Kirk-Othmer Encyclopedia of Chemical Technology.

DENTIFRICES

Dentifrices are compositions designed to be used with a toothbrush. The two essential functions of dentifrices are to remove dental stains and to introduce a fresh, cool, pleasant, and clean feeling into the oral cavity. In the 1960s, a third function was introduced, delivery to the dentition of the therapeutic chemical agent fluoride. Subsequently, agents offering specific therapeutic and nontherapeutic benefits were added to dentifrices. The three forms of marketed dentifrices are pastes (toothpastes), liquid concentrates, and powders. Pastes account for an overwhelming portion of the dentifrice market. Liquid concentrates and powders account for only a minor portion because they have disadvantageous dispensing characteristics and they do not provide a means to accurately and consistently dispense a dose of active agent.

Dentifrices and dental rinses have many common purposes and ingredients, thus dental rinses are discussed briefly herein.

0.1. Dental Plaque

Dental plaque, a mass of bacteria that develops around teeth in all people, is the primary cause of dental caries and diseases of the periodontium. Following dental prophylaxis, a tooth becomes covered with a thin film, or pellicle, selectively deposited from the saliva. Bacteria in the oral cavity attach to the pellicle. The early colonizers are predominantly gram-positive bacteria. The bacterial population increases and undergoes a predictable pattern of change as it approaches maturity. Supragingival and subgingival plaque masses are distinguishable. Supragingival plaque matures in about 10 to 12 days, at which time calcification of the mass may be observed (calculus, tartar). The maturation process may be altered by intervening events, such as toothbrushing. The microbial population may generate acids, which cause dental caries, and toxins, which cause irritation of the gingiva, depending on environmental and other factors.

Mechanical removal of plaque is the most effective measure against plaque-caused diseases, dental caries, and periodontal diseases. Even before the advent of fluoride treatments, it was assumed that a clean tooth does not decay. A toothbrush is effective in removing dental plaque and, for those individuals who optimize its use, it usually can adequately control plaque. Despite the proven efficacy of mechanical plaque removal, the amount of patient involvement is such that only about 30% of the population in developed countries and considerably less in undeveloped countries can be expected to adequately remove plaque (1). Hence, supplementary measures such as dentifrices and dental rinses are necessary.

Studies have shown that compliance with toothbrushing would be severely impaired if the brushing regimen did not include dentifrices. Thus, the role of dentifrices in plaque control is to enhance the toothbrushing experience and thereby enhance the results. Dentifrices have little direct effect on plaque removal or accumulation unless they contain agents that have specific antiplaque properties.

1. Toothpastes

Toothpastes are packaged in flexible tubes, other flexible containers, and mechanically operated pump dispensers. They are usually extruded as cylindrical ribbons of a cohesive, smooth paste, approximately 2.54 cm in length and weighing approximately 1.5 g. New or modified dispensing devices are continually introduced to increase consumer interest.

The addition of therapeutic or cosmetic agents to dentifrices has paralleled advances in knowledge about factors affecting the human dentition. Agents added to dentifrices can act directly on the host tooth structure or on specific oral accumulations, for example, the principal action of fluoride is on the tooth enamel. The primary action of an abrasive, however, is on an accumulated stained pellicle. Oral accumulations of interest to preventive dentistry are dental pellicles, dental plaque, dental calculus (tartar), microbial populations responsible for oral malodor, and oral debris (food residues, leukocytes, etc). Plaque is most important because of its potential to do harm.

1.1. General Toothpaste Formulation

The key functions of dentifrices, to remove dental stains and to freshen the oral cavity, are accomplished by abrasive cleaning and the masking or elimination of unpleasant oral odors. Materials designed to deliver antitartar, antiplaque, or anticaries benefits must be compatible with the ability of the dentifrice to fulfill those two functions.

Toothpaste contains an abrasive (qv), flavor, a humectant system, a surfactant, a binding and thickening agent, color, and one or more therapeutic or cosmetic agents.

