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2,955,985

DENTIFRICE COMPOSITIONS

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This invention relates to a dentifrice, and more particularly to a dentifrice in paste, powder or liquid form, which tends to reduce the normal susceptibility of the teeth to attack from acid.

It is generally accepted that dental caries result at least partially from the acids formed by microorganisms in the mouth in the course of their metabolism. These acids, when in contact with the teeth, attack the enamel of the teeth, dissolving the enamel, and result in tooth decay. A considerable amount of research effort has been devoted to find a means of protecting the teeth against the attack of these acids. Numerous proposals have been advanced to solve the problem. Those skilled in the dentifrice art are familiar with these proposals. One proposal was the incorporation of a basic ammonium salt in a dentifrice. These were known as the "ammoniated" dentifrices. Another was the use of chlorophyll in a dentifrice. Another was the incorporation of a so-called "anti-enzyme," such as sodium lauryl sulfate, into a dentifrice. While some of these proposals have given indications of being helpful, none of them has provided satisfactory protection of the teeth against the ravages of acids, such as are formed in the mouth.

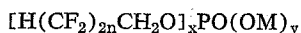
It is an object of the present invention to provide an improved dentifrice having the property of reducing the normal susceptibility of the teeth to acid attack.

It is another object of the present invention to incorporate in a dentifrice an agent affording protection to the teeth enamel against acid attack and resisting calculus formation on the teeth.

Other objects will be apparent to those skilled in the art from reading the description which follows.

The present invention is based upon the discovery that a dentifrice containing as an essential ingredient or component particular selected fluoroalkyl phosphates and their water-soluble salts will reduce the dissolving action of acids on dental enamel. Such a dentifrice also retards calculus formation and other deposits on the surface of the teeth.

These fluoroalkyl phosphates are the mono-, di- and tri-fluoroalkyl esters of phosphoric acids and their water-soluble salts. These esters are desirably esters of orthophosphoric acid of the formula:



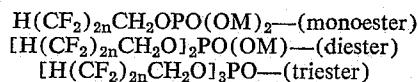
wherein n is an integer from 1 to 5, inclusive, x is an integer from 1 to 3, inclusive, y equals $3-x$, and M is hydrogen, an alkali-metal or an ammonium ion. The preferred esters are those in which n is an integer from 2 to 4, inclusive, x is 1, y is 2, and M is an alkali-metal or an ammonium ion, desirably the latter. The ammonium salt of 1,1,7-trihydroperfluoroheptyl phosphate has provided excellent results. The contemplated alkali-

metals are lithium, potassium and sodium, preferably the latter.

The esters of phosphoric acid and their water-soluble salts defined above will be referred to in this specification as the fluoroalkyl phosphates.

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The fluoroalkylphosphates contemplated for incorporation into the dentifrices of the invention fall within the following three types.



wherein n and M have the same definitions as above. As indicated above, the water-soluble salts of the monoesters, and particularly their ammonium salts, are preferred because of their greater water-solubility, whereas the triesters have substantially reduced solubility in water and are therefore not the preferred esters for use in the invention. The triesters, as a class, frequently are liquids and therefore are not as suitable in the preparation of dry powder dentifrices.

The selected fluoroalkyl phosphates and their water-soluble salts described above are known chemical compounds and per se do not constitute a part of this invention. These esters and their salts and their methods of preparation are described in U.S. Patent No. 2,597,702 of A. F. Benning. It is intended to incorporate by reference the entire disclosure of the patent into this specification. These esters may be produced by several methods, including the reaction between an appropriate fluorinated alcohol and phosphorus pentoxide or phosphorus oxychloride.

Among the preferred fluoroalkyl phosphates contemplated for employment in the dentifrices of the invention are: 1,1,7-trihydroperfluoroheptyl phosphate and its ammonium salt; 1,1,3-trihydroperfluoropropyl phosphate and its sodium salt; ammonium di-(1,1,3-trihydroperfluoropropyl) phosphate; tri-(1,1,3-trihydroperfluoropropyl) phosphate; ammonium di-(1,1,5-trihydroperfluoroamyl) phosphate; diammonium 1,1,9-trihydroperfluorononyl phosphate; diammonium 1,1,11-trihydroperfluoroundecyl phosphate, etc., and mixtures of them. The ammonium ion in the salts may be replaced with an alkali-metal ion to form the sodium, potassium or lithium salts.

While the concentration of the selected fluoroalkyl phosphate or its salts in the dentifrice may vary, best results are obtained where the selected phosphate constitutes between about 0.05% and 2.0%, and preferably between 1.0% and 1.8%, by weight of the total dentifrice composition. Below 0.05% the phosphate may be ineffective, and above 2.0% it may not be utilized efficiently.

