bitter notes. They effectively removed stain and had acceptable dentin abrasion. They contained flocculated particles of sodium aluminosilicate.

EXAMPLES 20 to 23

The following dentifrices were prepared:

EXAMPLE	*20*	*21*	*22*	*23*
Glycerine	10.0	10.0	10.0	10.0
Sorbitol	15.0	15.0	15.0	15.0
Maltitol (Active)	15.0	15.0	15.0	15.0
Dicalcium phosphate dihydrate	30.0	30.0	15.0	15.0
Anhydrous dicalcium phosphate	–	–	10.0	–
Calcined alumina	–	–	–	10.0
PLURONIC F-108	3.0	3.0	3.0	3.0
Xanthan	2.0	2.0	2.0	2.0
POLYOX WSR-301	–	0.2	0.2	0.2
Sodium mono-fluorophosphate	0.76	0.76	0.76	0.76
Titanium dioxide	0.4	0.4	0.4	0.4
Low menthol flavour	0.5	0.5	0.5	0.5
Water	Q.S. to 100	Q.S. to 100	Q.S. to 100	Q.S. to 100

The dentifrices of Examples 20 to 23 provided good, stable full-bodied foam. Those of Examples 21 to 23 (which contained the POLYOX material) had particularly fine, smooth texture. The foam from all these examples gave desirable mouth feel throughout the oral cavity during toothbrushing. Even though no sweetener was used, the dentifrices were quite sweet in taste.

EXAMPLES 24 and 25

The following opacified gel dentifrices were prepared:

	PARTS	
EXAMPLE	*24*	*25*
Maltitol (75% solution)	40.00	40.00
Sodium aluminosilicate (silica containing about 1% combined alumina) – Zeo 49B-Huber	18.00	18.00
PLURONIC F 108 Block Copolymer	3.00	3.00
Xanthan	1.70	1.70
POLYOX WSR 301 (Union Carbide)	0.20	–
Titanium dioxide	0.40	0.40
Flavour	0.50	0.50
Sodium saccharin	0.20	0.20
Deionized water	Q.S. to 100	Q.S. to 100

Both dentifrices provided stable full-bodied foam with good mouth feel; the mouth feel of dentifrice 24 being particularly satisfactory.

The dentifrices of Examples 24 and 25 were compared for ability to remove dental stain and for dentin abrasion, and the results are given in Table 1 below. The dentifrice of Example 24 containing the POLYOX material removed more stain with less dentin abrasion than the dentifrice of Example 25, without POLYOX material. In the dentifrice of Example 25, flocculated particles of sodium aluminosilicate form *in situ*.

TABLE 1

DENTIFRICE EXAMPLE	*PERCENT STAIN REMOVAL*	*RADIOACTIVE DENTIN ABRASION*
24	35	14
25	22	39

The stain removal test used was as follows:

Sections of human dental enamel were etched with 0.1N hydrochloric acid (HCl) for 2 minutes, rinsed with water, then wet with a dilute solution of stannous fluoride, wiped dry, and finally exposed to a stream of hydrogen sulphide gas which resulted in the deposition of a brown deposit of stannous sulphide. The amount of stain on the surface was measured with a Gardner Automatic Colour Difference meter. The surface was then brushed with a mechanical brushing machine for 500 reciprocal strokes with a slurry of a dentifrice and the residual stain measured with the meter. Finally, the stain which remained was completely removed with dental pumice and the reflectance of this surface was read. The ability of a dentifrice to remove the stain is expressed by the following equation:

$$\text{Percent Stain removed} = \frac{(Rd_{500\ \text{strokes}} - Rd_{\text{initial}})\ 100}{Rd_{\text{pumiced}} - Rd_{\text{initial}}}$$

where Rd_{initial}, $Rd_{500\ \text{strokes}}$, and Rd_{pumiced} are respectively the reflectance values measured on the initially stained surface, the surface after brushing for 500 reciprocal strokes and the surface after removing the residual stain by pumicing.

The radioactive dentine abrasion (RDA) values were obtained by a procedure based on a radioactive technique described in the literature; Stookey, C. K. and Muhler, J. C., J. Dental Research *47* 524-538 (1968).

EXAMPLE 26

The following dentifrice was prepared and compared with the dentifrice of Example 18.

