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TOOTH PASTE HAVING IMPROVED TOOTH CLEANING PROPERTIES

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ABSTRACT OF THE DISCLOSURE

Toothpaste, of the non-self-heating type and of the type which does not liberate oxygen in the presence of water, having improved tooth cleaning properties comprising a mild abrasive agent, in major proportion based upon the weight of the solid ingredients of the toothpaste, and at least 20%, by weight, of the total of the liquid ingredients of said toothpaste, of at least one water-soluble polyoxyalkyleneglycol having a molecular weight of at least 200.

Our invention relates to improved toothpastes which are characterized by substantially enhanced cleaning properties, with low abrasion characteristics. The toothpastes of the present invention are of the type which do not generate sensible heat on contact with water nor generate oxygen on contact with water. In this sense, they may be considered to be toothpastes of conventional character except for the improvements which are brought about by the present invention.

Conventional toothpaste formulations comprise a mixture of a number of solid ingredients with a mixture of a number of liquid ingredients all of which, together, produce a product of suitable paste consistency. The solid ingredients of the toothpaste formulation comprise one or more abrasives, and, in certain cases, detergents and miscellaneous ingredients such as gums, sweeteners, thickeners, etc., the abrasive constituting at least the major proportion, that is, in excess of 50% by weight, of the total of the solid ingredients of the toothpaste formulation. The liquid ingredients of the toothpaste formulation usually comprise water, humectant, and, commonly, very minor constituents such as flavors or flavoring oils.

Numerous efforts have been made to provide toothpastes which clean the teeth rapidly as well as impart an enhanced polish. One of such approaches lies in the selection of the abrasive ingredient or ingredient of the toothpaste formulation. The use of relatively harsher abrasives will sometimes result in a more rapid and more complete cleaning of the teeth brushed with toothpastes containing the same than if abrasives with a milder abrading action are used in the toothpastes. This type of approach to bring about more rapid and more complete cleaning of the teeth is undesirable because of the adverse effects on exposed dentin and oral health.

Accepted Dental Therapeutics 1969/70, published by the American Dental Society, discusses the function of an abrasive, and states that "Dentifrices should certainly be free from very harsh abrasives, such as materials that can scratch enamel." It further states "there has been a recent tendency to promote dentifrices on the basis of their ability to whiten or brighten teeth. Such claims appear to relate almost exclusively to the incorporation in the dentifrices of harsher abrasive agents such as calcium carbonate, anhydrous dibasic calcium phosphate, or silica.

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Highly abrasive products should not be used regularly by individuals having exposed cementum or dentin, or possibly, by individuals with restored tooth surfaces of the softer synthetic materials." It concludes that "there would appear to be no valid reason for the use of a dentifrice with a greater abrasiveness than is necessary to prevent residual accumulation on the teeth."

An early report concerning the abrasion properties of dentifrice cleaning and polishing agents was made in a paper entitled "Experiments and Observation on the Wasting of Tooth Tissue Variously Designated as Erosion Abrasion, Chemical Abrasion, Denudation, Etc.," Dent. Cosmos, 49:1–23; 109–124; 225–247; 1907, the author concluding commonly used dentifrices at that time were capable of producing damage to the teeth. Similar results were obtained by various later investigators.

Studies have also been made on the necessity of an abrasive in a dentifrice. Manly, R. S.: A Structureless Recurrent Deposit on Teeth, J. Dent. Res. 22:479–486, 1943, and McCauley et al., Clinical Efficacy of Powder and Paste Dentifrices, J. Amer. Dent. Assoc. 33:993–997, 1946, noted a high incidence of pellicle in persons using a nonabrasive dentifrice. Phillips and Van Huysen: Dentrifrices and the Tooth Surface, Amer. Perf. 50:33–41, 1948, reported a high incidence of tooth discoloration from the collection of material on the tooth surface. Vallotton, C. F.: An Acquired Pigmented Pellicle of the Enamel Surface, J. Dent. Res. 24:161–169, 1945, and Kitchin, P. C. and Robinson, H. B. G.: How Abrrasive Need a Dentifrice Be? J. Dent. Res. 27:501–406, 1948, reported that the teeth of about two thirds of the persons using a liquid dentifrice with no abrasive system had a variety of stains. Kitchin and Robinson in the same paper also found that only 4% of subjects brushing with water alone failed to form stains within a two week period. Dudding et al.: Patient Reactions to Brushing Teeth with Water, Dentifrice, or Salt and Soda, J. Periodont 31:386–392, 1960, found that toothbrushing without the use of a dentifrice resulted in pellicle formation in 93% of the subjects after a five week study compared to only 9% when a dentifrice was used. Kitchin and Robinson, in their evaluation of the ability of commercial dentifrices to prevent pellicle formation, suggested that the cleaning ability was related to abrasiveness to dentin.

