

STABLE ANTIPLAQUE DENTIFRICE WITH IMPROVED
FOAMING AND FLUORIDE STABILITY

- The present invention relates to an antiplaque
5. dentifrice containing a quaternary active ingredient and at least 1.5% and up to 2% betaine surfactant by weight, such as cocoamidopropylbetaine, lauramido-propylbetaine or cocobetaine, which enhances foaming and does not inactivate the antibacterial activity
 10. of the quaternary compound. Nonionic surfactants fail to afford sufficient foaming, and nonionic surfactants inactivate the quaternary antibacterial activity. Carbowax 600 (polyethylene glycol) and/or sorbitol replace propylene glycol and glycerin as humectant
 15. in order to afford stability to the betaine-containing composition. Also, carboxymethyl cellulose is preferably avoided because large organic molecules deactivate the quaternary compound. Nonionic gums such as hydroxy-ethylcellulose are used as gelling/thickening agent
 20. for the dental cream. More specifically, this composition is free of anionic and nonionic surfactants and contains only a minimal amount of glycerin, 1-10% and preferably 5-7% by weight as a fluoride stabiliser (when a fluoride compound is used) in a sole poly-
 25. ethylene glycol humectant-containing composition.

It has been found that the addition of a betaine surfactant to an antiplaque dental formulation based on quaternary active ingredients, improves the foaming characteristics thereof, without deactivating the

30. quaternary antimicrobial activity. It has additionally

- been found that humectants other than glycerin are required in the betaine system to effect cosmetic stability, specifically polyethylene glycol and/or sorbitol. The limitation of the gelling/thickening agent to nonionic gums such as hydroxyethylcellulose is also a necessary expedient.

- The ability of quaternary ammonium compounds to inhibit the formation of dental plaque is well documented. These compounds, however, present a problem when formulated in a dentifrice in that they are deactivated by traditional anionic surfactants such as sodium lauryl sulphate. Stable, clinically effective dental formulations have been made with quaternary ammonium compounds and nonionic surfactants but these formulations are very poor foamers and result in inferior products. Compositions containing anti-plaque quaternary ammonium compounds and nonionic surfactants are disclosed in U.S. Patents Nos. 4,080,441, 4,110,429, 4,118,472, 4,118,473, 4,118,475, 4,118,476 and British Patent No. 1,573,356.

- U.S. Patent No. 4,161,518 discloses a dentifrice composition for inhibiting plaque formation containing 0.05-1% by weight of a quaternary ammonium organosiloxane as the active antibacterial agent in a suitable vehicle containing suitable polishing agents, fluoride compounds, anionic surfactants, flavouring and sweetening agents, thickening agents such as carboxymethylcellulose, humectants such as glycerin, sorbitol and other polyhydric alcohols.

- U.S. Patent No. 3,988,435 discloses pharma-

ceutical compositions including a dentifrice containing a quaternary ammonium dihydrochalcone glucoside as the antibacterial agent having a sweet taste, as well as abrasives, surfactants including nonionics and

5. "derivatives of fatty amines with betaine structures," swelling, gelling or thickening agents such as hydroxy-alkylcellulose particularly hydroxyethylcellulose, polyethylene glycols, polypropylene glycols, etc., humectants such as sorbitol, mannitol, glycerin,
10. propylene glycol, colourants, and flavours.

- All of aforesaid cited patents simply list the conventional additives useful in dentifrice compositions. There is no disclosure of the use of the betaine as the exclusive surfactant in the production
15. of a high foaming dentifrice. There is also no disclosure nor recognition of the necessity to limit the humectant to polyethylene glycol and/or sorbitol, and the thickening agent to nonionic gums such as hydroxyethylcellulose, in order to obtain a cosmeti-
 20. cally stable dentifrice in a betaine-quaternary ammonium system.

- U.S. Patent No. 4,363,795 and its counterpart International Patent Publication No. WO 80/00057 to Wahlstam disclose a cleaning agent for dentine sur-
25. faces containing a quaternary ammonium compound, an ampholytic tenside which may be an imidazoline or a betaine and a sequestering agent of the aminocarboxylic acid type which has a synergistic effect as to the antibacterial properties of the treating
 30. solution. All the Examples are in the form of

cleaning solutions. There is no mention of dental creams, nor the use of humectants and thickening agents.

- U.S. Patent No. 4,130,637 discloses a specific group of betaine compounds, or a mixture of the said
5. betaine and its corresponding carboxylic acid quaternary ammonium salt in a 9:1 ratio, as non-staining anti-microbial antiplaque agents in a dentifrice vehicle containing the aforelisted conventional humectants and gelling agents, and a nonionic surfactant. This patent
10. fails to disclose the necessity of using a betaine surfactant exclusively, the specific nonionic gelling agent hydroxyethylcellulose and the specific humectant polyethylene glycol and/or sorbitol, in order to obtain a stable, high foaming quaternary-containing antiplaque
15. dentifrice.

