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STABLE FLAVOUR-CONTAINING DENTIFRICE

The present invention relates to reduction of migration and absorption of flavour from a dentifrice into plastic packaging materials, by including in the dentifrice polyvinyl pyrrolidone additive in small amounts, by forming a combination of flavour oil and PVP prior to its addition to the dentifrice.

5. The use of polyvinyl pyrrolidone (PVP) in dentifrice compositions as a thickener and binder is well known in the prior art as disclosed in U.S. patent no. 4,307,076 in an amount of at least 3% by weight; in U.S. patent no. 3,429,963, no. 3,970,747, no. 3,120,469 and no. 4,223,003 as one of several gelling agents, and in U.S. patent no. 4,376,762 as the water soluble binder in combination with a water insoluble binder in providing visible speckles in dentifrices.

10. Polyvinylpyrrolidone has also been used as an anti-staining agent in chlorophyll-containing dentifrice compositions as disclosed in U.S. patent no. 2,783,182, and British patents nos. 739,936 and 741,315.

15. However, the use of PVP in amounts representing 5% to 50% by weight of the total flavour oils, in combination with flavour oils, in dentifrice compositions, to minimise flavour loss in plastic packages has not been disclosed in the prior art.

20. It has unexpectedly been found that dentifrice compositions comprising flavour oil in combination with PVP has the unique property of reducing flavour migration and absorption into plastic packaging materials.

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The present invention aims to provide a flavour-containing dentifrice composition which reduces the migration and absorption of flavour into plastic packing material.

5. The present invention also aims to provide a flavour-stabilised dentifrice composition containing a flavour oil in combination with 5% to 50% PVP by weight of the total flavour oils.

10. The present invention also aims to provide a plastic-packaged flavour oil-containing dentifrice stabilised against flavour loss, containing about 12% PVP by weight of the total flavour oils, which minimises contact and migration of the flavour onto the inner surfaces of the package.

15. The present invention also aims to provide a dentifrice in paste, gel or cream form containing flavour oils in combination with 5% to 50% PVP by weight of the flavour oils.

20. A dentifrice according to the present invention, which has improved stability against flavour loss into plastic package components, comprises a premixed coacervate of flavour oils in combination with 5.0%-50% PVP by weight of the total flavour oils dispersed in a dental vehicle, preferably with the flavour oil colloiddally bound with the PVP. The composition may be in the form of a paste, gel, or cream dentifrice formulation.

25. More specifically, the present invention relates to a plastic-packaged composition stabilised against flavour loss, the composition comprising the
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- combination of a flavour oil and about 12.0% PVP by weight of the total flavour oils in the form of a premix, dispersed in a dental vehicle. This premix is preferably added to the dentifrice formulation as
5. a final step.

- The use of plastic laminate tubes and plastic pump dispensers in toothpaste packaging has resulted in a problem not usually encountered with metal packages, the absorption of dentifrice flavour
10. components into the plastic packaging materials. Manufacturers of dentifrice packages have attempted to minimise flavour absorption by using less permeable plastic packaging compositions wherever possible, but design and engineering constraints
15. prohibit the development of packages that are totally immune to flavour absorption. At least one toothpaste manufacturer has increased the level of flavour in their products, at extra cost, to make up for the flavour lost in the plastic package. An
20. ideal remedy for flavour absorption into plastic would be to tie up the flavour oil chemically in the toothpaste formulation to minimise contact and migration of the flavour onto the inner surfaces of the package.
25. It has now been found that the flavour loss from a plastic-packaged dentifrice is reduced when polyvinyl pyrrolidone is combined with the dentifrice flavour oil and said combination is incorporated into the dentifrice composition, preferably as the final
30. step in the formulation of the dentifrice.

