

"DENTIFRICE SACHET"

The present invention relates to a dentifrice
5 sachet. More particularly it relates to a laminated
plastic sachet which is subject to little or no delam-
ination when in contact with a paste or gel dentifrice.

For many years dentifrices have been commonly
packaged in flexible metal containers, such as
10 aluminium tubes, from which the dentifrice is readily
extruded as a ribbon upon application of mild manual
pressure.

More recently, other types of packages have been
widely used for toothpastes. These include plastic
15 dispensers operated by vacuum pressure or with a manual
pump as well as flexible plastic tubes.

Because of their form retaining properties and
light weight, laminated polyethylene tubes have been
the tubes of commercial choice. Nevertheless, the art
20 has encountered difficulties due to flavour loss from
toothpaste when in contact with a polyethylene tube
inner surface. Such difficulties have been overcome or
reduced, for instance by including among the toothpaste
ingredients polyvinyl pyrrolidone as an agent to reduce
25 flavour loss, as described in U.S. Patent 4,590,065 to
Piechote and Sparacio of Colgate-Palmolive Company.

As an alternative or additional means to reduce
dentifrice flavour loss in a plastic tube, the
structure of the plastic laminate package could also be
30 changed. In this regard, advantage could be taken of
the known flavour barrier properties of the polymeric
material marketed by Sohio Chemical Company as Barex
(Registered Trade Mark), a modified acrylonitrile

methvl acrylate copolymer. Thus, with a heat-sealed laminate tube having an outside to inside structure of polyethylene terephthalate/adhesive/aluminium foil/adhesive/low density polyethylene, flavour is lost
5 from a toothpaste toward the nearest adhesive layer; while with a heat-sealed laminate tube having the outside to inside structure polyethylene terephthalate/adhesive/aluminium foil/adhesive/Barex (Registered Trade Mark), flavour is substantially or essentially
10 completely retained within the toothpaste formulation. A dentifrice tube is described in British Patent 1,342,755 to Colgate-Palmolive Company of Barex (Registered Trade Mark) without layers laminated thereto, which provides reduced flavour loss.

15 An alternative form of packaging convenient for travel, is now coming into use; that is a dentifrice sachet, generally containing about 7-12 cc of dentifrice per plastic sachet package.

It is noted that G.D. Searle Company manufactured
20 a liniment under the name Icy Hot (Registered Trade Mark) in a plastic sachet having a Barex (Registered Trade Mark) inner layer.

In dentifrice sachets, the typical ratio of interior sachet surface to toothpaste volume is from
25 about 16:1 to about 9:1. This surface to volume ratio far exceeds the ratio of about 2.6:1 to about 0.9:1 or less which typically prevails in plastic toothpaste tubes. In situations when sachets are provided, an additional serious problem occurs with laminated poly-
30 ethylene packages; that is delamination occurs.

It is an advantage of this invention that a laminated Barex (Registered Trade Mark) sachet readily envelops dentifrice without being subject to substan-

tial delamination.

Other advantages of this invention will be apparent from consideration of the following disclosure.

5 In accordance with certain of its aspects this invention relates to a dentifrice sachet, the sachet comprising a heat-sealed laminated package having dentifrice therein, the said package having a plurality of layers adhesively laminated to one another in the
10 said laminated package, the inner surface of the said laminated package being an acrylonitrile methyl acrylate copolymer modified with butadiene acrylonitrile copolymer, the said sachet enveloping a dentifrice present in amount of 7-12 cc and the ratio of the
15 interior surface of the said laminated package to the volume of the said dentifrice being from about 16:1 to about 9:1.

The dental base or vehicle utilized in the present invention may be in the form of a paste or gel,
20 comprising known ingredients conventionally used in the dentifrice art.

