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(54) Title: ANTICALCULUS COMPOSITIONS

(57) Abstract

The present invention relates to oral compositions containing a mixture of certain polyphosphonates and a synthetic anionic polymeric carboxylate to provide enhanced anticalculus benefits.

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ANTICALCULUS COMPOSITIONS

TECHNICAL FIELD

The present invention relates to oral compositions containing a mixture of certain polyphosphonate and a limiting anionic polycarboxylate, which compositions provide unexpected anticalculus benefits.

BACKGROUND OF THE INVENTION

Dental calculus, or tartar as it is sometimes called, is a deposit which forms on the surfaces of the teeth at the gingival margin. Supragingival calculus appears principally in the areas near the orifices of the salivary ducts; e.g., on the lingual surfaces of the lower anterior teeth and on the buccal surfaces of the upper first and second molars, and on the distal surfaces of the posterior molars.

Mature calculus consists of an inorganic portion which is largely calcium phosphate arranged in a hydroxyapatite crystal lattice structure similar to bone, enamel and dentine. An organic portion is also present and consists of desquamated epithelial cells, leukocytes, salivary sediment, food debris and various types of microorganisms.

As the mature calculus develops, it becomes visibly white or yellowish in color unless stained or discolored by some extraneous agent. This is undesirable from an aesthetic standpoint.

A wide variety of chemical and biological agents have been suggested in the art to retard calculus formation or to remove calculus after it is formed. Mechanical removal of this material periodically by the dentist is, of course, routine dental office procedure.

The chemical approach to calculus inhibition generally involves chelation of calcium ions and/or crystal growth inhibition which prevents the calculus from forming and/or breaks down mature calculus by removing calcium.

The prior art discloses a number of chelating agents for this purpose. British Patent 490,384, February 15, 1937, discloses oral compositions containing ethylenediaminetetraacetic acid, nitrilotriacetic acid and related compounds including pyrophosphates as anticalculus agents. U.S. Patent 3,678,154, July 18, 1972 to

Widder et al. discloses oral compositions containing certain polyphosphonates and fluoride. U.S. Patent 3,737,533, June 5, 1973 to Francis discloses oral compositions containing certain carbonyl diphosphonates.

In addition to the above references, additional prior art discloses dentifrices and mouthwashes containing soluble pyrophosphate salts which have been included for a variety of purposes, some for providing an anticalculus benefit. Included among such references are U.S. Patent 2,941,926, June 21, 1960 to Salzmann et al. which discloses dental powders containing chlorophyll and pyrophosphate salts. U.S. Patent 3,137,632, June 16, 1964 to Schiraldi discloses toothpastes containing pyrophosphate salts. U.S. Patents 3,927,201 and 202, December 16, 1975 to Baines et al. and Harvey et al., respectively, disclose toothpastes which utilize soluble pyrophosphates as abrasives. U.S. Patents 4,244,931, January 13, 1981 and 4,247,526, January 27, 1981 to Jarvis et al. disclose pyrophosphate salts in dicalcium phosphate systems. Jap. Patent Application Disclosure No. 4945-1974 discloses soluble pyrophosphates in a variety of dentifrice systems. U.S. Patent 4,333,551, April 6, 1982 to Parran discloses tetraalkali metal salts in mouthwash compositions. U.S. Patent 4,515,772, May 7, 1985 to Parran, et al., discloses compositions containing soluble pyrophosphate salts as anticalculus agents. Diphosphonate materials have also been disclosed as anticalculus agents. See, for example, U.S. Patent 3,488,419, January 6, 1970 to McCune et al.

Although there have been a number of approaches disclosed for combatting calculus, there is still the desire and need to develop improved products possessing that property. The prior art while disclosing the use of diphosphonates and synthetic linear polycarboxylates provides no suggestion to use such materials in a mixture wherein the materials are present in amounts sufficient to achieve the desired level of anticalculus efficacy.

It is an object of the present invention to provide compositions which deliver an anticalculus benefit.