1.1.0.1. Abrasive.. Dentifrices have the unique ability to remove extrinsic tooth stains, which are caused by agents such as berries, tea, smoking, antibiotics, and certain bacteria as they attach to the dental pellicle. These stains can be removed only by abrasive cleaning; a toothbrush alone is not adequately effective. It has been shown that only 4% of a test population were able to maintain their teeth in an acceptably stain-free state without an abrasive and that 18% of the population were "heavy" stainers (2). However, colored materials found in dental plaque are removable without abrasives.

Many abrasive materials have been incorporated into dentifrices to remove stained pellicles. These are generally particles of insoluble inorganic materials and are characterized for dentifrice application by five interdependent parameters: particle size, shape, hardness, toughness, and chemical inertness. Particle size is limited by safety and comfort. The larger the particle, the more it abrades and the more readily it can be detected in the mouth as a gritty foreign material. Most abrasives for dentifrices have an average particle diameter of about 3 to 12 μm. Particles of 30 μm or larger are detected as gritty. The particle shape should be almost spherical, with no protuberances. Sharp points scratch the surface of the tooth. Hardness is governed by the hardness of dentin; on Mohs' scale the hardness of dentin is 2–2.5 and the hardness of dental enamel is 4–5. (Hardness values of talc [14807-96-6] and quartz [14808-60-7] are 1 and 7, respectively, on Mohs' scale). A hardness of about 2.5 for the abrasive material is adequate to assure that the stained pellicle is safely removed. Toughness is an expression of the tendency of the particle to break down under the force of toothbrushing. Some materials appear to be too hard for use as an abrasive. These can be used, however, if they break down during toothbrushing to particles too small to harm dentin or enamel.

An abrasive is usually chemically inert, neither interacting with other dentifrice ingredients nor dissolving in the paste or the mouth. Substances used as dentifrice abrasives include amorphous hydrated silica, dicalcium phosphate dihydrate [7789-77-7], anhydrous dicalcium phosphate [7757-93-9], insoluble sodium metaphosphate [10361-03-2], calcium pyrophosphate [35405-51-7], α-alumina trihydrate, and calcium carbonate [471-34-1]. These materials are usually synthesized to specifications for purity, particle size, and other characteristics; naturally occurring minerals are used infrequently. Sodium bicarbonate [144-55-8] and sodium chloride [7647-14-5] have also been employed as dentifrice abrasives.

Methods have been developed to quantify the abrasiveness of dental abrasives. Numerical values are assigned based on the amount of dentin removed by toothbrushing using a standardized slurry of abrasive or total dentifrice under standardized conditions, and comparison with a reference abrasive. One popular measure is the radioactive dentin abrasion value (RDA) (3). This value is obtained by subjecting an excised bovine tooth to a neutron flux, mounting segments of the irradiated tooth dentin in a special brushing machine, and brushing under standardized conditions. The amount of ^{32}P removed is compared with the amount of ^{32}P removed using a reference calcium pyrophosphate abrasive set at 500. The RDA of the total finished product is also measured, because the apparent abrasiveness of an abrasive can be modified by the presence of other ingredients of the formulation. Safe and effective RDA values are in the range of about 50 to 250.

1.1.0.2. Flavor. Dentifrices are used to refresh the oral cavity. Flavor oils and other flavoring materials are key to that function (see Flavors and spices). Generally recognized as safe (GRAS) flavors or flavors from approved lists are used. The most popular flavors are peppermint [8006-90-4], spearmint [8008-79-5], cinnamon [8006-79-9], and mixtures of these. Menthol is a principal constituent of the mint flavors and a source of refreshment and coolness. The concentration of the flavor in the dentifrice and the nature of substances added to bring out specific flavor notes and thereby make the flavor unique are significant concerns. The flavor must not be excessive; it must not burn too strongly. Also, the flavor must not be a sensitizer. Synthetic sweeteners are usually added, although regulatory concerns limit their selection; for example, cyclamate [100-88-9] is not used in the United States.

1.1.0.3. Humectant System. The humectant system comprises one or more liquids in which the other toothpaste ingredients are dispersed to provide a stable paste. The liquids are usually glycerol and 70% aqueous sorbitol. Propylene glycol [57-55-6] and polyethylene glycols are used occasionally. The liquids are used alone or in combination. Their water activity is such that they do not support bacteriological growth. The humectant system does not crystallize, and thus the final formulation does not dry out or cause the tube cap to lock to the nozzle.