Where the dentifrice is a paste or powder it is desirable to incorporate into the dentifrice a solid polishing agent, such as dicalcium phosphate, calcium pyrophosphate, tricalcium phosphate or powdered chalk (calcium carbonate), etc. Non-calcium-containing polishing agents, such as aluminum oxide, titanium dioxide, ground pumice, powdered nylon, etc., may be employed.

In addition to the selected fluoroalkyl phosphate and polishing agent (when desired), the dentifrice can contain as optional ingredients a soap or synthetic detergent as a surface tension depressant. Soaps of high molecular weight fatty acids, including, for example, sodium and potassium soaps of myristic, stearic and palmitic acids and the fatty acid mixtures of palm oil and coconut oil, as well as diglycol laurate, diglycol stearate and glycostearine, can be employed. Typical synthetic detergents include the alkyl sulfates and sulfonates having alkyl groups of from about 8 to about 18 carbon atoms, such as sodium lauryl sulfate, the sulfated fatty alcohols derived from coconut oil and palm oil, sodium cetyl sulfate, sulfated sperm oil fatty alcohols and sodium oleyl sulfate, sulfated glycerides, such as oleyl, stearic, palmitic and ricinoleic glycerides, usually in the form of mixed glycerides and sulfonated hydrocarbons having from 8 to 20 carbon atoms, such as sulfonated decanes, dodecanes and octadecanes. Particularly good results are obtained

with Tweens, such as Tween 20 which is the polyoxyethylene derivative of sorbitan, and Atlas G-2160 which is the polyoxyethylene derivative of mannitan. Another type is the Drucals, such as sodium lauryl isethionate, or sodium mixed alkyl isethionates.

Other optional conventional components of a dentifrice which may be present include flavoring materials, such as the flavoring oils (peppermint oil, etc.); sweeteners, such as sucrose, glucose, saccharin and sodium cyclamate, and harmless coloring materials, in proportions to give any desired taste or flavor or other effect.

In a preferred embodiment of the invention, the dentifrice is in the form of a paste, and in this event it will contain a carrier and softener and a binder in amounts to give the dentifrice a smooth texture and good flowability. Glycerin and sorbitol are preferred humectants, carriers and softeners, but syrup, glucose and invert sugars and honey can also be employed. As binders there can be used carboxymethylcellulose, gum tragacanth, sodium alginate, Irish moss, gum acacia, pectin, etc. Those skilled in the dentifrice art will know other carriers, softeners and binders. The pastes may be either of the aqueous type, containing substantial amounts of water (above 18%), or of the relatively anhydrous type, containing less than 5% water. Formulations are given below for both types.

In addition to pastes, the dentifrices of the invention may be in the form of powders or liquids. The main difference between a paste and powder is that the latter contains little or no water and usually no binder or softener. A liquid usually differs from a paste in that it is more fluid and it contains no solid polishing agent.

The following are general formulations of tooth pastes, powders and liquids of the type contemplated according to the present invention (parts are expressed in terms of parts by weight):

Aqueous tooth paste

	Parts by weight
Fluoroalkyl phosphate	0.05 to 2.0
Water	18 to 25
Binder	0.8 to 1.2
Polishing agent	40 to 50
Softener or humectant	20 to 25
Detergent	0 to 2
Sweetener	0.1 to 0.2
Flavoring oils	0.9 to 1.2

Relatively anhydrous tooth paste

	Parts by weight
Fluoroalkyl phosphate	0.05 to 2.0
Water	0 to 4.5
Binder	0.3 to 1.2
Polishing agent	45 to 70
Humectant	25 to 45
Detergent	0 to 2
Sweetener	0.03 to 0.10
Flavoring oils	0.9 to 1.2

Powder

	Parts by weight
Fluoroalkyl phosphate	0.05 to 2.0
Polishing agent	93.6 to 98
Detergent	1 to 3
Flavoring oils	0.85 to 1.2
Sweetener	0.1 to 0.2

Liquid

	Parts by weight
Fluoroalkyl phosphate	0.05 to 2.0
Water	60.1 to 92
Detergent	1.5 to 5
Softener	5 to 30
Binder or suspending agent	0.5 to 1.5
Flavoring agent	0.85 to 1.2
Sweetener	0.1 to 0.2

In order more clearly to disclose the nature of the present invention, specific examples illustrating the preparation of typical dentifrices will hereinafter be described. It should be understood, however, that this is done solely by way of example and is intended neither to delineate the scope of the invention nor limit the ambit of the appended claims. Unless otherwise stated, quantities of materials are referred to in terms of parts by weight. The materials are mixed together in accordance with the standard practice in the dentifrice art.