It is a further object of the present invention to produce an effective anticalculus product using a mixture of certain polyphosphonates and a synthetic anionic polycarboxylate which delivers improved anticalculus performance.

It is still a further object of the present invention to provide anticalculus products which are cosmetically acceptable and do not inhibit remineralization of the teeth.

It is still a further object of the present invention to provide effective methods for combating calculus.

These and other objects will become more clear from the detailed description which follows.

All percentages and ratios used herein are by weight unless otherwise specified. Also all measurements referred to herein are made at 25°C in the composition or on the pure material unless otherwise specified.

SUMMARY OF THE INVENTION

The present invention embraces an oral composition comprising:

(a) a safe and effective amount of certain polyphosphonate or a mixture of polyphosphonates;

(b) a safe and effective amount of a synthetic anionic polycarboxylate or mixture thereof;

(c) a safe and effective amount of a soluble fluoride ion source; and

(d) a pharmaceutically acceptable carrier.

The present invention also encompasses a method for retarding development of dental calculus.

DETAILED DESCRIPTION OF THE INVENTION

The compositions of the present invention comprise a mixture of a certain polyphosphonate(s) and a synthetic anionic polycarboxylate(s) in a pharmaceutically acceptable carrier.

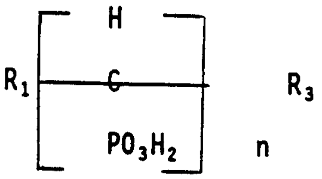
By "safe and effective amount" as used herein means sufficient amount of material to provide the desired benefit while being safe to the hard and soft tissues of the oral cavity.

By the term "comprising", as used herein, is meant that various additional components can be conjointly employed in the compositions of this invention as long as the listed materials perform their intended functions.

By the term "pharmaceutically acceptable carrier", as used herein, is meant a suitable carrier which can be used to apply the present anticalculus agents in the oral cavity without undue toxicity irritation allergic response and the like, commensurate with a reasonable benefit/risk ratio.

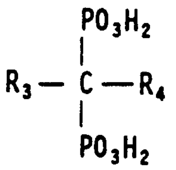
Polyphosphate Material

The polyphosphonates found useful in the present invention are those set forth in U.S. Patent 3,488,419, to McCune et al., January 6, 1970 incorporated herein in its entirety by reference. The polyphosphonates useful herein are selected from the group consisting of those of the formulae:



$$R_1\left[\begin{array}{c}H\\ C\\ PO_3H_2\end{array}\right]_n R_3$$

(I)



$$R_3-\overset{PO_3H_2}{\underset{PO_3H_2}{C}}-R_4$$

(II)

wherein R_1 and R_2 are hydrogen or CH_2OH; n is an integer of from 3 to 10; R_3 is hydrogen, alkyl containing from 1 to about 20 carbon atoms, alkenyl containing from 2 to about 20 carbon atoms, aryl (e.g., phenyl and naphthyl), phenylethenyl, benzyl, halogen (e.g., dimethylamino, diethylamino, N-hydroxy-N-ethylamino, acetylamino), $-CH_2COOH$, $-CH_2PO_3H_2$,

$-CH(PO_3H_2)$

(OH) or $-CH_2CH(PO_3H_2)_2$; R_4 is hydrogen, lower alkyl (e.g., methyl, ethyl, propyl, and butyl), amino, benzyl, halogen (e.g., chlorine bromine and fluorine), hydroxyl, $-CH_2COOH$, $-CH_2PO_3H_2$, or $-CH_2CH_2PO_3H_2$; or a pharmaceutically acceptable salt thereof such as alkali metal (e.g., sodium and potassium), alkaline earth metal (e.g., calcium and magnesium), and ammonium or low molecular weight substituted ammonium (e.g., mono-, di, and triethanolammonium) salts, and a carrier suitable for use in the oral cavity, the pH of the composition being within the range from about 5.0 to about 11.0.