- U.S. Patent Nos. 4,117,107 and 4,117,108 also disclose a specific group of betaine compounds and their salts as antiplaque agents in a dentifrice vehicle containing the conventional humectants and
20. gelling agents, as well as anionic/nonionic surfactants. There is no disclosure of an antibacterial quaternary ammonium compound, and a betaine surfactant exclusively. There is also no recognition of the specificity of humectant and gelling agent and the exclusion
25. of anionic/nonionic surfactants in a quaternary-betaine system, which is necessary in order to obtain a stable high foaming antiplaque dentifrice.

- Thus, none of the above cited prior art discloses a cosmetically stable antiplaque dentifrice
30. with improved foaming and fluoride stability containing

as the essential ingredients a cationic quaternary ammonium antiplaque compound, a zwitterionic betaine surfactant, a humectant compatible with the cationic antiplaque agent selected from the group consisting of polyethylene glycol and sorbitol, and the nonionic gelling agent hydroxyethylcellulose, in an aqueous vehicle containing a dental abrasive. Nor is there a prior art disclosure of the sorbitol humectant improving long term fluoride stability, nor the combination of small amounts of glycerin in a polyethylene glycol humectant improving long term fluoride stability.

We have now found that dental cream formulations containing antiplaque quaternary ammonium compounds may be stabilised and provide better foaming when betaine type surfactants replace the traditional anionic and nonionic surfactants. Humectants such as polyethylene glycol and sorbitol must replace the conventional glycerin for better cosmetic stability of the product. However, a small amount of glycerin may be used to chemically stabilise the fluoride-containing compound in a sole polyethylene glycol humectant. Nonionic gums such as hydroxyethylcellulose replace the anionic carboxymethylcellulose gelling agent which also has the potential to deactivate the quaternary compound.

The present invention aims to provide a better foaming antiplaque dentifrice based on quaternary active ingredients by the incorporation of a zwitterionic betaine surfactant as the foaming agent.

The present invention also aims to provide a cosmetically stable foaming antiplaque dentifrice

containing polyethylene glycol and/or sorbitol as humectant which is compatible with the betaine and the quaternary active ingredients.

5. This invention also aims to provide a stable foaming antiplaque dentifrice containing the nonionic gum, hydroxyethylcellulose, as gelling agent to stabilise the betaine quaternary ammonium system and to prevent deactivation of the quaternary active ingredient by the anionic sites in molecules of
10. carboxymethylcellulose.

- This invention also aims to provide a cosmetic (physical) and chemically stable foaming antiplaque dentifrice containing a fluoride-providing compound and sorbitol or minimal amounts of glycerin, (1-10% by weight) as stabilising agents for the fluoride-providing compound, without adversely affecting cosmetic stability of the dentifrice.
- 15.

- According to the present invention a stable antiplaque dentifrice with improved foaming which
20. is free of nonionic and anionic surfactants, comprises as the essential ingredients, an effective amount of an antiplaque quaternary ammonium compound, at least 1.5% by weight of a betaine surfactant, the betaine surfactant being the sole surfactant species, a
25. humectant selected from the group consisting of polyethylene glycol, sorbitol and mixtures thereof, a nonionic gelling agent such as hydroxyethylcellulose and preferably a fluoride-providing compound, in an aqueous vehicle containing a dental abrasive.
30. More specifically, the present invention relates to a stable antiplaque dentifrice formulation with improved foaming and fluoride stability which is free

- of nonionic and anionic surfactants, comprising an effective antimicrobial amount of a quaternary ammonium compound, at least 1.5% by weight e.g. about 1.5-2% by weight of a betaine surfactant, preferably about 0.05-2% by weight of a fluoride-providing compound, and sorbitol or 1 to 10% by weight of glycerine as a stabilizer for the fluoride providing compound, preferably about 20-30% by weight of a humectant selected from the group consisting of polyethylene glycol, sorbitol and mixtures thereof, and a nonionic gelling agent, e.g. about 0.5-2% by weight of hydroxyethylcellulose, preferably in an aqueous vehicle containing about 40-60% by weight of water-insoluble dental abrasive. The sorbitol component, which stabilises the betaine-quaternary ammonium system, also improves the long term fluoride chemical stability of the dentifrice. When the sole humectant is polyethylene glycol, a small amount of glycerin, as low as 1%, may be utilised to improve long term fluoride stability, without adversely affecting the cosmetic stability of the dentifrice.

- Cationic antibacterial materials are well known in the art. See, for instance, the section on "Quaternary Ammonium and Related Compounds" in the article on "Antiseptics and Disinfectants" in Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition (Volume 2, pages 632-635), incorporated herein by reference. Cationic materials which possess antibacterial activity (i.e. are germicides) are used against bacteria and have been used in oral composi-

7a.

tions to counter plaque formation caused by bacteria in the oral cavity.

