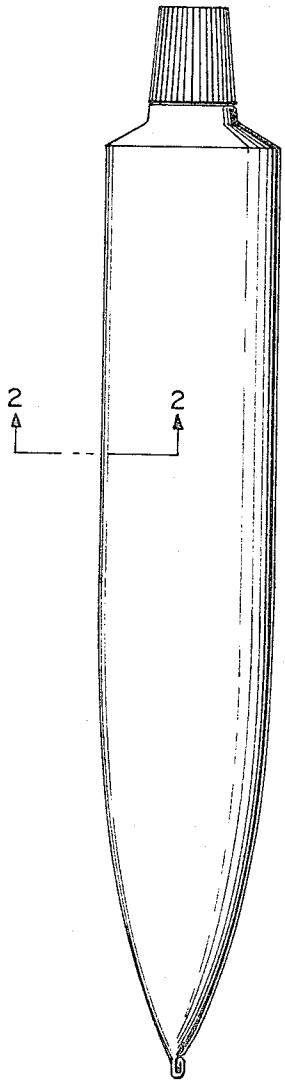
May 7, 1968 P. E. COPE ETAL 3,381,818

DENTIFRICE PACKAGE HAVING A LAMINATED FILM BODY

Original Filed Feb. 12, 1962

Fig. 1



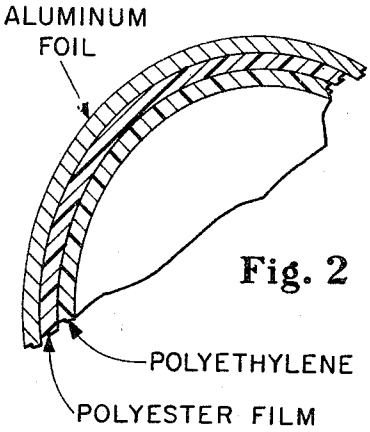


Fig. 2

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DENTIFRICE PACKAGE HAVING A LAMINATED FILM BODY

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Original application Feb. 12, 1962, Ser. No. 172,805. Divided and this application May 3, 1965, Ser. No. 452,920

4 Claims. (Cl. 206—84)

ABSTRACT OF THE DISCLOSURE

A package in which at least a portion of the package body is made from a three layer laminate system comprising an outer layer of aluminum foil, an intermediate layer of polyester film, and an inner layer of polyethylene. The package is particularly well suited for storing dentifrice products.

This is a division of application Ser. No. 172,805, filed Feb. 12, 1962, now abandoned.

This invention relates to a laminated film composed of several layers of material. More especially, the invention provides a laminated film material which can be used for packaging toothpaste containing stannous fluoride and like products.

It is common practice to package toothpaste for commercial sale in well-known collapsible tubes having a threaded spout and separable closure at one end and a crimped and sealed closure at the other end. Such tubes are commonly made from aluminum or lead by the well-known impact extrusion method. Many commercially available toothpaste products are currently marketed in this type of package.

In recent years, toothpaste products containing stannous fluoride as an anticaries agent have been introduced. In order to keep the stannous fluoride in the toothpaste composition, it was found necessary to make the toothpaste acidic with a pH in the range of from about 5.0 to about 4.5. It was found that in such an acid environment a reaction took place between the stannous fluoride and the aluminum in a typical collapsible tube. This significantly reduced the usual benefits derived from a toothpaste containing stannous fluoride. At the same time, it corroded the tube. As a consequence, toothpaste containing stannous fluoride has been preferably packaged in wax-coated lead collapsible tubes to avoid the undesirable reaction between product and package material. The wax lining also functioned to prevent the lead walls from bleaching the toothpaste dye. It was discovered however, that lead collapsible tubes had to be provided with a plastic neck or spout since the interior of the metal neck could not be adequately coated in the waxing operation and therefore the lead in the neck tended to react with components of the toothpaste. This tended to result in a very unattractive black smear on the outside of the spout which was considered detrimental to consumer acceptance. The plastic spout resolved this problem.