It is apparent from the foregoing studies on abrasion and cleaning that the usual method of increasing tooth cleaning generally results in a dentifrice having a high level of abrasion for dentin.

The abrasiveness of a dentifrice has most recently been determined by the so-called RDA method of Grabenstetter, et al., in their paper The Measurement of the Abrasion of Human Teeth by Dentifrice Abrasion: A Test Utilizing Radioactive Teeth, J. Dent. Res. 37:1060–1068, 1958. This method utilizes freshly extracted human teeth, which are irradiated, producing the radio nuclide, P^{32}, a high energy beta emitter with a half life of 14.3 days. This irradiated tooth is brushed with a mechanical toothbrush, across the dentin. Using a mica end-window Geiger-Muller counter for which the background estimated activity of a dried P^{32} source is 10^{-4} microcuries, it is possible to determine 10^{-7} g. of worn dentin in the abrasive slurry.

A recent paper by Stookey and Muhler, Laboratory Studies Concerning the Enamel and Dentin Abrasion Properties of Common Dentifrice Polishing Agents, J. Dent. Res. 47:524–532, 1968, utilized the RDA method to evaluate thirty-six commercial paste dentifrices. They found RDA values of 82 to 1019. There were eight prod-

ucts that could be classified as mildly abrasive, with a value of under 200, twenty-one products fell into the intermediate abrasiveness category, with dentin abrasion values ranging between 200 and 400, and seven products fell into the harsh abrasiveness category with dentin abrasion values over 400.

It has been discovered, in accordance with the present invention, that certain combinations of mild abrasive agents, and a water-soluble polyoxyalkyleneglycol, in a toothpaste with an RDA value of less than 200, exhibit improved and unique properties.

The present invention is based upon enhancing the cleaning and luster of teeth by means of the incorporation into a toothpaste, which contains a major proportion of one or more mild abrasives based on the weight of the solids of the toothpaste formulation, and at least 20%, by weight of the total of the liquid ingredients of the toothpaste formulation, of one or more polyoxyalkyleneglycols described in detail below. While the polyoxyalkyleneglycols may constitute the total of the liquid ingredients of the toothpaste, it is generally more desirable that they constitute only a part of the liquid ingredients of the toothpaste formulation, not less than 20% by weight of said liquid ingredients and, better still, from 35% to 60% of the total weight of the liquid ingredients of the toothpaste. Based on the weight of the finished toothpaste, the polyoxyalkyleneglycols will usually most desirably comprise from about 20% to about 30% although the percentages may be somewhat lower, usually not below about 15%, or somewhat higher, usually not more than 45%.

The polyoxyalkyleneglycols employed must be water-soluble and particularly desirable, but not necessarily, liquids at room temperatures. Various of them can be represented by the formula

$$HO—Alk—O—(Alk—O)_nH$$

where Alk is an alkylene radical containing from 2 to 4 carbon atoms, namely, ethylene, propylene or butylene, especially ethylene, and n is an integer such that the molecular weight of the polyoxyalkyleneglycol is at least 200 and so that the polyoxyalkyleneglycol is reasonably water-soluble or is soluble in the liquid ingredients of the toothpaste formulation. In the case of the polyoxyethyleneglycols, the subscript n is at least 4 and can be materially greater than 4 and, indeed, up to the point where the polyoxyethyleneglycol is a solid at room temperature. Illustrative polyoxyalkyleneglycols which are useful in the production of toothpastes in accordance with our invention are polyoxyethyleneglycols having molecular weights of about 200, 350, 400, 500, 600, 800 and 1,000 and, as stated above, still higher; tetraoxypropyleneglycol, pentaoxypropyleneglycol and tetraoxybutyleneglycol. Mixtures of the aforesaid polyoxyalkyleneglycols can also be utilized. Furthermore, polyoxyalkyleneglycols can be used in which there are present ethoxy and propoxy groups, or ethoxy and butoxy groups, or propoxy and butoxy groups, or all three of such groups as, for instance, 1 mole of dioxyethyleneglycol adducted with 3 moles of propylene oxide; 1 mole of polyoxyethyleneglycol 400 adducted with 1 mole of propylene oxide; 1 mole of dioxypropyleneglycol adducted with 6 moles of ethylene oxide, and the like. Particularly satisfactory are polyoxyethyleneglycols having molecular weights between about 400 and about 800. It is desirable to include with said latter polyoxyethyleneglycols, in any given toothpaste formulation made in accordance with the present invention, a smaller proportion of higher polyoxyethyleneglycols, such as those of a molecular weight of about 2,000 to about 6,000, generally in the range of about 5 to 12% by weight of the toothpaste. The polyoxyalkyleneglycols utilized pursuant to the present invention are not surfactants or surface active agents in the sense of which such terms are commonly used in the art. For purposes of the present invention, the polyoxyalkyleneglycols employed in the practice of the present invention will, in a 1% solution in water at 25° C., not reduce the surface tension of water to below 45 dynes/cm.

