July 28, 1942. R. H. WHITE 2,290,928

COLLAPSIBLE TUBE AND PROTECTIVE LINING THEREFOR

Filed March 28, 1941

Fig. 1.

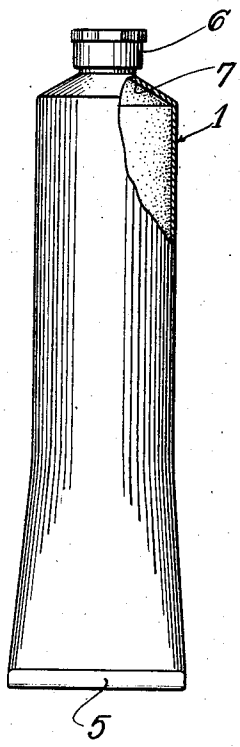
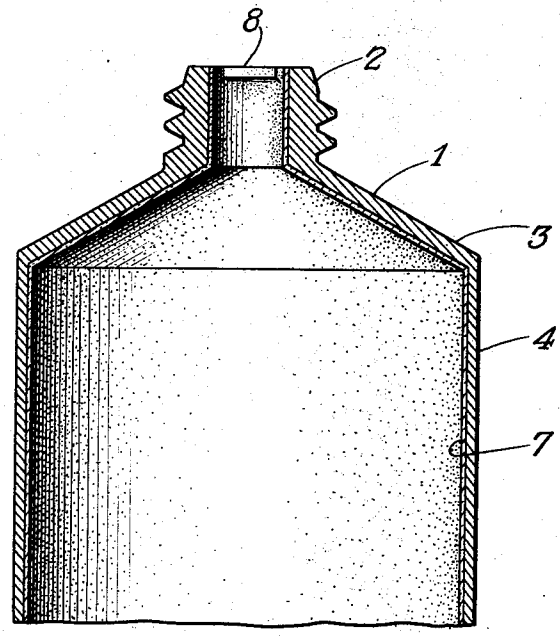


Fig. 2.



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COLLAPSIBLE TUBE AND PROTECTIVE LINING THEREFOR

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17 Claims. (Cl. 221—60)

This application is a continuation in part of pending application Serial No. 200,342, filed April 6, 1938.

My invention relates to collapsible tubes, that is, thin walled tubes of pliable material, such as tin, lead, aluminum, or alloys of metals, of the type used as containers for tooth pastes, shaving soaps, cold creams and other cosmetics, and to a lining for such tubes which will adequately protect the wall of the tube against corrosion over a long period of time.

Collapsible tubes of the above type are used for contents that vary widely in their chemical composition and which may be made of mixtures of materials each of which reacts differently on the metal or which, in combination, act differently than they act separately. Some of these substances are alkaline in reaction, some are acid and others contain various salts or solvents which deleteriously react with the material of the tube, occasionally eating the thin walls of the tube in one or more spots or areas and, in other cases, forming compounds therewith which either discolor the contents or the walls of the tube, or both, or are toxic or semi-toxic and absorbed by the tube contents.

It has been proposed heretofore to protect collapsible tubes with lacquer, varnish and the like coating for protection against, or resistance to, alkali, acids, salts and solvents. However, such coatings generally afford little or no resistance to the attacking compounds, such as shaving creams, dentifrices, certain cosmetics, food products, etc., which may contain one or several different and differently acting ingredients. For example, solutions of caustic soda or of potash, of stearic acid, of certain essential oils, or of salts, or of glycerine alone, may not readily attack such materials, yet shaving creams, dentifrices and similar materials which contain caustic soaps, fatty acids, essential oils, salts and glycerine, or various combinations of the above and other materials, will soften, blister and remove such films, leaving the metallic walls open to attack, particularly in view of the fact that the tube and its contents may be carried in stock or on the shelves of a wholesaler or retailer for long periods such as several months or several years.

My present invention overcomes the above difficulties and provides a tube and tube coating which are highly resistant to materials, or combinations of materials, that commonly form the contents of collapsible tubes and which, therefore, are immune, or substantially immune, to attack by a large number of such materials over long periods of time.

In my invention I provide an inner surface for a collapsible tube of thermoplastic polymerized rubber hydrocarbons, either of natural or artificial origin or modified by chemical treatment, which are hard and resinous. These materials may be coated as a thin film or coating on the inner surface of a metal walled tube. Among thermoplastic rubber hydrocarbons preferred as a lining for tubes in my invention are purified gutta-percha, balata, chlorinated rubber, either of natural or artificial origin, cyclized rubbers, such as caoutchouc treated with stannic chloride, halogenated acid of tin such as chloro-stannous acid and similar compounds or similar substances formed by treatment of rubber hydrocarbons with boron fluoride or fluo-boric acid or with rubber hydrocarbons treated with sulphonic acids to form resinous thermoplastic materials such as that known as "Vulcalock." An example of a cyclized rubber formed by treatment of caoutchouc with stannic chloride, halogenated acid of tin is that known heretofore as "Pliofform" or "Pliolite." A common characteristic of these various materials, even though they may have specific differences, is that they are hard, amorphous or resinous when cold and are thermoplastic, that is, they soften above certain temperatures and also have high resistance to a wide variety of alkaline and other materials.

Hydrocarbons of the above class and their derivatives may be applied to the inner surface of collapsible tubes by dissolving them, or a mixture of them, in a suitable solvent, spraying or otherwise coating the interior surface of the tube with the resulting solution and permitting the coating to dry by the evaporation of the solvent. In some cases a combination of two or more films may be employed as, for example, one such as the sulphonated rubber materials which are highly adherent to metals may be applied first to the tube surface and then covered with a second film more resistant to the materials with which the tube is to be filled.

Certain fillers may also be added to the solution of hydrocarbons, preferably finely divided or colloidal tin, tin oxides, or mixture of tin and tin oxides or bismuth or antimony. Tin or tin oxides have the advantage, when used with certain materials, or tubes having certain contents, of forming relatively insoluble oxidized tin compounds in contact with acid, alkali or sulphur compounds and soaps, and the more common corrosive agents to be found in tube contents.

They, therefore, add to the resistance of the coatings and slow or lengthen the attack of the contents on the protective surface or lining. Where hard, relatively brittle hydrocarbons are used as the body of the coating composition, small amounts of plasticizer such as castor oil or soya bean oil may be added but this is generally unnecessary even with materials which are apparently quite hard and brittle when cold.

The various features of the invention are illustrated in the accompanying drawing as applied to a common collapsible tube, in which Fig. 1 shows a side view of the tube, part of the thin wall being broken away to show the position of the protective film or coating on the inside of the tube, and Fig. 2 is a longitudinal section on an enlarged scale of the upper part of the tube.

In the accompanying drawing, the tube 1 is of the usual type having a relatively thick neck 2 and a relatively thin shoulder 3 and wall 4. The bottom of the tube is closed as at 5 and the neck or top is closed by means of a cap 6 threaded onto the neck 2. The inner surface of the tube is covered by a protective coating 7 of thermoplastic rubber hydrocarbons, such as those mentioned above, of one or more layers extending from the mouth or opening 8 in the neck 2 to the bottom edge of the tube. The coating thus protects every part of the inner surface of the tube that comes into contact with the contents thereof.

In applying the lining or coating to the tube, the rubber derivatives or rubber hydrocarbons are dissolved in a suitable solvent to form a solution of a body to correspond with the thickness of the lining to be formed. The following are examples of such solutions to be applied by spraying or otherwise to the inner surface of the tube.

Example I

1 ounce of gutta-percha is dissolved in 16 liquid ounces of carbon tetrachloride and then strained to remove impurities and coarse particles. A film formed by spraying this material onto the inner surface of a tube and dried, withstands the attack of 10% shaving soap solution for 550 to 600 hours. A film of .002 inch in thickness was unattacked by a 10% shaving soap solution after six weeks (1008 hours). The adhesion of this film to the wall of the tube may be improved by the addition of small amounts of a modified rubber cement such as "Bakelite BC 6052" or by first coating the tube with such cement.

Example II

A solution of 1¼ ounces of balata is made in 16 ounces of carbon tetrachloride and then filtered to remove impurities. Preferably, a purified balata is employed. This material sprayed onto the inner surface of a tube and dried, provided a protective lining that resists a 10% shaving soap solution from 650 to 700 hours. A film of .002 inch in thickness was unattacked by a 10% shaving soap solution after six weeks (1008 hours). Adhesion to the wall of the tube is also improved by the use of "Bakelite cement BC 6052."

Example III

Plioform such as Plioform 20 or Plioform 40 is dissolved in a suitable solvent, such as benzene or other hydrocarbon solvent, in about the ratio of 2¾ ounces of "Plioform" to 16 fluid ounces of benzene with about ½ ounce of castor oil as a plasticizer, and then sprayed and dried as above. A film formed of this material has a resistance to soap solution equivalent to that of balata.

Example IV

A halogenated rubber, that is one having one or more atoms of halogen, such as chlorine added or substituted in the rubber molecule, may also be used to form lining coatings. For example, a balata-like chlorinated rubber known by the trade name of "Parlon" is dissolved in 10° xylol, or commercial coal tar naphtha in the proportion of ¾ pound of "Parlon" per gallon of solvent and then sprayed to form a coating on the inner surface of the tube. Such a coating of .002 inch thickness had a resistance of over 1000 hours when tested with a 10% shaving soap solution.

It will be understood that any suitable solvent, such as the ketones or ethylene glycol may be substituted for the xylol in making a solution and that any suitable coal tar solvent may be used.

It will also be understood that thermoplastic products resulting from the treatment of rubber with other halogens than chlorine as, for example, fluorine, bromine or iodine may be used although the chlorinated rubbers are more available.

In each of the compositions tin or tin oxides can be added as fillers in small amounts as, for example, 2 to 2½ pounds per gallon of solution.

Small amounts of plasticizers compatible with the thermoplastic rubber material and preferably having slight or negligible absorption of water may be added. For example small amounts of drying, semi-drying or non-drying oils or mixtures of one or more of such oils may be added to coating solutions of cyclized rubber, "Pliolite" or "Plioform," sulphonated rubber, such as cyclized sulphonated rubber as "Vulcalock," chlorinated rubber or the natural hydrocarbon rubbers as balata and gutta percha. The upper limit for the addition of such plasticizers will be determined by the qualities of the lining and the nature of the plasticizers. For example China wood oil or oiticica oil may be used up to about 8 to 10% of the thermoplastic rubber. Beyond these limits it tends to separate. Castor oil or soya bean oil may be used up to about 4 to 5% of the content of thermoplastic rubber hydrocarbons. Above this limit the coating becomes too soft for most purposes.

Examples of non-drying oils, tri-cresyl phosphate or di-butyl phthalate or perilla oil may be used up to about 2 to 3% without impairing the quality of the coating or rendering it too soft for use. In the case of chlorinated thermoplastic rubber hydrocarbons an alkyd resin, such as glyptol resin No. 2466 or a phenolic resin, for example "Bakelite XR 5403," may be used up to 10% of the chlorinated rubber in some cases, or for some purposes. However, the use of plasticizers is not generally necessary and the amount that may be added would generally be very much below the above limits.

It will be understood that the test with 10% shaving soap solutions is an accelerated test and merely gives an indication of the protection afforded by the protective coatings. These coatings have been found to effectively protect the inner surfaces of collapsible tubes filled with contents ordinarily destructive to such tubes over long periods of time sufficient for all commercial purposes.