Paste or gel dentifrices may be based on aqueous or substantially non-aqueous systems. The former will usually include substantial proportions of finely
25 divided, solid polishing agent, surface active agent, gelling agent and some humectant vehicle, e.g. glycerine, sorbitol, polyethylene glycol of average molecular weight of about 600 and mixtures thereof and will be opaque, whereas the latter type will often be a
30 clear gel, containing a minor proportion of a visually clear particulate solid polishing agent, a larger proportion of humectant vehicle, surface active agent and gelling agent, with a minor proportion of water

(e.g. below 10% by weight) often being present.

The surface active agent, or detergent, present in the dentifrice may sometimes be cationic or amphoteric but will usually be anionic or nonionic. Of these compounds, the anionics are the most preferred. The anionic detergents or surface active agents also usually serve as foaming agents. Among the useful anionic detergents may be mentioned the higher fatty acid monoglyceride monosulphates, such as the sodium salts of the monosulphated monoglycerides of hydrogenated coconut oil fatty acid; higher alkyl sulphates, such as sodium lauryl sulphate; higher alkyl aryl sulphonates, such as sodium linear dodecyl benzene sulphonate; higher olefin sulphonates, such as sodium higher olefin sulphonate in which the olefin group is 12 to 21 carbon atoms; higher alkyl potassium sulphoacetates; higher fatty acid esters of 1,2-dihydroxypropane sulphonates, magnesium salt; the substantially saturated higher aliphatic acyl amides of lower aliphatic aminocarboxylic acid alkali metal salts, such as those having 12 to 16 carbon atoms in the fatty acyl radicals, higher alkyl poly-lower alkoxy (of 10 to 100 alkoxies) sodium sulphates; higher fatty acid sodium and potassium soaps of coconut oil and tallow, and the like. As may be noted, most frequently the detergents are sulphated or sulphonated compounds. Examples of useful anionic amides which may be employed are N-lauroyl sarcosine and the sodium, potassium and ethanolamine salts of N-lauroyl-, N-myristoyl, and N-palmitoyl sarcosines. In the above descriptions, "higher" refers to chain lengths of 12 to 22 carbon atoms, preferably of 12 to 18 carbon atoms and most preferably of 12 to 16 carbon atoms. Lower means 2 to

4 carbon atoms, preferably 2 to 3 carbon atoms and most preferably, two carbon atoms.

- The nonionic detergents include those containing chains of lower alkylene oxide, e.g. ethylene oxide or propylene oxide, in which there are present from 10 to 100 or more moles of lower alkylene oxide. Among such materials are the block copolymers of ethylene oxide, propylene oxide and propylene glycol, sold under the mark Pluronic (Registered Trade Mark); the alkyl phenyl polyethoxy ethanols, sold under the mark Igepal (Registered Trade Mark); mixed copolymers of ethylene oxide and propylene oxide, sold under the mark Ucon (Registered Trade Mark); and various other well known nonionics derived from fatty alcohols or acids and polyethylene oxide. The amphoteric or ampholytic agents include long chain (alkyl) amido-alkylene-alkylated amine derivatives, such as "Miranol", e.g. Miranol (Registered Trade Mark) C₂M; and cationic germicidal detergents, such as diisobutylphenoxyethoxyethyl dimethyl benzyl ammonium chloride, benzyl dimethyl stearyl ammonium chloride; and tertiary amines having a higher fatty alkyl group and two polyoxyethylene groups attached to the nitrogen thereof.

The detergents constitute about 0.5-5% and preferably 0.8 to 3% by weight of the dentifrice composition.

- Toothpastes and dental gels conventionally contain substantially water insoluble polishing agents or abrasives which are compatible with the formulation, in amounts from about 15-75% by weight of the total gel or paste formulation. Suitable polishing agents include anhydrous dicalcium phosphate, dicalcium phosphate dihydrate, tricalcium phosphate, insoluble sodium metaphosphate, crystalline silica, colloidal silica, complex aluminosilicates, aluminium hydroxide (including alumina trihydrate or hydrated alumina),

