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CONTAINER FOR TOOTHPASTE CONTAINING STANNOUS FLUORIDE AND PROCESS FOR REDUCING CORROSION THEREOF

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The present invention relates to a new and unexpected process for reducing the corrosiveness of inorganic fluorides to aluminum and to an improved toothpaste container capable of substantial resistance to the corrosiveness of stannous fluoride containing toothpastes.

It is a well known and highly troublesome fact that inorganic fluorides are corrosive to aluminum and aluminum base alloys, especially aqueous solutions of inorganic fluorides. This corrosiveness has caused numerous problems in the past and has resulted in particular difficulties recently due to the increased popularity of stannous fluoride containing toothpastes.

Impact extruded aluminum tubes are used in substantial volume for containing toothpastes. These tubes are not as pliable and subject to repeated deformation as the tin-lead alloy toothpaste tubes but their lower cost and ease of fabrication provides considerable impetus for their use. The new stannous fluoride containing toothpastes are highly corrosive to aluminum and result in pitting and sometimes perforation of the impact extruded tubes during storage. In addition, stannous fluoride containing toothpastes cause the formation of a dark corrosion product on the interior of the toothpaste container. This corrosion product often colors the toothpaste and makes it unacceptable to consumers.

Accordingly, it is an object of the present invention to provide an improved process for reducing the corrosiveness of inorganic fluorides to aluminum and aluminum base alloys.

It is a further object of the present invention to provide an improved aluminum toothpaste tube which is capable of substantial resistance to the corrosiveness of stannous fluoride containing toothpastes.

It is an object of the present invention to provide an improved aluminum toothpaste tube as aforementioned which does not result in pitting, perforation, or the formation of a dark corrosion product when in contact with stannous fluoride containing toothpastes.

Other objects and advantages of the present invention will appear hereinafter.

In accordance with the present invention it has been found that the foregoing objects and advantages of the present invention may be readily accomplished and a process obtained for reducing the corrosiveness of inorganic fluorides to aluminum which comprises contacting the fluoride with an aluminum base alloy containing at least 90 percent aluminum, and preferably at least 95 percent aluminum, and between 0.01 and 0.5 percent tin, with the tin preferably retained in solid solution to the maximum degree.

The improved toothpaste container of the present invention comprises an aluminum base alloy containing at least 90 percent aluminum and between 0.01 and 0.5 percent tin, with the tin preferably retained in solid solution to the maximum degree. In accordance with the present invention it has been further found that when a stannous fluoride containing toothpaste is kept in contact with the improved toothpaste container of the present invention surprisingly there is substantial reduction in, if not complete elimination of, pitting, perforation, and formation of dark corrosion products.

The present invention obtains marked and surprising improvement in the corrosion resistance with respect to any inorganic fluoride, for example, alkali metal or alkaline earth metal fluorides, such as sodium, potassium, cesium, calcium, barium, etc., and also magnesium, manganese, iron, tin, etc. The improvements obtained in accordance with the present invention are especially pronounced with aqueous solutions of inorganic fluorides, since the aqueous solutions are more highly corrosive.

Similarly, with regard to toothpastes containing stannous fluoride, the present invention encompasses the use of any toothpaste containing stannous fluoride. The present invention obtains marked improvement as aforesaid irrespective of the toothpaste used, as long as the toothpaste contains stannous fluoride. These toothpastes are widely available commercially under various trade names.

The improved toothpaste tube of the present invention comprises an aluminum base alloy containing at least 90 percent aluminum, and preferably at least 95 percent aluminum, and between 0.01 and 0.5 percent tin, with the tin preferably retained in solid solution to the maximum degree, i.e., about 0.1 percent.

The preferred manner of preparing the alloy is to heat the aluminum-tin sample at elevated temperatures, e.g., 620° C.±20° C. for a sufficient period of time to dissolve the maximum amount of tin. Generally, the heating period within the preferred temperature range may vary between 15 minutes and 24 hours. After the heating period the sample is cooled rapidly, e.g., by immersion in a large volume of water at ambient temperatures. For simplicity, this treatment may be termed "homogenization treatment." Further details of this homogenization treatment are fully disclosed in the copending United States Patent Applications Serial No. 60,166, filed October 3, 1960, and Serial No. 171,114, filed February 5, 1962. It is noted that "homogenization treatment" does not have to be applied at the final stage of processing, since it can be accomplished at previous convenient stages in the fabrication and can be succeeded by conventional thermal and mechanical treatments without invalidating its beneficial effects.

In accordance with the present invention it has been found that the preferred amounts of tin in the alloy are from 0.08 to 0.35 percent. Either high purity aluminum or aluminum of a lower purity may be readily used in the present invention. When lower purity aluminum is used it should contain a maximum of 0.1 percent silicon and a maximum of 1.0 percent iron, i.e., from 0.001 to 0.1 percent silicon and from 0.001 to 1.0 percent iron.

It should be further understood that the alloy of the present invention may contain in addition to the aluminum and tin and the impurities, other metal components. The critical aspect of the present invention is the use of an aluminum alloy containing at least 90 percent aluminum and tin in the aforementioned range, preferably retained in solid solution to the maximum degree. The use of other alloying ingredients to achieve particular results does not interfere with the surprising corrosion resistance of this alloy to inorganic fluorides. Exemplificative alloy ingredients and representative amounts thereof include: magnesium from about 0.001 to 7.0 percent; zirconium from about 0.001 to 0.3 percent; bismuth from about 0.001 to 0.3 percent; indium from about 0.001 to 0.5 percent; zinc from 0.001 to 0.01 percent; copper from 0.001 to 0.002 percent; silicon from 0.001 to 0.05 percent and manganese from 0.001 to 0.05 percent.