	PARTS
Maltitol (75% solution)	40.00 (30.00 active)
Sodium aluminosilicate (silica containing about 1% combined alumina) Zeo 49B – Huber	18.00
Calcined alumina	5.00
PLURONIC F-108	3.00
Xanthan	1.70
Titanium dioxide	0.40
Flavour	0.50
Sodium saccharin	0.10
Deionized water	Q.S. to 100

The dentifrices of Examples 18 and 26 both provided stable full-bodied foam with good mouth feel; the mouth feel of the dentifrice of Example 18 being particularly satisfactory.

Stain removal and radioactive dentin abrasion results were carried out using the procedure described for Table 1 on the dentifrices of Examples 18 and 26 and the results are given in Table 2 below. The results indicate the superiority of the dentifrice of Example 18 containing the POLYOX material showing higher stain removal with similar dentin abrasion.

TABLE 2

DENTIFRICE EXAMPLE	*PERCENT STAIN REMOVAL*	*RDA*
18	65	47
26	44	41

EXAMPLES 27 and 28

The following dentifrices were prepared;

	PARTS	
EXAMPLE	*27*	*28*
Maltitol (80%)	59.0	59.0
Deionized water	10.74	10.74
Sodium monofluorophosphate	0.76	0.76
Sodium saccharine	0.25	0.25
Sodium carboxymethyl chloride	0.35	0.35
Polyethylene glycol (CARBOWAX (Registered Trade Mark) 600)	3.0	3.0
Silica xerogel (SYLOID (Registered Trade Mark) 74)	18.0	–
Sodium aluminosilicate (silica containing about 1% combined alumina)– Zeo 49B–Huber	–	18.0
Sodium lauryl sulphate	1.2	1.2
Flavour	1.2	1.2

The refractive index of SYLOID (Registered Trade Mark) 74 in the dentifrice of Example 27 and Zeo 49B in the dentifrice of Example 28 is within about 0.005 units of that of the liquid vehicle of each dentifrice.

Each of the dentifrices is initially shiny and clear. However, after one week at room temperature, the dentifrice of Example 27, containing silica xerogel, becomes dull in appearance and upon being left exposed to air becomes opaque white-like colour and quite hard. Under these same conditions, the dentifrice of Example 28 remains shiny and clear and continues to have desirable flow characteristics.

EXAMPLES 29 to 31

The following visually clear dentifrices were prepared in which the refractive index of the polishing agent is within 0.005 unit of that of the liquid vehicle.

EXAMPLE	PARTS 29	30	31
Maltitol (73%)	62.0	–	–
Maltitol (80%)	–	60.0	48.0
Deionized water	7.24	16.6	22.6
Sodium monofluorophosphate	0.76	0.76	0.76
Sodium saccharin	0.25	0.24	0.24
Sodium benzoate	0.50	–	–
Sodium carboxymethyl cellulose	0.35	0.4	–
Xanthan	–	–	1.4
Polyethylene glycol (CARBOWAX (Registered Trade Mark) 600)	3.00	–	–
Sodium aluminosilicate (silica containing about 1% combined alumina) Zeo 49A in Example 29 and Zeo 49B in Examples 30 and 31–Huber	18.00	20.00	20.00
Silica thickener (SYLOID (Registered Trade Mark) 244)	5.50	–	–
sodium lauryl sulphate	1.20	1.20	1.20
Flavour	1.20	0.80	0.80

CLAIMS

1. A dentifrice comprising about 20-80% by weight of a liquid humectant vehicle, about 0.5-7% by weight of xanthan gum and about 1-10% by weight of a surface active agent, the said surface active agent being a nonionic polyoxyethylene - polyoxypropylene block copolymer surface active agent.

2. A dentifrice as claimed in Claim 1 in which resinous poly (ethylene oxide) is present in an amount of about 0.05-5% by weight.

3. A dentifrice as claimed in Claim 2 in which about 0.1-1.5% by weight of the said resinous poly (ethylene oxide) is present.

4. A dentifrice as claimed in Claim 1, 2 or 3 in which the said block copolymer is a solid material.

5. A dentifrice as claimed in Claim 4 in which the said solid block copolymer contains about 80% by weight polyoxyethylene and the molecular weight of the said polyoxypropylene is about 3250.

6. A dentifrice as claimed in Claim 4 in which the said solid block copolymer contains about 70% polyoxyethylene and the molecular weight of said polyoxypropylene is about 2250.

