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# PACKAGING OF MATERIALS AND MEANS THEREFOR

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The present invention relates to improvements for the packaging in aluminum containers of materials normally reactive with aluminum and means for rendering this combination non-reactive and stable upon aging, as hereinafter described and claimed. As a particular embodiment, the invention comprises a fluoride dentifrice normally reactive with aluminum in an aluminum container having on its inner surfaces a film of an alkaline metal aluminate effective to prevent said reaction and form a compatible combination.

The packaging and storing of ordinary toothpastes and similar pasty materials in collapsible aluminum tubes is known. These aluminum containers possess certain advantages over the use of lead tubes or the like with regard to cost and the inherent properties of the metals.

It is known that certain fluoride compounds have a beneficial effect on the teeth and tend to inhibit tooth decay. Soluble fluoride compounds have been incorporated in pasty dental materials such as toothpastes. In the packaging and storing of toothpastes containing soluble fluorides, it has now been found that it is not practical to use aluminum containers commercially. The packaging of fluoride toothpastes in aluminum containers creates a problem since the materials are not compatible and produce a chemical reaction resulting in adverse effects, both upon the product and upon the container. The inter-action of the fluoride toothpaste with the inner aluminum surfaces results in the evolution of hydrogen, bloating of the collapsible tube, discoloration of the product and other adverse effects which prohibit the practical utilization of fluorides in aluminum tubes. In general, therefore, fluoride toothpastes have been packaged in waxed-lead tubes or the like whereas the use of collapsible aluminum tubes has been restricted to the packaging of toothpastes which do not contain fluorides.

In accordance with the present invention, it has been found that materials normally reactive with aluminum surfaces such as fluoride toothpastes may be packaged in aluminum containers so as to prevent said reaction and achieve a stable product by a method which comprises treating said aluminum surfaces adapted to contact said toothpaste with an aqueous solution of an alkaline metal base effective to form a film of alkaline metal aluminate thereon, and thereafter filling the same with the pasty product. A preferred embodiment comprises a fluoride toothpaste in an aluminum container having on its inner surfaces a calcium aluminate film formed as a reaction product which is inert with respect to said fluoride toothpaste. Various other preferred embodiments will be apparent in the following description.

The treated aluminum surfaces having the film or coating of calcium aluminate or like reaction product thereon is inert and non-reactive with the fluoride toothpaste. It is substantially non-porous and impermeable upon aging so as to prevent or inhibit the reaction between the fluoride toothpaste and the aluminum metal. As a result, the fluoride toothpaste in the treated aluminum container maintains its utility and cosmetic character. While the invention is described herein with particular reference to the packaging of fluoride toothpaste and the like, it is obvious that it is applicable to the treatment of aluminum containers for the packaging of other materials of a similar nature such as cosmetic creams, pastes, etc.



The treating agent is a solution of the alkaline metal base in water which reacts with the aluminum and forms the protective film as a reaction product. In general, it is preferred to use an inorganic calcium base such as calcium hydroxide (including oxide forming the hydroxide in aqueous solution) because it forms a most insoluble film. The calcium hydroxide solution or the like has been found to react with the aluminum surface so as to form a coating which is a calcium aluminum complex and is accordingly designated as a calcium aluminate herein. Other inorganic bases such as barium hydroxide and lithium hydroxide which produce hydroxyl ions in solution also have been found to form similar coatings. According, the term "alkaline metal base" refers herein to the alkaline earth metal and alkali metal bases releasing hydroxyl ions in aqueous solution and which react with said aluminum and result in the formation of the alkaline metal aluminum complex film. On the other hand, alkaline metal salts such as the chlorides, acetates and the like were tried with unsatisfactory results. The aqueous solution of base should be free from amounts of salts which prevent the desired reaction of the metal with the aluminum, including salts which are deposited per se as coatings on the aluminum since such salt coatings tend to be more porous, soluble and reactive with fluorides.

The aluminum containers are treated with the alkaline metal base solution in any suitable manner so as to form the desired reaction product on the inner surfaces of the container which are adapted to come into contact with the pasty material. The usual method of producing soft collapsible aluminum tube containers involves extruding the tubes from a slug or piece of relatively pure aluminum metal (99.5+% aluminum) and thereafter subjecting the extruded tube to an annealing treatment so as to produce a soft flexible tube. The mouth is shaped and threaded and a screw cap applied thereto. The bottom end is open and the treating solution may be added to this open end while the tube is inverted so as to permit the necessary contact between the materials. Alternatively, the aluminum container may be treated while the cap end is still solid if the subsequent processing does not adversely affect the film.

