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W. C. RAINER ET AL

3,202,307

PLASTIC LINERS

Filed Dec. 31, 1954

FIG.1.

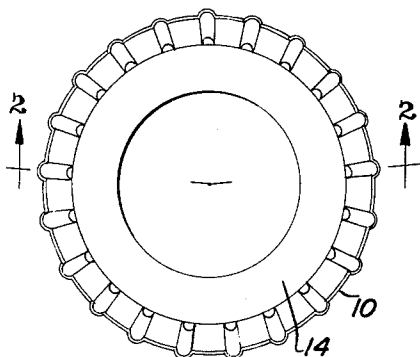


FIG.2.

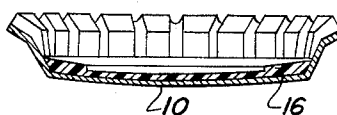


FIG.3.

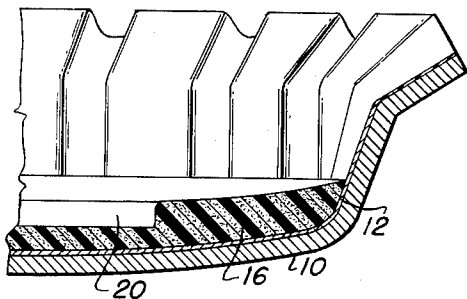


FIG.4.

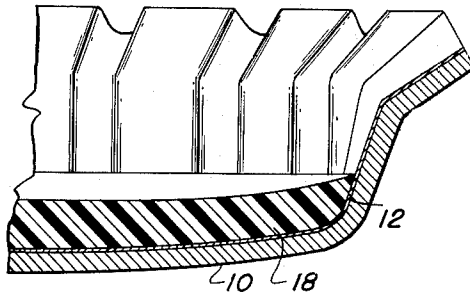
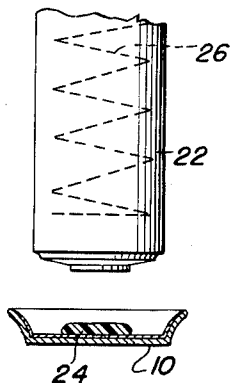


FIG.5.



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PLASTIC LINERS

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6 Claims. (Cl. 215—39)

This invention relates to closures, particularly to closures of the crown type.

The cushion sealing liner for crown type closures is conventionally made of cork. While cork has many desirable properties, which render it an excellent cushion liner, it has the disadvantage that a large part of the cork supply must be imported.

Accordingly, a primary object of the present invention is to provide a substitute for cork as a cushion liner for crown type closures.

Another object of the invention is to prepare a cap having an improved plastic cushion liner.

A further object is to prepare a synthetic cushion liner having all the desirable properties of cork for this purpose.

A still further object is to reduce bottle leakage by providing a cap having a cushion liner which is somewhat flowable under capping pressure.

Another object of the invention is to provide a cap having a cushion liner which will adhere to the metal surface of the cap or to the conventional lacquer coating on the interior of the cap shell or which will adhere to an adhesive applied on the metal or lacquer coating.

An equally important object is to provide a cap having a liner which will be inert with respect to a variety of foods, beverages and medicinals, and which will not impart taste, odor or color to the contents of the bottle.

A further object is to provide a cap and cushion liner that can be formed on conventional machinery.

While the present invention is primarily directed to making caps of the crown type and it is in this form that it finds its greatest utility, it also is useful in preparing caps of the screw-on, lug or press-on type.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

In the past, there have been several proposals for replacing the conventional cork liners by materials, such as natural rubber, polyethylene, vinyl chloride plastisols and porous polyethylene. None of these proposals have achieved commercial success to the present time.

It has now been found that, by the use of appropriate conditions, it is possible to prepare substitutes for cork which approach and, in some cases, even excel cork as cushion liners, more especially as cushion liners for crown

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type shells. While several different types of material have been found to be satisfactory as cushion liners, it should be understood that these materials are not necessarily equivalent, as in many cases, they have different properties, varying degrees of effectiveness and are prepared in different ways. These differences will become evident during the subsequent description in the specification.

For the two extreme conditions normally encountered in bottle use with crowns having cork liners, the following ranges of values have been found:

15	Temperature (° F.)	30-170
	Bottle, pressure (p.s.i.)	0-120
20	Load on crown (total force (tension) in the side wall of the steel crown when the bottle is under pressure) (lbs.)	62-102.5
	Load on liner (total force on the gasket liner when the bottle is under pressure) (lbs.)	62-61+
25	Stress in crown (tensile stress in steel of side wall of crown) (p.s.i.)	1800-3000
	Pressure in liner (compressive stress) (pressure in gasket) (p.s.i.)	240-237
30	Compression in liner made of cork (percent)	60-58

From these figures, it is evident that the compressibility of the conventional cork liner, in comparison with the compressibility of the crown, is so high that there is very little change in the compression of the liner with variation of the bottle pressure. The large compression of the cork liner and its relative independence of internal pressure contribute materially to its sealing abilities.

It has been found that it is desirable for a cork substitute to be a soft, compressible material. It has also been found that a closed-cell foamed polymeric material is particularly desirable, as it can be varied in compressibility and hardness to meet varying requirements simply by adjusting the amount of foaming agent. Additionally, it is less dense than unfoamed resin and, hence, is more economical to use than the corresponding unfoamed resin or rubber. Again, not every foamed material can be employed, but only those materials which have the necessary combination of properties, such as those above outlined.

Neoprene (polychloroprene) was tested as a liner in a conventional metal crown. The neoprene liner of slightly smaller diameter than the crown cap was molded into the cap, using a conventional molding die employed with cork crown liners. The neoprene proved to be an excellent liner, even in the absence of an adhesive. Six ounce bottles, containing Coca Cola, Seven Up and Carbonated Water, having a 0.066 inch thick neoprene liner, were cycled daily between 34° F. and 167° F. for seven days. There was no leakage in any of the bottles.

The neoprene liners employed had been prepared by curing, in the absence of sulfur, the following composition:

Neoprene GN (non-staining) -----	100	5
MgO (Heavy) -----	4	
Furnace Black (semi-reinforcing) -----	100	
Dibutyl phthalate -----	15	
Zinc oxide (fast curing) -----	5	10

The proportion of neoprene to the other materials is open to considerable variations. Thus, there can be used 0 to 150 parts of furnace black or other conventional filler; 0 to 0 parts of dibutyl phthalate or other conventional modifier; 4 to 150 parts of MgO or equivalent material and 0 to 100 parts of zinc oxide per 100 parts of neoprene.

The variation in pressure between individual bottles was small, even for highly carbonated beverages.

Plastisols or paste resins, based upon polymers and copolymers of vinyl chloride (which, it should be noted, is an ester) also have been found to be effective as liners. However, not all of these plastisols were equally effective. There are significant variations, depending upon the type of polymer and type and amount of plasticizer and, to some extent, the type of filler.

A plastisol may be described as being a mixture of a resin or other high polymer with a plasticizer in which it is essentially insoluble at room temperature or very slowly soluble at room temperature, but in which it is essentially completely soluble at some elevated temperature or slowly soluble on standing at room temperature. When such a mixture is heated, the resin dissolves in the hot plasticizer and, when the solution cools, a permanent gel is formed.

Of the plastisols based on polyvinyl chloride or its copolymers, the most effective ones were prepared from Exon 654 and Vinylite QYNV. Plastisols of Pliovic AO, Vinylite VYHH, and Marvinol MX 3001, were in some instances, too viscous for the incorporation of fillers. It is desirable for commercial use, that the resin should be capable of dilution with relatively inexpensive fillers. Plastisols of Geon 121 were approximately ten times as viscous (Brookfield viscosimeter) as those of Exon 654 and Vinylite QYNV at the same ratio of resin to plasticizer. Santizer B-16 (butyl phthalyl butyl glycolate) and 141 (an arylalkyl phosphate) gave plastisols of lower viscosity than E-15 ethyl phthalyl ethyl glycolate) and M-17 (methyl phthalyl ethyl glycolate) and, hence, are more desirable than the latter two plasticizers. Santizer B16 plastisols, when cured, produced products with better physical properties than 141.

Acetyl tributyl citrate and diisobutyl adipate are both excellent plasticizers. Di-2-ethylhexyl phthalate also was good, but it imparted in some cases an odor to 0.075 inch sheets cured at 150° C. for one minute. Acetyl tributyl citrate imparted no odor, but gave clear strong sheets. Dioctyl phthalate (di-2-ethylhexyl phthalate) also gave clear strong sheets.

The formulation employed for preparing these sheets and for measuring the viscosities previously mentioned is:

Exon 654 -----	100	Parts
Plasticizer -----	125	
Calcium stearate -----	3	70

When measured at 37 to 40° C., the viscosities obtained with various plasticizers in the above formulation are given in Table I below.

TABLE I

Plasticizer:	Viscosity, c.p.s.
Santizer B-16 -----	940
Santizer E-15 -----	3,750
Santizer M-17 -----	250,000
Santizer 141 -----	340
Di-2-ethyl hexyl phthalate (DOP) -----	380
Acetyl tributyl citrate -----	480
Diisobutyl adipate -----	410

Other plasticizers can be employed, provided they do not impart a viscosity substantially above 25,000 c.p.s. (Brookfield, spinner #4, 60 r.p.m.) in the above formulation at 40° C. Examples of such plasticizers are dicapryl phthalate, butyl benzyl phthalate, dioctyl azelate, dioctyl adipate, trioctyl phosphate, alkyl aryl phosphates, e.g., tricresyl phosphate, didecyl phosphalate, di-dodecyl phthalate, didecyl adipate, didecyl azelate, hydrogenated terphenyl, tetra hydro furfuryl esters (e.g., the adipate), low viscosity saturated and unsaturated polyesters (e.g., polyethylene glycol adipate and adipate-maleate), and mixtures of ether two or more primary plasticizers or one or more primary plasticizers with one or more secondary plasticizers.

The fillers yielding the lowest viscosity of plastisol and the best properties on curing are talc, Fuller's earth and calcium carbonate. Cork fines can be employed for certain purposes as a filler. Other operative fillers are inorganic materials, such as mica, clay, fibrous magnesium silicate, zeolites, glass fibers, carbon black, powdered charcoal, SiO₂ and diatomaceous earth, and organic materials, such as wood flour, lignin, lignin sulfonates, paper pulp, regenerated cellulose, finely ground straw, finely divided barks, such as Douglas fir bark or any fraction thereof, especially the cork fraction, shell, flours, e.g., walnut shell flour and other vegetable matter.