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An experiment was conducted to determine the effect on flavour emulsification in a conventional toothpaste formula when the flavour oil is first gelled with PVP. The formula aqueous phase

5. consisting of water, glycerine, sodium MFP (mono-fluorophosphate), tetra sodium pyrophosphate, sodium benzoate and sodium lauryl sulphate was prepared and divided into two equal parts. Flavour oil was added to one part (0.84% level on a finished formula basis)
10. and the same flavour oil gelled with 0.1% PVP (representing 12.0% of the flavour oils) was added to the other part, both under moderate agitation. After standing for a few hours, the flavour oil gelled with 0.1% PVP, separated from the aqueous phase and formed
15. a distinct top layer while the unmodified flavour oil remained well dispersed. PVP remains bound with the flavour oil, instead of becoming solubilised into the aqueous phase. It became apparent that flavour oil tied up with PVP may reduce flavour migration/
20. sorption into plastic. Although the PVP/flavour oil gel separates in the aqueous phase, when the remaining formula components consisting of conventional gum binders and abrasives, are added to complete the dentifrice composition, the PVP/flavour
25. oil gel remains evenly dispersed in the compositions.

- The PVP used in the present invention may be of any molecular weight grade or physical form. PVP is a water soluble polymerised N-vinyl-pyrrolidone to any desired molecular weight or degree of polymer-
30. isation, having an average molecular weight from

- about 5,000 to approximately 1,000,000. It is conventionally in the form of a solid powder or flake, but can also be supplied in an aqueous solution. Although the PVP may be of any molecular weight, it is preferable to use high molecular weight PVP, above 50,000 and preferably within the range of about 60,000 to approximately 1,000,000. It is soluble in cold water and in a variety of organic alcohols, acids, ether-alcohols, ketone-alcohols, chlorinated hydrocarbons, esters and ketones; but is insoluble in hydrocarbons, flavour oils and some ethers, chlorinated hydrocarbons, ketones and esters. The amount of PVP utilised to tie up the flavour oil may be within the range of 5.0% to 50.0% by weight of the flavour oils and preferably about 12.0% by weight of the flavour oils. Although the exact nature of the mechanism by which the PVP ties up the flavour oil is not known, it is believed to form a coacervate with the flavour oil, i.e. an aggregate of colloidal droplets held together by electrostatic forces. This resembles a gel in appearance, but is not a true gel. However, the combination of flavour oil and PVP will be referred to as a gel. The formation of a coacervate of PVP and flavour oils is unexpected and unique. The preference of the PVP to combine with the flavour oils instead of dissolving in the aqueous medium is unexpected, because of the insolubility of the PVP in flavour oils, which presupposes no interaction therebetween.

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The invention extends to a coacervate useful in dental compositions of flavour oil and 5 to 50% by weight of polyvinyl pyrrolidone based on the total weight of flavour oils.

5. Any suitable flavour oil or mixture thereof may be used in the present invention. Examples of flavour oils include oils of spearmint, peppermint, wintergreen, sassafras, clove, sage, eucalyptus, marjoram, cinnamon, lemon and orange, and mixtures thereof e.g. preferably a mixture of oil of
10. peppermint and oil of spearmint. The flavouring oils are water-insoluble and are emulsified into the dentifrice formulation under moderate agitation in amounts of 0.01 to 5% by weight and preferably about
15. 0.5-3% by weight.

The dental base or vehicle utilised in the present invention may be in the form of a paste or gel, comprising known ingredients used conventionally in the dentifrice art.

20. Paste or gel dentifrices may be based on aqueous or substantially non-aqueous systems. The former will usually include substantial proportions of finely divided, solid polishing agent, surface active agent, gelling agent and some non-aqueous vehicle,
25. e.g., glycerol, sorbitol, and will be opaque, whereas the latter type will often be a clear gel, containing a minor proportion of a visually clear particulate solid polishing agent, a larger proportion of non-aqueous vehicle, surface active agent and gelling
30. agent, with a minor proportion of water often being present.