- Among the most common of these antibacterial antiplaque quaternary ammonium compounds is benzethonium chloride, also known as Hyamine 1622 or
5. diisobutylphenoxyethoxyethyl dimethyl benzyl ammonium

- chloride, and cetyl pyridinium chloride. In an oral preparation this material is highly effective in promoting oral hygiene by reducing formation of dental plaque and calculus, which is generally accompanied
5. by a reduction in periodontal diseases. Other cationic antibacterial agents of this type are those mentioned; for instance, in U.S. Patent Nos. 2,984,639, 3,325,402, 3,431,208 and 3,703,583 and British Patent No. 1,319,396.
 10. Other antibacterial antiplaque quaternary ammonium compounds include those in which one or two of the substituents on the quaternary nitrogen has a carbon chain length (typically an alkyl group) of some 8 to 20, typically 10 to 18, carbon atoms while the
 15. remaining substituents have a lower number of carbon atoms (typically an alkyl or benzyl group), such as 1 to 7 carbon atoms, typically methyl or ethyl groups. Dodecyl trimethyl ammonium bromide, benzyl dimethyl stearyl ammonium chloride, cetyl pyridinium chloride
 20. and quaternised 5-amino-1,3-bis (2-ethylhexyl)-5-methyl hexa hydro-pyrimidine are typical quaternary ammonium antibacterial agents.

- The dentifrice formulations of the present invention contain an effective amount of the anti-
25. plaque quaternary ammonium compound, preferably about 0.01-5%, and most preferably 0.025-1% by weight of the composition.

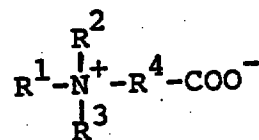
- The ability of quaternary ammonium compounds to inhibit the formation of dental plaque is well known.
30. However, they are deactivated by the anionic surfactants such as sodium lauryl sulphate conventionally used in dentifrice formulations. The substitution of nonionic surfactants for the anionic surfactants eliminates the

deactivation problem but results in products with poor foaming.

5. The incorporation of betaine surfactants into antiplaque dental formulations based on quaternary active ingredients unexpectedly improves the foaming of these formulations without deactivating the quaternary antibacterial agents.

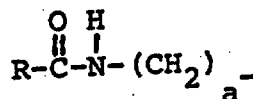
The betaine component of present dentifrice composition preferably has the general formula:

10.



15. wherein R^1 represents an alkyl group having 10 to about 20 carbon atoms, preferably 12 to 16 carbon atoms or the amido radical:

20.



wherein R represents an alkyl group having about 10 to 20 carbon atoms and a is the integer 1 to 3; R^2 and R^3 each represent an alkyl group having 1 to

25. 3 carbon atoms and preferably 1 carbon atom; R^4 represents an alkylene or hydroxyalkylene group having from 1 to 4 carbon atoms and, optionally, one hydroxyl group. Typical alkyldimethyl betaines include decyl betaine or 2-(N-decyl-N,N-dimethylammonio) acetate,
30. coco betaine or 2-(N-coco-N,N-dimethylammonio) acetate,

myristyl betaine, palmityl betaine, lauryl betaine, cetyl betaine and stearyl betaine. The amidobetaines similarly include cocoamidoethyl betaine, cocoamidopropyl betaine and lauramidopropyl betaine.

5. The betaines, which are zwitterionic materials, function as a foaming agent in the quaternary-containing dentifrice compositions of the present invention. They act cationically over a wide pH range, but do not deactivate the quaternary antimicrobial activity. This is shown by in vitro tests using wool swatches, which simulate human skin and oral tissue, as the absorptive material in the Red 80 Stain test, J. Soc. Cosmet, Chem. 31, 271-278 (Sept., Oct. 1980). Wool has the same type of absorptive properties as oral tissue due to similar isoelectric and isoionic points.

- Using the Red 80 Dye Test, the following experiment illustrates that the betaine surfactant does not deactivate the quaternary. The Red 80 Stain Test was performed using a solution of cocoamidopropyl betaine alone, benzethonium chloride alone, and a mixture of cocoamidopropylbetaine and benzethonium chloride. The degree of staining of the wool swatches treated with benzethonium chloride alone and the mixture of benzethonium chloride and betaine was nearly equal, and both were stained darker than the cocoamidopropyl betaine treated swatch. This indicates that benzethonium chloride is a "stronger" cationic compound than the betaine i.e. it has a greater attraction to the wool than the betaine, indicating that the betaine
- 20.
 - 25.
 - 30.

does not deactivate the benzethonium chloride.

5. However, wool swatches treated with a mixture of benzethonium chloride and the anionic surfactant, sodium lauryl sulphate, exhibit no staining (no red colour retention) indicating complete deactivation of the benzethonium chloride by the anionic surfactant.

10. The degree of staining of the wool swatches treated with a mixture of benzethonium chloride and the nonionic surfactant, polyoxyethylene (20 moles ethylene oxide) sorbitan di-iso stearate, was substantially equal to that of the benzethonium chloride alone. This indicates that the benzethonium chloride is not deactivated by the nonionic surfactant.

15. In addition to the non-interference exhibited by the betaines with the quaternary activity, laboratory foam tests have shown that formulations containing both the quaternary ammonium compound and the betaine, foam 2 to 3 times better than the nonionic quaternary ammonium formulations. The foam index for nonionic
20. quaternary ammonium compositions is about 20, whereas the foam index for betaine quaternary ammonium compositions is about 40-60. The foam test used herein comprises placing 1 gram of the test dentifrice in 10 ml of 175 PPM water at 90°F (32°C) in a 100 ml
25. graduated cylinder, shaking for 15 seconds and reading the foam height.