1.1.0.4. Surfactant. The primary purpose of a surfactant in toothpaste is to create a foam while the teeth are brushed. This foam provides an enjoyable sensation. Secondarily, the surfactant helps remove material dislodged by the toothbrush, and it may have minor effects on plaque accumulation (see Surfactants).

The surfactant most commonly used is the anionic detergent sodium lauryl sulfate. Other surfactants that have been used include sodium dodecylbenzene sulfonate [25155-30-0], sodium *N*-lauroyl sarcosinate or Gardol [137-16-6], and sodium cocomonoglyceride sulfonate [3694-90-4]. Cationic and nonionic surfactants are not used for several reasons, including incompatibility with the abrasive system and lack of high foaming capability.

1.1.0.5. Binding and Thickening Agent. The rheological properties of a dentifrice are primarily determined by the agent used to bind and thicken the product and allow its extrusion as a firm, but easily dispersible, ribbon. A well-formulated toothpaste exhibits a high yield point and thixotropy, that is, it is easily liquified (see Rheological measurements). Gums and resins are employed to obtain the desired thickening and binding. Each has a characteristic rheological spectrum and lends structure to the toothpaste accordingly. Gums and resins widely used include acrylic acid polymers, carrageenan [9000-07-1], sodium carboxymethyl cellulose [9004-32-4], xanthan gum [11138-66-2], and hydrated silica [10279-57-9]. Each is available in several variations having different properties. Selection of an optimal gum or resin along with the selection of appropriate other ingredients results in a paste that extrudes with the application of minimal pressure to form a smooth, cohesive ribbon, which stands up on the toothbrush bristles and breaks down and disperses quickly in the mouth during brushing.

1.1.0.6. Color. Colorants used in dentifrices are regulated by the Food and Drug Administration. They are FD&C (food, drug, and cosmetic) or D&C (drug and cosmetic) (see Colorants for food, drugs, cosmetics, and medical devices).

1.1.0.7. Special Active Agents. Toothpastes are vehicles for agents that provide special therapeutic and nontherapeutic effects. The scope of these agents has increased dramatically since the 1960s and research continues.

Fluoride added to a compatible dentifrice base at a level of 1000 ppm has been clinically proven to reduce the incidence of dental caries by about 25% on average, even in areas where the water supply is fluoridated (4). Elevation to 1500 ppm increases the protection. Sources of fluoride approved for use in dentifrices are sodium fluoride [7681-49-4] (0.22%), sodium monofluorophosphate (0.76%), and stannous fluoride [7783-47-3] (0.41%). The Food and Drug Administration regulates fluoridated dentifrices as drugs and has established parameters for safe and effective products. Compatibility of the fluoride with the abrasive is an important requirement.

Several agents delivered via toothpaste inhibit the accumulation of dental calculus. Pyrophosphate salts, with or without a methoxyethylene–maleic acid copolymer, and zinc salts have given positive results in clinical trials (5). Pyrophosphates were added as potassium or sodium pyrophosphate or mixtures at a level of about 2–6%. The zinc salt was zinc citrate [546-46-3] (0.5–2.0%) or zinc chloride [7646-85-7] (2.0%). The products all contained fluoride in addition to the calculus inhibitor. The anticaries activity of the fluoride was not compromised (6).

Dentifrices are also vehicles for agents that alleviate dentinal hypersensitivity. Among the materials that have given positive results in clinical tests are potassium nitrate [7757-79-1] (5%) and strontium chloride [10476-85-4] (10%).

An antimicrobial agent that reduces dental plaque and can be delivered effectively from toothpaste is a combination of Triclosan [3380-34-5] (0.2% in the toothpaste) and zinc citrate (0.5%) (7). This agent influenced plaque accumulation and reduced the incidence of gingival bleeding in clinical tests. Additional dentifrices for improved gingival health are in the offing.