It is obvious that the invention is not restricted to the treatment of collapsible aluminum tubes since it is applicable to other aluminum or aluminum alloy containers which are particularly adaptable to dispense material therefrom. Such aluminum containers are the tubular containers used in pressurized products known as aerosol containers and suitable for the packaging of various creams, pastes, sprays, etc. In the usual method of preparing such aerosol containers, the extruded tube has an opening for a dispenser on the top with a solid bottom wall. The container is then filled with the treating solution to overflow or to any desired level.

In the treatment of the aluminum containers, the aqueous solution of alkaline metal base is permitted to contact the inner surfaces of the aluminum tube for a sufficient length of time to form the desired reaction product as a complete film. The calcium aluminate film or the like is produced spontaneously by reaction of the base with the aluminum. To some extent, the thickness of the film is controlled by the solubility of the base in the solution and the time that the materials are in contact. In general, the deposited film should be less than the thickness of the walls of the collapsible tubes which are of the order of about 0.004–0.005 inch, and preferably not substantially in excess of about one-half the tube wall thickness, e.g., 0.0004 to 0.002 inch. In general, the alkaline metal bases do not exhibit appreciable solubility in water so that it is convenient to employ solutions which initially are approximately saturated, particularly using the more water-insoluble alkaline earth metal bases such as calcium hydroxide, though solutions of any practical concentrations may be employed.

The period of time to form the reaction product on the aluminum surfaces is variable. In general, the reaction product starts to form within a few minutes and the film is sufficiently formed within about one-half hour, though longer periods such as one and two hours may be employed if desired. It is unnecessary to continue to build up a relatively thick film such as occurs after three hours in view of the satisfactory nature of films achieved with a lesser time treatment. It has been found that the reaction can be conveniently conducted at room temperature, e.g., about 25° C., with attendant advantages. It is unnecessary to heat or cool the ingredients during the treating step though conditions such as time and temperature may be suitably modified provided the desired product is obtained.

Thereafter, the residual aqueous solution is poured or otherwise removed from the containers. It is preferred to wash or rinse the containers with water for general cleansing purposes. It is advantageous to dry the coating and, thus, the tubes are preferably subjected to a suitable drying temperature for a sufficient period of time. For example, it is sufficient ordinarily to insert or pass the tubes through an oven at a temperature from about 100° F. to 212° F. for up to an hour. A preferred drying operation comprises drying at about 140° F. for about 15–30 minutes.

The treated aluminum containers are then filled with the fluoride toothpaste or similar product in the usual manner and the open end is sealed or closed by known means.

The fluoride-containing toothpastes and the like comprise usually a water-soluble fluoride compound admixed with a polishing material, a surface-active agent and a quantity of liquids which are proportioned to form a creamy mass of desired consistency which is suitable for dispensing from the aluminum container, e.g., extrudible from a collapsible aluminum tube. Any water-soluble fluoride compound may be employed such as sodium fluoride or a tin fluoride such as stannous flouride, stannous chlorofluoride and the like. Various polishing materials are known in the art such as insoluble sodium metaphosphate, hydrated alumina, and calcium pyrophosphate. The insoluble sodium metaphosphate is preferably admixed with a minor proportion of an insoluble calcium or magnesium-containing polishing agent. The surface-active agents are usually foaming detersive materials. Examples of known dentifrice surface-active agents are sodium N-lauroyl sarcoside, sodium lauryl sulfate and sodium coconut monoglyceride sulfonate. The liquids in the toothpaste will comprise chiefly water and a humectant such as glycerine, sorbitol, propylene glycol or the like including suitable mixtures thereof. In general, the amount of fluoride is from about 0.05 to 2%, the polishing agent



is about 20–80%, the surface-active agent is about 0.5 to 10%, and the liquid content is about 20–80%, these amounts being by weight of the dental formulation.

Further examples of fluoride dentifrices containing the indicated ingredients in the amounts by weight specified below which may be packaged in the treated aluminum containers are as follows:

| Ingredients | I | II |
|---|---|---|
| Sodium fluoride | 0.2 | |
| Stannous fluoride | | 0.4 |
| Polishing agent | 51 | 41 |
| Detergent | 2 | 1.5 |
| Glycerine | 29 | 10 |
| Sorbitol | | 15 |
| Water | 14 | 29 |

The formulations contain also small amounts of flavor, preservatives and gum which are usual ingredients in a commercial dental cream.