propane-1,2,3-triphosphonic acid;
butane-1,2,3,4-tetraphosphonic acid;
hexane-1,2,3,4,5,6-hexaphosphonic acid;
hexane-1-hydroxy-2,3,4,5,6-pentaphosphonic acid;
hexane-1,6-dihydroxy-2,3,4,5-tetraphosphonic acid;
pentane-1,2,3,4,5-pentaphosphonic acid;
heptane-1,2,3,4,5,6,7-heptaphosphonic acid;
octane-1,2,3,4,5,6,7,8-octaphosphonic acid;
nonane-1,2,3,4,5,6,7,8,9-nonaphosphonic acid;
decane-1,2,3,4,5,6,7,8,9,10-decaphosphonic acid;
and the pharmaceutically acceptable salts of these acids, e.g., sodium, potassium,calcium, magnesium, ammonium, triethanolammonium, diethanolammonium, and monoethanolammonium salts.

Among the operable polyphosphonates encompassed by the above Formula (II) are
ethane-1-hydroxy-1,1-diphosphonic acid;
methanediphosphonic acid;
methanehydroxydiphosphonic acid;
ethane-1,1,2-triphosphonic acid;
propane-1,1,3,3-tetraphosphonic acid;
ethane-2-phenyl-1,1-diphosphonic acid;
ethane-2-naphthyl-1,1-diphosphonic acid;
methanephenyldiphosphonic acid;
ethane-1-amino-1,1-diphosphonic acid;
methanedichlorodiphosphonic acid;
nonane-5,5-diphosphonic acid;
n-pentane-1,1-diphosphonic acid;
methanedifluorodiphosphonic acid;
methanedibromodiphosphonic acid;
propane-2,2-diphosphonic acid;
ethane-2-carboxy-1,
1-diphosphonic acid;
propane-1-hydroxy-1,1,3-triphosphonic acid;
ethane-2-hydroxy-1,1,2-triphosphonic acid;
propane-1,3-diphenyl-2,2-diphosphonic acid;
nonane-1,1-diphosphonic acid;
decane-1,-hydroxy-1,1-diphosphonic acid

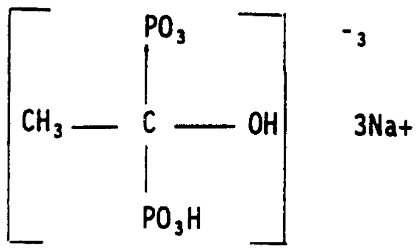
hexadecane-1,1-diphosphonic acid;
pent-4-ene-1-hydroxy-1,1-diphosphonic acid;
octadec-9-ene-1-hydroxy-1,1-diphosphonic acid;
3-phenyl-1,1-diphosphonoprop-2-ene;
octane-1,1-diphosphonic acid;
dodecane-1,1-disphosphonic acid;
phenylaminomethanediphosphonic acid;
naphthylaminomethanediphosphonic acid;
N,N-dimethylaminomethanediphosphonic acid;
N-(2-hydroxyethyl)-aminomethanediphosphonic acid;
N-acetylaminomethanediphosphonic acid;
aminomethanediphosphonic acid;

and the pharmaceutically acceptable salts of these acids, e.g., sodium, potassium, calcium, magnesium ammonium, triethanolammonium, diethanolammonium and mono-ethanolammonium salts.

and the pharmaceutically acceptable salts of these acids, e.g., sodium, potassium, calcium, magnesium ammonium, triethanolammonium, diethanolammonium and mono-ethanolammonium salts.

Mixtures of any of the foregoing phosphonic acids and/or salts can be used in the compositions of this invention.

Ethane-1-hydroxy-1,1-diphosponic acid, an especially preferred polyphosphonate, has the molecular formula $CH_3C(OH)(PO_3H_2)_2$. (According to nomenclature by radicals, the acid might also be named 1-hydroxyethylidene diphosphonic acid.) The most readily crystallizable salt of this acid is obtained when three of the acid hydrogens are replaced by sodium. Preferred salts for the purpose of this invention are the trisodium hydrogen salt which has the structure:



$$\left[CH_3 - \overset{PO_3}{\underset{PO_3H}{C}} - OH \right]^{-3} \quad 3Na^+$$

and the disodium salt.

The trisodium hydrogen salt normally crystallizes as the hexahydrate which loses some water during air-drying to yield a mixture of the hexa- and monohydrate averaging 3 to 4 molecules of water of hydration. The polyphosphonate is used as an effective amount generally from about 0.1 about 6% preferably from about .5 to about 2.0%.

Synthetic Polycarboxylate

The synthetic anionic polycarboxylates employed herein are well known, being employed in the form of their free acids or partially or preferably fully neutralized water soluble alkali metal (e.g. potassium and preferably sodium) or ammonion salts. Preferred are 1:4 to 4:1 copolymers of maleic anhydride or acid with another polymerizable ethylenically unsaturated monomer, preferably methyl vinyl ether (methoxyethylene) having a molecular weight (M.W.) of about 30,000 to about 1,000,000. These copolymers are available for example as Gantrez (AN 139(M.W. 500,000), A.N. 119 (M.W. 250,000) and preferably S-97 Pharmaceutical Grade (M.W. 70,000), of GAF Corporation.

Other operative polymeric polycarboxylates include those such as the 1:1 copolymers of maleic anhydride with ethyl acrylate, hydroxyethyl methacrylate, N-vinyl-2-pyrollidone, or ethylene, the latter being available for example as Monsanto EMA No. 1103, M.W. 10,000 and EMA Grade 61, and 1:1 copolymers of acrylic acid with methyl or hydroxyethyl methacrylate, methyl or ethyl acrylate, isobutyl vinyl ether or N-vinyl-2-pyrrolidone.

Additional operative polymeric polycarboxylates disclosed in above referred to U.S. Patent Nos. 4,138,477 and 4,183,914, incorporated herein by reference, include copolymers of maleic anhydride with styrene, isobutylene or ethyl vinyl ether, polyacrylic, polyitaconic and polymaleic acids, and sulfoacrylic oligomers of M.W. as low as 1,000 available as Uniroyal ND-2.

Suitable generally are polymerized olefinically or ethylenically unsaturated carboxylic acids containing an activated carbon-to-carbon olefinic double bond and at least one carboxyl group, that is, an acid containing an olefinic double bond which readily functions in polymerization because of its presence in the monomer molecule either in the alpha-beta position with respect to a carboxyl group or as part of a terminal methylene grouping. Illustrative of such acids are acrylic, methacrylic, ethacrylic, alpha-chloroacrylic, crotonic, beta-acryloxy propionic, sorbic, alpha-chlorsorbic, cinnamic, beta-styrylacrylic, muconic, itaconic, citraconic, mesaconic, glutaconic, aconitic, alpha-phenyl-acrylic, 2-benzyl acrylic, 2-cyclohexylacrylic, angelic, umbellic, fumaric, maleic acids and anhydrides. Other different olefinic monomers copolymerizable with such carboxylic monomers include vinylacetate, vinyl chloride, dimethyl maleate and the like. Copolymers contain sufficient carboxylic salt groups for water-solubility.

Other suitable carboxylates include the Carbopol® materials sold by B. F. Goodrich such as Carbopol 934, 936, 940 and 941.

The synthetic anionic polymeric polycarboxylate component is mainly a hydrocarbon with optional halogen and O-containing substituents and linkages as present in for example ester, ether and OH groups, and when present is generally employed in the instant compositions in approximate weight amounts of 0.05 to 3%, preferably 0.05 to 2%, more preferably 0.1 to 2%.

Water Soluble Fluoride Ion Source

Water-soluble fluoride compounds in the present compositions are present in an amount sufficient to give a fluoride concentration of from about 0.0025% to about 5.0% by weight, preferably from about 0.005% to about 2.0% by weight, to provide anticaries efficacy. Preferred fluorides are sodium fluoride, stannous fluoride, indium fluoride, and sodium monofluorophosphate. Norris et al., U.S. Patent 2,946,735, issued July 26, 1960 and Widder et al., U.S. Patent 3,678,154, issued July 18, 1972 disclose such salts as well as others. Both patents are incorporated herein by reference. Fluorides serve to combat caries as well as to inhibit pyrophosphatase as does the synthetic anionic polycarboxylate.