Even the wax-lined lead tube with plastic spout created problems unless made under carefully controlled and precise conditions. For example, the wax lining was subject to flaking as the toothpaste tube was squeezed and manipulated so that a certain amount of wax lining material was extruded. This gave an undesirable appearance to the toothpaste as it was being used. In addition, the flaking off of the wax exposed the lead wall of the tube and this also had its drawbacks due to the undesirable

reactions that can occur between the lead and the toothpaste.

In order to overcome these problems, it was deemed desirable to form a collapsible tube from web material by the use of the processes and apparatus described in U.S. Patents 3,207,651 and 3,128,215 issued to Charles R. Hood and Jean E. Schaefer, and entitled, respectively, Apparatus and Method of Forming Tubing From a Continuous Web and Apparatus and Method for Flame-sealing a Thermoplastic Top to a Laminated Tube Body. The said patents are commonly owned by the assignee of the present application.

In the formation of collapsible tubes by the above apparatus and methods it was discovered that no web or film materials were available which could be processed by these methods and which would satisfactorily hold a toothpaste containing both stannous fluoride and typical flavoring materials such as lavamenthe, spearmint rectified, methyl salicylate, cinnamic aldehyde and the like. A variety of laminates were tested using aluminum foil as an outer layer bonded to polyethylene or nylon as an inner layer in a two-layer system; polyethylene and nylon of many diverse types were tested in these laminate systems. None of these laminates possessed the peculiar combination of properties essential to a satisfactory material for fabricating an acceptable package for stannous fluoride toothpaste containing typical flavoring materials as used therein. The flavoring materials are especially difficult to package since they are very penetrating and tend to cause deterioration of many plastic film materials rather quickly.

It is, of course, well known that many types of plastic and metal films can be laminated to obtain a desired combination of properties. However, the packaging of a stannous fluoride toothpaste containing certain flavoring ingredients such as lavamenthe, spearmint rectified, methyl salicylate, etc., is such an unusual problem that the classic approach to finding a proper combination of materials was not feasible in this instance. In order to create a satisfactory material, it was necessary, among other things, to develop a laminate which provided an oxygen barrier to prevent air from entering the package, thereby causing the product to deteriorate when stored in the package for comparatively long periods of time. Another factor was the need for a laminate material which would be a satisfactory moisture barrier so that the product would not dry out; the moisture barrier is also necessary to prevent moisture in the product from penetrating the inner laminate layer thereby causing delamination of the several layers. In the packaging of toothpaste products which contain detergents and flavor oils among other things, it was discovered that these ingredients are especially difficult to retain as they will permeate most plastic film materials, thereby causing delamination of the package and some deterioration of the scent and flavor of the product. Another factor was the tendency of components of stannous fluoride toothpaste to react with many metals so that metal foils used in a laminate system must be properly protected to avoid chemical attack by the product. In addition to all these requirements, the laminated packaging material had to be heat-sealable in order that it could be handled by the methods and apparatus above cited as well as any others that contemplate package fabrication by the use of well-known heat sealing techniques.

In addition to the many requirements and properties needed for satisfactory product storage as outlined above, it was also neccessary to find a laminate material which would be acceptable to the average consumer. Most consumers are conditioned to squeezing and folding up a col-

lapsible tube as the product inside is used. If a plastic material alone is used to make a tube, it will generally have a high degree of resiliency which gives it the ability to spring back to its original shape after a portion of the product has been squeezed out. This action will automatically draw air into the tube after it is squeezed and the air will tend to adversely affect the toothpaste. It also makes it very difficult to squeeze out product after only about 20% of the original contents remain in the tube. In a laminate for collapsible tubes, it was also considered desirable to "build in" consumer acceptance-type characteristics such as dead fold properties, etc., in order that the finished tube, if desired, will act and feel similar to present well-known metal collapsible tubes formed by the impact extrusion process. On the other hand, a completely resilient tube or one having an intermediate degree of dead fold properties could be used for toothpaste where the tube is to be stored in inverted position, for example.