magnesium phosphate, magnesium carbonate, calcium carbonate, calcium pyrophosphate, bentonite, talc, calcium silicate, calcium aluminate, aluminium oxide, aluminium silicate, and silica xerogels and hydrous gels. Most of the polishing agents mentioned are most useful in the preparation of opaque dentifrices but some of them, such as colloidal silicas, especially the silica xerogel and hydrous colloidal silicas, as well as complex sodium aluminosilicates, including those characterised as containing a low amount (e.g. about 0.7-1.5% by weight) of combined alumina, may be utilized in the manufacture of clear gel dentifrices, because their indices of refraction approximate to those of other dentifrice constituents, particularly the liquid vehicle. If desired, clear gel dentifrices may be made less clear or opacified by including therein, opacifying agents and/or substantial water contents (e.g. at least about 10% by weight). When gel dentifrice is employed in the present invention, prevention of delamination and flavour retention is excellent. When a cream dentifrice is employed, substantial improvement in reducing delamination and flavour loss is observed compared to the situation when a polyethylene sachet is used.

25 In dental gel or toothpaste dentifrice formulations, the liquid vehicle and solids should necessarily be proportioned to form a gel or creamy mass of desired consistency, which for instance is readily extrudible from an opened sachet upon application of mild manual pressure. In general the liquids in the dental gel or toothpaste will comprise chiefly water, glycerine, sorbitol, polyethylene glycol 400 or 600 or propylene glycol, including suitable mixtures thereof, such as

glycerine and sorbitol in a weight ratio of about 0.25:1 to about 3:1, typically about 0.25:1 to about 0.8:1. It is advantageous usually to use a mixture of both water, and a humectant such as glycerine, or sorbitol or mixtures thereof. The total liquid content will generally be about 20-75% by weight of the formulation. In gel dentifrices the amount of water (excluding that water which may be used to dissolve sorbitol) is often below 10% by weight, e.g. about 2-5%. In paste dentifrices, the amount of water generally is at least 10%, typically about 15-25%. It is preferred to use also a gelling agent in dental creams such as the natural and synthetic gum-like materials, e.g. Irish Moss, gum tragacanth, sodium carboxymethylcellulose, polyvinylpyrrolidone, iota-carrageenan, xanthan gum or starch. Irish Moss and sodium carboxymethylcellulose are compatible particularly and are preferred gelling agents. The gelling agent or gum content is usually in an amount up to about 10% and preferably about 0.3-5% by weight of the formulation. Fillers such as pyrogenic silica and silica aerogel may also be used, typically in amounts up to about 10% by weight to supplement the gelling agent, particularly in dentifrices. These colloidal silica aerogels which include Syloid (Registered Trade Mark) 244 and 266 and Aerosil (Registered Trade Mark), and the pyrogenic silica sold as Cab-O-Sil (Registered Trade Mark) may be used as thickening agents, typically, in amount of about 5-10% by weight. The silica, Sylox (Registered Trade Mark) 15 is also a desirable thickener.

Any suitable flavour oil or mixture thereof may be used in this invention. Examples of flavour oils

- include oils of spearmint, peppermint, wintergreen, sassafras, clove, sage, eucalyptus, marjoram, cinnamon, lemon and orange. The flavouring oils are water-insoluble and are emulsified into the dentifrice formulation under moderate agitation in amounts of 0.01 to 5% by weight and preferably about 0.5-3% by weight, and most preferably about 0.8 - 1.3% by weight. Desirably, the flavour contains a mixture of spearmint and peppermint oils (typically, about 3:1 to 1:3 by weight) which may be supplemented with alpha-ionone, wintergreen or the synthetic substantial equivalent thereof, methyl salicylate, and the like.