EXAMPLE I

The following is an example of a tooth paste formulation:

Ingredient:	Parts by weight
Monoammonium 1,1,7-trihydroperfluoroheptyl phosphate	1.0
Deionized water	22.9
Soluble saccharin	0.15
Carboxymethylcellulose (HV-120)	1.0
Dicalcium phosphate	49.0
Sorbitol	23.05
Sodium lauryl sulfate	1.8
Flavoring oils	1.10

EXAMPLE II

The following is an example of a series of tooth paste formulations:

Ingredient	A	B
Ammonium di-(1,1,5-trihydroperfluoramyl) phosphate	1.80	
Diammonium 1,1,9-trihydroperfluorononyl phosphate		1.80
Deionized water	22.90	22.90
Soluble saccharin	0.15	0.15
Carboxymethylcellulose (HV-120)	1.0	1.0
Dicalcium phosphate	50.0	50.0
Sorbitol	23.05	23.05
Flavoring oils	1.10	1.10

EXAMPLE III

The following is an example of a series of tooth paste formulations:

Ingredient	A	B	C	D
Monoammonium 1,1,7-trihydroperfluoroheptyl phosphate	1.8	0.9	1.0	1.0
Water	22.90	22.90	22.8	22.5
Soluble saccharin	0.15	0.15	0.15	0.15
Carboxymethylcellulose (HV-120)	1.0	1.0	1.0	1.0
Dicalcium phosphate	50.0	50.0	49.9	49.65
Sorbitol	23.05	23.05	23.05	23.05
Drucal (CHD)—(a mixture of sodium lauryl isethionate and sodium myristyl isethionate)		0.9		
Sodium lauryl sulfate			1.0	1.50
Flavoring oils	1.1	1.1	1.1	1.1

EXAMPLE IV

The following is an example of a tooth paste formulation which is relatively anhydrous, i.e., having less than 5% water:

Ingredient:	Parts by weight
Monoammonium - 1,1,7 - trihydroperfluoroheptyl phosphate	1.55
Water, deionized	4.35
Glycerin U.S.P.	41.0
Saccharin, soluble U.S.P.	0.05
Carbomethylcellulose (HV-120)	0.50
Dicalcium phosphate	50.85
Sodium lauryl sulfate	1.80
Flavoring oils	1.0

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EXAMPLE V

The following is an example of a series of tooth powder formulations:

Ingredient	A	B
Monoammonium-1,1,7-trihydroperfluoroheptyl phosphate.....	1.8	1.5
Dicalcium phosphate.....	95.5	95.5
Polyoxyethylene sorbitan.....	1.5	2
Soluble saccharin.....	0.15	0.15
Flavoring oils.....	1.05	0.85

EXAMPLE VI

The following is an example of a series of liquid dentifrice formulations:

Ingredient	A	B
Monoammonium-1,1,7-trihydroperfluoroheptyl phosphate.....	1.5	1.5
Sorbitol.....	20.0	15.0
Water.....	75.0	79.5
Carboxymethylcellulose (HV-120).....	1.0	1.0
Soluble saccharin.....	0.15	0.15
Polyoxyethylene sorbitan.....	1.5	1.5
Flavoring oils.....	0.85	1.0

The terms and expressions employed are used as terms of description and not of limitation, and it is not intended, in the use of such terms and expressions, to exclude any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed.

What is claimed is:

1. A dentifrice comprising a dentifrice vehicle and at least about 0.05% by weight of a fluoroalkyl phosphate of the formula:



wherein n is an integer from 1 to 5, inclusive, x is an

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integer from 1 to 3, inclusive, y equals $3-x$, and M is a member selected from the class consisting of hydrogen, an alkali-metal ion and an ammonium ion.

2. A dentifrice comprising a dentifrice vehicle and at least about 0.05% by weight of a fluoroalkyl phosphate of the formula:



wherein n is an integer from 1 to 5, inclusive, and M is a member selected from the class consisting of hydrogen, an alkali-metal ion and an ammonium ion.

3. A dentifrice is accordance with claim 1, in which the vehicle is a paste.

4. A dentifrice in accordance with claim 1, in which the vehicle is a powder.

5. A dentifrice in accordance with claim 1, in which the vehicle is a liquid.

6. A dentifrice in accordance with claim 1, which also contains a polishing agent.

7. A dentifrice in accordance with claim 1, which also contains a surface tension depressant.

8. A dentifrice in accordance with claim 7, wherein the surface tension depressant is a synthetic detergent.

9. A dentifrice in accordance with claim 1, which also contains a binder.

10. A dentifrice in accordance with claim 1, wherein the fluoroalkyl phosphate is monoammonium-1,1,7-trihydroperfluoroheptyl phosphate.

References Cited in the file of this patent

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