An object of this invention, therefore, is the provision of a laminated material for packaging stannous fluoride toothpaste and like products containing flavor oils and/or other components which are sensitive to oxygen and tend to react with many common metal packaging materials. Another object is to provide for the packaging of toothpaste and similar products in a laminated material which can be fabricated into collapsible tube form by methods and apparatus which have already been developed. Still another object is the provision of a laminated material which may be fabricated into either a resilient collapsible tube or one having a desired degree of dead fold properties to permit the consumer to squeeze, roll and fold the tube as the product is used, thereby increasing the convenience and ease of emptying the tube. These and other objectives will appear more clearly hereinafter.

The foregoing objects are realized by the present invention which, briefly stated, comprises a laminated material which can be fabricated into a collapsible tube body, the laminate being composed of an outside layer of rolled sheet aluminum, an intermediate layer adhered to the outside layer, said intermediate layer being highly resistant to the transmission of flavor oils, and an inner layer adhered to the intermediate layer, said inner layer being highly resistant to water vapor transmission and being heat-sealable so that the material can be handled, processed and formed into a package by the use of conventional heat sealing techniques.

The accompanying drawing illustrates a preferred embodiment of the invention wherein:

FIGURE 1 is a side elevation of a collapsible tube made from the preferred laminate of the invention; and

FIGURE 2 is a fragmentary cross section taken on the line 2—2 of FIGURE 1 which has been legended to describe the several layers of the preferred laminate system.

A laminate composed of at least three layers has been found satisfactory for packaging stannous fluoride toothpaste such as described, for example, in U.S. Patent 2,876,166, issued to William H. Nebergall. The outer layer of the laminate is a continuous film of aluminum foil which serves as a very effective oxygen barrier to prevent air permeation and resultant product oxidation and deterioration. The aluminum foil layer must be at least thick enough to act as a satisfactory oxygen barrier. The thickness may be as much as 5 mils but above that it is uneconomical at present to use an aluminum foil layer in this type of laminate system. A preferred thickness for the aluminum foil layer is in the range of from about .35 mil to about 3 mils. The greater the thickness, the more this layer will contribute to the dead fold properties of the finished material. The outside surface of the foil can be decorated or printed with the trademark of the product in the package as well as other advertising and instructional matter. If desired, the aluminum outer surface can be covered with a protective coating of heat-sealable material such as polyethylene or the like.

The aluminum foil is adhered to an intermediate layer which is preferably a polyester film. A polyester film which is the condensation polymer of ethylene glycol and terephthalic acid has been found very satisfactory for this purpose. Such films are described in bulletin TR–1 (dated November 1955) published by E. I. du Pont de Nemours & Company. The films are sold by Du Pont under the trademark Mylar. The polyester film is highly resistant to the transmission of flavors, perfumes, oil and fats. Consequently, when bonded to aluminum foil, there is little tendency for the flavor and perfume elements to permeate the polyester film to cause delamination from the aluminum foil outer layer. It has been found that a polyester film can be bonded to aluminum foil by the use of any well-known thermoplastic adhesives such as polyethylene, polyvinylidene chloride and their equivalents. A polyester film having a thickness of at least about .5 mil is preferred for good results.

The inner layer of the laminate composite is preferably polyethylene due to its heat-sealable properties as well as its impreviousness to water vapor transmission. The polyethylene perferred for purposes of this invention is a medium density, normally solid, crystalline polymer of the formula $(CH_2)_x$. High-density polyethylene, i.e., having a density greater than 0.92–0.93 may also be used, however, as well as polyethylene having lower densities. In general, any type of polyethylene may be used herein. For example, in addition to the preferred type of polyethylene, polyethylene formed by copolymerizing ethylene with minor amounts of aliphatic unsaturated hydrocarbons, such as propylene, butylene, isobutylene and the like, and polymers formed by copolymerizing ethylene with small quantities of other polymerizable compositions such as styrene, vinyl acetate and similar types of vinyl unsaturated compounds, are suitable for purposes of this invention. Other polymerized alkene products such as polypropylene and other equivalents can be used for the inner layer.

