

UNITED STATES PATENT OFFICE

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DENTIFRICE COMPOSITIONS

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1 The present invention relates to dentifrices and more particularly to dentifrices in paste, powder or liquid form which contain microcrystalline aluminum hydroxide as an essential cleansing and polishing agent. This application is a continuation-in-part of our copending applications, Serial No. 645,950, filed February 6, 1946, now abandoned, and Serial No. 750,362, filed May 24, 1947, now abandoned.

Dentifrices are usually mixtures which assist the toothbrush in cleaning the surfaces of the teeth. Such mixtures contain cleansing, scouring and polishing ingredients and their properties and proportions largely constitute the measure of value of the dentifrice. While it is recognized that a certain amount of scouring is desirable in order to remove accumulated film, it is undesirable to employ an ingredient therein which is excessively abrasive due to deleterious effects produced on the teeth and tooth structure. On the other hand, too little scouring power in the dentifrice renders it valueless for cleansing purposes. At the same time it is recognized that in addition to purely cleansing and scouring actions, it is desirable that the dentifrice polish the teeth and give a luster thereto.

Various agents for cleansing, scouring and polishing have heretofore been incorporated in dentifrices, including precipitated chalk, calcium phosphates, magnesium carbonate, oxide and hydroxide, kaolin, fuller's earth, sodium borate and perborate, finely powdered pumice, silica, soaps and synthetic detergents. Some of these agents, moreover, have been used in colloidal, hydrated and gel form. All of these materials when used in large amounts as the sole cleansing, scouring and/or polishing agent in a dentifrice suffer from the disadvantage of being either inordinately abrasive, or else ineffective in cleansing, scouring and/or polishing power. Moreover, certain of them, such as chalk, magnesium carbonate and oxide, when used in the necessary amount, leave a disagreeable, chalky aftertaste or astringent feeling in the mouth. The excessive abrasiveness of certain cleansing, scouring and/or polishing agents is a function of relatively large particle size, angular particle shape and hardness. Some agents are so hard that they scratch the tooth surfaces and produce only a matte-like finish. Other agents are used as relatively large particles which tend to damage the tooth surface and produce a matte-like effect, particularly since such particles frequently have a shape which presents sharp points, acute angles and acicular configurations. When soap

2 or a synthetic detergent is employed as the principal dentifricial ingredient, the resulting dentifrice, although having cleansing power, lacks adequate scouring and polishing power. These and other related factors must be taken into account in compounding or formulating a dentifrice. It is for such reasons that existing dentifrices either are excessively abrasive and therefore inherently harmful, particularly when used one or more times daily as a part of a regular dental hygiene program, or have inadequate scouring and polishing power. There is, therefore, a difficult problem involved of balancing the formulation to give optimum effects which has not been completely or satisfactorily solved heretofore so far as we are aware.

An object of this invention therefore is to provide improved dentifrices having effective cleansing, scouring and polishing action without harmful effects on the teeth.

Another object of the invention is to incorporate in a dentifrice an agent affording satisfactory scouring and polishing action without excessive abrasiveness and having desirable qualities of particle size, particle shape and hardness.

A further object of the invention resides in a dentifrice which can be safely used one or more times daily and which is capable of imparting a high luster to the surfaces of the teeth without adversely affecting the tooth enamel or the gums.

A still further object of the invention resides in the provision of a dentifrice with an essential component which is comparatively soft and is in the form of submicroscopic particles which are free from objectionably sharp points, acute angles and acicular configurations.

Our invention is predicated upon the discovery that dentifrices containing as an essential ingredient thereof a major portion of microcrystalline aluminum hydroxide the particle size of which is largely or substantially entirely submicroscopic, and mainly in the range of 0.025–0.5 microns, exhibit markedly different and exceptional properties with respect to cleaning, scouring, polishing and restoring natural luster to teeth without causing objectionable abrasion or damaging the tooth enamel or structure.