Pharmaceutically Acceptable Carrier

The carrier for the polyphosphonate and the synthetic anionic polycarboxylate can be any vehicle suitable for use in the oral cavity. Such carriers include the usual components of mouthwashes, toothpastes, tooth powders, prophylaxis pastes, lozenges, gums and the like and are more fully described hereinafter. Dentifrices and mouthwashes are the preferred systems.

The abrasive polishing material contemplated for use in the present invention can be any material which does not excessively abrade dentin. These include, for example, silicas including gels and precipitates, calcium carbonate, dicalcium orthophosphate dihydrate, calcium pyrophosphate, tricalcium phosphate, calcium polymetaphosphate, insoluble sodium polymetaphosphate, hydrated alumina, and resinous abrasive materials such as particulate condensation products of urea and formaldehyde, and other such as disclosed by Cooley et al. in U.S. Patent 3,070,510, December 25, 1962, incorporated herein by reference. Mixtures of abrasives may also be used.

Silica dental abrasives, of various types, can provide the unique benefits of exceptional dental cleaning and polishing performance without unduly abrading tooth enamel or dentin. Silica abrasive materials are also exceptionally compatible with sources of soluble fluoride and polyphosphonates. For these reasons they are preferred for use herein.

The silica abrasive polishing materials useful herein, as well as the other abrasives, generally have an average particle size ranging between about 0.1 to 30 microns, preferably 5 and 15 microns. The silica abrasive can be precipitated silica or silica gels such as the silica xerogels described in Pader et al., U.S. Patent No. 3,538,230, issued March 2, 1970 and DiGiulio, U.S. Patent No. 3,862,307, June 21, 1975, both incorporated herein by reference. Preferred are the silica xerogels marketed under the tradename "Syloid" by the W. R. Grace & Company, Davison Chemical Division. Preferred precipitated silica materials include those marketed by the J. M. Huber Corporation under the tradename, "Zeodent", particularly the silica carrying the designation "Zeodent 119". These silica abrasives are described in U.S. Patent No. 4,340,583, July 29, 1982, incorporated herein by reference.

The abrasive in the compositions described herein is present at a level of from about 6% to about 70%, preferably from about 15% to about 25% when the dentifrice is a toothpaste. Higher levels, as high as 90%, may be used if the composition is a toothpowder.

Flavoring agents can also be added to dentifrice compositions. Suitable flavoring agents include oil of wintergreen, oil of peppermint, oil of spearmint, oil of sassafras, and oil of clove. Sweetening agents which can be used include aspartame, acesulfame, saccharin, dextrose, levulose and sodium cyclamate. Flavoring and sweetening agents are generally used in dentifrices at levels of from about 0.005% to about 2% by weight.

Dentifrice compositions can also contain emulsifying agents. Suitable emulsifying agents are those which are reasonably stable and foam throughout a wide pH range, including nonsoap anionic, nonionic, cationic, zwitterionic and amphoteric organic synthetic detergents. Many of these suitable surfactants are disclosed by Gieske et al. in U.S. Patent No. 4,051,234, September 27, 1977, incorporated herein by reference.

Water is also present in the toothpastes of this invention. Water employed in the preparation of commercially suitable toothpastes should preferably be deionized and free of organic impurities. Water generally comprises from about 10% to 50%, preferably from about 20% to 40%, by weight of the toothpaste compositions herein. These amounts of water include the free water which is added plus that which is introduced with other materials such as with sorbitol.

In preparing toothpastes, it is necessary to add some thickening material to provide a desirable consistency. Preferred thickening agents are carboxyvinyl polymers of the type mentioned previously herein, xanthan gum, carrageenan, hydroxyethyl cellulose and water soluble salts of cellulose ethers such as sodium carboxymethyl cellulose and sodium carboxymethyl hydroxyethyl cellulose. Natural gums such as gum karaya, gum arabic, and gum tragacanth can also be used. Colloidal magnesium aluminum silicate or finely divided silica can be used as part of the thickening agent to further improve texture. Thickening agents in an amount from 0.5% to 5.0% by weight of the total composition can be used.