- Various other materials may also be incorporated into the dental vehicle. Examples thereof are
15. fluorine-containing compounds such as stannous fluoride, potassium stannous fluoride (SnF_2KP), sodium hexafluorostannate, stannous chlorofluoride, sodium fluoride and sodium monofluorophosphate. These materials, which dissociate or release fluorine-containing ions in water, may be present in the dental vehicle in an effective, but non-toxic amount, usually within the range of about 0.1-5% by weight. Other additives include preservatives such as sodium benzoate, chlorophyll compounds, silicones, ammoniated
 20. materials such as urea and diammonium phosphate, antibacterial agents such as benzethonium chloride and other quaternary antibacterial compounds, sweeteners such as sodium saccharin, sodium cyclamate or the like and colouring and opacifying agents. These additives may be used in
 25. amounts which do not adversely affect the properties and characteristics of the dentifrice in accordance with the present invention. Each constituent may be present in minimal amounts of up to a maximum of
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5% by weight and preferably up to 1% by weight of the formulation.

The combination of sodium fluoride, pyrophosphate, for instance from a mixture of tetrapotassium pyrophosphate and tetrasodium pyrophosphate and a copolymer of maleic anhydride and polymethyl vinyl ether, available from GAF Company under the trademark Gantrez (Registered Trade Mark), is particularly desirable for inclusion in the dentifrice in order to reduce calculus formation.

The dentifrice typically has a pH of about 4-10, preferably about 5.5 to 8.5.

The dentifrice of this invention is prepared by conventional methods of making toothpaste and dentifrice gel. More specifically, a toothpaste may be prepared by forming a gel with carboxymethylcellulose and water, adding thereto with mixing the powdered materials and humectant, followed by the addition with mixing of polishing agent, then the surfactant and then the flavour oil. The dentifrice is then placed into a laminated plastic sachet having an inner layer of Barex (Registered Trade Mark) plastic, which sachet is then heat-sealed to completely envelop the dentifrice.

The sachet which is employed generally has the structure of "one dose" packages which are provided in industry for purposes such as dispensing pharmaceuticals or cosmetics in a sanitary manner, to contain food condiments such as ketchup, mustard, mayonnaise, etc. in amount suitable for use during a single meal and the like.

A disposable or throw-away type packet containing a disposable toothbrush coated with a toothpaste and enclosed in an envelope was described in U.S. Patent

2,512,001. In U.S. Patent 3,534,887 a disposable denture care packet was described and in U.S. Patent 3,670,927 a sealed envelope for supplying dosage amounts of oral hygienic liquid compositions was described.

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In U.S. Patent 4,236,652 plastic laminate dispenser package for small amounts of flowable products such as foods, wherein an interior surface is composed of an imperforate, uniaxially oriented polymeric film such as Barex (Registered Trade Mark) is described. In the present invention the entire interior surface is composed of such a barrier layer.

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In a desirable sachet of the present invention, the flexible top layer of the sachet package may be comprised of flexible plastic sheeting such as polyethylene, paper, polyesters such as polyethylene terephthalate, Cellophane (Registered Trade Mark), polypropylene and combinations of such materials in multi-layered laminations. Similarly, the flexible material may be coated with plastic coatings to convey specific characteristics, as described. In a preferred embodiment the upper layers comprise a multi-layer structure of polyethylene or polyethylene terephthalate polymer with a metal foil adhesively secured thereto. The foil is preferably coated on both sides with heat sealable adhesive lacquers or otherwise conditioned to improve adhesion.

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The bottom or inner layer constituting the rigid or semi-rigid face of the package is a uniaxially oriented copolymer of acrylonitrile-methacrylate with butadiene-acrylonitrile copolymer, for instance available commercially as Barex (Registered Trade Mark) from Sohio.

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The sachet package may be transparent or opaque.

- Two laminates are adhered together, generally by heat sealing to envelop the dentifrice packaged therein. At least one of the laminated portions is scored for easy opening by tearing, bending or folding. If desired, a
5. line of ink may be printed on the film in the area superimposed over the scored area and printed indicia may direct the consumer on how to best tear, fold or bend the package to open it. The laminate bearing the scoring may be fully scored throughout the laminate
10. structure or it may be scored only in the outer portion of the laminate with the bottom layer remaining imperforate prior to opening as described in U.S. Patent 4,236,652.

