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METHOD OF TREATING COLLAPSIBLE ALUMINUM TUBE CONTAINERS

William Thomas Egan, Fanwood, N. J., and Russell Park McGhie, New York, and Frederick William Schneider, Woodhaven, N. Y., and Warren William Sweet, Pompton Plains, N. J., assignors to Colgate-Palmolive Company, a corporation of Delaware

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This invention relates to metal containers and more particularly to a method of treating collapsible tube containers made of aluminum metal, or a suitable alloy thereof, to render the same resistant to corrosion and suitable for packaging tooth paste, shaving cream and similar paste-like products. The invention will be described with particular reference to the treatment of collapsible aluminum tubes for packaging tooth paste, but it will be obvious that the invention is applicable to the treatment of like metal containers for packaging other materials of a similar nature.

In the packaging and merchandising of tooth pastes and similar pasty products which contain water-soluble salts and the like substances which tend to attack aluminum, the problem of corrosion becomes a serious one 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 inside of the aluminum tubes. The walls of such 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 inner linings such as cellulose acetate, fibreless cellulose hydrate, phenolic-type lacquers and the like film-forming coatings have been employed, but the use of inner liners substantially increases the costs of the merchandise, and such coatings are often attacked by the contents of the container. It is difficult, moreover, to form a continuous unbroken protective liner or coating on the inner surface of the collapsible tube which 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. 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

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may become contaminated with lead which is toxic. Aluminum metal on the contrary is practically non-toxic and can be suitably formed into tubes which are soft and admirably adapted for use as collapsible tube containers without such protective inner coatings except where corrosion is 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, no commercially practicable, low-cost and simple method has been devised heretofore for treating collapsible aluminum tubes to render the same corrosion resistant and applicable for packaging paste-like compositions which tend to corrode aluminum.

In the usual method of producing soft collapsible aluminum tubes, it is customary to extrude the tubes from a slug or piece of relatively pure aluminum metal (99.5% 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 metal 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 the annealing treatment alone, as applied to collapsible aluminum tube containers, is not sufficiently effective to overcome this corrosion problem when the tubes are filled with electrolytic pastes such as contained in tooth paste and the like products.

In accordance with the present invention, it has been found, after considerable experimenting and testing, that a collapsible aluminum tube container having improved resistance to corrosion is produced by wetting the tube with water and subjecting the wet tube to a temperature sufficient to cause the film of water on the aluminum metal surfaces to boil. The process is relatively inexpensive to carry out and no special equipment is required. Treatment of a collapsible aluminum tube container as described results in the production of a container which is sufficiently resistant to corrosion so that it can be used for packaging tooth paste and the like products without the necessity of employing protective liners or auxiliary coatings on the inside of the tube as aforementioned.

A preferred manner of treating a collapsible aluminum tube container to render the same corrosion resistant in accordance with this invention comprises immersing the tube in water so that the surfaces of the metal become coated with

a film of water and thereafter introducing the wet tube into a chamber which is heated above the temperature of boiling water to cause the film of water on the surfaces of the tube to boil forming steam. A number of tubes ordinarily will be treated at the same time, the tubes being wet with water and then heated rapidly to a temperature which causes the film of water on the aluminum metal surfaces of the tubes to boil, thus subjecting the metal surfaces to the action of boiling water and steam. Heating of the tubes may be effected in any suitable manner, but a preferred method comprises placing the wet tubes in a heated oven such as commonly used for annealing collapsible aluminum tubes. The presence of air or oxygen during the heat treatment is beneficial, tending to enhance the results obtained.

Aluminum tube containers which are to be rendered corrosion resistant in accordance with this invention may be treated at any suitable time prior to filling the containers. The treatment, for instance, may be performed either before or after annealing the containers. A convenient time for carrying out the process, and that which is generally preferred is during the annealing treatment. Such method of heat treating the aluminum tube containers while initially wet with a film of water is conveniently referred to hereinafter as "wet annealing."