Although the microcrystalline aluminum hydroxide which forms the essential polishing agent of our new dentifrices affords some cleansing action, we have found that for some types of teeth that are difficult to clean it is preferably used in combination with a relatively minor proportion of an agent which serves to augment the cleansing action and to afford adequate but

not excessive scouring action. As such a supplementary cleansing and scouring agent we employ a relatively soft, water-insoluble, tasteless powder having a particle size of about 5-30 microns. This corresponds roughly to a mesh size of 325 to 600 or somewhat finer. For the purpose we preferably employ crystalline aluminum hydroxide, although, but less desirably, other agents such as aluminum oxide, calcium carbonate, dicalcium phosphate, tricalcium phosphate or calcium sulfate can be used. The particle size of the supplementary cleansing and scouring agent, which comprises only a minor quantity of our dentifrice compositions, is considerably larger than the particle size of the aforesaid microcrystalline aluminum hydroxide, which comprises a major portion of our dentifrice compositions. The particle size of the microcrystalline aluminum hydroxide will be discussed more in detail hereinbelow. Hereinafter in the specification and claims, in order to differentiate between the two foregoing mentioned types of aluminum hydroxide of different particle size, the aluminum hydroxide which is used in a major proportion as a cleansing and polishing agent in our dentifrices will be referred to as microcrystalline aluminum hydroxide; and the aluminum hydroxide of larger particle size, used as a supplementary cleansing and scouring agent in a minor proportion in our dentifrice composition, will be referred to as crystalline aluminum hydroxide.

In preparing our dentifrices we have found that best results are obtained when one part of the aforesaid additional cleansing and scouring agent of larger particle size is incorporated with about five to twenty-five parts of the microcrystalline aluminum hydroxide.

It is, therefore, an additional object of this invention to produce a new and useful dentifrice composition which comprises a major portion of microcrystalline aluminum hydroxide as a cleansing and polishing agent and a minor portion of a supplementary cleansing and scouring agent.

A still further object of the invention resides in providing a dentifrice containing both a major quantity of microcrystalline aluminum hydroxide $\text{Al}(\text{OH})_3$ and a minor quantity of crystalline aluminum hydroxide $\text{Al}(\text{OH})_3$ of larger particle size, in order to remove or prevent the formation of stains on teeth which are difficult to clean and polish or keep clean and polished.

We have found that the addition of preferably about one part of crystalline aluminum hydroxide $\text{Al}(\text{OH})_3$ of 5-30 micron particle size per ten parts of microcrystalline aluminum hydroxide provides a dentifrice composition which not only has those properties and advantages set forth hereinabove for the dentifrice compositions containing microcrystalline aluminum hydroxide as the only cleansing and polishing agent but, in addition, is characterized by the fact that the conjoint use of the minor quantity of this crystalline aluminum hydroxide of larger particle size along with a major quantity of the microcrystalline aluminum hydroxide $\text{Al}(\text{OH})_3$ gives an enhanced and vastly superior cleansing, scouring and polishing action which not only brings all types of teeth to their fully polished condition but which removes and/or prevents the formation of stains which frequently arise in connection with some types of teeth.

The microcrystalline aluminum hydroxide employed in our dentifrices has the chemical form-

ula $\text{Al}(\text{OH})_3$. It exists in two crystalline modifications, the alpha form or hydrargillite and the beta form or bayerite. These crystalline forms are well known to crystallographers, the alpha form comprising monoclinic prisms (Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green & Co., 1940, vol. V, p. 275) and the beta form being a metastable configuration which is in time transformed into the alpha form (Thorpe and Whitley, "Thorpe's Dictionary of Applied Chemistry," Longmans, Green and Co., 4th edition, 1937, vol. I, p. 284). Generally the two crystalline modifications are found together since the relative amounts of each depend upon the conditions of precipitation of the aluminum hydroxide. Microcrystalline aluminum hydroxide is odorless and tasteless. It is inert and insoluble in water, has good properties of absorption and is much less abrasive than precipitated chalk, which is usually employed as the standard for comparison.

Due to its finely divided state, the commercially available microcrystalline aluminum hydroxide is apparently not screened by the usual sieving methods, but rather is graded to size by differential particle weight methods. This may explain why commercial samples unless blended, show a particle size distribution which roughly follows the well-known probability distribution law. Thus it is not practical to specify the particle size in an exact fashion clearly defining the limits of particle size, but it is possible to specify the average or mean diameter of the particles, and to indicate the spread of particle size distribution.

A representative sample of microcrystalline aluminum hydroxide upon examination for particle size under the electron microscope affords the following data:

Size, microns	Per cent	Per cent larger than size indicated
>0.5	0.384	0.4
0.4 - 0.5	2.115	2.5
0.3 - 0.4	5.192	7.7
0.25 - 0.3	4.807	12.5
0.2 - 0.25	6.346	18.8
0.15 - 0.2	8.846	27.7
0.1 - 0.15	12.692	40.4
0.075 - 0.1	12.884	53.2
0.05 - 0.075	22.5	75.7
0.025 - 0.05	22.115	97.9
<0.025	2.115	99.99
	99.996	

From the above data it can be readily determined that the apparent mean particle size of this particular specimen of microcrystalline aluminum hydroxide is 0.103 micron.