7. A dentifrice as claimed in any one of Claims 1 to 6 in which about 1.5 to 3.0% by weight of xanthan gum is present.

8. A dentifrice as claimed in any one of Claims 1 to 7 which contains a siliceous polishing material.

9. A dentifrice as claimed in Claim 8 which contains about 5 to 50% by weight of the siliceous polishing material.

10. A dentifrice as claimed in Claim 8 or Claim 9 in which the said siliceous polishing material is a complex alkali metal aluminosilicate.

11. A dentifrice as claimed in any one of Claims 1 to 7 in which the said liquid humectant vehicle comprises glycerine, sorbitol, maltitol or a mixture thereof.

12. A dentifrice as claimed in any one of Claims 1 to 11 in which maltitol is present as humectant.

13. A dentifrice as claimed in any one of Claims 1 to 12 which contains maltitol as humectant and 5-50% by weight of a complex alkali metal aluminosilicate polishing agent and is visually clear.

14. A dentifrice containing a siliceous polishing agent and poly (ethylene oxide) as defined herein.

15. A dentifrice comprising about 20-80% by weight of a liquid humectant vehicle, about 5-50% by weight of a siliceous polishing material and about 0.05-5% by weight of a resinous poly (ethylene oxide), the said dentifrice containing flocculated particles formed by the said siliceous polishing material in the presence of the said poly (ethylene oxide).

16. A dentifrice as claimed in any one of Claims 1 to 15 which contains resinous poly (ethylene oxide) having a reduced viscosity of at least 0.5 as measured at a concentration of 0.2 gram of the said poly (ethylene oxide) in 100 millilitres of acetonitrile at 30°C.

17. A dentifrice as claimed in Claim 14, 15 or 16 in which the said resinous poly (ethylene oxide) is present in amount of about 0.1-1.5% by weight.

18. A dentifrice as claimed in any one of Claims 14 to 17 in which the siliceous polishing material is a complex alkali metal aluminosilicate having a refractive index of from 1.44 to 1.47.

19. A dentifrice as claimed in Claim 18 in which the said alkali metal aluminosilicate is sodium aluminosilicate wherein silica is combined with about 0.1-3% alumina.

20. A dentifrice as claimed in any one of Claims 15 to 19 the said flocculated particles having an apparent particle size of about 44 to 177 microns.

21. A dentifrice as claimed in any one of Claims 14 to 20 in which maltitol is present as humectant.

22. A dentifrice containing a siliceous polishing agent and maltitol as humectant.

23. A dentifrice containing a vehicle comprising about 0.5-10% by weight of a solid portion of gelling agent and about 50-94.5% by weight of a liquid portion comprising (a) a humectant wherein maltitol of refractive index of about 1.48 is present as the sole or major non-water component of the said liquid vehicle and (b) water in amount to provide a refractive index to the said liquid vehicle of between about 1.44 and about 1.47, the said dentifrice also containing about 5-50% by weight of a complex alkali metal aluminosilicate polishing agent having a refractive index between about 1.44 to about 1.47, the said dentifrice being visually clear.

24. A dentifrice as claimed in any one of Claims 1 to 23 containing maltitol present in aqueous solution containing at least about 73% by weight of maltitol.

25. A dentifrice as claimed in Claim 24 in which maltitol is present in aqueous solution containing about 73-85% by weight of maltitol.

26. A dentifrice as claimed in any one of claims 23 to 25 in which the maltitol solution comprises about 65-100% by weight of the non-water portion of the said liquid vehicle and the water portion of the said liquid vehicle comprises about 5-25% by weight of the said dentifrice, the water in the said water portion being separately added to that water which

is used to dissolve the humectant.

27. A dentifrice as claimed in any one of Claims 22 to 26 in which the alkali metal aluminosilicate is sodium aluminosilicate.

28. A dentifrice as claimed in Claim 27 in which the said sodium aluminosilicate contains about 0.1-3% alumina in combination with silica.

29. A dentifrice as claimed in any one of Claims 1 to 28 containing sodium aluminosilicate which contains about 1% alumina in combination with silica.

30. A visually clear dentifrice as claimed in any one of Claims 22 to 29 in which the refractive index of the said alkali metal aluminosilicate is within 0.005 units of that of the said liquid vehicle.

31. A dentifrice as claimed in Claim 1, Claim 15 or Claim 23 substantially as specifically described herein with reference to the accompanying Examples.

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