The following examples are additionally illustrative of the present invention and it will be understood that the invention is not limited thereto:

*Example I*

A number of collapsible aluminum tubes suitable for packaging toothpaste having a screw cap on top and open on the bottom are inverted and filled with a saturated calcium hydroxide solution. Within a few minutes at room temperature a film starts to form on the inner walls of the aluminum tube. After two hours of this treatment, the liquid is removed from the tubes which are rinsed with tap water and dried in an oven at 140° F. for a period of about 60 minutes. The film is a calcium aluminate and has a wall thickness of about 0.001 inch.

The treated tubes are filled with a fluoride dental cream as indicated comprising a suspension of a polishing agent in an aqueous vehicle containing water, glycerine, detergent and having 0.2% sodium fluoride. At the same time, control samples are prepared with the same dental cream using untreated aluminum tubes. The tubes are sealed in the usual manner.

After aging for a number of weeks at 100° F., the control samples in the untreated aluminum tubes showed severe signs of chemical reaction, including bloating of the package, etching of the aluminum walls and discoloration of the product. The treated tubes with the calcium aluminate coating are satisfactory and do not exhibit the above defects.

*Examples II—III*

The procedure of Example I is repeated using similar solutions of barium hydroxide and lithium hydroxide separately in place of the calcium hydroxide. Both of these solutions result in the deposition of similar coatings effective for the packaging of the fluoride dentifrice.

Although the present invention has been described with reference to particular embodiments, it will be apparent to those skilled in the art that variations and modifications can be substituted therefor without departing from the principles and true spirit of the invention.

What is claimed is:

1. A process of packaging pasty material in an aluminum container, said material being normally reactive with aluminum, which comprises treating the inner surfaces of the aluminum container with an alkaline metal base releasing hydroxyl ions in aqueous solution for a period of time sufficient to form a film of an alkaline metal aluminate upon the inner surfaces of said container, separating the solution therefrom, and filling said treated aluminum container with said pasty material.

2. A process of packaging a fluoride dental composition in an aluminum container, said composition being normally reactive with aluminum, which comprises treating the inner surfaces of said aluminum container with an

aqueous solution of an inorganic calcium base releasing hydroxyl ions in aqueous solution for a period of time sufficient to form a reaction product as a film on said inner aluminum surfaces, drying said film and filling said aluminum container with said fluoride material.

3. A process of packaging a fluoride toothpaste in a collapsible aluminum tube which comprises treating the inner surfaces of said collapsible aluminum tube with an aqueous solution of an alkaline earth metal base for a period of time sufficient to form a reaction product as a film on said inner aluminum surfaces, separating said solution therefrom, and adding said fluoride toothpaste to said tube.

4. A package comprising an aluminum container having present therein a pasty material which is normally reactive with said aluminum, said aluminum container having a film of an alkaline metal aluminate on the inner surfaces thereof to inhibit reaction of said pasty material and aluminum.

5. A dentifrice comprising a fluoride-containing dental composition in an aluminum collapsible tube for dispensing said composition, said collapsible tube having a film of an alkaline metal aluminate on the inner surfaces thereof.

6. A dentifrice in accordance with claim 5 wherein said film comprises a calcium aluminate.

7. A process of packaging material in an aluminum container, said material being normally reactive with aluminum, which comprises treating the inner surfaces of the aluminum container with an alkaline metal base releasing hydroxyl ions in aqueous solution for a period of time sufficient to form a film of an alkaline metal aluminate upon the inner surfaces of said container, separating the solution therefrom, and filling said treated aluminum container with said material.



8. A process in accordance with claim 7 wherein said base is a solution of calcium hydroxide in water.

9. A package comprising an aluminum container having present therein a material which is normally reactive with said aluminum, said aluminum container having a film of an alkaline metal aluminate on the inner surfaces thereof to inhibit reaction of said material and aluminum.

10. A package comprising a collapsible aluminum container having present therein a material which is normally reactive with said aluminum, said aluminum container having a film of a calcium aluminate on the inner surfaces thereof to inhibit reaction of said material and aluminum.

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