The dry ingredients of the toothpastes of our invention contain one or more abrasive such as precipitated calcium carbonate, dibasic calcium phosphate, tribasic calcium phosphate, calcium pyrophosphate, calcium sulfate, hydrated alumina, insoluble sodium metaphosphate, and the like, the abrasive constituting the major proportion of the total of the dry ingredients or the major proportion of the total of the solids of the toothpaste formulation. The RDA value of the abrasives selected should not be in excess of 200 for best results in accordance with the present invention.

In addition, commonly it is the practice to include one or more detergents or surfactants in the toothpaste formulation and where such is a normally solid product, or contains solids, as will usually be the case, it is considered as constituting a dry ingredient of the toothpaste formulation. Commonly used detergents or surfactants include, by way of illustration, soaps, sodium lauryl sulfoacetate, sodium lauryl sulfate, sulfocolaurate, sodium salts of sulfated monoglyceride (of coconut oil fatty acids), and sodium N-lauroyl sarcosinate.

Other normally solid ingredients which, commonly, are incorporated into toothpastes are binders, which are usually hydrophilic colloids. Among such binders are, for instance, gum arabic, ghatti, gum karaya, gum tragacanth, Irish moss, (Na) alginates, bentonite, Veegum, methyl cellulose and sodium carboxymethylcellulose. It has been found that metallic, particularly aluminum, soaps of fat-forming fatty acids, especially aluminum octoate, are exceptionally satisfactory. Indeed, in those instances where aluminum soaps, such as aluminum octoate, are employed, they appear to coact with the polyoxyalkyleneglycols to further enhance the polish and luster of the brushed teeth. They also function effectively to stabilize the paste character of the toothpaste at the elevated temperatures which are at times encountered in shipping and storage of the toothpastes. Where employed, they will usually be used in a proportion of about 1 to about 12% by weight of the toothpaste. Where aluminum soaps are included in the toothpaste formulations of the present invention, care must be exercised, if water is to be incorporated into the toothpaste formulation, that too much water be not employed since it may destroy the desired gel structure imparted by the aluminum soaps.

The liquid ingredients of the toothpastes of our invention, in addition to the water-soluble polyoxyalkyleneglycols, desirably also include one or more of glycerin, propylene glycol and sorbitol solutions, or mixtures of the same, which are utilized for, in addition to their well-known humectant properties, their ability to improve taste and mouth feel. In certain cases, it may be desirable to include small proportions of water which, generally, will not be in excess of about 5% but, in certain cases, may be appreciably greater, of the weight of the liquid ingredients of the formulation, in the toothpaste formulations of our invention. The water serves mainly to counteract or reduce possible adverse tastes that may otherwise tend to be imparted to the toothpaste by particular polyoxyalkyleneglycols which are utilized in said toothpastes.

Various supplemental ingredients can, of course, be incorporated into the toothpastes to obtain particular effects and they may be of liquid or solid character. Illustrative of such supplemental ingredients are perfumes, dyes or other colorants, antidecay agents such as fluorides and stannous salts, and enzymes, etc.

The following examples are illustrative of toothpastes in accordance with our invention. It will be understood that numerous other toothpastes can be made following the guiding principles and teachings disclosed herein. Unless otherwise specified, all parts are in terms of weight.