In the following table the results of test data are given showing the improved corrosion resistance of collapsible aluminum tube containers which were treated in accordance with the method of this invention prior to being filled with tooth paste. The heat treatment for both wet and dry tubes was the same in each case. Tubes which were to be wet annealed were immersed in water immediately prior to transferring them to the annealing oven. Upon removal of the heated tubes from the annealing oven they were allowed to air cool gradually to room temperature. They were then filled with tooth paste and stored at room temperature for six weeks, and at the end of that time examined for corrosion. The results are tabulated as follows:

	No. of Tubes Tested	Heat Treatment, 1160 °F., for Twenty Minutes	No. of Tubes Showing Corrosion after Six Weeks' Storage	Percent Tubes Corrosion Free
Run #1 (control)	144	Annealed (Dry)	53	63.2
Run #2	71	Annealed (Wet)	3	95.8
Run #3	66	do	1	98.5

As the tabulated results show, aluminum tubes which were subjected to wet annealing have greatly increased resistance to corrosion as compared with like tubes which were annealed dry as commonly practiced. While the reason for this increased resistance is not exactly 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 in accordance with the method herein described to provide a collapsible aluminum tube having improved resistance to corrosion.

In carrying out the process with a tube which has been formed, for example by extrusion as commercially practiced, the surfaces of the aluminum tube are suitably cleaned of foreign matter, including any lubricant such as is commonly employed during the extrusion process, so that the surfaces of the tube, particularly on the inside, are clean and can be thoroughly wet with water. Cleaning of the tubes may be effected in any suitable manner as by washing with conventional cleaning solutions, for example using an aqueous alkali metal phosphate or carbonate solution, or suitable mixture thereof, and such as emulsify and remove greases and/or other foreign matter. The cleaned aluminum tube is then rinsed with water to remove the cleaning solution leaving a film of water on the surfaces, or if allowed to dry the tube is again wet with water, then introduced into the annealing oven. In some instances the cleaning operation may be performed by heating the tube to a temperature sufficiently high to volatilize and burn off organic matter after which the tube is washed with water to remove carbon and residual matter formed during heating and remaining on the surfaces of the tube. In this manner the surfaces of the tube are freed of foreign matter so that a continuous film of water will be left on the surfaces upon the application of water or aqueous solutions thereto.

The water employed for application to the aluminum tubes prior to annealing may comprise ordinary soft or hard waters and may contain, or have added thereto, small amounts of a surface-active agent if desired to enhance the wetting properties. It is preferred however, that the water or aqueous solution employed for this purpose be relatively pure and free from sediment or solid matter which would lower the efficiency of the process. Distilled water may be used to advantage where the cost is not prohibitive. Instead of immersing the aluminum tube in water, wetting of the tube may be effected by other methods such as by employing a water spray, or by suitably condensing water vapor on the surfaces of the tube prior to introducing the same into an annealing oven.

The temperature to which the collapsible aluminum tube is subjected during the process generally lies within a range of about 250° and 1250° F., the preferred temperature of treatment being between about 900 and 1200° F. The duration of the heating will vary depending upon the temperature, but preferably is on the order of about three to thirty minutes at temperatures above 900° F. Lower temperatures, for example between about 250° and 750° F. may be employed with a correspondingly longer duration of heating. It is important, however, that the temperature and duration of heating be sufficient to cause the film of water on the tube to boil or flash off rather than merely evaporate to produce a tube having improved corrosion resistance. By carrying out the process in accordance with the invention, a soft, annealed aluminum container is provided which has excellent resistance to corrosive attack. The invention also makes possible the production of collapsible aluminum tube con-

tainers which are particularly useful for packaging tooth paste and similar products such as cosmetic creams, pastes, etc., which under the conditions of storage and use tend to corrode aluminum metal surfaces.

Although a preferred method for treating collapsible aluminum tubes has been particularly described, it is to 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 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 wetting the surfaces, all of which are free from an artificially deposited coating of aluminum oxide, of a collapsible tube of aluminum of a purity of at least 99.5% with water, thereafter subjecting the tube while thus wet with water to an annealing temperature between about 250° F. and 1200° F. for a period of time sufficient to provide a tube which is readily flexed and which has increased resistance to corrosion, 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 the steps of wetting the surfaces, all of which are free from an artificially deposited coating of aluminum oxide, of a collapsible tube of aluminum of a purity of at least 99.5% with water, thereafter subjecting the wet tube to an annealing temperature above the boiling point of water for a period of time of approximately 3 to 30 minutes whereby a flexible tube is attained and the corrosion resistance of the tube is increased, and then filling said collapsible aluminum tube with said corrosive pasty material.

WILLIAM THOMAS EGAN.
RUSSELL PARK McGHIE.
FREDERICK WILLIAM SCHNEIDER.
WARREN WILLIAM SWEET.

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