We have found that microcrystalline aluminum hydroxide having a mean particle size below approximately 0.3 micron and having a distribution such that less than 5-10% of the particles are larger than 0.5 micron is especially efficacious. This is in sharp contrast with the comparatively large size of the particles of the cleansing, scouring and polishing agents in existing commercial dentifrices. In such commercial dentifrices seldom are particles of less than 1 micron in diameter encountered and the usual size is in the range of 2-10 microns.

Microcrystalline aluminum hydroxide is essentially of such fine particle size as to be beyond the resolving power of the microscope. In order to determine the physical characteristics of the

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microcrystalline aluminum hydroxide, we have therefore had it subjected to X-ray diffraction studies to learn as much as possible about the internal symmetry and crystal structure of the material, and to electron microscope studies to characterize as far as possible the average external shape and size of the particles. The results can best be interpreted on the basis that the particles of microcrystalline aluminum hydroxide are loose agglomerates of crystallites, each crystallite individually being so minute, of the order of .001 to .01 of micron in diameter, as to be close to the limits of resolving power of the electron microscope and also to give only diffuse X-ray diffraction patterns. These individual crystallites are probably composed of relatively few molecules, possibly of the order of 10-50 per crystallite. The agglomerates of crystallites vary in size and correspond to the particles whose size range in a representative sample has been indicated above. These agglomerates, when large enough for observation under the electron microscope have external configurations which approximate spherical symmetry. In other words, these agglomerates—the particles of the microcrystalline aluminum hydroxide—do not show an ellipsoidal or columnar form and no axis is significantly longer than any other axis. The particles, therefore, are accordingly free from sharp points, acute angles, and acicular configurations. The X-ray diffraction pattern shows lines characteristic both of the alpha and the beta forms of aluminum hydroxide, indicating that a mixture of the two forms is present. According to our studies, the relative proportions of these two forms may vary considerably without affecting the efficacy of the microcrystalline aluminum hydroxide as used in our dentifrices.

The hardness of the microcrystalline aluminum hydroxide particles is not directly measurable but it is known that they are relatively soft in nature and probably somewhat less than 2-3 on the Mohs' scale. They are believed to have a hardness of about $\frac{2}{3}$ that of chalk and about $\frac{1}{2}$ that of aragonite, on the basis of the macrocrystals.

Microcrystalline aluminum hydroxide having the form and particle size referred to above, as an ingredient in dentifrice compositions, gives an excellent, hitherto unattainable luster and polish to the surfaces of the teeth without harmful or damaging effects and without scratching or unduly abrading the teeth or tooth structure. Tests show that a mirror polish is produced by our new dentifrice in contrast to the ground-glass or matte type of surface which results from treatment with customary dentifrices and agents such as calcium carbonate and the calcium phosphates.

The microcrystalline aluminum hydroxide with or without a minor quantity of the hereinabove described supplementary cleansing and scouring agent, may be incorporated into dentifrice compositions in any suitable manner depending upon whether a paste, powder, liquid, chewing gum or other dental preparation is to be produced. For this purpose we add appropriate proportions of surface-active agents, binders, excipients or plasticizers, flavoring materials, sweetening agents, coloring material and lubricants. By a plasticizer, I mean a liquid which when mixed with powdery constituents affords a paste such as glycerol or propylene glycol, such heavy liquids used alone or diluted with water. Other heavy paste-forming liquids as mentioned hereinbelow

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may be used as plasticizer. The various combinations of these ingredients may be conveniently termed dentifrice vehicles, adjuvants or bases (and are so referred to hereinafter) and together with the cleansing, scouring and polishing agent, or agents, make up the dental paste, powder, liquid, chewing gum or other dental preparation.

Our invention is further illustrated by the following examples. All parts are by weight.

Example 1

Tooth powder.—90 parts of microcrystalline aluminum hydroxide having a mean particle size of approximately 0.1 micron and 0.1 part of saccharin are thoroughly mixed in a mechanical mixer such as a ribbon type powder mixer and sifter. Then 5 parts of powdered, neutral white soap are mixed in, followed by 3.5 parts of flavoring such as methyl salicylate.

When in the foregoing preparation 81 parts of microcrystalline aluminum hydroxide plus 9.0 parts of crystalline aluminum hydroxide are used in place of the 90 parts of microcrystalline aluminum hydroxide, the resulting composition has an enhanced scouring and cleansing action, while retaining its high polishing characteristics.

Example 2.

