Patented Mar. 16, 1954

2,671,995

UNITED STATES PATENT OFFICE

2,671,995

PACKAGING OF MATERIALS

William Thomas Egan, Fanwood, N. J., assignor to Colgate-Palmolive Company, Jersey City, N. J., a corporation of Delaware

No Drawing. Application October 22, 1949, Serial No. 123,085

2 Claims. (Cl. 53—5.5)

1

This invention relates to improvements in the packaging of materials in metal containers and more particularly to the packaging of paste-like materials in collapsible tube containers made of aluminum, or a suitable alloy thereof, the aluminum tubes being treated prior to filling to render the same resistant to the corrosive attack of such products. The invention will be described with particular reference to the packaging of tooth paste, but it will be obvious that the invention is applicable to the packaging of other materials of a similar nature such as cosmetic creams, pastes, etc.

In the packaging and merchandising of tooth paste and similar products which contain water-soluble salts and the like substances which attack aluminum, corrosion becomes a serious problem when such products are packaged in collapsible aluminum tube containers. The corrosive attack usually manifests itself in the form of pitting which represents a severe form of localized attack, the corrosion taking place on the inner surfaces of the tubes. The walls of collapsible aluminum tubes are purposely made very thin, usually on the order of about four or five thousandths of an inch or less in thickness, in order to conserve metal and provide a tube which is easily flexed and collapsed during use. The thinness of the walls of such a collapsible tube, although desirable for certain purposes, shortens the time when a tube may fail by corrosion, as for example, where the corrosive attack is so extreme that actual perforation of the thin walls of the tube takes place. Such a tube, moreover, is easily flexed and dented during handling and storage producing local stresses and work hardened areas in the metal walls which appear to induce corrosive attack at such areas.

To overcome this corrosion problem, protective linings such as cellulose acetate, fibreless cellulose hydrate, phenolic-type lacquers and the like film-forming coatings have been employed, but such methods substantially increase the cost of the container which, of course, is undesirable inasmuch as such tubes are not refilled, being discarded after using up the contents. Aside from the cost angle, the inner liner coatings are often attacked by the contents of the container. It is also difficult to form a continuous unbroken protective liner or coating on the inner surfaces of such collapsible aluminum tubes which will provide adequate protection thereof and not tend to peel or flake off when the tubes are flexed and collapsed in the usual manner during use.

Other forms of collapsible tubes also have been

2

employed, for example tinned lead tubes, but such tubes are expensive and have the added disadvantage that the contents of the container may become contaminated with lead which is toxic. Aluminum metal on the other hand is practically non-toxic and can be suitably formed into tubes which are soft and particularly adapted for use as collapsible tube containers where corrosion is not encountered.

While numerous methods for treating aluminum and aluminum oxide surface coatings to improve their resistance to corrosion have been described in the literature and patents relating to aluminum, insofar as known heretofore, no commercially practicable and simple method has been devised for treating collapsible aluminum tube containers in the packaging of paste-like compositions to provide a tube which is resistant to the corrosive attack of such compositions.

In the usual method of producing soft, collapsible aluminum tube containers, it is customary to extrude the tubes from a block or piece of relatively pure aluminum metal (99.5+per cent aluminum) and thereafter subject the extruded tube to an annealing treatment so as to change the crystalline structure of the metal and produre a soft, flexible tube which is readily collapsed and rolled upon itself. While it is known that annealing of aluminum metal which has been cold-worked improves its resistance to corrosion, it has been observed that such annealing treatment alone of collapsible aluminum tubes does not provide sufficient resistance to the corrosive attack of electrolytic pastes such as contained in tooth paste and the like products.

In accordance with the present invention it has been found, after considerable experimental work, that a collapsible aluminum tube container having exceptionally good resistance to the corrosive attack by such paste-like products is produced by immersing the tube in boiling water or a boiling aqueous solution prior to filling the tube. The treatment not only increases the corrosion resistance of the aluminum tube but removes impurities from the surface of the tube which may otherwise initiate electrolytic action and localized corrosion. In addition the treatment provides a tube having a clean and sterilized surface for receiving the paste-like product which is desirable. There is, moreover, no need of employing protective liners or auxiliary coatings on the inside of the tube as aforementioned.

A preferred manner of packaging tooth paste in a collapsible aluminum tube container in ac-

cordance with this invention comprises immersing the aluminum tube in boiling water for a period of from about one-half to two hours, and after removing the tube and allowing it to dry, filling the same with tooth paste. A number of tubes ordinarily are treated at the same time, the treatment being carried out preferably after such aluminum tubes have been annealed. If desired, however, the boiling water treatment of the tubes may be performed prior to the annealing treatment, or at some other time prior to filling the same with the paste-like product.

The following example illustrates the improved corrosion resistance of collapsible aluminum tube containers which were subjected to a boiling water treatment and thereafter filled with tooth paste in accordance with this invention.

Three batches each comprising about 65 aluminum tube containers were placed horizontally in a cylindrical glass rack open at each end, the tubes having been annealed but undecorated and uncapped. The glass rack and tubes were then suitably suspended in a stainless steel pot containing boiling distilled water, the tubes remaining completely submerged in the boiling water for one and a half hours. Following this treatment, the tubes were removed from the bath, drained dry and after filling with tooth paste were stored at room temperature until tested for corrosion resistance. All the tubes were filled simultaneously to eliminate possible filling variations. At the same time a corresponding quantity of each of the three original batches of tubes, which had not been treated with boiling water, were filled with dental cream as control samples.