Through the above invention the inner surface of tubes may be coated with a thin lining which

protects the surface of the tube from contact with alkaline or other corrosive materials while at the same time the lining coating, which may be extremely thin, adheres closely to the tube wall and may bend with it without danger of separating or cracking. The coating also has the advantage that it is not sticky but has a hard smooth surface and may thus be used on the usual filling machines and may be kept free from dust and may be sterilized.

By thus protecting the wall of the tube from contact with the tube contents a greater freedom of choice in the selection of materials for the tube is made possible. Provided the inner surface of the tube, of whatever material it may be, has a surface of appreciable thickness, for example .002 inch of the above thermoplastic rubber hydrocarbons, whether of the natural occurring material such as balata or gutta-percha or of rubber that has been cyclized by a suitable treatment of caoutchouc, either of natural or artificial origin, or chlorinated and thus made thermoplastic and of a hardness equal to that of balata, such tubes are sufficiently resistant to resist attack by alkalies or by an alkaline material packed in such tubes over a period of time much beyond the normal life of such tubes. Owing to the adhesion and flexibility of the coating it forms a substantially integral structure with the tube wall.

What I claim is:

1. A collapsible tube having an inner coating resistant to corrosive and fatty materials, and comprising a flexible, polymerized, rubber hydrocarbon treated with a reagent of the class consisting of stannic chloride, a halogenated acid of tin, boron fluoride, fluo-boric acid and sulphonic acids.

2. A collapsible tube having an inner coating resistant to corrosive and fatty materials, and comprising a flexible, polymerized, rubber hydrocarbon treated with a reagent of the class consisting of stannic chloride, a halogenated acid of tin, boron fluoride, fluo-boric acid and sulphonic acids and finely divided tin.

3. A collapsible tube having an inner coating resistant to corrosive and fatty materials, which comprises a flexible, thermoplastic rubber hydrocarbon.

4. A collapsible tube having an inner coating resistant to corrosive and fatty materials, and comprising a member of the class consisting of "Plioform," balata and gutta-percha.

5. A collapsible tube having an inner coating resistant to corrosive and fatty materials, and comprising a member of the class consisting of "Plioform," balata and gutta-percha, and a plasticizer.

6. A collapsible tube having an inner coating resistant to corrosive and fatty materials, and comprising "Pliolite."

7. A collapsible tube having an inner coating resistant to corrosive and fatty materials, and comprising balata.

8. A collapsible tube having an inner coating resistant to corrosive and fatty materials, and comprising gutta-percha.

9. A collapsible tube having an inner coating resistant to corrosive and fatty materials, and comprising a member of the class consisting of "Plioform," balata, and gutta-percha, a plasticizer and a cementing material.

10. A collapsible tube having thin flexible walls comprising a flexible thermoplastic rubber hydrocarbon facing the interior of said tube.

11. A collapsible tube having a flexible inner wall surface resistant to corrosive and fatty materials and comprising a member of the class consisting of balata, gutta-percha and a thermoplastic chlorinated India rubber.

12. A collapsible tube having flexible walls the inner surface of which comprises a member of the class consisting of "Plioform," balata and gutta-percha.

13. A collapsible tube having a flexible inner wall surface resistant to corrosive and fatty materials and comprising a thermoplastic chlorinated India rubber.

14. A collapsible tube having a flexible inner wall surface resistant to corrosive and fatty materials and comprising a thermoplastic halogenated India rubber.

15. A collapsible tube having a flexible inner wall surface resistant to corrosive and fatty materials and comprising gutta-hydrocarbons.

16. A collapsible tube having an inner coating resistant to corrosive and fatty materials, which comprises a flexible, thermoplastic rubber hydrocarbon and a small quantity of a plasticizer.

17. A collapsible tube having an inner coating resistant to corrosive and fatty materials, which comprises a flexible, thermoplastic rubber hydrocarbon and a small quantity of a plasticizer containing a small quantity of oil compatible with said thermoplastic rubber.

RAYMOND H. WHITE.