The polyethylene coating can be applied to the polyester film heretofore mentioned by the extrusion technique described in TAPPI, 39, p. 366 (June 1956). The polyethylene layer will adhere well to the polyester film intermediate layer by the use of this method of application. Alternately, the polyethylene film layer can be adhered to the polyester film layer by extruding a thin layer of molten polyethylene or polyvinylidene chloride between the polyethylene film and the polyester film. The details of this latter process are well known to persons skilled in the art of laminating plastic films. An inner polyethylene film layer of at least .5 mil thick has been found satisfactory for accomplishing the objects of the invention. The maximum thickness of the polyethylene inner layer is actually determined on the basis of economy and performance. It may be as much as 8 mils or more if necessary.

It is also possible to purchase a heat-seable laminate consisting of polyester film (a condensation polymer of ethylene glycol and terephthalic acid) and intermolecularly bonded polyethylene. Such films are available commercially from the Minnesota Mining and Manufacturing Company of St. Paul, Minn., under the trademark Scotchpak. The Scotchpak polyester-polyethylene film composite is available in type A (having polyethylene on one side only of the polyester film) and type B (having polyethylene on both sides of the polyester film). Type A Scotchpak polyester film is available in thicknesses ranging from 1.5 to 4.5 mils and type B Scotchpak polyester film is available with a thickness of 2.5 mils. All of the aforementioned types of Scotchpak polyester-polyethylene composite films are satisfactory for purposes of this invention and can be adhered to an outer layer of aluminum sheet material by the methods heretofore described.

From the above it will be evident that the preferred laminate of this invention is a three-layer system composed from outside to inside of aluminum foil, a poly-

ester film (as described herein) and polyethylene. This system has been found very satisfactory for packaging a stannous fluoride toothpaste product as described in the above-cited Nebergall patent and containing the flavoring materials heretofore mentioned. However, a collapsible tube fabricated from this laminate by the methods and apparatus described heretofore, will not neceessarily have the dead fold and other properties normally associated with such containers. In some applications, a resilient laminated tube will be entirely satisfactory. In other cases, it may be desired to "build in" dead fold and other properties normally associated with impact extruded metal collapsible tubes. One way to obtain these properties is to use a relatively thick, such as 5 mils, aluminum foil layer. This same objective can be achieved in a more economical way by providing a filling and bonding layer between the aluminum foil and the polyester film while at the same time using a relatively thin aluminum foil layer such as 2 mils. The filling and bonding layer must adhere well and must be interposed outside of the flavor impervious polyester film. Excellent results are obtainable by the use of a filling and bonding agent containing from about 10% to about 40% of a vinyl resin which is the copolymer of ethylene and vinyl acetate such as available from E. I. du Pont de Nemours & Company, under the trademark Elvax. The remainder of the filling and bonding layer is a paraffin wax. A preferred filling and bonding composition is composed of 25% of a copolymer of ethylene and vinyl acetate and 75% paraffin wax. A paraffin wax such as type AT 171 manufactured by the Atlantic Refining Company of Philadelphia, Pa., has been found satisfactory.

After combining the polyester film with the polyethylene, the aluminum foil is laminated to the polyester film layer with the filling and bonding layer interposed. The filling and bonding material of the above-mentioned composition is normally a solid at room temperature. It is first heated and then applied uniformly to a thickness of from about .5 to 7 mils. The aluminum foil and polyester film layer are then bonded together under heat and pressure between sealing rolls. The composition is then cooled to room temperature by conventional cooling rolls or the like. This results in a laminate system having the desired dead fold and other physical properties that can be made into an acceptable collapsible tube for packaging a stannous fluoride toothpaste product.

The following specific examples will further illustrate the principles, practice and advantages of the present invention.

EXAMPLE I

A laminate film was made consisting of successive superposed layers of 2 mil polyethylene, 3.2 mil aluminum foil, 2 mil polyethylene, 5 mil polyester film and an inner layer of 2 mil polyethylene. The polyester film was bonded to the adjoining polyethylene films by a .1 mil layer of polyvinylidene chloride. The laminate was made by conventional laminating techniques.

This laminate was made into square pouches measuring 4" x 6". Each pouch was filled with a stannous fluoride toothpaste having the following composition:

	Percent by weight
Calcium pyrophosphate	39.00
Stannous pyrophosphate	1.00
Stannous fluoride	0.40
Sorbitol	20.00
Synthetic detergent	1.50
Glycerine	10.00
Sodium carboxymethyl cellulose	1.05
Magnesium aluminum silicate	0.40
Flavor ingredients comprising: Lavamenthe (2-cyclohexalcyclohexanone), methyl salicylate (including about 1% vanilla), cassia (cinnamic aldehyde), and spearment rectified	0.85
Minor ingredients	0.55
Water	Balance

In filling the pouches with the above product, contamination of the heat seal areas was avoided.