- A typical example of resins available as Barex
15. (Registered Trade Mark) which may be employed in the sachet packages of the present invention is the nitrile-rubber modified acrylonitrile-methyl acrylate copolymer Barex (Registered Trade Mark) 210, which is about 73-77 parts by weight acrylonitrile and about 27-
20. 23 parts by weight methyl acrylate modified with about 8-10 parts by weight of a butadiene-acrylonitrile copolymer which is about 70% by weight derived from butadiene.

- The top and bottom laminates of the sachet are each generally about 50-100 microns thick. Typically the flexible
25. outer layer, for instance of polyethylene terephthalate is about 10-15 microns thick. The intermediate metal foil, preferably aluminium, is typically about 5-20 microns thick and the adhesives on each side of the foil may be about 15-25 microns thick for the adhesive to the flexible outer layer and about 2-5 microns thick
30. to the inner barrier layer. The layer of acrylonitrile methyl acrylate copolymer typically has a thickness of about 25-60 microns.

The invention may be put into practice in various

ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples. All amounts and proportions are by weight except as otherwise indicated.

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EXAMPLES 1A and 1B

The gel dentifrice set out in Table 1 below is prepared:

TABLE 1

	<u>Ingredients</u>	<u>Parts</u>
10	Glycerine	25.00
	Sorbitol (70%)	38.29
	Polyethylene Glycol 600	3.00
	Sodium Carboxymethyl Cellulose	0.35
	Sodium Benzoate	0.50
15	Sodium Monofluorophosphate	0.76
	Sodium Saccharin	0.20
	Water (Deionized)	3.00
	Titanium Dioxide	0.50
	Silica containing 1% combined alumina	18.00
20	Silica Aerogel (Syloid 244)	5.00
	Calcined Alumina	2.00
	Colour Solution (0.1%)	0.70
	Sodium Lauryl Sulphate	1.20
	Flavour	1.00
25	pH 6.5	
	Specific Gravity	1.36

Separate portions of 12.8 grams, corresponding to 9.41 cc of the above gel dentifrice are placed in sachets having an inner layer of the acrylonitrile methyl acrylate copolymer modified with butadiene-acrylonitrile copolymer sold under the name Barex (Registered Trade Mark) 210 (Example 1A) and in sachets having an inner layer of low density polyethylene

(Density = 0.925 g/cc) (Example 1B) and the sachets are then heat sealed. The surface of the sachets in contact with the gel dentifrice is 112 cm², providing a plastic surface to dentifrice volume ratio of 13.1:1.

5 (Sachet surface based on 2 interior sides.)

The structure of the Barex (Registered Trade Mark) sachet (Example 1A) from outer layer to inner layer is as set out in Table 2:

TABLE 2

10	<u>Layer</u>	<u>Thickness in Microns</u>
	Polyethylene Terephthalate	12
	White Low Density Polyethylene	18
	Adhesive	
	Aluminium Foil	9
15	Adcoat (Registered Trade Mark)	3
	Adhesive (Morton Thiokol)	
	Barex (Registered Trade Mark)	51
	Copolymer	

20 The structure of the polyethylene sachet (Example 1B) from outer layer to inner layer is as set out in Table 3:

TABLE 3

	<u>Layer</u>	<u>Thickness in Microns</u>
	Polyethylene Terephthalate	12
25	Ethylene Acrylic Acid	21.3
	Aluminium Foil	15-17
	Adcoat (Registered Trade Mark)	3.3
	adhesive (Morton Thiokol)	
	Low Density Polyethylene	25.4

30 The Barex (Registered Trade Mark) sachets of Example 1A containing the gel dentifrice retain their integrity very well over a period of 24 weeks at room temperature and 9 weeks at 49°C, while the dentifrice

5. also remains phase and flavour stable. On the other hand the sachets of Example 1B containing the gel dentifrice having an inner layer of polyethylene quickly undergo delamination within 4 weeks at room temperature and within 3 weeks at 49°C, while the dentifrice also did not remain phase and flavour stable. Similar extensive delamination occurs even when the inner polyethylene layer is twice as thick as 25.4 microns or more.