The surface active agent, or detergent, present

- in the dentifrice may sometimes be cationic or amphoteric but will usually be anionic or nonionic. Of these compounds, the anionics are the most preferred. The anionic detergents or surface active agents also usually serve as foaming agents. Among the useful anionic detergent may be mentioned the higher fatty acid monoglyceride monosulphates, such as the sodium salts of the monosulphated monoglycerides of hydrogenated coconut oil fatty acid; higher alkyl sulphates, such as sodium lauryl sulphates; higher alkyl aryl sulphonates, such as sodium linear dodecyl benzene sulphonates; higher olefin sulphonates, such as sodium higher olefin sulphonates in which the olefin group is 12 to 21 carbon atoms; higher alkyl potassium sulphoacetates; higher fatty acid esters of 1,2-dihydroxypropane sulphonates, magnesium salt; the substantially saturated higher aliphatic acyl amides of lower aliphatic aminocarboxylic acid alkali metal salts, such as those having 12 to 16 carbon atoms in the fatty acyl radicals, higher alkyl poly-lower alkoxy (of 10 to 100 alkoxies) sodium sulphates; higher fatty acid sodium and potassium soaps of coconut oil and tallow, and the like. As is noted, most frequently the detergents are sulphated or sulphonated compounds. Examples of useful anionic amides which may be employed are N-lauroyl sarcosine and the sodium, potassium and ethanolamine salts of N-lauroyl-, N-myristoyl, and M-palmitoyl sarcosines. In the above descriptions, "higher" refers to chain

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lengths of 12 to 22 carbon atoms, preferably of 12 to 18 carbon atoms and most preferably of 12 to 16 carbon atoms. Lower means 2 to 4 carbon atoms, preferably 2 to 3 carbon atoms, and most preferably, 2 carbon atoms.

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The nonionic detergents include those containing chains of lower alkylene oxide, e.g. ethylene oxide, propylene oxide, in which there are present from 10 to 100 or more moles of lower alkylene oxide. Among such materials are the block co-polymers of ethylene oxide, propylene oxide and propylene glycol, sold under the mark Pluronic (Registered Trade Mark); the alkyl phenyl polyethoxy ethanols, sold as Igepals; mixed co-polymers of ethylene oxide and propylene oxide, sold under the mark Ucon (Registered Trade Mark); and various other well known nonionics derived from fatty alcohols or acids and polyethylene oxide.

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The amphoteric or ampholytic agents include long chain (alkyl) amido-alkylene-alkalated amine derivatives, such as "Miranol", e.g. Miranol (Registered Trade Mark) C₂M; and cationic germidical detergents, such as diisobutylphenoxyethoxyethyl dimethyl benzyl ammonium chloride, benzyl dimethyl stearyl ammonium chloride; and tertiary amines having a higher fatty alkyl group and two polyoxyethylene groups attached to the nitrogen thereof.

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The detergents constitute about 0.5-5% and preferably up to 3% by weight of the dentifrice composition.

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Toothpastes, and dental gels contain conventionally substantially water insoluble polishing agents or abrasives which are compatible

with the formulation, in amounts from about 15-75% by weight of the total gel or paste formulation.

- Suitable polishing agents include anhydrous dicalcium phosphate, dicalcium phosphate dihydrate, tricalcium phosphate, insoluble sodium metaphosphate, crystalline silica, colloidal silica, complex aluminosilicates, aluminium hydroxide (including alumina trihydrate or hydrated alumina), magnesium phosphate, magnesium carbonate, calcium carbonate, calcium pyrophosphate, bentonite, talc, calcium silicate, calcium aluminate, aluminium oxide, aluminium silicate, and silica xerogels. Most of the polishing agents mentioned are most useful in the preparation of opaque dentifrices but some of them, such as colloidal silicas, especially the silica xerogels which include a low combined alumina content, and complex sodium aluminosilicates, may be utilised in the manufacture of clear gel dentifrices, because their indexes of refraction approximate those of the rest of the dentifrice constituents in an appropriate vehicle.

- The invention also extends to a dentifrice containing silica or silicious materials and a premix of flavour oil and PVP or a coacervate of flavour oil and 5 to 50% by weight PVP based on the total weight of flavour oils.