Claims for safety and efficacy of therapeutic dentifrices are regulated by the Food and Drug Administration. The Council on Dental Therapeutics of the American Dental Association reviews products and grants a Seal of Acceptance to those products deemed worthy.

1.1.1. Specific Toothpaste Formulations

Two types of toothpaste formulation predominate. Type 1 is a low abrasive—high solvent toothpaste (Table 1); type 2 is a high abrasive—low solvent toothpaste (Table 2). The most important differences are the ratio of humectant to abrasive and the nature of the abrasive. Type 1 dentifrices were introduced nationally to the U.S. market in 1970 and now constitute the predominant type. Type 2 dentifrices represent a popular earlier formulation, in which economic and scientific considerations related to the abrasive and humectant favored use of a maximum amount of the abrasive component. All type 1 dentifrices of the early 1990s contain an amorphous hydrated silica powder as the abrasive. Type 2 dentifrices may contain one or more of many insoluble minerals.

1.1.2. Gels

Amorphous hydrated silicas of a purity and structure typical of those used in type 1 dentifrices and the liquid portion (humectant system) of type 1 dentifrices both have approximately the same refractive index, ie, about 1.47. As a result, the type 1 dentifrices represented in Table 1 are inherently transparent or translucent. In the marketplace it has become popular to refer to such dentifrices as gels. For marketing reasons some companies have chosen to opacify these products, with titanium dioxide, for example. The opacified products are identical in functionality, structure, and all other ways, except opacity, to their translucent or transparent counterparts.

Table 1. Type 1 Dentifrices[a]

Function	Ingredient	CAS Registry Number	Amount, %
abrasive	silica xerogel (hydrated silica)	[10279-57-9]	14.00
humectant system	sorbitol, 70%	[50-70-4]	46.72
	glycerol, 96%	[56-81-5]	20.90
	poly(ethylene glycol) 1450	[25322-68-3]	5.00
surfactant	sodium lauryl sulfate	[151-21-3]	1.50
binder and thickener	carboxymethylcellulose, grade 9MX	[9004-32-4]	0.30
	silica aerogel	[7631-86-9]	8.00
flavor	flavor oils		2.00
	sodium saccharin		0.20
preservative	sodium benzoate	[532-32-1]	0.10
anticaries agent	sodium monofluorophosphate	[10163-15-2]	0.78
color solution	FD&C, D&C dyes in water		0.50

[a] Ref. 8.

Table 2. Type 2 Dentifrices[a]

Function	Ingredient	CAS Registry Number	Amount, %
abrasive	α-alumina trihydrate	[12252-70-9]	55.0
humectant system	glycerol	[56-81-5]	20.0
	water	[7732-18-5]	21.6
surfactant	sodium lauryl sulfate	[151-21-3]	1.5
binder and thickener	sodium carboxymethylcellulose	[9004-32-4]	1.0
flavor	flavor oils		0.9

[a] Ref. 9.

2. Dental Rinses

Dental rinses, as discussed here, do not include gargles and other liquids that are indicated for inflammation and diseases of the throat and are unrelated to dental plaque.

The primary function of a dental rinse is to clean and refresh the mouth. With few exceptions dental rinses marketed in the early 1990s also fulfill important secondary functions. Some contain agents that inhibit or destroy oral microbial populations that aid in generating dental plaque or oral malodor. Other rinses deliver fluoride to the teeth to prevent the development of caries. A relatively new rinse is used before toothbrushing to enhance the efficacy of brushing. Dental rinses can also deliver active agents that cannot be provided by toothpaste because of chemical incompatibility between the agent and the toothpaste ingredients. For example, sodium fluoride and calcium-containing abrasives are incompatible, as are sodium lauryl sulfate (an anionic detergent) and chlorhexidine [55-56-1] (an active cationic antimicrobial agent).

The amount of a product introduced into the oral cavity is substantially greater with a dental rinse than with a dentifrice, the action of swishing the rinse assures thorough distribution of the agent to accessible oral surfaces.

An oral dental rinse generally consists of water, alcohol, a humectant, an emulsifier, flavor, color, and an active agent. Water is the primary vehicle. The alcohol provides bite and is also a formulation aid. The humectant improves the feel in the mouth and also prevents locking of the cap to the container between uses; glycerin or noncrystallizing sorbitol may be satisfactory. The emulsifier is a nonionic type, for example, a

polyoxyethylene–polyoxypropylene block copolymer or a polyoxyethylene sorbitan fatty acid ester. Flavors are generally a type of mint or cinnamon. Colors are FD&C or D&C.

Active agents vary according to use. For controlling bad breath, zinc salts, sodium lauryl sulfate, and flavors are used. To destroy oral microorganisms, chlorhexidine, cetylpyridinium chloride [123-03-5], and benzalkonium chloride [68391-01-5] are valuable. Essential oils, such as thymol [89-83-8], eucalyptol [470-82-6], menthol, and methyl salicylate [119-36-8] reduce plaque-related gingivitis (see Oils, essential). Sodium fluoride aids in caries control.

Chlorhexidine is the most potent oral antimicrobial agent available. It has side effects and is sold only with a prescription. It is active delivered from a rinse, but a compatible toothpaste vehicle for chlorhexidine has yet to be developed.

A dental rinse containing sodium lauryl sulfate, marketed to be used before toothbrushing, removes some plaque directly and makes residual plaque easier to remove by brushing.

Claims for oral dental rinses are regulated by the Food and Drug Administration whether they are marketed as drugs or cosmetics. The Council on Dental Therapeutics of the American Dental Association reviews oral rinses, and may authorize use of the Seal of Acceptance for a product.

3. Economic Aspects

The dentifrice market in the United States was valued at about $1.5 billion at the retail level in 1991. The oral rinse market has a value of about $850 million.

Usage patterns for dentifrices vary considerably from country to country. A large portion of the market is concentrated in the industrialized countries; however, even the most undeveloped countries have markets for dentifrices, generally centered on the larger urban areas. The scale of toothpaste manufacture is variable and is directly related to market size and marketing practice. Toothpaste can be made by batch, continuously, or in combinations. Plants with outputs of 110 t or more daily have been operated, but are an exception. Toothpastes vary considerably in composition around the world, and any single enterprise may market several brands with different properties.

The strongly research-oriented dentifrice market is dominated by a few primary companies. The industry funds efforts to develop products with superior cosmetic and therapeutic performance. The four principal manufacturers of toothpaste worldwide are Procter & Gamble, Unilever, Colgate-Palmolive, and Beecham. Numerous smaller companies and private-label houses also exist.

The incidence of dental caries has decreased dramatically in recent years. It has fallen to such an extent as to reduce the need for professional dental health services related to caries significantly. The cause is not clear, but water fluoridation, addition of fluoride to toothpaste, and other modes of fluoride administration are generally conceded to be important contributors to the phenomenon and the American Dental Association recommends use of a fluoride toothpaste for all patients (10).

Toothpaste usage patterns are highly variable, even within reasonably homogeneous populations. In the United States, for example, studies have shown that about 50% of people who brush their teeth brush twice a day, 10–25% brush more than twice a day, and somewhat less than 30% brush less than twice a day (11). On average, Americans use roughly 0.9 kg of toothpaste per brusher per year. There is also tremendous variation in the effect of toothpaste because of the huge variability in motivation, brushing time, brushing proficiency, amount of toothpaste used per application, toothbrush condition, and other factors.

4. Tooth Whitening Agents

Tooth whitening preparations are available by dentist's prescription and over the counter. Many products are marketed as systems comprising toothpastes and treatment pastes or gels. The whitening agent in most is 10% carbamide peroxide [35220-04-3], which reacts with water to release hydrogen peroxide. The hydrogen peroxide liberates free-oxygen radicals, which bleach the dental enamel. Some preparations contain calcium peroxide [1305-79-9]as the bleaching agent (see Bleaching agents). The products have undisputed efficacy. Some dental authorities have questioned their safety, hypothesizing that long-term chronic exposure to hydrogen peroxide can result in ill effects. However, human clinical trials to substantiate this hypothesis have not yet been forthcoming, and appropriately formulated and tested whitening products must be considered safe when used in accordance with directions (12, 13).

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