The present invention contemplates the use of the alloys of the present invention as a toothpaste container or tube with the stannous fluoride containing toothpaste in contacting relationship therewith and contained therein. The particular shape of the toothpaste container or tube is

not critical and in addition, naturally, the alloy of the present invention may contain the usual descriptive or writing material on the exterior portion thereof, which descriptive material is useful in commercial distribution.

A particular advantage of the present invention is the inexpensive character of the alloy and the fact that it readily accepts descriptive material and color on the exterior portion thereof. In addition, the toothpaste containers of the present invention are non-toxic and have the other characteristics desirable in aluminum toothpaste containers.

The improvements of the present invention will be more readily apparent from a consideration of the following illustrative examples.

Example 1

This example describes a representative preparation of an aluminum alloy containing 0.2 percent tin in a form suitable for use in a toothpaste tube, with the tin retained in solid solution to the maximum degree.

High purity tin, 45.36 grams, was added to 22,640 grams of molten 99.995 percent pure aluminum at a temperature of 1300° F. The melt was thoroughly mixed by mechanical stirring and degassed with dry chlorine. The degassed melt was cast to a cross section thickness of 3 x 6½", by the Direct Chill method into a water-cooled copper mold. After cooling, the ingot was preheated at 1148°±5° F. for 16 hours, removed and cooled in still air to room temperature. The ingot was then scalped to a thickness of 2⅝", ultrasonically inspected and found to be free of defects. The scalped ingot was hot rolled to a thickness of 0.062" and air cooled. The 0.062" thick strip was cold rolled to a final thickness of 0.023", homogenized at 1148°±5° F. for four hours and quenched in still water. After quenching, the strip was cleaned and roller levelled. When subsequently analyzed, the alloy contained 0.20 percent tin, 0.0021 percent iron and less than 0.001 each of silicon and copper.

Example 2

The alloy prepared in Example 1 was coupled to a mild steel cathode in sodium chloride solution. This procedure contemplates high galvanic currents on the order of ½ to 1 milliamp per sq. centimeter of steel cathode. Small additions of sodium fluoride were then made to the electrolyte. It was totally unexpected that the fluoride additions instead of increasing the galvanic current in the cell reduced them substantially to less than 0.1 milliamp per sq. centimeter so that the aluminum base alloy appeared to become almost passive. This shows that the normally accelerating action of aqueous inorganic fluorides on the corrosion rate of pure and alloyed aluminum is not observed with the alloy of the present invention. In fact, a distinct and surprising inhibiting or passivating action is observed.

Example 3

Aluminum foil, 1145 alloy, of the type used in aluminum toothpaste tubes was stored in contact with samples of two commercial toothpastes, represented by the symbols Toothpaste A and Toothpaste B, both containing stannous fluoride, and a third commercial toothpaste, Toothpaste C, containing an organic fluoride. The samples were stored over water, so that the toothpaste would not dry out, for a period of three months. It was found after the storage period that the aluminum was blackened and perforated when in contact with the toothpaste containing stannous fluoride, i.e., Toothpaste A and Toothpaste B. Little or no attack occured from Toothpaste C, i.e, the toothpaste containing the organic fluoride.

Example 4

Example 3 was repeated using 1100 aluminum alloy samples. The results were substantially the same as Example 3 with the 1100 alloy substantially blackened by contact with Toothpaste A and Toothpaste B, but not significantly attacked by Toothpaste C. There was some pitting of the 1100 alloy as evidenced with contact with Toothpaste A and Toothpaste B.

Example 5

Examples 3 and 4 were repeated utilizing the alloy of Example 1. The alloy was substantially unattacked and completely unpitted by contact with all three toothpastes, even those containing stannous fluoride.

This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

What is claimed is:

1. A process for reducing the corrosiveness of an inorganic fluoride to aluminum which comprises contacting the fluoride with an aluminum base alloy containing at least 90 percent aluminum and between 0.01 and 0.5 percent tin.

2. A process according to claim 1 wherein the tin is retained in solid solution to the maximum degree.

3. A process according to claim 2 wherein the tin is present in an amount between 0.08 and 0.35 percent.

4. A process for reducing the corrosiveness of stannous fluoride containing toothpaste to aluminum containers which comprises contacting the stannous fluoride containing toothpaste with an aluminum container comprising an aluminum base alloy containing at least 90 percent aluminum and between 0.01 and 0.5 percent tin.

5. A process according to claim 4 wherein the tin is retained in solid solution to the maximum degree.

6. A process according to claim 5 wherein the tin is present in an amount between 0.08 and 0.35 percent.

7. A process for reducing the corrosiveness of stannous fluoride containing toothpaste to aluminum tubes which comprises contacting the stannous fluoride containing toothpaste with an aluminum tube comprising an aluminum base alloy containing at least 90 percent aluminum, between 0.08 and 0.35 percent tin, with the tin retained in solid solution to the maximum degree, and a maximum of 0.1 percent silicon and 1.0 percent iron.

8. An improved aluminum containing toothpaste container capable of substantial resistance to the corrosiveness of stannous fluoride containing toothpaste which comprises an aluminum base alloy containing at least 90 percent aluminum and from 0.01 to 0.5 percent tin.

9. An improved toothpaste tube according to claim 8 wherein the tin is retained in solid solution to the maximum degree.

10. An improved toothpaste tube according to claim 9 wherein the tin is present in an amount between 0.08 and 0.35 percent.

11. An improved aluminum containing toothpaste tube capable of substantial resistance to the corrosiveness of stannous fluoride containing toothpaste which comprises an aluminum base alloy containing at least 90 percent aluminum, between 0.08 and 0.35 percent tin, with the tin retained in solid solution to the maximum degree, and a maximum of 0.1 percent silicon and 1.0 percent iron.

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