- In dental gel or toothpaste dentifrice formulations, the liquids and solids should necessarily be proportioned to form a creamy mass of desired consistency, which for example is extrudable from a collapsible laminate tube or pump dispenser. In

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5. general, the liquids in the dental gel or toothpaste will comprise chiefly water, glycerine, sorbitol, polyethylene glycol, or propylene glycol 400, including suitable mixtures thereof. It is advantageous usually to use a mixture of both water, and a humectant such as glycerine, or sorbitol or mixtures thereof. The total liquid content will generally be about 20-75% by weight of the
10. formulation. It is preferred to use also a gelling agent in dental creams such as the natural and synthetic gum-like materials, e.g. Irish Moss, gum tragacanth, sodium carboxymethylcellulose, polyvinylpyrrolidone, xanthan gum, or starch. Irish Moss and sodium carboxymethylcellulose, are compatible
15. particularly and are preferred gelling agents. The gum content is usually in an amount up to about 10% and preferably about 0.3-5% by weight of the formulation. Fillers such as pyrogenic silica and silica aerogel may also be used, typically in amounts
20. up to about 10% by weight to supplement the gelling agent. These colloidal silica aerogels which include Syloids 244 and 266 and Aerosil (Registered Trade Mark) and the pyrogenic silica sold as Cab-O-Sil (Registered Trade Mark) may be used as gelling and
25. thickening agents.

- Various other materials may also be incorporated into the dental vehicle. Examples thereof are
30. fluorine-containing compounds such as stannous fluoride, potassium stannous fluoride (SnF_2KP), sodium hexafluorostannate, stannous chlorofluoride, sodium fluorozirconate and sodium monofluoro-

- phosphate. These materials, which dissociate or release fluorine-containing ions in water, may be present in the dental vehicle in an effective, but nontoxic amount, usually within the range of about
5. 0.1-5% by weight. Other additives include preservatives such as sodium benzoate, chlorophyll compounds, silicones, ammoniated materials such as urea and diammonium phosphate, antibacterial agents such as benzethonium chloride and other quaternary
 10. antibacterial compounds, sweeteners such as sodium saccharin, colouring. These additives may be used in amounts which do not adversely affect the properties and characteristics of the dentifrice in accordance with the present invention. Each constituent may be
 15. present in minimal amounts of up to a maximum of 5% by weight and preferably up to 1% by weight of the formulation.

- The dentifrice of the present invention is prepared by methods of making toothpaste, and dental
20. creams. More specifically, a toothpaste may be prepared by forming a gel with carboxymethylcellulose and water, adding thereto with mixing the powdered materials and humectant, followed by the addition with mixing of polishing agent and then the
 25. surfactant, and then the flavour oil premixed with the PVP, and tubing the final mixture or packaging in plastic material.

- In the practice of this invention to promote oral hygiene, the dentifrice according to this
30. invention is applied regularly to dental enamel by

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brushing the teeth for 30-90 seconds at least once daily.

The invention may be put into practice in various ways and a number of specific embodiments will be

5. described to illustrate the invention with reference to the accompanying examples. The compositions are prepared in the usual manner and all amounts and proportions referred to herein and in the appended claims are by weight unless otherwise specified. The
10. flavour oil is admixed with the PVP prior to the addition of this gelled combination to the dentifrice formula

Examples 1 and 2

Toothpaste

Table 1

15.	<u>Ingredient</u>	<u>Ex. 1</u>	<u>Ex. 2</u>
		%	%
	Deionised water	24.49	24.39
	Glycerine (99.5%)	22.00	22.00
20.	Sodium Monofluorophosphate	0.76	0.76
	Carboxymethylcellulose 7MF	1.00	1.00
	Tetrasodium Pyrophosphate	0.25	0.25
	Sodium saccharin	0.20	0.20
	Sodium benzoate	0.50	0.50
25.	Sodium lauryl sulphate	1.20	1.20
	Dicalcium phosphate dihydrate	48.76	48.76
	Flavour ¹	0.84	0.84
	Polyvinylpyrrolidone ²	-----	0.10