30. The zwitterionic betaines are completely compatible with the quaternary antimicrobial antiplaque agents, and impart deterative and improved foaming properties to the quaternary-containing dentifrice

- composition without deactivating the antimicrobial properties thereof. The amount of betaine effective in the production of improved foaming may be varied from about 1.5-2% active ingredient by weight of the
5. total formulation. Greater amounts of betaine adversely affect the taste of the dentifrice.

- Cosmetic problems of stability are incurred with all zwitterionic-containing dentifrices, such as crimp leakage of flavour. The flavour oozes and is
10. not solubilised in the zwitterionic surfactant.

- Accordingly, in order to effect cosmetic (physical) stability of the betaine system, a specific group of humectants which includes polyethylene glycol, sorbitol or mixtures thereof must be used.
15. Glycerin and propylene glycol alone provide insufficient cosmetic stability to the betaine system. The humectant system constitutes about 20-30% by weight and preferably 20-25% by weight of the dentifrice and is selected from the group consisting of polyethylene glycol, sorbitol and mixtures thereof.
20. thereof.

- Another essential ingredient in dentifrice compositions of the present invention is a gelling agent which is a nonionic gum, in an amount up to
25. 5% by weight and preferably about 0.5-2%. It has been found that large organic anionic molecules such as carboxymethylcellulose have the potential to deactivate the quaternary antibacterial activity. Accordingly, hydroxyethylcellulose, which is a
30. nonionic small organic molecule, effects a stable

pituitous gel in the betaine quaternary ammonium system of the present invention, and is the preferred gelling agent. Other nonionic gelling agents may be used such as hydroxymethylcellulose.

5. It has been found that only by utilising the specific combination of ingredients of betaine, polyethylene glycol and/or sorbitol humectant and nonionic gelling agent, can a stable antiplaque dentifrice with improved foaming based on the quaternary antibacterial compounds, be obtained.

10. The fluoride-providing compounds, which are preferably additional ingredients in dentifrice compositions of the present invention, are characterised by their ability to release fluoride ions in water and by
15. substantial freedom from reaction with other compounds of the dentifrice. Among these materials are inorganic fluoride salts, such as soluble alkali metal, alkaline earth metal and heavy metal salts, for example, sodium fluoride, potassium fluoride, ammonium fluoride, lead
20. fluoride, a copper fluoride such as cuprous fluoride, zinc fluoride, a tin fluoride such as stannic fluoride or stannous chlorofluoride, barium fluoride, sodium fluorosilicate, ammonium fluorosilicate, sodium fluorozirconate, sodium monofluorophosphate, aluminium
25. mono- and di-fluorophosphate, and fluorinated sodium calcium pyrophosphate. Alkali metal and tin fluorides, such as sodium and stannous fluorides, sodium mono-fluorophosphate and mixtures thereof, are preferred.

30. The amount of the fluoride-providing compound is dependent to some extent, upon the type of compound,

- its solubility, and the dentifrice, but it must be a nontoxic amount. In a solid oral preparation, such as a toothpaste or dental cream, an amount of such compound which releases a maximum of 1% by weight of the preparation is considered satisfactory. Any suitable minimum amount of such compound may be used, but it is preferable to employ sufficient compound to release from 0.005% to 1%, and preferably about 0.1% of fluoride ion. Typically, in the cases of alkali metal fluorides and stannous fluoride, this component is present in an amount up to 2% by weight, based on the weight of the preparation, and preferably in the range of from 0.05% to 1%. In the case of sodium monofluorophosphate, the compound may be present in an amount up to 7.6% by weight, more typically 0.76%.

- It has additionally be found that the long term chemical fluoride stability in a sorbitol based humectant or a mixed surfactant system containing polyethylene glycol and at least 5% sorbitol is markedly improved over a polyethylene glycol based humectant, wherein its fluoride stability is marginal but acceptable. However, the use of small amounts of glycerin, about 1-10% and preferably 5-7% by weight in a polyethylene glycol based humectant markedly improved long term fluoride stability without adversely affecting the cosmetic stability of present dentifrice formulation. The glycerin component herein functions as, and is used as a chemical stabiliser for the fluoride ingredient only when polyethylene glycol is used as the sole humectant.

- Based on the three week results of the 120°F (49°C) aging study, 5% glycerin improves the fluoride stability 25% without adversely affecting cosmetic stability. The mechanistic reason why the presence of some glycerin improves the fluoride stability is unclear. Fluoride stability data after 12 weeks at 100°F (37°C) further confirms the significant improvement with the use of small amounts of glycerin in the dentifrice. Table 1 clearly shows this improved fluoride stability in a polyethylene glycol humectant system.

TABLE 1

		Soluble Fluoride Content				
15.	Glycerin: Polyethylene Glycol	Initial	3 wks @ 100°F	6 wks @ 100°F	9 wks @ 100°F	12 wks @ 100°F
	0:20	0.093	0.077	0.068	0.063	0.057
	1:19	0.088	0.081	0.074	0.066	0.066
20.	3:17	0.093	0.082	0.074	0.069	0.067
	5:15	0.093	0.081	0.077	0.071	0.070
	10:10	0.094	0.086	0.083	0.080	0.077

- It has also been found that increase in the glycerin content results in decreases in pH as shown in Table 2.