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EXAMPLE 2

- Results corresponding to those set forth in Example 1 in regard to Barex (Registered Trade Mark) sachets (Example 2A) (see Table 2) and to polyethylene sachets (Example 2B) (see Table 3) are observed when 12.8 g corresponding to 9.34 cc of the high water gel dentifrice set out in Table 4 is packaged in the same sized sachets (surface to dentifrice volume ratio = 12:1):

TABLE 4

	<u>Ingredients</u>	<u>Parts</u>
20.	Glycerine	15.000
	Sorbitol (70%)	19.657
	Polyethylene Glycol 600	5.000
	Iota Carrageenan	0.600
	Tetrapotassium Pyrophosphate	4.500
25.	Tetrasodium Pyrophosphate	1.500
	Maleic anhydride/Polymethyl Vinyl Ether	6.670
	Copolymer (Gantrez S-97) (15% Solution)	
	Sodium Fluoride	0.243
	Sodium Saccharin	0.400
30.	Titanium Dioxide	0.200
	Water (Deionized)	20.530
	Hydrous Silica Gel	16.000
	Silica Aerogel	7.700

Sodium Lauryl Sulphate	1.200
Colour Solution (0.5%)	0.050
Flavour	1.150

pH 7.00

Specific Gravity 1.37

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EXAMPLE 3

15 g corresponding to 10 cc of the paste dentifrice set out in Table 5 are packaged in the Barex (Registered Trade Mark) sachet described in Example 1 which is sized the same as in Example 1:

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TABLE 5

<u>Ingredients</u>	<u>Parts</u>
Deionized Water	24.49
Glycerine (99.5%)	22.00
Sodium Monofluorophosphate	0.76
15. Carboxymethylcellulose Sodium Salt	1.00
Tetrasodium Pyrophosphate	0.25
Sodium Saccharin	0.20
Sodium Benzoate	0.50
Sodium Lauryl Sulphate	1.20
20. Dicalcium Phosphate Dihydrate	48.76
Flavour	0.89
Specific Gravity	1.5

The layers of the Barex (Registered Trade Mark) sachet remain essentially laminated to each other with little loosening of the layers.

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CLAIMS

1. A dentifrice sachet, the sachet comprising a heat-sealed laminated package having dentifrice therein, the said package having a plurality of layers adhesively laminated to one another in the said laminated package, the inner surface of the said laminated package being an acrylonitrile methyl acrylate copolymer modified with butadiene-acrylonitrile copolymer, the said sachet enveloping a dentifrice present in amount of 7-12 cc and the ratio of the interior surface of the said laminated package to the volume of the said dentifrice being from about 16:1 to about 9:1.

2. A dentifrice sachet as claimed in Claim 1 in which the said dentifrice is a gel dentifrice.

3. A dentifrice sachet as claimed in Claim 1 in which the said dentifrice is a toothpaste.

4. A dentifrice sachet as claimed in Claim 1, 2 or 3 in which the said dentifrice contains about 0.5-3% by weight of a flavour oil.

5. A dentifrice sachet as claimed in Claim 4 in which the said gel dentifrice contains about 0.8-1.3% by weight of a flavour oil.

6. A dentifrice sachet as claimed in Claim 4 or Claim 5 in which the said flavour oil comprises a mixture of peppermint and spearmint oils.



* C L M S *

7. A dentifrice sachet as claimed in any one of Claims 1 to 6 in which the layers of the said laminated package from the outer layer to the inner layer having a surface in contact with the said dentifrice are: (1) polyethylene terephthalate; (2) adhesive; (3) aluminium foil; (4) adhesive; (5) acrylonitrile methyl acrylate copolymer.

8. A dentifrice sachet as claimed in any one of Claims 1 to 7 in which the said layer of acrylonitrile methyl acrylate copolymer has a thickness of about 25-60 microns.

9. A sachet of dentifrice as claimed in Claim 1 substantially as specifically described herein with reference to Example 1A, 2A or 3.



* C L M S *