Tooth powder.—By proceeding in accordance with the directions of Example 1 but substituting 2-2.5 parts of a synthetic detergent such as sodium lauryl sulfoacetate instead of the soap, a tooth powder with high polishing power is obtained.

Example 3

Tooth powder.—The dentifrice of Examples 1 or 2 may be put in the form of small, discrete granules by procedures of generally known types. For example, an aqueous slurry prepared by mixing 50 parts of microcrystalline aluminum hydroxide, 2 parts of sodium lauryl sulfoacetate, 0.1 part of saccharin and 0.1 part of gum tragacanth may be dried by evaporation below 60° C., as by spray drying. The dried product is then screened until all granules pass through a 40 mesh screen and are retained by an 80 mesh screen.

Example 4

Tooth paste.—90 parts of high grade propylene glycol (pharmaceutical quality) and 170 parts of 4% low-viscosity methyl cellulose solution are thoroughly mixed. Into the solution are stirred 0.5 part of saccharin and 4.5 parts of flavoring such as oil of birch. The resulting solution is added to 175 parts of microcrystalline aluminum hydroxide and the mass is mixed in a dough mixer and passed through a colloid mill.

Example 5

Tooth paste.—A gel is formed of 1.5 parts of gum tragacanth and 50 parts of water. 64 parts of glycerin, 0.18 part of saccharin and 1.5 parts of flavoring such as oil of peppermint are added and mixed. 84 parts of microcrystalline aluminum hydroxide are mixed into the liquid, followed by 2 parts of powdered, neutral white soap. The resulting mass is put through a colloid mill.

Example 6

Liquid dentifrice.—30 parts of microcrystalline aluminum hydroxide of substantially submicroscopic particle size is homogenized in a solution containing 5 parts of alcohol U. S. P., 3 parts of low-viscosity methyl cellulose, 3 parts of sodium

lauryl sulfate, and sufficient coloring, flavoring and water to make 80 parts of solution. The homogenization may be conveniently carried out in a blender of the Waring type.

Also exemplary of our invention is the composition that results when in the above preparation about 3 parts of the microcrystalline aluminum hydroxide is replaced by about 3 parts of crystalline aluminum hydroxide.

Example 7

Tooth paste.—A dentifrice composition containing a minor quantity of alumina as the supplementary cleansing agent contains the following ingredients in substantially the following amounts:

Ingredient	Approximate per cent by weight
Aluminum Hydroxide $Al(OH)_3$ (microcrystalline).....	42.50
Alumina (Aluminum oxide) Al_2O_3	2.00
Glycerin.....	25.00
Water.....	24.50
Sodium lauryl sulfoacetate (or other synthetic sulfate or sulfonate type of anionic detergent).....	1.00
Flavor.....	0.70
Tragacanth.....	0.50
Methyl para-Hydroxybenzoate.....	0.10
Saccharin, soluble.....	0.05
Phosphoric acid H_3PO_4 (100%)—enough to produce a pH value of 6.5 to 7.5.	

Example 8

TOOTH PASTE

Ingredient	Approximate per cent by weight
Aluminum Hydroxide $Al(OH)_3$ (microcrystalline).....	39.00
Aluminum Hydroxide $Al(OH)_3$ (crystalline).....	4.00
Glycerin.....	25.00
Water.....	26.00
Sodium lauryl sulfoacetate (or other synthetic sulfate or sulfonate type of anionic detergent).....	1.00
Flavor.....	0.70
Tragacanth.....	0.50
Methyl para-Hydroxybenzoate.....	0.10
Saccharin, soluble.....	0.05
Phosphoric acid H_3PO_4 (100%)—enough to produce a pH value of 6.5 to 7.5.	

From the foregoing illustrative examples it will be appreciated that microcrystalline aluminum hydroxide constitutes a major proportion of our new dentifrices and that, in the case of a powder dentifrice, the microcrystalline aluminum hydroxide is the predominating ingredient. Thus our new dentifrices are characterized by being largely or, in some cases, almost wholly composed of the cleansing, scouring and polishing agent or agents and thus differ markedly from dentifrices known to us which utilize a very minor and often insignificant proportion of special cleansing, scouring and polishing agents. The microcrystalline aluminum hydroxide content or the sum content of microcrystalline aluminum hydroxide and additional cleansing and scouring agent of our dentifrices ranges generally from about 25–30% in the case of liquid dentifrices to about 90–95% in the case of powders. Our new dentifrices enjoy the further advantage of being largely or almost wholly composed of an amphoteric material having no pronounced acid or basic qualities.

Various modifications can be made from the foregoing examples without departing from our invention. For instance, instead of soap, sodium lauryl sulfoacetate, or sodium lauryl sulfate, some other surface-active agent could be used, such as the amine and metal salts of alkyl sul-

fates and sulfonated fatty alcohols, the amine and metal salts of aliphatic sulfonic acids and aliphatic-substituted aromatic sulfonic acids, the fatty acid amides of dialkylaminoalkylamines, basically substituted esters of fatty acids, and the like. Other flavoring materials may also be employed, including vanillin; oil of cinnamon, clove, anise, fennel, lavender, and eucalyptus; thymol, menthol, camphor, and other terpenes.

10 Binders, excipients and lubricants that are satisfactory in the dentifrices that we contemplate comprise all such substances generally employed in such a manner, including gum karaya, Irish moss, gum acacia, agar-agar, salts of carboxymethyl cellulose, esters of polyhydroxy compounds such as sorbitol citrate, diethylene glycol diborate, mannitol oleate and the like, pectin, sorbitol syrup, corn starch, glycerite of starch, glycerite of sodium stearate, sodium alginate, 20 gelatin, glycols, fatty acid esters of glycerine and glycols, mineral oil, petrolatum, alcohol and similar materials. Besides saccharin, other sweetening agents such as sugar, starch and sugar syrups, honey, dulcitol and lactose may be employed. 25 Chicle or compositions of chicle and other chewing gum ingredients, such as corn syrup, form satisfactory bases for incorporating microcrystalline aluminum hydroxide in chewing gum.

30 We claim:

1. A dentifrice comprising microcrystalline aluminum hydroxide having a particle size substantially in the range of 0.025 to 0.5 microns, a dentifrice vehicle and a detergent.

35 2. A dentifrice comprising microcrystalline aluminum hydroxide, a dentifrice vehicle and a detergent, the particles of said microcrystalline aluminum hydroxide being in the form of agglomerates of crystallites and having a mean diameter of not more than approximately 0.3 micron.

40 3. A dentifrice powder comprising microcrystalline aluminum hydroxide having a particle size averaging approximately 0.1 micron, a dentifrice vehicle and a detergent.

45 4. A dentifrice paste comprising microcrystalline aluminum hydroxide having a particle size averaging approximately 0.1 micron, a dentifrice vehicle, a surface-active agent and a plasticizer.

50 5. A liquid dentifrice dispersion comprising microcrystalline aluminum hydroxide having a particle size averaging approximately 0.1 micron, a liquid vehicle and a surface-active agent.

55 6. A dentifrice containing as an essential cleansing and polishing agent microcrystalline aluminum hydroxide of a particle size mainly in the range of 0.025–0.5 micron and averaging approximately 0.1 micron and a dentifrice vehicle, said microcrystalline particles being characterized by freedom from acute angles, sharp points and acicular configurations, and by being softer than chalk, the microcrystalline aluminum hydroxide ranging from about 25–95% of the dentifrice.

60 7. A dentifrice comprising as essential ingredients thereof a major proportion of microcrystalline aluminum hydroxide, a minor proportion of a supplementary cleansing and scouring agent, said supplementary cleansing and scouring agent being a relatively soft, water-insoluble, tasteless powder having a particle size of 5–30 microns and a dentifrice vehicle.

75 8. A dentifrice comprising as essential ingredients thereof microcrystalline aluminum hydroxide, a supplementary cleansing and scouring

agent in the ratio of about 1 part by weight of the latter ingredient to about 5 to 25 parts of the former, said supplementary cleansing and scouring agent being a relatively soft, water-insoluble, tasteless powder having a particle size of 5-30 microns and a dentifrice vehicle.

9. A dentifrice comprising as essential ingredients thereof a major proportion of microcrystalline aluminum hydroxide having a mean diameter of not more than approximately 0.3 micron, a minor proportion of crystalline aluminum hydroxide having a particle size of about 5 to 30 microns and a dentifrice vehicle.

10. A dentifrice comprising as essential ingredients thereof microcrystalline aluminum hydroxide having a particle size in the range of 0.025-0.5 micron and averaging approximately 0.1 micron, crystalline aluminum hydroxide having a particle size of about 5 to 30 microns in the ratio of about 1 part of the latter ingredient to about 5 to 25 parts of the former, and a dentifrice vehicle.

11. A dentifrice paste comprising as essential ingredients thereof microcrystalline aluminum hydroxide having a particle size in the range of 0.025-0.5 micron and averaging approximately

0.1 micron, crystalline aluminum hydroxide having a particle size of about 5 to 30 microns in the ratio of about 1 part of the latter ingredient to about 10 parts of the former, and a dentifrice vehicle.

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