TABLE 2

	<u>Glycerin:Polyethylene Glycol</u>	<u>pH 9 wks @ 120°F</u>
5.	0:20	9.8
	1:19	9.7
	3:17	9.4
	5:15	9.4
	10:10	8.9

10.

The dentifrice of the present invention, which is a toothpaste or dental cream, contains conventional water-insoluble polishing materials or dental abrasives, in amounts from about 20-75% and preferably about 40-

15. 60% by weight of the total formulation. Suitable examples of dental abrasives or polishing materials include sodium metaphosphate, potassium metaphosphate, tricalcium phosphate, dihydrated calcium phosphate, anhydrous dicalcium phosphate, calcium pyrophosphate, 20. magnesium orthophosphate, trimagnesium phosphate, calcium carbonate, alumina, hydrated alumina, aluminium silicate, zirconium silicates, silica, bentonite, and mixtures thereof, such as a mixture of hydrated alumina and calcined alumina.

25. The dentifrice of the present invention may also contain conventional additional ingredients such as colouring or whitening agents, preservatives, flavouring or sweetening materials, and ammoniated materials such as monoammonium glycyrrhizinate. These 30. additional ingredients may each be added to the dentifrice in minimal amounts of up to 5% by weight, and

preferably up to 1%, provided they do not interfere with the foaming, antiplaque and stability properties of the finished product.

- The dentifrice of the present invention is
5. prepared by conventional methods of making toothpaste and/or dental creams. More specifically, a toothpaste may be prepared by forming a gel with hydroxyethyl-cellulose and water, adding thereto with mixing the powdered materials including the fluoride compound
 10. and humectant, followed by the addition with mixing of polishing agent and then the betaine and flavour, and inserting the final mixture in the toothpaste tube.

- In the practice of this invention to promote
15. oral hygiene, the dentifrice according to this invention is applied regularly to dental enamel by 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
20. will be described to illustrate the invention with reference to the following 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
25. otherwise indicated.

EXAMPLE 1

A dentifrice having the composition given in Table 3 is made up.

TABLE 3

	<u>Ingredients</u>	<u>%</u>
	Hydroxyethylcellulose	1.0
5.	Carbowax 600 ¹	20.0
	Na Saccharin	0.2
	MFP ²	0.76
	CAB ³ (35% A.I.)	3.5
	Dicalcium Phosphate	49.0
10.	BZCl ⁴	0.5
	D.I. H ₂ O	24.04
	Flavour	1.0

Notes on Table 3

15.

¹Polyethylene glycol, mol. weight 600²Sodium monofluorophosphate³Cocoamidopropyl betaine⁴Benzethonium chloride

20.

The hydroxyethylcellulose and water are premixed for 10 minutes to form a gel. The powdered materials MFP, BZCl and saccharin, and the Carbowax humectant are added to the gel and mixed for 10 to 20 minutes.

25. The gelled mixture is added to dicalcium phosphate and mixed for 20 minutes at speed 8 in a Ross agitator. The betaine and flavour is added to the mixture and mixed for 5 minutes at speed 6 in the Ross agitator. The resultant dental cream which is cosmetically
30. attractive is inserted into tubes.

- Aging tests performed on this product in lined tubes at room temperature, at 40°F (4.5°C) and 100°F (38°C) for 9 weeks, and in unlined tubes at 120°F (49°C) for 9 weeks, showed it to have excellent cosmetic stability.

EXAMPLE 2

A dentifrice having the composition given in Table 4 is made up.

TABLE 4

<u>10. Ingredients</u>	<u>%</u>
Hydroxyethylcellulose	1.1
Carbowax 600	20.0
Na Saccharin	0.2
MFP	0.76
15. CAB (35% A.I.)	5.7
Dicalcium Phosphate	46.8
BZCl	0.5
H ₂ O	24.04
Flavour	1.0

20.

This dental cream is prepared in accordance with the procedure of Example 1. This product has a pH of 6.7 and a foam height of 55, but does not taste good.

25.

EXAMPLE 3

A dentifrice having the composition given in Table 5 is made up.

TABLE 5

<u>Ingredients</u>		<u>%</u>
	Hi Sweet peppermint	1.0
	MAG ¹	0.1
5.	BZCl	0.5
	MFP	0.76
	Na Saccharin	0.2
	H ₂ O	23.44
	PEG 600 ²	20.0
10.	Natrosol ³ (Registered Trade Mark)	1.0
	Dicalcium phosphate	49.0
	CAB (30% A.I.)	4.0

Notes on Table 5

15.

¹ Monoammonium glycyrrhizinate² Polyethylene glycol, molecular weight 600³ Hydroxyethylcellulose

20.

This dental cream is prepared according to the procedure of Example 1, except that the pH is adjusted to 8.5 with dilute NaOH for hydration purposes, after the polyethylene glycol is added to the gelled premix.

The resultant cream looks good, has a foam

25.

height of 38-40, and shows excellent stability using aging tests over a period of 12 weeks at 100°F (38°C) as well as at 140°F (60°C) in unlined tubes for 3 weeks.

EXAMPLE 4

This is a comparison example.

