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## PACKAGING OF MATERIALS

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This invention relates to the packaging of materials in metal containers and more particularly to the packaging of paste-like materials in collapsible tube containers made of aluminum metal, or a suitable alloy thereof, the aluminum tubes being treated prior to the filling operation to render them resistant to the corrosive attack of said materials. The invention will be described with particular reference to the packaging of tooth paste, but it will be obvious that the invention is applicable for 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 appears 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. Such methods, however, substantially increase the cost of the collapsible tube containers 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 coatings are often attacked by the contents of the container. It is also difficult to form a continuous unbroken protective lining or coating on the inner surface of a collapsible aluminum tube such as will provide adequate protection to the material and not tend to peel or flake off when the tube is flexed and collapsed in the usual manner during use.

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Other forms of collapsible tubes also have been employed such as 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 readily deformed 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 generally to aluminum, no commercially practicable, low-cost and simple method has been devised heretofore 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 contained, it is customary to extrude the tubes from a slug or piece of relatively pure aluminum metal (99.5+ percent aluminum) and thereafter subject the extruded tube to an annealing treatment so as to change the crystalline structure of the metal and produce 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 produce a tube having 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 that a collapsible aluminum tube container having greatly improved resistance to the corrosive attack by such paste-like products is produced by treating the collapsible tube with steam preferably at atmospheric or superatmospheric pressures, including ordinary variations due to altitude and meteorological conditions, prior to filling the same with the paste-like product. Steaming of the collapsible aluminum tube provides a tube having greatly improved resistance to over-all as well as localized corrosion, and such as results from prolonged contact with corrosive paste-like material. The steam treatment, furthermore, effects the removal of minute segregated impurities from the metal surfaces of the tube. These impurities often cause local electrolytic solution of the surrounding metal to take

place in the presence of electrolytes such as are generally contained in pastes and cream-like products.

A preferred manner of packaging tooth paste in a collapsible aluminum tube container in accordance with this invention comprises pretreating the tube prior to filling by subjecting the tube to the action of steam or saturated water vapor for a time effective to provide increased corrosion resistance of the metal tube surfaces. This usually takes about half an hour or more, and when carried out under ordinary atmospheric pressure conditions the tube preferably is treated for about an hour and a half to two hours. A number of tubes ordinarily are treated at the same time, the treatment being performed usually after the aluminum tubes have been annealed. If desired, however, the treatment of the tubes with steam may be effected before the same are annealed, or at some other time prior to filling the tubes with tooth paste or the like product.

In the following table the results of test data are given showing the improved corrosion resistance of collapsible aluminum tube containers which were steam treated prior to being filled with paste corrosive to aluminum. In all cases the steam treatment was carried out at atmospheric pressure. To obtain comparative tests, a number of tubes were left untreated as control samples.

Three batches (A), (B) and (C) were tested. In batches designated (A) and (B) the aluminum tubes were of commercial grade being made from practically pure aluminum (99.7%) and annealed to provide a soft, flexible metal tube. Tubes (A) were supplied by one manufacturer and tubes (B) by another. In batch (C) the aluminum tubes used were of commercial grade, but in this instance each tube was filled with a paste which was extremely corrosive to aluminum. The results are tabulated as follows:

| Batch | Number of Tubes | Treatment | Percent Tubes Corrosion Free |
|---|---|---|---|
| A-1 (control) | 144 | | 56% after 4 months. |
| A-2 | 66 | Steamed 2 hours | 97% after 4 months. |
| B-1 (control) | 72 | | 82% after 4 months. |
| B-2 | 66 | Steamed 2 hours | 98% after 4 months. |
| C-1 (control) | 15 | | 6% after 3 months. |
| C-2 | 13 | Steamed 2 hours | 92% after 3 months. |

As the tabulated results indicate, collapsible aluminum tubes which were subjected to steam treatment prior to filling with pasty material show exceptionally good resistance to corrosion after several months storage, and even when subjected to a highly corrosive paste. 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 tubes which provides the increased resistance to 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 steam prior to filling with tooth paste in accordance with this invention.

In carrying out the process with a tube which has been formed for example by extrusion as commercially practiced and 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. After cleaning the tube, it is then placed in a closed chamber filled with steam and subjected to steaming for about an hour or more as required to produce a tube having increased resistance to corrosion.

Cleaning of the aluminum metal tubes may be effected in any suitable manner such as by washing the same with conventionl cleaning solutions, for example aqueous alkali metal phosphate and/or carbonate solutions such as emulsify and remove grease and other foreign matter. The removal of organic and readily volatilizable impurities from the surfaces of the tube may, if desired, be effected by heating the tube to a temperature sufficient to volatilize and burn off such extraneous matter. The cleaning step, however, may be omitted and is not essential to the process but may be used to advantage where the surfaces of the tube are contaminated with impurities which are difficult to remove during the steam treatment.

When the steam treatment is carried out above atmospheric pressure a suitable pressure vessel or chamber is employed. Treatment of collapsible aluminum tubes in an atmosphere of steam at approximately 15 pounds gage pressure for one-half hour has been found effective for increasing the corrosion resistance of the tubes. Steam at higher temperatures may be used if desired. In the preferred method the treatment comprises the use of saturated steam at atmospheric pressure which avoids the use of an autoclave or the like high pressure equipment.

The duration of treatment using steam at ordinary atmospheric pressure is usually of greater length than with the use of superheated steam. By carrying out the packaging process in accordance with this invention, a packaged tooth paste product is provided which can be stored for long periods of time without encountering serious corrosion difficulties such as heretofore described. The invention further provides a relatively simple method of treating aluminum tube containers preparatory to filling the same which makes it possible to use collapsible aluminum metal tubes for marketing tooth paste and the like materials which tend to corrode aluminum. The improvement, moreover, provides a simple and economical method of treating collapsible aluminum tube containers so as to improve their corrosion resistance to such an extent that they may be utilized to package materials which are corrosive to aluminum surfaces without the necessity of using inner liners and/or special coatings as heretofore described.

Although a preferred method of treating collapsible aluminum tubes preparatory to filling the same with paste-like materials such as tooth paste has been described, it will be understood that suitable variations of the method may be utilized 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, the same being limited only as particularly called for in the appended claims.

What is claimed is:

1. A process of packaging pasty material in a collapsible aluminum tube container, said material being corrosive to aluminum metal surfaces, which comprises the steps of subjecting an annealed, collapsible tube of aluminum of a purity of at least 99.5% to the action of steam 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, which material is corrosive to aluminum metal surfaces, comprising subjecting an annealed, collapsible tube of aluminum of a purity of at least 99.5% to an atmosphere of steam at atmospheric pressure for a period of time of approximately one-half to two hours whereby the resistance to corrosion of the aluminum metal surfaces is effectively increased, and filling said collapsible aluminum tube with said corrosive pasty material.

3. A process of packaging pasty material in a collapsible aluminum tube container, which material is corrosive to aluminum metal surfaces, comprising subjecting an annealed collapsible tube of aluminum of a purity of at least 99.5% to an atmosphere of superheated steam for a period of time of approximately one-half to two hours to increase substantially the resistance of the aluminum metal surfaces to corrosion when



filled with said material, and filling said collapsible aluminum tube with said corrosive pasty material.

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