Reference samples were prepared by filling conventional 5 oz. wax-coated lead tubes with toothpaste from the same batch as used in filling the pouches.

Filled pouches and reference samples were stored in a constant temperature room at 80° F. and a pouch and a reference sample were removed every two months. The pouches were evaluated for laminate bond strength and the product in the pouches was tested for flavor difference against the product in the reference samples. The results of this example and those of Examples II to VIII are given in Tables I and II following Example VIII.

The following test procedures were used to determine laminate bond strength and flavor difference between test and reference samples.

Laminate bond strength.—After removal from the constant temperature room, the pouch was cut open and the product was removed. The center of the pouch was cut into strips about 1" wide. These strips were examined for adhesion between the aluminum foil layer and the plastic film layers. The aluminum foil layer was manually peeled off from the laminate. The force required for peeling was compared with the force required for peeling the aluminum foil from the same laminate stored at room temperature but not in contact with any product. If the force required to peel samples was about equal, the stored laminate material was deemed satisfactory.

Flavor difference between test samples and reference sample.—A slurry of toothpaste in water at room temperature is made from the product stored in the pouch and from the product stored in the reference sample. In each case the slurry is made by adding 1 part toothpaste to 10 parts water. The slurry from the reference sample is divided and placed in two flasks; one is marked standard and the other remains unmarked. The slurry of paste made from the pouch-stored sample is kept separately, but is also unmarked. Persons on the flavor panel are first asked to taste the slurry marked standard. All the persons are then asked to taste the unmarked slurry made from the reference sample and the unmarked slurry made from the pouch-stored sample. Alternate persons taste the unmarked reference sample before the unmarked sample made from the pouch-stored product. The panelists are asked which of the unmarked samples taste differently as compared to the taste of the slurry marked standard. If no substantial difference is detectable, the flavor difference is deemed not detectable.

EXAMPLE II

The same procedure was followed as in Example I except that the pouches and reference samples were stored at a constant temperature of 100° F. The laminate was evaluated in the same manner as in Example I with the results shown in Tables I–II.

EXAMPLE III

The same procedure was followed as in Example I, except that the pouches and reference samples were stored at a constant temperature of 120° F. and tested after 2 months. The laminate was evaluated in the same manner as in the previous samples with the results shown in Tables I–II.

EXAMPLE IV

A laminate film was made consisting of successive superposed layers of 1 mil aluminum foil, 1 mil polyethylene, .5 mil polyester film and 1 mil polyethylene. The 1 mil polyethylene, .5 mil polyester film, 1 mil polyethylene component was type 25B13 Scotchpak heat sealable polyester film obtained from Minnesota Mining & Manufacturing Company. The laminate was otherwise made by conventional laminating techniques. Thereafter, the same filling and storage procedures were followed as in Ex-

ample I. The laminate was evaluated in the same manner as in the previous examples with the results shown in Tables I–II.

EXAMPLE V

The same procedure was followed as in Example IV except that the pouches and reference samples were stored in a constant temperature of 100° F. The laminate was evaluated in the same manner as in the previous examples with the results shown in Tables I–II.

EXAMPLE VI

The same procedure was followed as in Example IV except that the pouches and reference samples were stored at a constant temperature of 120° F. for 2 months. The laminate was evaluated in the same manner as in the previous examples with the results shown in Tables I–II.