30.

Example 3 is repeated except that glycerin replaces the polyethylene glycol humectant. This

product gives a foam height of 46, but shows trace separation in 3 days at 140°F (60°C) and a wetness and separation at the neck of the tube at 120°F (49°C) in 3 weeks. This product is cosmetically unstable.

5.

EXAMPLE 5

A dentifrice having the composition given in Table 6 is made up.

TABLE 6

	<u>Ingredients</u>	<u>%</u>
10.	H ₂ O	21.14
	Natrosol	1.3
	Propylene glycol	20.0
	Na Saccharin	0.2
	BZCl	0.5
15.	MAG	0.1
	MFP	0.76
	Dicalcium phosphate	50.0
	CAB (30% A.I.)	5.0
	Flavour	1.0
20.		

25. This dental cream is prepared according to the procedure of Example 1 except that the propylene glycol humectant is mixed with the premix gel for only 10 minutes. The resulting product is good in appearance and foaming with a foam height of 44. However, it's instability is clearly evident by separation, wetness along the ribbon and clip leakage in 3 weeks at 8°F (-13°C) and 40°F (4.5°C) and slight yellowing at 110°F (43°C) and 120°F (60°C) within 3 weeks.

EXAMPLE 6

A dentifrice having the composition given in Table 7 is made up.

TABLE 7

5.	<u>Ingredients</u>	<u>%</u>
	H ₂ O	19.68
	Natrosol	1.1
	Carbowax 600	20.0
	Na Saccharin	0.2
	BZCl	0.5
10.	MAG	0.1
	MFP	0.76
	Dicalcium phosphate	50.0
	CAB (30% A.I.)	6.66
	Flavour	1.0

15.

This dental cream is prepared according to the procedure of Example 1.

The resulting product is slightly thick but exhibits good foaming and stability.

20.

EXAMPLE 7

A dentifrice having the composition given in Table 8 is made up.

TABLE 8

25.	<u>Ingredients</u>	<u>%</u>
	H ₂ O	21.34
	Natrosol	1.1
	Carbowax 600	20.0
	Na Saccharin	0.2
	BZCl	0.5
30.	MAG	0.1

TABLE 8 (Cont.)

	<u>Ingredients</u>	<u>%</u>
	MFP	0.76
	$\text{Ca}_2\text{P}_2\text{O}_7^1$	50.0
5.	CAB (30% A.I.)	5.0
	Flavour	1.0

Notes on Table 8

10. ¹Calcium pyrophosphate

This dental cream is prepared according to the procedure of Example 1.

15. The resulting cream is thick and grainy, which may be due to the corseness of the calcium pyrophosphate dental abrasive.

EXAMPLE 8

A dentifrice having the composition given in Table 9 is made up.

TABLE 9

	<u>Ingredients</u>	<u>%</u>
20.	H_2O	17.68
	Natrosol	1.1
	Carbowax 600	20.0
	Na Saccharin	0.2
25.	BZCl	0.5
	MAG	0.1
	MFP	0.76
	Dicalcium phosphate dihydrate	42.0
	Anhydrous Dicalcium phosphate	10.0
30.	CAB (30% A.I.)	6.66
	Flavour	1.0

EXAMPLE 9

A dentifrice having the composition given in Table 10 is made up.

TABLE 10

5.	<u>Ingredients</u>	<u>%</u>
	Carbowax 600	20.0
	Natrosol	1.1
	Na Saccharin	0.2
	MAG	0.1
10.	BZCl	0.5
	H ₂ O	17.68
	MFP	0.76
	Hydrated Alumina	42.0
	Calcined Alumina	10.0
15.	Cocoamidopropyl betaine (30% A.I.)	6.66
	Flavour	1.0

pH 8.3

This product shows complete stability after
20. aging for 9 weeks at room temperature, 40°F (4.5°C),
100°F (38°C) and 120°F (49°C).

EXAMPLES 10 and 11

Dentifrices having the compositions given in Table 11 are made up.

25.

TABLE 11

	<u>Ex. 10</u>	<u>Ex. 11</u>
<u>Ingredients</u>	<u>%</u>	<u>%</u>
PEG 600	20.0	20.0
Natrosol	1.1	1.3
30. Na Saccharin	0.3	0.3

TABLE 11 (Cont.)

	<u>Ingredients</u>	Ex. 10 %	Ex. 11 %
	Hydrated Alumina	42.0	42.0
5.	Calcined Alumina	10.0	10.0
	CAB (30% A.I.)	5.0	5.0
	MFP	0.76	0.76
	Flavour	1.0	1.0
	H ₂ O D.I.	19.27	19.27
10.	BZCl	0.5	0.5
	Red 40 (1% solution)	0.07	0.07

EXAMPLE 12

A dentifrice having the composition given in

15. Table 12 is made up.

TABLE 12

	<u>Ingredients</u>	%
	Sorbitol (70% aqueous solution)	28.0
	Natrosol	1.1
20.	Na Saccharin	0.3
	BZCl	0.5
	MFP	0.76
	Alumina	42.0
	Calcined Alumina	10.0
25.	CAB (30% A.I.)	5.0
	Flavour	1.0
	H ₂ O	11.34
	Initial pH 7.4	
	3 weeks pH 7.5	
30.	6 weeks pH 7.6	

- This product exhibits complete stability at 8°F (-13°C) and 40°F (4.5°C) for a period of 9 weeks but slight wet cap at 110°F (43°C) and 120°F (49°C) after 3-9 weeks. In addition to the good physical stability of this product, the active ingredient content (ionic fluoride and the benzethonium chloride) remains stable as evidenced by the substantially stable pH.