It is also desirable to include some humectant material in a toothpaste to keep it from hardening. Suitable humectants include glycerin, sorbitol, and other edible polyhydric alcohols at a level of from about 15% to about 70%.

Another preferred embodiment of the present invention is a mouthwash composition. Conventional mouthwash composition components can comprise the carrier for the anticalculus agents of the present invention. Mouthwashes generally comprise from about 20:1 to about 2:1 of a water/ethyl alcohol solution and preferably other ingredients such as flavor, sweeteners, humectants and sudsing agents such as those mentioned above for dentifrices. The humectants, such as glycerin and sorbitol give a moist feel to the mouth. Generally, on a weight basis the mouthwashes of the invention comprise 5% to 60% (preferably 10% to 25%) ethyl alcohol, 0% to 20% (preferably 5% to 20%) of a humectant, 0% to 2% (preferably 0.01% to 0.15%) emulsifying agent, 0% to 0.5% (preferably 0.005% to 0.06%) sweetening agent such as saccharin, 0% to 0.3% (preferably 0.03% to 0.3%) flavoring agent, and the balance water.

Suitable lozenge and chewing gum components are disclosed in U.S. Patent No. 4,083,955, April 11, 1978 to Grabenstetter et al., incorporated herein by reference.

Other optional components useful in the present invention are pyrophosphate salts such as those described in U.S. 4,515,772, May 7, 1985 to Parran et al. incorporated herein by reference. Also useful are nonionic antimicrobials such as triclosan described in U.S. 4,894,220, January 16, 1990 to Nabi et al. Both patents are incorporated herein by reference.

The pH of the present compositions and/or its pH in the mouth can be any pH which is safe for the mouth's hard and soft tissues. Such pH's are generally from about 3 to about 10, preferably from about 4 to about 8.5.

METHOD OF MANUFACTURE

The carrier compositions of the present invention can be made using methods which are common in the oral products area.

For example, toothpaste compositions may be prepared by mixing part of the humectant and water together and heating to 66°-71°C. The fluoride source, if present, is then added along with the sweetener, the synthetic anionic polycarboxylate or copolymer and the polyphosphonate, the opacifier and the flavor. To this mixture is added the abrasive which is mixed in well. The thickener is then slurried with the remainder of the humectant and milled prior to being added to the other components.

COMPOSITIONS USE

The present invention in its method aspect involves applying to the oral cavity safe and effective amounts of the anticalculus agents. Generally an amount of at least about 0.025 grams of the polymer and at least about 0.150 grams of the polyphosphonate salt(s).

The following examples further describe and demonstrate preferred embodiments within the scope of the present invention. The examples are given solely for illustration and are not to be construed as limitations of this invention as many variations thereof are possible without departing from the spirit and scope thereof.

EXAMPLES I - IV

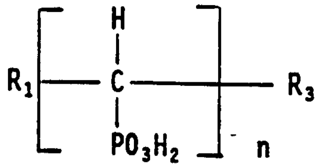
The following are compositions representative of the present invention.

	Weight %			
Component	I	II	III	IV
Sorbitol (70% Aqueous Solution)	35.000	35.000	35.000	35.000
Sodium Fluoride	0.243	0.243	0.243	0.243
Glycerin	5.000	5.000	5.000	5.000
Ioto Carrageenan	0.750	0.750	0.750	0.750
Sodium Saccharin	0.280	0.280	0.280	0.280
EHDP	1.000	1.250	1.700	1.750
Polyacrylic Acid (LMW-45N)[1]	14.700	14.700	14.700	14.700
Titanium Dioxide	0.500	0.500	0.500	0.500
Flavor	1.044	1.044	1.044	1.044
Precipitated Silica	20.000	20.000	20.000	20.000
Sodium Alkyl Sulfate (27.4% Aqueous Solution)	4.000	4.000	4.000	4.000
Sylox 15	2.000	2.000	2.000	2.000
Water	q.s. 100.000%	100.000%	100.000%	100.000%

[1]: Offered by Rohm and Haas as LM-45N having mass average molecular weight of 4500. A solution of 45.6% solids is used.