EXAMPLE VII

A laminate film was made consisting of successive superposed layers of 1 mil aluminum foil, a 2 mil filling and bonding layer consisting of a blend of 25% of a vinyl resin which is the copolymer of ethylene and vinyl acetate and 75% paraffin wax, .5 mil polyester film and 1.5 mils polyethylene. The filling and bonding layer was made from 25% Elvax vinyl resin obtained from E. I. du Pont de Nemours & Company, and 75% AT 171 wax obtained from the Atlantic Refining Company. The .5 polyester film, 1.5 polyethylene component was type 20A5 Scotchpak heat sealable polyester film obtained from Minnesota Mining and Manufacturing Company. The laminate was otherwise made by conventional laminating techniques. Pouches and reference samples were made and stored as in Example I except that the pouches and reference samples were stored at 100° F. The laminate was evaluated in the same manner as in the previous examples with the results shown in Tables I–II.

EXAMPLE VIII

The same procedure was followed as in Example VII except that the pouches and reference samples were stored in a constant temperature of 120° F. The laminate was evaluated in the same manner as in the previous examples with the results shown in Tables I–II.

Any variation or modification of the invention as described above which conforms to the spirit of the invention is intended to be included within the scope of the claims.

What is claimed as new is:

1. A dentifrice package at least a portion of which has a laminated film body, said laminated film comprising a laminate system composed of at least three layers, the outer layer of the system being aluminum foil, said outer layer being at least thick enough to act as an effective oxygen barrier to prevent air permeation and resultant oxidation and deterioration of the dentifrice product, said outer layer being limited to a maximum thickness of about 5 mils, an intermediate layer adhesively bonded to said outer layer, said intermediate layer consisting essentially of a polyester film which is the condensation polymer of ethylene glycol and terephthalic acid, said polyester film having a thickness of at least 0.5 mil and being highly resistant to the transmission of flavor constituents in said dentifrice thereby preventing delamination of the bond between the intermediate layer of polyester film and the outer layer of aluminum foil, an inner layer of polyethylene having a thickness of from about 0.5 mil to about 8 mils and being highly resistant to water vapor transmission, said package containing a dentifrice product in contact with its inner layer of polyethylene, said dentifrice including a plurality of flavoring ingredients and water and being subject to deterioration by prolonged contact with oxygen.

2. A dentifrice package as claimed in claim 1 wherein the laminated film forms the body of a collapsible tube.

3. A dentifrice package as claimed in claim 2 wherein the laminated film has a filling and bonding layer interposed between the outside layer of aluminum foil and the intermediate layer of flavor impervious polyester film, said filling and bonding layer containing from about 10% to about 40% of a vinyl resin which is the copolymer of ethylene and vinyl acetate with the remainder paraffin wax, said filling and bonding layer having a thickness ranging from about 0.5 mils to about 7 mils, said filling and bonding layer giving the body of the collapsible tube improved feel and dead fold properties when the collapsible tube is filled with a dentifrice product.

TABLE I.—LAMINATE BOND STRENGTH

Example (°F.)	1 month	2 months	4 months	6 months
I (80)		Satisfactory	Satisfactory	Satisfactory.
II (100)		do	do	Moderate deterioration.
III (120)		Severely delaminated.	(1)	(1)
IV (80)		Satisfactory	Satisfactory	Satisfactory.
V (100)		do	do	Moderate delamination.
VI (120)		Severely delaminated.	(1)	(1)
VII (100)	Satisfactory	Satisfactory	Satisfactory	(2)
VIII (120)	do	(2)	(2)	(2)

[1] Test discontinued.
[2] Test in progress.

TABLE II.—FLAVOR DIFFERENCE BETWEEN TEST SAMPLE AND REFERENCE SAMPLE

Example (°F)	1 month	2 months	4 months	6 months
I (80)		Not detectable	Not detectable	Not detectable.
II (100)		do	do	Do.
III (120)		do	(1)	(1)
IV (80)		do	Not detectable	Not detectable.
V (100)		do	do	Do.
VI (120)		do	(1)	(1)
VII (100)	Not detectable	do	Not detectable	(2)
VIII (120)	do	(2)	(2)	(2)

[1] Test discontinued.
[2] Test in progress.

4. A dentifrice package as claimed in claim 3 wherein the dentifrice composition within said package contains stannous fluoride in an acid environment.

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T. R. SAVOIE, *Assistant Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,381,818 May 7, 1968

Paul E. Cope et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, line 54, "5 mil polyester film" should read -- .5 mil polyester film --.

Signed and sealed this 23rd day of September 1969.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents