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F. CLEMENT ET AL
COATED COLLAPSIBLE TUBES
Filed Oct. 11, 1965

3,441,057

Fig. 1

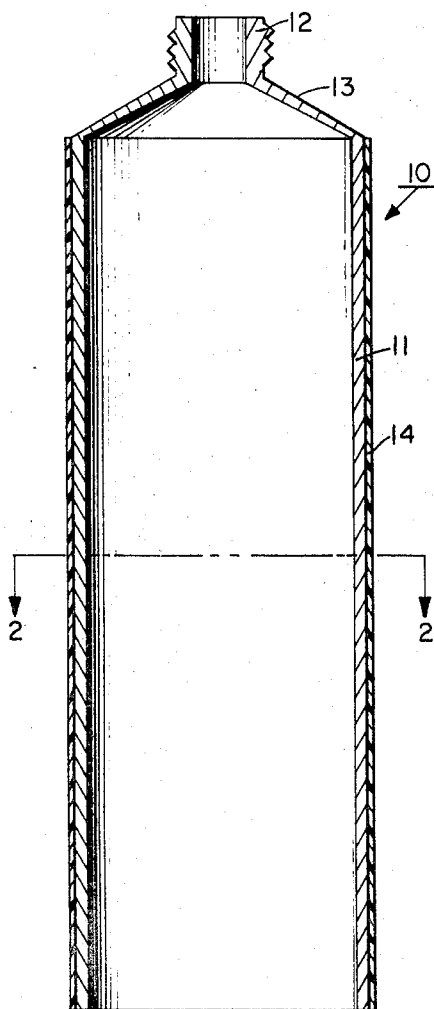


Fig. 2

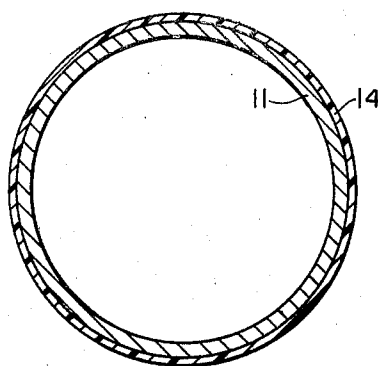
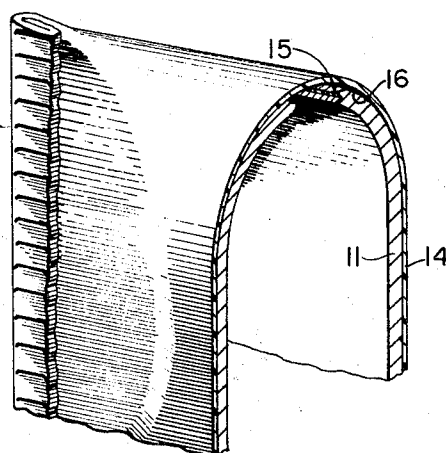


Fig. 3



INVENTORS

Finn Clement
Paul E. Cope

BY *Arthur J. Morgan*
AND *John V. Gorman* ATTORNEYS

1

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COATED COLLAPSIBLE TUBES

Finn Clement and Paul E. Cope, Cincinnati, Ohio, assignors to The Procter & Gamble Company, Cincinnati, Ohio, a corporation of Ohio

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5 Claims

ABSTRACT OF THE DISCLOSURE

An imperforate, elastomeric coating applied to the exterior of a metallic collapsible tube to prevent leakage of the product therein contained in the event of cracking of the metallic tube wall. The preferred coating is based on a solvent-soluble polyesterurethane resin.

This invention relates to collapsible containers. More particularly, the invention relates to collapsible metallic tubes having elastomeric coatings uniformly applied to the exterior thereof to increase the resistance of the tube to flexurally induced cracking and to prevent product leakage in the event that such cracking occurs.

Collapsible metallic tubes have found widespread use as packages for paste, jelly, or cream-type semi-solid products by reason of the fact that these products may be conveniently dispensed by squeezing the tube, thereby extruding the product through a closable orifice at one end thereof. Various metals, among which are lead, tin, aluminum, and alloys thereof, have been used to form the bodies of such tubes.

In the course of using packages of this type it is frequently found that the repeated flexing, folding, squeezing, or rolling-up of the tube material to force the contents to dispensing position results in the formation of cracks and breaks in the tube wall. These cracks and breaks can be caused by fatigue failure of the metal, which type of failure is usually induced by repeated applications of stress with the result that subsequent squeezing of the tube may cause the product to be extruded through these breaks. Cracks and breaks can also occur at the edges of folds, particularly where two successive folds are made at right angles to each other. In the latter case the break would not necessarily be caused by fatigue failure of the metal due to repeated folding but would be a reflection of the ductility of the metal. These conditions whereby cracks or breaks are formed are undesirable in that the product may extrude onto the user's hand or be otherwise wasted by not passing through the dispensing orifice. This can occur even though a protective coating is interiorly applied since the sharp metal edges surrounding a break may be able to cut through these coatings. The interior coatings do not provide any protection to the user from the sharp edges frequently found in the areas where such breaks have occurred but generally serve merely to prevent direct contact between the tube and its contents so that chemical reaction between the product and the tube, because of incompatibility of the product and the tube material, can be avoided. The exterior coatings previously used on such tubes have been limited to those of a decorative nature, such as various enamels, lacquers, and inks, which have been employed to impart attractive colors to the surfaces of the tubes and provide identification of the products therein contained.

One approach to the problem of tube splitting has been to increase the tube wall thickness in an attempt to increase resistance to cracking. This approach, however, is unsatisfactory in that the tubes thereby increase in price due to the additional material necessary and may become too expensive for practical use. Also, the

2

increase in wall thickness makes the tube sidewall stiffer, thereby presenting difficulty in dispensing the contents.

Accordingly, it is an object of this invention to provide a coated collapsible tube having improved resistance to leakage due to flexurally induced cracking in the metal sidewall thereof.

Another object of the invention is to provide a coated tube which is capable of being readily decorated by printing or other decoration techniques without the necessity of added surface treatments.

A further object of the invention is to provide a coated collapsible tube with improved resistance to leakage due to cracking, and which will permit product to be readily dispensed therefrom without excessive pressure or manipulation of the tube.

Another object of the invention is to provide a coated collapsible tube which will not cut the hands of the user when cracked as a result of the application of excessive flexural loads.

Still another object of the invention is to provide a coated collapsible tube wherein the coating is adapted to be easily applied to the exterior of the tube by existing coating application techniques.

Briefly stated, in accordance with one aspect of the present invention, a collapsible metallic tube is provided with an imperforate, elastomeric coating which improves resistance of the tube to leakage due to cracking caused by flexure of the tube body when in use. The coating is uniformly applied to the exterior of the cylindrical portion of the tube and is adherently bonded thereto in such a manner that the tensile strength of the coating is greater than the bond strength between the tube and the coating.

While the specification concludes with claims particularly pointing out and distinctly claiming the subject matter regarded as forming the present invention, it is believed the invention will be better understood from the following description taken in connection with the accompanying drawing in which:

FIGURE 1 is a longitudinal sectional view of a coated collapsible tube embodying the instant invention;

FIGURE 2 is a transverse sectional view of the tube of FIGURE 1 taken along line 2—2; and

FIGURE 3 is an enlarged fragmentary sectional view of a fracture in the wall of a tube provided with the coating of the instant invention.

Referring now to the drawing, and particularly to FIGURES 1 and 2, there is shown an unfilled and uncrimped collapsible tube 10 of substantially cylindrical cross-section and generally symmetrical in nature having an elongated cylindrical wall 11 of finite length, a neck 12 having a substantially cylindrical bore therethrough to permit the product to be packaged within tube 10 to be expelled and dispensed therefrom, and a sloping shoulder 13 interconnecting the neck 12 and the wall 11 and providing a transition from the relatively smaller neck 12 to the relatively larger wall 11. The neck 12 is externally threaded and adapted to receive an internally threaded cap (not shown) although various other closure arrangements and devices can also be used as is well known to those skilled in the art.

The tube 10 can be made from the metals commonly employed for such purposes, as, for example, lead, tin, or aluminum, or alloys thereof, and is made by methods well known in the art. A thin, uniform, substantially imperforate coating 14 of extensible, resilient material covers the external surface of the tube wall 11. The coating 14 can be applied as a solution by dipping, brushing, roller coating or other convenient method. Depending upon the properties of the coating applied it can be air-dried or oven-dried until it has set. Although the entire exterior of the tube except the threads can be coated, it is only

necessary to coat wall 11 to achieve the benefits of this invention as it is this area where manipulation and flexure of the tube takes place and where tube cracking due to such handling can occur. The coating is preferably about 1 mil (0.001 inch) in thickness although coatings as low as about 0.4 mil (0.0004 inch) have been found to provide improved resistance to leakage. Of course, thicker coatings will also improve resistance to leakage. The preferred range of coating thickness for both economy and performance is from about 0.4 mil to about 4 mils, i.e., about 0.0004 inch to about 0.004 inch. The usual range of tube wall thickness is from about 2.5 mils to about 8 mils (i.e., about 0.0025 inch to about 0.008 inch), depending upon the size of the tube under consideration and the material from which it is made.

The effect of the coating is illustrated in FIGURE 3 in which is shown a break or fracture 15 in tube wall 11. When the break 15 occurs and fluid pressure is transmitted therethrough, the coating 14 peels or pulls away from the tube wall 11 in the area of the wall immediately surrounding the break and stretches, when subjected to fluid pressure from the tube interior, to cover the fracture and thereby prevent the product inside the tube from extruding therethrough onto the user's hand. The peeling or pulling away of the coating 14 from the tube wall 11 in the area of the break forms a small pocket 16 of the coating 14 which pocket is in communication with the break 15.

In order to preclude excessive localized thinning and possible fracture of the coating where it stretches to cover breaks, it is necessary that the tensile strength of the coating be greater than the peel strength of the bond between the coating and the tube wall, i.e., it must be easier to peel the coating than to rupture it. This relationship permits the requisite peeling described above in the formation of the pocket 16 which results in the distribution of the tensile load over a greater area as a result of which the unit tensile stress is reduced. Generally the tensile strength of the coating ranges from about 500 p.s.i. to about 9000 p.s.i.

It has been found that it generally is easier to control peel or bond strength than it is tensile strength since there are numerous substances available which will promote adhesion without causing major changes to other properties. On the other hand, a change in coating tensile strength could result in deleterious effects to other important coating properties such as elongation or toughness. Without the regulation of the adhesion of the coating to the tube wall to permit the peeling described above, the coating would have to have an ultimate tensile strength considerably greater than that which is required with the present invention.

The preferred range of peel or bond strength for peeling the coating from the tube is from about 0.5 to about 9 pounds per inch of width at a rate of peeling of 5 inches per minute and in a plane parallel to the tube surface such that the peeled coating undergoes a 180° change in direction. This range of peel strength has been found to provide the adhesion necessary to preclude premature delamination of the coating from the tube at the lower limit and still permit satisfactory peeling of the coating at the upper limit to provide increased resistance to leakage.

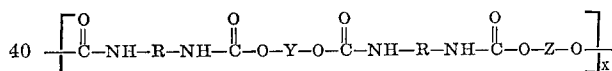
The peel strength can be readily ascertained by testing specimens of coated tube walls to determine their resistance to peeling. In this connection, the neck and shoulder of a coated tube are removed and the tube wall cut lengthwise to form a flat sheet. Next, one inch wide strips are cut lengthwise from the flat sheet. A small section of coating is initially peeled from one end of the one inch wide specimen and the specimen is then placed in a tensile tester with one jaw of the tester attached to the small section of peeled coating and the other jaw attached to the section of the tube wall specimen from which the coating has been peeled. The coating is caused to be

peeled from the remainder of the tube wall in a plane parallel to the specimen being tested and in such a manner that the part of the coating which has been peeled from the tube wall specimen overlies that part of the coating which has not been peeled, thereby subjecting the coating to a 180° change in direction.

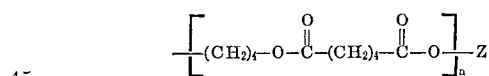
A coating which is adapted to function in the manner hereinabove discussed must, in addition to the tensile strength-peel strength relationship described, possess certain other physical properties in order that the full benefits of the instant invention may be achieved. Since the coating contemplated by the instant invention improves tube wall leakage resistance by stretching to cover breaks which may develop in the wall, the coating used must be sufficiently elastic to sustain both the repeated flexing which the tube wall undergoes and the extension necessary to cover tube wall breaks.

Also of significance is the abrasion resistance of the coating, which must be sufficient to preclude attrition of the coating as a result of the chafing action of the sharp edges of a break in the tube wall. This is necessary to prevent excessive thinning of the coating and consequent rupture thereof under the pressure applied when dispensing the product.

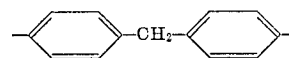
The preferred coating material having all of the requirements noted above utilizes as the basic functional ingredient thereof a solvent-soluble, thermoplastic, polyesterurethane elastomer which is substantially free of crosslinks, such as that described in U.S. Patent 2,871,218, issued Jan. 27, 1959 to Charles S. Schollenberger, the disclosure of which is incorporated herein by reference. This resin is essentially linear and is characterized by having hydrogen bonds between the molecules as opposed to cross-links. Chemically, the preferred resin has a weight average molecular weight of between about 30,000 and about 60,000 and can be characterized by the following structural formula:



where Y is



R is



and Z is an alkylene radical having from 2 to 10 carbon atoms and n and x are such that the molecular weight is in the above range.

The physical characteristics of a preferred specific embodiment of this resin as employed in Example II include tensile strength of about 5800 p.s.i., minimum elongation of about 500%, and a modulus at 300% elongation (tensile strength at 300% strain) of about 1300 p.s.i. In addition, the Taber abrasion test for determining abrasion resistance (ASTM No. D1044-49-T using Taber CS-17 wheels, 5000 cycles, 1000 gram load, at 73° F.) when conducted with this polyesterurethane material results in a loss of about five milligrams of this material. This abrasion property may be compared with that of polyester film, which loses about 29 milligrams, low density polyethylene, which loses about 70 milligrams, and plasticized polyvinyl chloride, which loses about 187 milligrams, all as a result of the same ASTM test. In addition to the poorer abrasion resistance, the latter resins are not effective in providing the improved resistance to leakage of this invention.

Since the preferred elastomer can be dissolved in solvents and is substantially free of cross-links, a coating solution can be prepared therewith which will have virtually indefinite pot life and there will consequently be no need to employ a curing step following the application

of the coating. A solution of the coating can be made with solvents and diluents having a medium to high hydrogen bonding value, among which the following have been found to be satisfactory: cyclohexanone; 1,4-dioxane; acetone; and dimethyl formamide. Preferably the coating solution contains from about 5% to about 90% of solvent based on the weight of the resin. In addition to solvents and diluents, various other substances can be added to the coating solution, if desired, to alter its characteristics or properties. For example, it has been found that the addition of a small amount of epoxy resin, such as Epon 826, a low molecular weight epoxy resin which is a condensation product of epichlorohydrin and bisphenol-A and is obtainable from the Shell Chemical Company, New York, N.Y., or phenoxy resin, such as PKDA-8500, a high molecular weight thermoplastic resin comprising a polyhydroxy ether derived from bisphenol-A and epichlorohydrin, and obtainable from the Union Carbide Corporation, Chemicals and Plastics Division, New York, N.Y., improves the adhesion of the resulting coating to collapsible tubes; suitable amounts are from about .0025% to about 1% by weight of the polyesterurethane resin (solvent-free basis). Suitable pigments, such as titanium dioxide, can be added if desired to impart opacity or color to the coating but are not necessary. Other ingredients such as polycarbodi- amide, synthetic silicas and waxes, and anionic surfactants can be added if desired to obtain resistance to weathering, reduction of blocking, and substrate wetting, respectively, but are not necessary to achieve the benefits of this invention.

EXAMPLE I

Material:	Percent by weight
Polyesterurethane resin -----	18.53
Titanium dioxide -----	18.53
Dimethyl formamide -----	30.25
Acetone -----	30.25
Blue pigment -----	0.01
Epoxy resin (Epon 826) -----	0.345
Dicyandiamide -----	0.345
Melamine formaldehyde resin (Uformite MM-55 available from the Rohm & Haas Company, Philadelphia, Pa.) -----	1.740

The polyesterurethane resin is of the type hereinabove described in detail and is specifically characterized by having a weight average molecular weight of about 40,000 and wherein the alkylene radical Z is $(CH_2)_6$. In preparing the coating solution, the polyesterurethane resin is first thoroughly dissolved in the acetone and dimethyl formamide. The titanium dioxide is added to the solution to impart a white color thereto and is intimately mixed therewith. The remaining ingredients are then added and intimately mixed with the pigmented solution in order to provide a homogeneous coating solution. The blue pigment is added to improve the whiteness appearance of the resulting coating while the epoxy resin serves to improve the adhesion of the coating to the tube wall. The melamine formaldehyde resin imparts surface gloss and marproofness to the resulting coating and the dicyandiamide is employed as a stabilizer against the action of moisture and light. The sequence of addition of the blue pigment, epoxy resin, dicyandiamide and melamine formaldehyde resin to the pigmented solution is immaterial, it being only necessary that they be intimately intermixed therewith. After the coating solution has been prepared as hereinabove described, collapsible lead alloy tubes are cleaned with alcohol to remove extrusion lubricant and are suitably plugged at the bottom to preclude the deposition of coating on the interior of the sidewall. The tubes are then dipped into the coating solution up to the shoulder, removed, and the excess coating solution allowed to drain off for a few seconds. The coated tubes are then air dried for four minutes at room temperature and then oven dried for seven minutes at 310° F. to

evaporate the dimethyl formamide and acetone and leave a tough, white, substantially uniform, substantially imperforate elastic coating on the tubes. Since the solvents are used are hygroscopic in nature and tend to absorb the moisture which results from the combustion of hydrocarbon fuels, and since the presence of water in the coating solution adversely affects the adhesion of the coating to the tube, the drying is preferably accomplished in an electric oven where moisture is not produced.

After applying the above-described coating solution to standard, 5 oz. capacity lead alloy collapsible tubes having a wall thickness of about 7 mils, by the technique indicated, the resultant coating averages about 1.5 mils in thickness and the tubes can be crushed an average of about 45 times before a leak develops. Tubes of the same size without the coating forming a part of the instant invention but having the presently commercially used printing and decorative exterior coating fail after being crushed an average of only about 14 times.

Leakage resistance can be determined by means of a crush test in which the sidewalls of the presently used tubes and the sidewalls of the coated collapsible tubes of the instant invention are each subjected to repeated axial compression and extension. A record is kept to determine the average number of times each type of tube is so manipulated before failure occurs. When a vacuum of about 7 inches of mercury can no longer be retained in the tube, the wall has failed. In performing this test, a tube is held at each end and restrained so that only axial motion is possible. The neck of the tube is connected to a U-tube mercury manometer to indicate the pressure within the tube while the lower, open end of the tube is plugged off to prevent air leakage therethrough. The U-tube is then connected to the neck of the collapsible tube by means of flexible tubing in which a two-way valve is located so that the interior of the collapsible tube can be connected either to the U-tube manometer or, alternatively, vented to the atmosphere. In operation, the two-way valve is initially opened to vent the tube to the atmosphere after which the tube is crushed axially to a given length. The two-way valve is then turned so that the manometer is connected to the collapsed tube. The tube is then partially extended toward its original length, thereby creating a vacuum within the tube and causing the mercury U-tube to be unbalanced. The tube is maintained at the partially extended position for about two seconds and if the mercury columns remain unbalanced during this period then no leakage through the tube wall has occurred. Similarly, if the U-tube does not become unbalanced upon partial extension of the collapsed tube or during the two second time interval, a leak in the tube sidewall is indicated. Next, the tube is again vented to the atmosphere and fully extended to its original length. This cycle is repeated until sidewall leakage is indicated, at which time the test is terminated.

EXAMPLE II

A coating solution having the following composition was prepared in accordance with the method described in Example I:

Material:	Percent by weight
Polyesterurethane resin -----	9.72
Titanium dioxide -----	13.89
Cyclohexanone -----	71.31
Blue pigment -----	0.01
Phenoxy resin (PKDA-8500) -----	4.16
Melamine formaldehyde resin (Uformite MM-55) -----	0.91

The polyesterurethane resin used in this coating solution had a weight average molecular weight of about 38,000 (number average molecular weight of about 36,000) and can be represented by the structural formula presented above wherein Z is $(CH_2)_4$. The coating solution was applied to standard 5 oz. capacity lead alloy tubes having a wall thickness of about 7 mils by means of a conven-

tional roller coater apparatus for coating collapsible tubes. The coated tubes were then oven dried at 285° F. for 11 minutes. The resulting coating was about 1 mil in thickness and the tubes were crushed an average of about 50 times before a leak developed. This is to be compared with tubes having the present printing and decoration but not the coating of this invention, which tubes failed after being crushed an average of about only 14 times. The leakage resistance of both types of tubes was determined by using the crush test hereinbefore described.

EXAMPLE III

A coating solution having the following composition can be prepared:

Material:	Percent by weight
Polyesterurethane resin	17.0
Dimethylformamide	41.5
Acetone	41.5

The polyesterurethane resin used in this coating solution has a weight average molecular weight of about 45,000 and can be represented by the structural formula presented above wherein Z is (CH₂)₈. The dimethylformamide and acetone are mixed together and the resin slowly added thereto while the solvent mixture is being stirred. Aluminum alloy tubes of 5 oz. capacity and wall thickness of 4 mils are prepared and coated according to the procedure described in Example I. The coated tubes are then air dried for four minutes at room temperature followed by an oven drying in an electric oven for seven minutes at 300° F. to evaporate the solvents and leave a tough, clear, polyesterurethane coating on the tubes. The resulting coating averages about 1 mil in thickness and the coated tubes can be crushed by the technique described in Example I an average of about 49 times before a leak develops. This is to be compared with tubes of the same size but having the presently used decorative exterior coating which fail after having been crushed an average of only about 14 times.

The thickness of the coating obtained can be readily varied by changing the viscosity of the coating solution as by altering the amount of solvent used. Since some of the coating solutions discussed in the examples incorporate titanium dioxide, the resulting tube coatings are white in color. Further decoration can be readily accomplished by conventional printing techniques such as offset lithography, silk screening, and the like, or by the addition of other pigments.

The preferred polyesterurethane resin is also advantageous from a decoration standpoint in that it results in a coating which is a polar material. A polar material is composed of molecules having a positive charge at one end and a negative charge on the other. Although these molecules have no overall charge, the polarity thereof results in an additional attractive force to bind them to other polar molecules. Since printing inks are also polar, it follows that this coating can be readily printed without further surface treatment or preparation as is frequently the case with other coating systems. As an example, polyethylene is non-polar and is therefore difficult to print without employing well-known surface preparation techniques such as treatment of the polyethylene articles by exposure to the oxidizing portion of a flame or by exposure to a corona discharge.

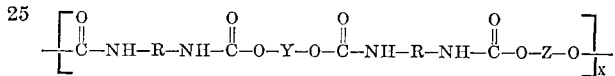
The foregoing coating formulations can be modified or changed to suit particular circumstances. Different resins

having the mechanical properties described can be used in conjunction with different solvents to provide a coating of the character described. It is also possible to apply a suitable coating without making a solution system, as, for example, by extruding a coating onto the surface of the metal and then forming the same into a tube.

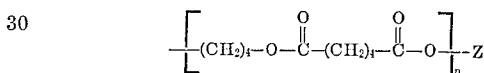
What is claimed is:

1. A collapsible metallic tube having a uniform, exterior, substantially imperforate elastomeric protective coating comprising a polyesterurethane compound as the basic functional ingredient thereof, said polyesterurethane compound having a weight average molecular weight of from about 30,000 to about 60,000 and being solvent-soluble and free of cross-links, said coating being adherently bonded to said tube and having a tensile strength greater than the bond strength between said coating and said tube whereby to permit said coating to peel from small areas of said tube surrounding any cracks formed therein and thereby distribute the localized tensile stress induced in the coating over a sufficient area to prevent rupture of said coating and leakage therethrough.

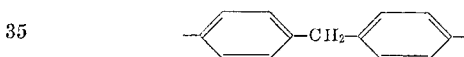
2. The collapsible metallic tube of claim 1 wherein said polyesterurethane compound has the following structural formula:



wherein Y is



R is



Z is an alkylene radical having from 2 to 10 carbon atoms, and x and n are such that the weight average molecular weight ranges from about 30,000 to about 60,000.

3. The collapsible metallic tube of claim 2 in which the bond strength of said coating lies in a range of from about 0.5 to about 9 pounds per inch of width at a peeling rate of 5 inches per minute.

4. The collapsible metallic tube of claim 3 in which said coating has a thickness in the range of from about 0.0004 to about 0.004 inch.

5. The collapsible metallic tube of claim 4 in which said coating is polar by nature so that it is decorable with a polar printing ink without additional surface treatment.

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ALFRED L. LEAVITT, *Primary Examiner*.

J. R. BATTEN, JR., *Assistant Examiner*.

U.S. Cl. X.R.

117—94, 132; 222—107