EXAMPLE 1

	Parts
Polyoxyethyleneglycol 400	23.275
Polyoxyethyleneglycol 4000	5
Glycerin	23.275
Dicalcium phosphate dihydrate	40
Aluminum octoate	5
Sodium saccharin	0.75
Methyl "Paraben" (methyl ester of parahydroxy benzoic acid)	0.18
Propyl "Paraben" (propyl ester of parahydroxy benzoic acid)	0.02
"Maprofix" 563 (anhydrous sodium lauryl sulfate)	1.5
Flavoring	1

Any suitable procedure can be used to produce the toothpaste from the above formulation. One suitable way is to place the first three listed ingredients into a mixer and heat to about 55 to 60° C. to melt the polyoxyethyleneglycol 4000. The mixture is transferred to another container and allowed to cool to about 35° C. under conditions of mixing. The dicalcium phosphate dihydrate, the sodium saccharin, the methyl "Paraben" and the propyl "Paraben" are then blended in, with stirring, then the aluminum octoate is added, a vacuum of about 25" is drawn and mixing is effected at high speed for about 20 minutes after which the "Maprofix" 563 is added. The mixing is continued under stirring for about 3 to 5 minutes. The temperature rises to about 50° C. during the two last-mentioned mixing steps. The flavoring is mixed in, and then the mixture is pumped into a large tank from which it is filled into conventional toothpaste containers.

Other well known mixing procedures for producing toothpastes can be employed, as such or with minor variations. Thus, for instance, the binder, previously wetted with the humectants, is admixed, under slight heating if desired, with and dispersed in the remaining liquid portion of the toothpaste formulation (except for the flavoring) containing the sodium saccharin and such preservative as may be utilized. The resulting gel is then admixed, in a suitable mixer, with the abrasive, the latter being added gradually to the gel, until homogeneity is obtained. Finally, the flavor and the detergent are added and mixed uniformly through the mass. The latter may then be milled, deaerated, and filled into toothpaste tubes.

EXAMPLE 2

	Parts
Polyoxypropyleneglycol 400	23.25
Dicalcium phosphate dihydrate	42
Glycerin	23.25
Lauryl sodium sulfate	2
Carboxyvinyl polymer ("Carbopol 934")	1
Sodium saccharin	0.5
Water	7.5

Flavoring as desired.

EXAMPLE 3

	Parts
Polyoxyethyleneglycol 600	22.3
Aluminum hydroxide gel (20% water)	53
Glycerin	23
Lauryl sodium sulfate	1
Sodium saccharin	0.1

The improved cleaning properties of the toothpaste formulations of the present invention have been confirmed by tests. Thus, by way of illustration, a test was made with human volunteers to measure the cleaning ability of a typical toothpaste of the invention vs. the cleaning ability of a commercial strongly abrasive toothpaste. Subjects did not brush from the previous day, had the oral residual accumulations stained, were scored, brushed their teeth with the test dentifrices, had remaining oral residual accumulations stained, and were rescored.

	Toothpaste of Example 1	Commercial toothpaste
RDA value	128	472
Number subjects	31	32
Average initial score	2.0323	1.9375
Average score after brushing	.8065	.7188
Average cleaning score	−1.3226	−1.2187

The foregoing test demonstrates that the cleaning ability of the low RDA value mild abrasive dentifrice made in accordance with the present invention was at least as good as that of the high RDA value strongly abrasive dentifrice.

Another test, similar to that outlined in U.S. Pat. No. 2,773,801, was used to measure the stain removing ability of toothpastes made according to the present invention. Cigarettes were smoked by a mechanical device, and the tars were collected. These tars were dissolved in acetone to a uniform concentration. The tars in the acetone were then placed on porous porcelain. The stain was set with water and brushed with water to a point where water alone removed no more stain. The stained porcelain was then brushed with the test toothpastes identified in the following table and diffuse reflectance values initially and at intervals to 15,000 strokes were recorded. The numerical values in said table are reported in terms of percent reflectance value of an unstained porcelain strip as a standard of 100%.

TABLE

Porcelain strip:	Percent reflectance
Unstained	100
(a) Brushed with toothpaste of Example 1 of present application (RDA 129)	98
(b) Brushed with toothpaste of Example 1 of Pat. No. 2,773,801	94.5
(c) Brushed with strongly abrasive commercial toothpaste (RDA 472) used in the above-described first test	89
(d) Brushed with a commercial toothpaste containing about 5.5% polyoxyethylene glycol 400 (described below) (RDA 149)	79

The superior stain-removing property of low abrasive toothpastes made in accordance with the present invention is clear from the foregoing tests.

It heretofore has been known to prepare and commercially market toothpastes containing, in addition to (a) a major proportion of an abrasive, based on the weight of the dry ingredients of the toothpaste, (b) liquid ingredients comprising a humectant, and a substantial amount of water, generally of the order of about 40 to 45%, and also containing about 11% of a polyoxyethyleneglycol of a molecular weight of the order of about 400, said percentages being by weight of the (b) or liquid phase of the toothpaste (about 5.5% by weight of the toothpaste). The apparent function of the polyoxyethyleneglycol in the foregoing known toothpastes is to assist in solubilizing the flavor constituents used in the toothpaste formulation. In any event, such proportions of polyoxyethyleneglycol are ineffective to achieve a cleaning enhancement or polishing effect on the teeth (note test of toothpase (d) in the foregoing table), and, as stated above, a minimum of almost twice that quantity is required. Indeed, it is particularly advantageous, in the practice of the present invention, as has been pointed out above, that the polyoxyethyleneglycol constitute from about 30 to 60% of the total weight of the liquid ingredients of the toothpaste.

It has also heretofore been known, as shown in U.S. Pat. No. 2,501,145, to produce nonaqueous toothpastes containing perborate which, in use, in the presence of water, release oxygen. To increase the stability of said toothpastes against premature release of oxygen, aldehydic

inactivating agents and polyoxyethyleneglycols of a molecular weight in the range of 300 to 2,000 are included in the toothpaste compositions, polyoxyethyleneglycols of viscous character being included to provide a suitable base for the toothpaste. Furthermore, it has been known, as shown in U.S. Pat. No. 3,250,680 to produce nonaqueous toothpastes of the self-heating type containing finely divided solid adsorbent materials capable of sorbing water exothermically, such as silica gel, and a liquid nonaqueous vehicle which is inert to said adsorbent particles, such as polyoxyethyleneglycols and polyoxypropyleneglycols which melt at temperatures no higher than 75° C., such vehicles being employed in small proportions in the toothpaste, generally of the order of less than 3%. These prior known disclosures provide no teaching nor suggestion of the present invention which is based upon the discovery that certain polyoxyalkyleneglycols when used in certain proportions in otherwise conventional toothpastes and especially in conjunction with mild abrasives, to wit, those having an RDA value of not more than 200, and better still, not more than about 150, bring about wholly unexpected improvements in the cleaning of teeth and removal of stains.

The term "toothpaste," as used in the claims, will be understood to mean toothpastes which are not of the self-heating type and are not of the oxygen-liberating type.

What is claimed is:

1. A toothpaste containing (a) a major proportion of a toothpaste abrasive based on the weight of the solids of said toothpaste, said toothpaste abrasive having an RDA value of not more than 400, (b) at least one paste-forming ingredient, and (c) at least 20%, by weight of the total of the liquid ingredients of said toothplaste, of at least one water-soluble polyoxyalkyleneglycol having a molecular weight of at least 200, the alkylene radicals of said polyoxyalkyleneglycol containing from 2 to 4 carbon atoms,

said polyoxyalkyleneglycol constituting at least about 15% by weight of the toothpaste, and an aluminum soap of a fat-forming fatty acid.

2. A toothpaste according to claim **1** in which the polyoxyalkyleneglycol is a polyoxyethyleneglycol having a molecular weight of about 400.

3. A toothpaste according to claim **1**, in which the aluminum soap is aluminum octoate.

4. A toothpaste according to claim **1**, in which the polyoxyalkyleneglycol is a polyoxyethyleneglycol and wherein said toothpaste contains about 20% to 30% by weight of said polyoxyethyleneglycol, said polyoxyethyleneglycol having a molecular weight of about 400, and in which the aluminum soap is aluminum octoate.

5. A toothpaste containing (a) a major proportion of an abrasive based on the weight of the solids of said toothpaste, said brasive having an RDA value of not more than 200, (b) an aluminum soap of a fat-forming fatty acid, and (c) at least 20% by weight of the total of the liquid ingredients of said toothpaste of a water-soluble polyoxyalkyleneglycol, said polyoxyalkyleneglycol comprising a mixture of polyoxyethyleneglycols and wherein said toothpaste contains from about 30 to about 60% of polyoxyethyleneglycol 400, based on the weight of the total of the liquid ingredients of the toothpaste, and from about 5 to about 12% of polyoxyethyleneglycol 4000 based on the weight of said toothpaste.

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RICHARD L. HUFF, Primary Examiner