Good stabilizers are Thermolite 31 (thio organic tin compound), and Stayrite #90 (a mixture of metallic soaps, predominately calcium, aluminum and zinc stearates with a minor amount of other fatty acid salts) and alkyl and aryl thin compounds, dibutyl tin oxide, calcium, magnesium and aluminum and zinc soaps used singly or in combination. Salts of the higher saturated fatty acids, e.g., stearic acid, are preferred. Tin compounds, such as dibutyl tin oxide, are also efficacious. Sodium phosphate, cadmium and barium epoxy compounds, diphenyl urea, and alaphenyl indole are also good. Calcium stearate was satisfactory when employed at concentrations of 3% on the resin. Other conventional stabilizers for the vinyl chloride resins, such as those recited in Schildknecht "Vinyl and Related Polymers" (1952) can also be used.

The proportions of the various materials, preferably should be in the following range:

Vinyl chloride polymer or copolymer -----	100	Parts
Plasticizer -----	60 to 150	
Filler -----	0 to 150	
Stabilizer -----	1 to 10	

When a filler is employed, preferably it is present in an amount of 20 to 100 parts per 100 parts of resin.

Preferably, at least 100 parts of plasticizer are employed per 100 parts of resin.

Unichrome 219 PX (a butadiene-acrylonitrile- rubber

lacquer) was found to be an excellent adhesive for bonding polyvinyl chloride plastisols to either lacquered or unlacquered crown caps. For best results, the Unichrome, as a 1 to 10 solution in acetone, or Goodrich A 458B should be applied to the metal and then baked 10 minutes at 170° F. Other satisfactory adhesives include chlorinated rubber (Parlon), copolymers and terpolymers of vinyl chloride with monomers containing polar groups, e.g., vinyl acetate (this may be partially hydrolyzed later to obtain —OH groups for linking the polymer to metal through isocyanate groups (especially triisocyanates)), acrylonitrile, dialkyl maleates (e.g., diethyl maleate), dialkyl fumarates (e.g., diisopropyl fumarate), and polyurethanes, e.g., (adipic acid reacted with excess ethylene glycol then with p,p' diphenyl methane diisocyanate). Other good adhesives are neoprene, blends of polyvinyl chloride and butadiene-acrylonitrile polymers (latex), cyclized natural rubber, e.g., Vulcalock.

B. F. Godrich adhesive A 458B, Hycar-phenolic lacquer (rubbery butadiene-acrylonitrile and phenolformaldehyde blend) is an excellent adhesive for bonding polyvinyl chloride to lacquered and unlacquered steel plate. It is as good as Unichrome 219 PX for bonding to unlacquered shells and even better as an adhesive for lacquered shells. For satisfactory bonding, the plastisol should be cured at 170° C. In typical tests, the results were as follows. The value of adhesive was based on the force required to pull the strips apart.

Adhesive	Metal	Baking	Results
1. A 458B	Plain	None	Fair.
2. A 458B	Lacquered	do	Good.
3. A 458B	Plain	170°, 10 min.	Very good. ¹
4. A 458B	Lacquered	170°, 10 min.	Do. ¹
5. Unichrome	Plain	170°, 10 min.	Do.
6. Unichrome	Lacquered	170°, 10 min.	Good.
7. Unichrome	Plain	170°, 10 min.	Very good. ¹
followed by A 458B.	Lacquered	170°, 10 min.	Do. ¹
8. A 458B followed by	Plain	170°, 10 min.	Good.
Unichrome.	Lacquered	170°, 10 min.	Do.

¹ The bonded strips of metal could not be separated by "hand-pull."

The conventional lacquers can be employed in forming lacquered caps. One such lacquer is a vinyl lacquer, e.g., 80% of a vinylchloride-vinylacetate copolymer (87% vinylchloride) together with 20% of an oleoresinous modifier, e.g., tung oil modified phenyl phenol-formaldehyde, dissolved in an organic solvent, such as 70% xylene and 30% isophorone with 20% solids. More volatile solvents, such as toluene, methylethyl ketone and methyl isobutyl ketone can also be employed. As an alternative lacquer there can be used 80% of a vinylchloride-vinyl acetate-maleic anhydride terpolymer prepared from monomers in the respective ratios of 87:12:1 together with 20% of an o-cre-sol-formaldehyde resin dissolved in any of the above mentioned solvents or mixture of solvents. Especially effective liners have been made by foaming polyvinylchloride plastisols with blowing agents to give preferably closed-cell products. Sheets of uniform porosity can be obtained with water and bicarbonates, e.g., sodium and ammonium bicarbonates or by using carbon dioxide or other inert gas under pressure, or supersaturated solutions of carbon dioxide or other inert gas in the liquid phase of the plastisol. Other foaming agents which can be used are potassium bicarbonate, ammonium nitrate,

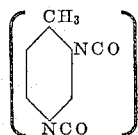
barium nitrite, azo, compounds, e.g., diazoaminobenzene, BL-353 and azobisisobutyronitrile (Porofor N), sodium formate, ammonium benzoate; alpha, alpha'-azobisisobutyronitrile, 1,3-bis(o-xenyl)triazene, 1,3-bis (p-xenyl)-triazene, sodium bicarbonate mixed with a higher fatty acid, e.g., oleic acid, isocyanates, e.g., 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, or phenyl mono isocyanate mixed with water. Other blowing agents are hydrazine, hydrazine hydrate, hydrazine salts, e.g., hydrazine acetate, oxalate, acetate, phosphate, formate, salicylate, malonate, stearate and sulfate, hydrazides of organic sulfonic acids, e.g., p-toluene sulfonic acid hydrazide, propane sulfonic acid hydrazide, urea oxalate, a urea and biuret mixture, nitroso compounds, such as dinitrosopentamethylene tetramine (Unicel D), N-nitroso beta amino ketones, e.g., N-nitroso triacetone amine, N-methyl N-nitroso diacetone amine (the nitroso amines are preferably used with a basic accelerator, e.g., triethanolamine), diphenyl-4,4'-di(sulfonyl azide), azosulfones, arylazotriaryl methanes, bicarbonates, e.g., sodium bicarbonate, mixed with cyanamide and its polymers, such as dicyandiamide and melamine; cyclic ethylene carbonate, organic peroxides, e.g., benzoyl peroxide, dinitroso pentamethylene tetramine, bis benzene bis(sulfonyl hydrazide), Vynafoam 8910 (a mixture of Pliovic AO and a blowing agent).