The corrosion test data results obtained with the batches of untreated and treated aluminum tube containers, as described, are tabulated as follows:

Percent of tubes showing pinhole corrosion

Batch	Untreated Tubes		Treated Tubes	
	After 1½ Mo.	After 4½ Mo.	After 1½ Mo.	After 4½ Mo.
(A)	37	44	0	0
(B)	13	18	0	1½
(C)	11	11	0	1½

As the tabulated results indicate, aluminum tubes which were subjected to the boiling water treatment prior to filling with tooth paste show exceptional good resistance to corrosion after over four months storage. While the reason for this increased resistance is not definitely known it is believed that the improvement is brought about due to the removal of impurities from the metal surface and the production of a relatively thick continuous non-porous oxide and/or hydroxide layer over the surfaces of the aluminum metal which resists attack by corrosive substances.

The collapsible aluminum tubes may be formed in any suitable manner, a number of different processes being known, and such preformed tubes thereafter treated with boiling aqueous solution prior to filling with tooth paste in accordance with the invention.

In carrying out the process with a tube which has been formed, for example, by extrusion as commercially practiced and subsequently annealed, the surfaces of the aluminum tube are suitably cleaned of grease and foreign matter including any lubricant such as commonly employed during the extrusion process. The tube is then immersed in a bath of boiling water for a time effective to provide increased resistance to corrosion.

Cleaning of the aluminum metal tubes may be accomplished in any desired manner such as by washing with conventional cleaning solutions, using for example an aqueous alkali metal phosphate or carbonate solution, and such as emulsify and remove grease and/or other foreign matter. Removal of organic and volatilizable impurities from the surfaces of the tube, if desired, may be effected by merely heating the tube to a temperature sufficient to volatilize and burn off such extraneous matter, and thereafter subjecting the tube to boiling water. The cleaning step, however, may be omitted and is not essential to the process but can be used to advantage where the surfaces of the tube are contaminated with impurities which are difficult to remove during the boiling water treatment.

The water or aqueous solution employed for treating the collapsible aluminum tubes need not be distilled water and ordinary soft or hard waters may be used for this purpose. Further, if desired, the wetting properties of such aqueous solutions may be enhanced by the addition of surface-active agents. The treating solution may also contain varying but small amounts of suitable water-soluble additives such as oxidizing agents, silicates, phosphates, etc.

The temperature of the boiling solutions during treatment of the tubes will usually be about 100° C. or above depending upon the soluble matter in solution and atmospheric pressure conditions. In general, however, the solution temperature will not be above about 125° C. Temperatures somewhat below 100° C. may be employed but the results obtained are not as good as where the tubes are treated for a like period wherein the treating solution is maintained at the boiling point. The duration of treatment will vary depending upon the particular composition and surface condition of the metal tube used as well as the temperature of the treating solution. Preferably the tubes will be kept immersed in the boiling aqueous solution for about thirty minutes or more, and such as effective to produce the desired corrosion resistance properties without substantially altering the softness and flexibility characteristic properties of the collapsible tubes.

Employing the method described in the packaging of tooth paste, a finished package of tooth paste is provided which can be stored for long periods of time without encountering the corrosion difficulties described. An improved collapsible aluminum tube container, moreover, is produced which is especially useful for packaging and marketing paste-like materials which tend to cause corrosion of aluminum metal surfaces when stored in contact therewith.

Although a preferred method of treating collapsible aluminum tube containers preparatory to filling the same with paste-like materials such as tooth paste has been described, it will be understood that variations of the method may be used to accomplish the same purpose by those skilled in the art and that such variations and modifications are intended to be included in the present invention, being limited only as specifically called for in the appended claims.

What is claimed is:

1. A process of packaging pasty material in a collapsible aluminum tube container, which material is corrosive to aluminum metal surfaces,

comprising the steps of immersing an annealed, collapsible tube of aluminum of a purity of at least 99.5% whose surfaces are free from artificially deposited coatings of aluminum oxide in a boiling water bath for a period of time of approximately one-half to two hours whereby the corrosion resistance of the aluminum metal surfaces of the tube is substantially increased, and then filling said collapsible aluminum tube with said corrosive pasty material.

2. A process of packaging pasty material in a collapsible aluminum tube container, said material being corrosive to aluminum metal surfaces, which comprises subjecting an annealed, collapsible tube of aluminum of a purity of at least 99.5% whose surfaces are free from artificially deposited coatings of aluminum oxide to the action of boiling water for a period of time of approximately one-half to two hours whereby the surface of said aluminum tube is provided with increased resistance to corrosion, and filling said collapsible aluminum tube with corrosive pasty material.

WILLIAM THOMAS EGAN.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,912,175	Blough	May 30, 1933
2,086,993	Barrett	July 13, 1937
2,091,419	Schroeder	Aug. 31, 1937
2,104,222	Decker	Jan. 4, 1938
2,279,252	Slunder	Apr. 7, 1942
2,403,426	Douty et al.	July 2, 1946
2,465,443	Gide	Mar. 29, 1949
2,475,945	Clark et al.	July 12, 1949
2,502,441	Dodd et al.	Apr. 4, 1950
2,516,685	Douty et al.	July 25, 1950

FOREIGN PATENTS

Number	Country	Date
872,562	France	Feb. 16, 1942

OTHER REFERENCES

Mellor: "Comprehensive Treatise on Inorganic and Theoretical Chemistry," vol. V, page 205, published 1924 by Longmans, Green and Company, New York. (Copy in Div. 59.)

Babor and Lehrman: "General College Chemistry," page 541, published 1940 by Thomas Y. Crowell Co., New York. (Copy in Div. 59.)