EXAMPLE 13

- A dentifrice having the composition given in Table 13 is made up.

TABLE 13

<u>Ingredients</u>	<u>%</u>
H ₂ O	21.14
Natrosol	1.3
15. Sorbitol	20.0
Na Saccharin	0.2
BZCl	0.5
MAG	0.1
MFP	0.76
20. Dicalcium phosphate dihydrate	50.0
CAB (30% A.I.)	5.0
Flavour	1.0

- The resultant cream exhibits a foam height of 42 and no flavour separation after 9 weeks at 120°F (49°C). This product is completely stable at 8°F (-13°C) and 40°F (4.5°C) for a period of 9 weeks, but exhibits traces of a wet cap at 110°F (43°C) and 120°F (49°C) after 3 to 9 weeks.

EXAMPLE 14

A dentifrice having the composition given in Table 14 is made up.

TABLE 14

5.	<u>Ingredients</u>	<u>%</u>
	Natrosol	1.1
	Na Saccharin	0.3
	BZCl	0.5
	MFP	0.76
10.	Carbowax 600	10.0
	Sorbitol (70%)	10.0
	H ₂ O deionized	19.34
	Hydrated Alumina	10.0
	Calcined Alumina	42.0
15.	Flavour	1.0
	CAB (30% A.I.)	5.0

EXAMPLE 15

A dentifrice having the composition given in Table 15 is made up.

TABLE 15

	<u>Ingredients</u>	<u>%</u>
	Natrosol	1.1
	Na Saccharin	0.3
25.	MFP	0.76
	BZCl	0.5
	Carbowac 600	15.0
	Sorbitol (70%)	5.0
	H ₂ O	19.34
30.	Hydrated Alumina	42.00

TABLE 15 (Cont.)

	<u>Ingredients</u>	<u>%</u>
	Calcined Alumina	10.0
	Flavour	1.0
5.	CAB (30% A.I.)	5.0

- This product which contains 5% sorbitol, exhibits 84% soluble fluoride recovery at 12 weeks at 100°F (38°C), as compared to 61% fluoride recovery (an acceptable level) for the systems using polyethylene glycol alone as the humectant under the same conditions, e.g. Examples 1 to 11. This indicates that the presence of sorbitol, in amounts as low as 5% (70% A.I.), provides superior fluoride stability.

15. EXAMPLES 16 - 20

Dentifrices having the compositions given in Table 16 are made up.

		<u>TABLE 16</u>				
		<u>16</u>	<u>17</u>	<u>18</u>	<u>19</u>	<u>20</u>
20.	<u>Ingredients</u>	<u>%</u>	<u>%</u>	<u>%</u>	<u>%</u>	<u>%</u>
	Polyethylene Glycol (Carbowax 600)	15	17	19	10	20
	Glycerin	5	3	1	10	-
	Hydroxyethyl cellulose	1.10	1.10	1.10	1.10	1.10
25.	Sodium Monofluorophosphate	0.76	0.76	0.76	0.76	0.76
	Sodium Saccharin	0.30	0.30	0.30	0.30	0.30
	Benzethonium chloride	0.50	0.50	0.50	0.50	0.50
	Hydrated Alumina	42	42	42	42	42
30.	Calcined Alumina	10	10	10	10	10

TABLE 16 (Cont.)

Example	16	17	18	19	20
Ingredients	%	%	%	%	%
CAB (30% A.I.)	5	5	5	5	5
5. Flavour	1	1	1	1	1
Water	19.34	19.34	19.34	19.34	19.34
Fl ⁻ content ¹	0.07	0.067	0.066	0.077	0.057

Note on Table 16

10. ¹Chemical stability of the above formulations after accelerated aging for 12 weeks at 100°F (38°C) as determined by the percentage of Fl⁻ content.

15. All the above formulations are effective against plaque related bacteria while possessing improved foaming characteristics, cosmetic stability and chemical stability. The presence of a small amount of glycerin, as low as 1% by weight, enhances the chemical stability of the fluoride in the polyethylene glycol humectant-containing dentifrice over the acceptable fluoride stability in the absence of glycerin (Example 20).

20. Variations in the above formulations may be made. For example, other betaines such as lauramido-propyl betaine, coco betaine and the like may be substituted for the cocoamidopropyl, betaine in the examples. Similarly, other abrasives may be substituted for the specific abrasives in the examples. Likewise, other fluoride-containing compounds such as sodium fluoride or potassium fluoride, may be substituted for the sodium monofluorophosphate in the specific examples.
- 25.
- 30.

CLAIMS

1. A stable antiplaque dentifrice with improved foaming which is free of nonionic and anionic surfactants, comprising as the essential ingredients an effective amount of an antiplaque quaternary ammonium compound, at least 1.5% by weight of a betaine surfactant, the betaine surfactant being the sole surfactant species, a humectant selected from the group consisting of polyethylene glycol, sorbitol and mixtures thereof, and a nonionic gelling agent in an aqueous vehicle containing a dental abrasive.

2. A stable antiplaque dentifrice with improved foaming and fluoride stability which is free of nonionic and anionic surfactants, comprising an effective amount of an antiplaque quaternary ammonium compound, at least 1.5% by weight betaine surfactant, a humectant selected from the group consisting of polyethylene glycol, sorbitol and mixtures thereof and a nonionic gelling agent, the betaine surfactant being the sole surfactant species, a fluoride-providing compound and sorbitol or 1 to 10% by weight of glycerine as a stabiliser for the fluoride providing compound.

3. A dentifrice as claimed in Claim 1 which contains 1.5-2% by weight of the betaine.



31.

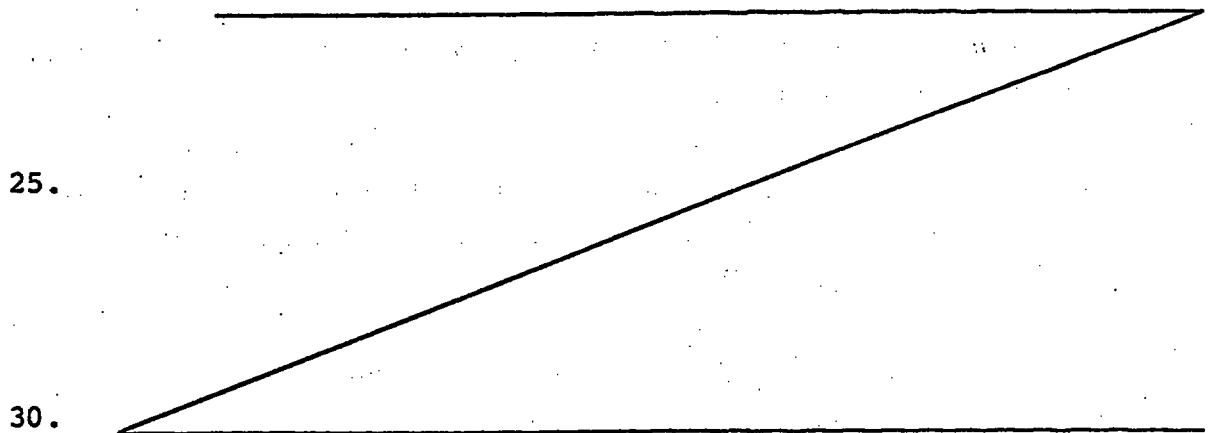
4. A dentifrice as claimed in Claim 1 or Claim 2, in which the nonionic gelling agent is hydroxyethylcellulose.

5. 5. A dentifrice as claimed in any one of Claims 1 to 4 which contains 0.5 to 2% by weight of the nonionic gelling agent.

10. 6. A dentifrice as claimed in any one of Claims 1 to 5, containing 20-30% by weight of the humectant.

15. 7. A dentifrice as claimed in any one of Claims 1 to 6, in which the humectant is polyethylene glycol having a molecular weight of about 600.

20. 8. A dentifrice as claimed in any one of Claims 1 to 6, in which the humectant is sorbitol.





9. A dentifrice as claimed in any one of Claims 1 to 8 which contains about 40-60% by weight of a water-insoluble dental abrasive.
5. 10. A dentifrice as claimed in any one of Claims 1 to 8, in which the dental abrasive is dicalcium phosphate.
10. 11. A dentifrice as claimed in any one of Claims 1 to 10, in which the antiplaque agent is benzethonium chloride.
15. 12. A dentifrice as claimed in any one of Claims 1 to 11 which contains 0.01 to 5% of the antiplaque agent.
20. 13. A dentifrice as claimed in Claim 1 or any one of Claims 3 to 12 when dependant on Claim 1 which contains a fluoride-providing compound.
25. 14. A dentifrice as claimed in Claim 2 or Claim 13 containing 0.05-2% by weight of the fluoride-providing compound.
30. 15. A dentifrice as claimed in Claim 13 or Claim 14, in which the fluoride-providing compound is sodium monofluorophosphate.
16. A dentifrice as claimed in Claim 2 or Claim 13 when dependant on any one of Claims 1 to 6, in which the numectant is a mixture



of polyethylene glycol and at least 5% sorbitol.

17. A dentifrice as claimed in Claim 2 or Claim 13 when dependant on any one of Claims 1 to 6 in which the humectant is polyethylene glycol and 1-10% by weight of glycerin as fluoride stabiliser.

18. A dentifrice as claimed in any one of Claims 1 to 17, in which the betaine is cocoamid-propyl betaine.

19. A dentifrice as claimed in any one of Claims 1 to 9, which contains an abrasive, the abrasive being alumina.

20. A dentifrice as claimed in Claim 19, in which the abrasive is a mixture of hydrated alumina and calcined alumina.

21. A dentifrice as claimed in Claim 1 substantially as specifically described herein with reference to the Examples.
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