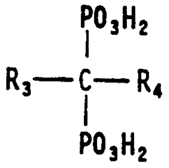
CLAIMS:

1. An anticalculus oral composition comprising:
   (a) a safe and effective amount of a polyphosphonate selected from the group consisting of those of the formulae:



$$R_1\left[\begin{array}{c} H \\ | \\ -C- \\ | \\ PO_3H_2 \end{array}\right]_n R_3$$

(I)



$$R_3-\overset{PO_3H_2}{\underset{PO_3H_2}{C}}-R_4$$

(II)

wherein R_1 and R_2 are each hydrogen or CH_2OH; n is an integer of from 3 to 10; R_3 is hydrogen, alkyl containing from 1 to about 20 carbon atoms, alkenyl containing from 2 to about 20 carbon atoms, phenyl, naphthyl, phenylethenyl, benzyl, halogen, amino, dimethylamino, diethylamino, N-hydroxy-N-ethylamino, acetylamino,

$-CH_2COOH$,

$-CH_2PO_3H_2$, $-CH(PO_3H_2)(OH)$ or

$-CH_2CH(PO_3H_2)_2$

R_4 is hydrogen, lower alkyl, amino, benzyl, halogen, hydroxyl, $-CH_2COOH$, $-CH_2PO_3H_2$, or $-CH_2CH_2PO_3H_2$; or a pharmaceutically acceptable salt thereof;

   (b) a safe and effective amount of a synthetic anionic polycarboxylate which is a copolymer of maleic anhydride and benzyl methyl ether and having a molecular of less than about 1,000,000;
   (c) a safe and effective amount of a water soluble fluoride ion source; and
   (d) a pharmaceutically acceptable carrier.

2. An anticalculus composition according to Claim 1 wherein the polyphosphonate is ethane-1-hydroxy-1,1-diphosphonic acid or a pharmaceutically acceptable salt thereof.

3. An anticalculus composition according to either of Claims 1 or 2 wherein the fluoride ion source is selected from the group consisting of sodium fluoride, sodium monofluorophosphate, stannous fluoride, and mixtures thereof.

4. An anticalculus composition according to any of Claims 1-3 wherein the polycarboxylate is selected from the group consisting of polyacrylic acid, polyvinyl methyl ether maleic anhydride copolymers and mixtures thereof.

5. An anticalculus composition according to any of Claims 1-4 which is in the form of a toothpaste.

6. An anticalculus composition according to any of Claims 1-5 which in addition contains a dental abrasive.

7. An anticalculus composition according to any of Claims 1-6 wherein the fluoride ion source is sodium fluoride.

8. An anticalculus composition according to any of Claims 1-7 wherein the dental abrasive is a silica dental abrasive.

9. An anticalculus composition according to Claim 4 which is in the form of a mouthrinse.

10. An anticalculus composition according to Claim 9 which in addition contains a humectant and ethanol.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 93/05521

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 A61K7/16

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	A61K

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	EP,A,0 341 662 (THE B.F. GOODRICH COMPANY) 15 November 1989 see the whole document ---	1-10
Y	US,A,5 096 699 (A. GAFFAR) 17 March 1992 see the whole document ---	1-10
Y	EP,A,0 236 827 (BLENDAX-WERKE R. SCHNEIDER GMBH & CO.) 16 September 1987 see the whole document -----	1-10

° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
27 AUGUST 1993	09.09.93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	SIERRA GONZALEZ

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9305521
SA 75811

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 27/08/93
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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		AU-A- 3456389	09-11-89
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		CA-A- 2058053	21-06-92
		CN-A- 1062653	15-07-92
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		JP-A- 4334314	20-11-92
		US-A- 5208009	04-05-93
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		JP-A- 62212314	18-09-87

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82