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Notes on Table 1

- 1 Consisting predominantly of oil of peppermint, oil of spearmint, menthol.
- 2 Luviskol K-90, BASF, Inc., Average M.W. greater
5. than 1,000,000

- The effect on flavour absorption into plastic between unmodified flavour oil and flavour oil gelled with 0.1% PVP in a toothpaste based on dicalcium phosphate dihydrate as abrasive/polishing component was measured instrumentally on a gas chromatograph. One method measures the quantity of flavour released into the headspace of a toothpaste package; and another method measures the quantity of flavour absorbed by a section of a laminate toothpaste tube.
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- The quantity of flavour released into the headspace of a toothpaste package measured 2.96 ± 0.11 G.C. units of flavour for Example 1, and 2.74 ± 0.08 G.C. units for Example 2 (0.1% PVP). These results are statistically significantly different at the 99% confidence level.
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- Example 2 with 0.1% PVP inhibits the release of flavour from the dentifrice into a laminate tube by 16%, which is significant at the 95% confidence level, when compared to Example 1 without PVP.
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Examples 3 to 6Dentifrice Gel

<u>Ingredient</u>		<u>Ex. 3</u>	<u>Ex. 4</u>	<u>Ex. 5</u>	<u>Ex. 6</u>
	Sorbitol (70%)	41.49	41.39	41.10	41.00
5.	Glycerine	25.0	25.0	18.0	18.0
	Silica containing low combined alumina	18.0	18.0	18.0	18.0
	Silica thickener	5.5	5.5	5.5	5.5
	Polyethylene glycol 600	3.0	3.0	3.0	3.0
10.	Deionised water	3.0	3.0	3.0	3.0
	Sodium lauryl sulphate	1.2	1.2	1.2	1.2
<u>Ingredient</u>		<u>Ex. 3</u>	<u>Ex. 4</u>	<u>Ex. 5</u>	<u>Ex. 6</u>
	Sodium monofluoro- phosphate	0.76	0.76	0.76	0.76
15.	Flavour ³	0.69	0.69	-----	-----
	Sodium benzoate	0.50	0.50	0.50	0.50
	Sodium carboxymethyl cellulose	0.35	0.35	0.35	0.35
	Sodium saccharin	0.30	0.30	0.20	0.20
20.	FD&C Blue #1 (1% aqueous)	0.20	0.20	-----	-----
	Titanium dioxide	0.01	0.01	0.5	0.5
	Polyvinylpyrrolidone	-----	0.10	-----	0.10
	Flavour ¹	-----	-----	0.89	0.89

25. Notes on Table 3

1 See note 1 on Table 1

3 Consisting predominantly of oil of spearmint, oil of peppermint, anethole.

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- Each of the silica abrasive gel formulae was evaluated in aluminum tubes, laminate tubes and pump dispensers under accelerated conditions. After nine weeks of aging no form of separation/leakage was seen in the PVP formulae while the formulae without PVP exhibited clip and cap wet in the tubes and piston wetness or button wetness in the dispenser. It appears that by tying up the flavour oil, the reaction that causes separation/leakage of silica formulae, as well as flavour loss in the laminate tubes and pump dispensers is significantly decreased.

- This unique combination of flavour oil and PVP has the unexpected ability of reducing flavour loss into plastic package components, as well as reducing separation/leakage of silica formulae in tubes and dispensers.

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CLAIMS

1. A coacervate useful in dental compositions of flavour oil and 5 to 50% by weight of polyvinylpyrrolidone based on the total weight of flavour oils.

2. A composition as claimed in Claim 1, in which the polyvinylpyrrolidone has an average molecular weight of 5,000 to approximately 1,000,000.

3. A composition as claimed in Claim 1, in which the polyvinylpyrrolidone has an average molecular weight of about 60,000 to approximately 1,000,000.

4. A composition as claimed in Claim 1, 2 or 3, in which the polyvinylpyrrolidone constitutes about 12.0% by weight of the flavour oils.

5. A dentifrice composition having improved stability against flavour loss into plastic package components comprising a premix of flavour oil with 5% to 50% by weight of the total flavour oils of polyvinylpyrrolidone dispersed in a dental vehicle.

6. A dentifrice composition as claimed in Claim 5 in which the premix of flavour oil and 5 to 50% by weight of polyvinylpyrrolidone based on the total weight of flavour oils, is a coacervate.



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7. A dentifrice composition as claimed in Claim 6 in which the flavour oil is colloiddally bound with the polyvinylpyrrolidone.

5. 8. A dentifrice as claimed in Claim 5, 6 or 7 in which the flavour oil constitutes about 0.5-3.0% by weight of the composition.

10. 9. A dentifrice as claimed in Claim 5, 6, 7 or 8, in which the polyvinylpyrrolidone has an average molecular weight of 5,000 to approximately 1,000,000.

15. 10. A dentifrice as claimed in any one of Claims 5 to 9, in which the polyvinylpyrrolidone has an average molecular weight of about 60,000 to approximately 1,000,000.

20. 11. A dentifrice as claimed in any one of Claims 5 to 10, in which the polyvinylpyrrolidone constitutes about 12.0% by weight of the flavour oils.

25. 12. A dentifrice as claimed in any one of Claims 5 to 11, which is in the form of a toothpaste containing 15-75% by weight of a water insoluble polishing agent.

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13. A dentifrice as claimed in any one of Claims 5 to 11, which is in the form of a dental gel containing 15-75% by weight of water insoluble polishing agent.

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14. A dentifrice as claimed in any one of Claims 5 to 13, containing 0.5-5% by weight of surfactant.

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15. A dentifrice as claimed in any one of Claims 5 to 14, containing a liquid content of 20-75% by weight of the composition.

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16. A toothpaste as claimed in any one of Claims 12 or 14 or 15 when appendant to Claim 12, in which the said polishing agent is dicalcium phosphate dihydrate.

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17. A dental gel as claimed in any one of Claims 13 or 14 or 15 when appendant to Claim 13, in which the said polishing agent is silica containing combined alumina.

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18. A dentifrice as claimed in any one of Claims 5 to 17, containing 0.1-5% by weight of a fluorine-containing compound capable of releasing fluoride ions in water.

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19. A dentifrice as claimed in any one of Claims 5 to 18, in which the said flavour oil comprises a mixture of oil of peppermint and oil of spearmint.

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20. A dentifrice as claimed in Claim 5 substantially as specifically described herein with reference to the Examples.

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21. A method of preparing a dentifrice as claimed in any one of Claims 5 to 20, which comprises admixing the flavour oil and the polyvinylpyrrolidone to form a premix, followed by admixing the said premix with the other formula components, and tubing or packaging the final mixture in plastic material.

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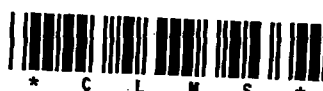
22. A method as claimed in Claim 21, in which the said plastic material is a collapsible laminate tube.

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23. A method as claimed in Claim 21, in which the said plastic material is a pump dispenser.

24. A plastic packaged dentifrice composition having improved stability against flavour loss into plastic package components comprising a premix of flavour oil with about 5-50% by weight of the total flavour oils of polyvinylpyrrolidone, dispersed in a dental vehicle.

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25. A plastic packaged dentifrice as claimed in Claim 24, in which the said plastic package is a collapsible laminate tube.

5. 26. A plastic packaged dentifrice as claimed in Claim 23, in which the said plastic package is a pump dispenser.

10. 27. A dentifrice containing silica or silicious materials and a premixed coacervate of flavour oil and PVP.

15. 28. A dentifrice containing silica or silicious materials and a premix of flavour oil and PVP or a coacervate as claimed in any one of Claims 1 to 4.

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