Toxic and hazardous foaming agents should be avoided for food uses.

The foaming agent is normally used in an amount of 1 to 20%, based on the polyvinyl chloride or other polymer in preparing foamed sheets. When water is used in the foaming composition, non-toxic emulsifiers, such as non-ionic detergents, including sorbitan, sesqui-oleate, sorbitan monostearate (Span 60) (relatively poor), glycerol mannitan laurate (Atlas NNO), (very good), polyoxyethylene sorbitol oleate-laurate (Atlas 1045A) (very good), sorbitan laurate, the Tweens, i.e., ethylene oxide condensation products or sorbitan and mannitan esters of higher fatty acids may be used. In general, non-ionic detergents with a high hydrophiliclyophilic balance may be used, e.g., polyoxyethylene stearate, polyoxyethylene sorbitol-laurate, polyoxyethylene sorbitan monopalmitate and the corresponding mono-oleate and mono-laurate, as well as the corresponding trilaurate, trioleate and tristearate, alkyl phenol-alkylene oxide condensation products, p-isooctyl phenol-10-ethylene oxide and Tergitol NPX are examples of this type of detergent, dodecyl alcohol-16-ethylene oxide, polyethylene glycol esters of higher fatty acids, such as Acco Emulsifier No. 5, glyceryl mono-stearate, propylene glycol monostearate (Aldo 25), glycerol oleo-stearate, polyoxyethylene lauryl ether (Brij-35). Anionic detergents also can be used, such as Aerosol OT (dioctyl ester of sodium sulfosuccinic acid), sodium salt of dihexyl sulfosuccinate, Aersol 18 (n-octadecyl sodium sulfosuccinate), sodium lorol sulfonate, sulfonated fatty acid amides and fatty alcohol amine sulfates. Mixed cationic-anionic detergents, such as N-dodecyl beta-alanine can be employed as can straight cationic detergents, such as cetyl pyridinium chloride and bromide, diisobutyl-phenoxy-ethoxy ethyl dimethyl benzyl ammonium chloride and other quaternary ammonium halides, long chain fatty acid amides containing multiple amine groups, e.g., Intracol O, alkyl polyoxyethylene glycol amines, alkylated amides, e.g., Michelene 20, can be employed in amounts from 0.025% to 5%, based on the polyvinyl chloride. (All parts and percentages in the specification and claims are by weight, unless otherwise indicated.)

In place of foamed polyvinyl chloride plastisols, less preferably other foamed polymers can be used, such as polystyrene, plastisols from cellulose ethers, e.g., ethyl cellulose and cellulose esters, e.g., cellulose acetate and cellulose nitrate. Cellulose acetate-butyrate and cellulose acetate-sorbate plastisols are considerably better than

straight cellulose acetate plastisols in performance, toluene diisocyanate



or similar isocyanate modified polyesters (these are prepared by reacting toluene diisocyanate with polyesters having hydroxy end groups) e.g., ethylene glycol or propylene glycol adipic acid polymers. Other examples of foamed polymers are polyvinyl butyral, polyethylene (under controlled conditions), terpolymers, e.g., maleic acid reaction products of copolymers of vinyl chloride with vinyl acetate, trichloroethylene, alkyl acrylates, e.g., methyl or ethyl acrylates, vinylidene chloride, dialkyl maleates, e.g., dimethyl or diethyl maleate, diethyl fumarate, diethyl chloro maleate, acrylonitrile, divinylbenzene or copolymers of any of these unsaturated compounds with vinyl chloride rather than terpolymers can be employed, copolymers and terpolymers of styrene with any of the above monomers or with small amounts of unsaturated oils, e.g., tung oil and oiticica oil, polyvinyl acetals, e.g., polyvinyl butyral, styrene-butadiene copolymers, e.g., GR-S, polyisoprene, isoprene copolymers, polyvinylidene chloride and copolymers of vinylidene chloride with any of the above monomers, styrenated alkyl resins, polyisobutylene, polyurethanes, linear polyamides, e.g., polymeric hexamethylene adipamide, polyesters, e.g., polymeric ethylene terephthalate, and blends of condensation of polymers with natural or synthetic rubber.

The preferred polymers as indicated are polyvinyl chloride and copolymers of vinyl chloride with not more than 10% and usually not more than 5% of a copolymerizable ethylenically unsaturated monomer.

The curing cycles for filled, unfilled and foamed plastisols of polyvinyl chloride embrace the following ranges:

Mold temperature -----° C. 100 to 200
Curing time -----minutes. 1/10 to 5
Mold pressure -----lbs./sq. inch. 0 to 10,000

The preferred conditions for curing sheets from which the liners are cut are:

Mold temperature -----° C. 130 to 200
(Most preferably, 170° C.)
Curing time -----seconds. 1 to 30
Mold pressure -----lbs./sq. inch. 100

The liners are cut from the sheet, e.g., by a cutting die, and preferably, have a diameter less than that of the undersurface of the top of the crown shell. The liners are simultaneously positioned and centered in the shells. The shells may be heated, e.g., to a temperature of 200° to 300° F. to render the bottom surface of the disc sufficiently tacky to adhere the disc to the shell. Then, the liners are subjected to a molding pressure of about 100 lbs./sq. inch to 500 lbs./sq. inch. The molding die, preferably, has a stepped face and can be a plunger of the type conventionally employed in the crown cap art to produce a liner having a central recess and a relatively thicker rim adjacent the skirt wall, so as to provide a greater amount of inner material for engagement with a lip of a bottle to insure an adequate seal. This method of molding also reduces the amount of material required in the disc, the amount in the center of the liner constituting merely a thin coating serving the same purpose as the well known crown center spot. The molding die or plunger also may be heated, e.g., to 150° to 300° F. If desired, the molding

plunger can be a conventional one without the step. In such case, the final crown will not have a center recess.

Instead of curing the unfoamed plastisol in the cap, it is frequently advantageous to partially or completely cure the plastisol as a button or disc (usually solid) of the proper weight. The partial or complete curing can be carried out for example as the buttons travel on an endless belt through a heated oven or as they travel around heated forming plates. Each button is then inserted into an individual crown cap, either cold or, preferably, while still hot. By using a preheated cap and a preheated plunger for shaping the liner, the button is pressed into the desired shape in a very short time. In the case of partially cured buttons, the simultaneous completion of the cure is accomplished. Surprisingly, it has been found that, even a fully cured button of a polyvinyl chloride plastisol, e.g., from 100 parts of Exxon 654, 125 parts Santicizer B 16 and 3 parts of calcium stearate, can be reshaped, e.g., at 180° C. in a crown cap with the preheated plunger. The cured plastisol assumes the new shape with no tendency to return to its original shape on cooling. The use of precured plastisols in units of the proper size has the advantage over curing the plastisol in the cap in that the curing of the plastisol need not be synchronized with subsequent insertion of the plastic unit into the crown cap followed by the shaping operation. Consequently, the molding machinery need not be tied up for as great a length of time as when curing is accomplished in the cap shell.

Alternatively, the plastisol can be inserted in the crown in the form of a liquid or paste and cured in place by using a die as above, either or both of the die and crown caps are preferably heated to hasten curing. This method is especially advantageous in preparing foamed liners.

Molding pressure is not normally critical and when foamed liners are formed in situ, using pressurized carbon dioxide or other inert gas, some leakage should be permitted to let the carbon dioxide come out. The pressure need only be high enough to give the proper form to the liner. The necessary pressure, consequently, will vary slightly with different materials.

Referring to the drawings:

FIGURE 1 is a bottom elevation of a cap provided with one of the improved liners.

FIGURE 2 is a sectional view of the cap taken along line 2—2 shown in FIGURE 1 having a liner made from a foamed polymer.

FIGURE 3 is an enlarged broken away sectional view of a cap having a liner made from a foamed polymer.

FIGURE 4 is a broken away sectional view, similar to FIGURE 3, but having an unfoamed polymer liner and without a center recess.

FIGURE 5 shows a stepped die about to be applied to a cap containing a plastisol.

In the drawings, the numeral 10 indicates a metal cap shell of the crown type having a lacquer coating 12 and a polymeric cushion liner 14. The polymer can either be foamed 16 (FIGURES 2 and 3) or unfoamed 18 (FIGURE 4). The polymeric material can be molded so as to form a center recess as at 20, although this is not essential.

Referring to FIGURE 5, there is shown a stepped die or plunger 22 about to be applied to a cap 10 having a blob of polyvinyl chloride plastisol 24 in the center thereof in order to spread and cure the plastisol. The die can be heated as by electrical heating element 26.

In preparing the compositions of the following Table II, the mixing of the plastisol was effected by stirring for one minute in an Oster Blender. The viscosity of the plastisols was measured, immediately after mixing, with a Brookfield viscosimeter, Model RVF.

0.5 grams of each of the plastisol compositions was placed in a conventional crown cap and cured for 10 minutes at 170° C.

TABLE II
Resin and plasticizer compositions

Composition	Parts	Viscosity, Centipoises	Temp., degrees	Remarks
1. Geon 121..... E-15..... Calcium Stearate.....	100 125 3	20,000	30	Cure soft, moderately tough, full of gas bubbles, plastisol set up at room temp., in 4 days.
2. Exon 654..... E-15..... Ca. St.....	100 125 3	3,750	30	Cure same as #1, viscosity of plastisol 40,000 after 1 day, set up 4 days.
3. Plivoc AO..... E-15..... Ca. St.....	100 125 3	(¹)	-----	Cure same as #1.
4. Marvinol MX 3001..... E-15..... Ca. St.....	100 125 3	(²)	-----	Do.
5. QYNV Blend 466..... E-15..... Ca. St.....	100 125 3	920	30	Do.
6. VYHH..... E-15..... Ca. St.....	100 125 3	(³)	-----	Discarded as unsuitable for making liners.
7. Exon 654..... B-16..... Ca. St.....	100 125 3	940	30	Cure same as #1.
8. Exon 654..... M-17..... Ca. St.....	100 125 3	250,000	-----	Do.
9. Exon 654..... Santicizer 141..... Ca. St.....	100 125 3	340	30	Cure soft, moderately tough.
10. QYNV blend 771..... E-15..... Ca. St.....	100 125 3	1,100	30	Cure same as #1.
11. QYNV blend 466..... Santicizer 141..... Ca. St.....	100 125 3	440	28	Cure opaque moderately tough.

¹ Thick paste.² Medium paste.³ Dry cakey mass.

The characteristics of several of the vinyl chloride polymers employed in the above Table II are as follows:

Geon 121 is a polyvinyl chloride having a limiting intrinsic viscosity $[\eta]_0$ of 1.2 and a molecular weight of 89,000; Exon 654 is a vinyl chloride-trichloroethylene copolymer (at least 95% vinyl chloride) $[\eta]_0$ of 1.2 and a mol. wt. of 89,000; Plivoc AO is a vinyl chloride-dialkyl maleate copolymer (at least 95% vinyl chloride); VYHH is a vinyl chloride-vinyl acetate copolymer (87% vinyl chloride) $[\eta]_0$ of 0.44 and mol. wt. of 20,000.

Other typical vinyl chloride polymers are Geon 101 $[\eta]_0$ of 1.13 and mol. wt. 82,000; Geon 202 $[\eta]_0$ of 0.80 and mol. wt. of 49,000; Geon 205 $[\eta]_0$ of 0.51 and mol. wt. of 25,000; and Vinylite VYNV (copolymer of 95% vinyl chloride-5% vinyl acetate) $[\eta]_0$ of 1.87 and mol. wt. 174,000. There can be employed a vinyl chloride-trichloroethylene copolymer containing less than 10% of trichloroethylene.

All of the above polymers are capable of forming plastisols. It has previously been proposed to employ polyvinyl chloride plastisols in making liners for crown caps. However, the prior art workers never disclosed the molecular weights or limiting intrinsic viscosity of the polymers. To obtain compositions which can be formed into liners on a commercial scale, we have found that the molecular weight and limiting intrinsic viscosity are of a critical nature. The limiting intrinsic viscosity $[\eta]_0$ should be between 0.50 and 1.20 and the molecular weight should be between 25,000 and 90,000 to give compositions which can be satisfactorily blended with fillers or readily converted to the cured state upon the application of heat, while, at the same time, not being too readily dissolved in the plasticizer at room temperature.

Any conventional paste-forming vinyl chloride polymer or copolymer having the requisite characteristics can be employed. Copolymers should contain at least 90% of vinyl chloride and, preferably, at least 95% of vinyl chloride.

The ratio of plasticizer to resin has little influence on viscosity of the mixture if the ratio is 1:1 or greater. There is a sharp increase in viscosity at lower ratios of plasticizer to resin. The ratio of plasticizer to resin is prefer-

ably between 0.6 to 1 and 1.5 to 1 and most preferably is at least 1:1. In any event, the ratio of plasticizer to resin should be such as to give a viscosity at 30° C. of between 300 c.p.s. and 25,000 c.p.s., preferably between 900 c.p.s. and 15,000 c.p.s.

The viscosity of the plastisol increases with time after mixing. Part of the increase in viscosity is attributed to thixotropy, since remixing in the blender reduces the viscosity to almost the original value. Such mixtures which have been allowed to stand can be re-used after remixing, provided the viscosity then is still in the operative range.

The effects of plasticizer-resin ratio, temperature and time after mixing are shown in Table III below.

TABLE III
Factors affecting plastisol viscosity

1. Different Plasticizer-resin Ratios.

	Calcium Stearate	Parts B-16	Parts Exon 654	Viscosity	Temp.
A.....	3	150	100	880	40°
B.....	3	125	100	940	30°
C.....	3	100	100	1,020	36°
D.....	3	75	100	152,000	30°

2. Effect of Temperature on Mix 1 C above:

Temperature	Viscosity
10°.....	2,180
15°.....	1,850
25°.....	1,280
36°.....	1,020
45°.....	980

3. Effect of Time after Mixing, Mix 1 C.

Time after Mixing	Temperature	Viscosity
Immediately.....	36°	1,020
15 minutes.....	31°	1,720
1 hour.....	32°	1,900
2 hours.....	31°	3,030
Remixing in blender.....	31°	1,440

Various fillers can be incorporated in the plastisols. To be satisfactory, the filler should not increase the viscosity of the composition beyond the operative range and should not adversely affect the cure or adversely affect the adhesion to lacquered crown caps to too great a degree. Among the most satisfactory fillers, as previously indicated, are Fuller's earth, talc and calcium carbonate.

The filled compositions described in Table IV below were cured for 10 minutes in crown caps at 170° C., using 0.5 gram of the composition in each cap.

TABLE IV
Experimental fillers

Formulation:	Grams
Santicizer B-16.....	100
Exon 654.....	100
Calcium stearate.....	3
Filler.....	Variable as below.....

	Filler	Quantity, grams	Viscosity (Brookfield)	Temp., deg.	Cure
1.....	Glass fiber.....	25	Very thick paste.....		Very tough.
2.....	Glassfloss.....	5	Medium paste.....		Do.
3.....	Wood flour.....	25	5,500.....	46	Moderately tough, odor present.
4.....	do.....	50	150,000.....	43	Do.
5.....	Fuller's earth.....	50	520.....	37	Cure fairly tough, hard.
6.....	do.....	100	3,400.....	37	Do.
7.....	do.....	150	148,000.....	40	Do.
8.....	Talc.....	50	3,700.....	40	Do.
9.....	do.....	100	7,600.....	47	Do.
10.....	do.....	150	Very thick paste.....		Do.
11.....	Talc ¹	125	208,000.....	25	Do.
12.....	Talc ¹	125			No difference noticeable.
13.....	Parlon (chlorinated rubber) ²	0.5			Cure opaque, but rubbery, tough.
14.....	#13 50 ml. toluene ²	50	145,000.....	30	Cure translucent otherwise about same as #13.
15.....	Darco G-60, activated carbon.....	25	360,000 (thick paste).....		Cure fair.
16.....	CaCO ₃ , powdered.....	50	2,800.....	46	Cure fairly tough, hard.
17.....	do.....	100	16,500.....	45	Do.
18.....	do.....	150	195,000.....	45	Do.
19.....	ZnO.....	50	10,000.....	40	Opaque, white, fairly tough, hard.
20.....	ZnO.....	75	33,000 (solid paste).....	40	Fairly tough, hard, opaque, white.
21.....	SiO ₂ , rubber grade.....	15	Medium paste.....		Fairly tough.
22.....	Marasperse CB (calcium sodium lignin sulfonate).....	50	1,860.....	40	Poor adhesion, otherwise ok.
23.....	Marasperse CB.....	100	6,600.....	45	Do.
24.....	Marasperse CB.....	150	36,000.....	45	Do.
25.....	Marasperse C (calcium lignin sulfonate).....	100	150,000.....	45	Crumbly, very poor adhesion.
26.....	Indulin A (sulfate lignin).....	50	8,400.....	40	Very poor adhesion and cohesion.
27.....	Indulin A.....	100	160,000.....	40	Do.
28.....	Bentonite.....	50	4,400.....	42	
29.....	Asbestol (fibrous magnesium silicate).....	50	27,000.....	42	

¹ Compositions 11 and 12 were made by blending in a sigma mixer for 15 minutes.

² Compositions 13 and 14 were very sticky.

Formulation No. 9 of Table IV was cured into sheets. Liners 0.037 inch in thickness were cut from these sheets and inserted in lacquered shells without the use of an adhesive. Soda water (Canada Dry) bottles (6 oz.) were chilled to 4° C., uncapped and recapped with the prepared crowns. The bottles were cycled between room temperature and 75° C. five times over a period of five days

without leakage. The same excellent results were obtained by repeating the tests using a lower temperature of 2° C. The pressure for the Canada Dry soda water bottles ranged from 60 p.s.i. at 26° C. to 165 p.s.i. at 75° C. Soda water was chosen for this test because it presents more rigorous testing conditions, e.g., ability to withstand the development of leaks at higher pressures, than do the cola drinks, for example, in which the pressures developed are not nearly as high. For example, at 75° C. a cola beverage (Coca-Cola) develops a pressure of only approximately 115 p.s.i.

Paper flock, calcium carbonate and cork fines were further tested as fillers for plastisols, in preparing cured sheets. The fillers were added to the plastisol, mixed one minute in an Aster blender, and the viscosity of the blend measured. Sheets 0.075 inch thick of each mix were cured at 150° C. for one minute. Only the calcium carbonate gave plastisols of a desirable low viscosity. The results are shown in Table V below.

TABLE V
Fillers for PVC

Formulation:	Parts
Exon 654.....	100
Sant. B-16.....	100
Cal. stearate.....	3
Filler.....	as indicated

	Filler	Quantity	Viscosity, cps.	Remarks
1.....	Cork fines.....	40 parts.....		Bulk vol. of 40 g. cork was 800 ml. The plastisol formed a coating around cork. The cured sheet resembled cork liner in appearance.
2.....	do.....	80 parts.....		Similar to No. 1.
3.....	Surfex MM (calcium carbonate).....	50 parts.....	5,500 at 38° C.....	White, medium hard sheet.
4.....	Paper flock.....	10 parts.....	26,600 at 44° C.....	Straw-colored sheet.

Linears made from a sheet of the cork fines filled plastisol of No. 1 (Table V), 0.075 thick were cycled without leakage. The cork fines had a particle size less than 2 mm. Liners of this type are commercially attractive, as they employ a normally waste product, namely, the cork fines.

Polymers containing chlorine, such as polyvinyl chloride, for example, decompose to some extent with the formation of undesirable decomposition products, such as hydrogen chloride, at elevated temperatures. Accordingly, it is frequently desirable to add a small amount of stabilizer to prevent such decomposition and consequent discoloration. The stabilizer should be non-toxic if the liner containing it is intended for use in bottling beverages. The stabilizers in Table V were tested for their stabilizing effect on Exon 654 upon heating 15 minutes at 170° C. Calcium stearate, a non-toxic stabilizer was found to give excellent results, particularly, at 3% concentration, based on the resin. Sodium bicarbonate gave good results, although not as good as calcium stearate. However, sodium bicarbonate is a foaming agent and it has the advantage that it can serve the dual function of stabilizer and foaming agent in preparing foamed vinyl chloride plastisol liners. Dibutyl tin oxide also gave excellent results as did mixtures of sodium bicarbonate with either calcium stearate or dibutyl tin oxide. Foaming with the bicarbonate was suppressed to a considerable extent by using such mixtures.

TABLE VI

Stabilizer for polyvinyl chloride plastisols

Formulation:	
Exon 654.....	5 parts.
B-16.....	5 parts.
Stabilizer.....	0.005 parts=0.1% of resin. 0.025 parts=0.5% of resin. 0.075 parts=1.5% of resin. 0.15 parts=3% of resin.

	Stabilizer	Percent of resin	Appearance of product
1.....	Control, no stabilizer.....	-----	Dark brown.
2.....	Calcium stearate.....	0.1	Do.
3.....	do.....	0.5	Medium brown.
4.....	do.....	1.5	Amber.
5.....	do.....	3	Light cream.
6.....	V-1-N (A strontium containing compound described on page 32 of "Stabilizers" publ. by Advance Solvents & Chemical Corp.).....	0.1	Medium dark brown.
7.....	do.....	0.5	Medium brown.
8.....	do.....	1.5	Tan.
9.....	do.....	3	Center cream, edges tan.
10.....	Dibutyl tin oxide.....	0.1	Medium dark brown.
11.....	do.....	0.5	Do.
12.....	do.....	1.5	Light cream.
13.....	do.....	3	Do.
14.....	Zinc oxide.....	0.5	Center tan, edges black.
15.....	do.....	1.5	Center light tan, some black around edges.
16.....	do.....	3	All very light tan.
17.....	Calcium carbonate.....	0.5	Dark brown.
18.....	do.....	1.5	Medium brown.
19.....	do.....	3	Light brown.
20.....	Sodium bicarbonate.....	0.5	Medium brown.
21.....	do.....	1.5	Light tan, slight foaming.
22.....	do.....	3	Deep cream, considerable foaming.
23.....	do.....	6	Deep cream, slightly more foaming.
24.....	do.....	12	Deep cream, about same as #23 regarding foaming.
25.....	(Dibutyl tin oxide.....	1.5	} Light color, slight foaming.
	(Sodium bicarbonate.....	6	
26.....	(Calcium stearate.....	3	} Light color, no foaming.
	(Sodium bicarbonate.....	6	

Stannous stearate proved to be an unsatisfactory stabilizer, even at 3% on the resin for protecting Exon 654. It can be used to some extent in other formulations.

Stayrite No. 90 protected this resin against discoloration at the 3% level.

Thermolite No. 31 is an even better stabilizer, 1.5% of this material proved to be adequate. This is an outstanding stabilizer for use with polyvinyl chloride liner compositions.

Paraplex G-62 (a polymeric ester-epoxide), specifically a glycol-sebacate-epoxide is also a good stabilizer,

It has been found that the plycerol ester of hydrogenated rosin reduces the migration of the plasticizer in unfoamed polyvinyl chloride plastisols. In general, 5 to 10% of the plycerol ester is employed, based on the resin. Preferably 10% of plycerol ester is used. A typical formulation is:

	Parts
Exon 654	100
Santicizer B-16	125
Calcium stearate	3
Glycerol ester of hydrogenated rosin	10

As previously indicated, the use of foamed polyvinyl chloride plastisols gives liners with outstanding properties. Various blowing agents were effective, some more so than others. Typical blowing agents have been pointed out previously. Blowing agents based on organic nitrogen compounds, which liberate free nitrogen, generally produced good foam but may, in some instances, impart odor or "off flavor" and, consequently, be undesirable for many uses for this reason. They also, in some instances, produced foamed sheets which were discolored yellow which again may be undesirable for some purposes.

As will be appreciated, curing time and pressure of cure affect uniformity and fineness of porosity. Preferably, the curing time is between $\frac{1}{10}$ minute and $\frac{1}{2}$ minute, the pressure between 0 lb./sq. inch and 500 lbs./sq.

inch, and the temperature between 130° C. and 180° C., although the temperature is not generally critical. Naturally, there will be some variation in these values, depending on the particular blowing agent employed.

Foams, based upon the use of water or aqueous bicarbonate solution, were improved by employing emulsifiers which aid in the formation of water-in-oil emulsions. Such emulsifiers include the materials recited below as well as those mentioned previously. The nonionic emulsifiers in general are preferred.

Specific emulsifiers of this type, which proved satisfactory in forming foamed sheets with a density of 0.6 grams/cc., using ammonium bicarbonate solution as a blowing agent, are Triton X-177 (an alkylphenoxy-polyether alcohol), nonylphenyl ether of polyethylene glycol, Ethofat 60-15 (a higher fatty acid, including caprylic acid, stearic acid, intermediate acids between these two acids, and oleic acid-ethylene oxide condensate), Ethomid 60-15 (a condensate similar to Ethofat 60-15, but with the acids replaced by their amides), Tergitol NPX (an alkylphenyl polyethylene glycol ether), Methocel 4000 c.p.s. (methyl cellulose) and Elvanol 50-42 (polyvinyl alcohol).

Liners cut from cured sheets foamed with aqueous ammonium bicarbonate or with Vynafoam were inserted in lacquered shells. The liners were 0.037 inch in thickness and no adhesive was used. There was no pressure loss when bottles of Canada Dry carbonated water were recycled five times between room temperature and 75° C., employing these crowns.

The following Table VII illustrates that, for satisfactory blowing, conditions should be controlled. The best results are illustrated by Nos. 33 and 34. As is evident from No. 32, merely bubbling Dry Ice through the plasticizer did not give a good blow.

TABLE VII

Foamed PVC plastisols

Sheets of foamed polyvinyl chloride were prepared by the following procedure: Surface active agent and blowing agent were added to 100.75 grams of plastisol in an Oster blender and mixed 30 seconds. 15 grams of the

ticizer, it is desirable to introduce the carbon dioxide under pressure as disclosed hereinafter.

As previously indicated, curing temperature has little or no effect on the density of foam in the normal temperature range in foaming polyvinyl chloride plastisols with aqueous ammonium bicarbonate solutions. Foams cured at 110° C. had a density of 0.66 grams/cc., whereas those cured from the same composition at 150° C. had a density of 0.62 grams/cc.

The ratio of resin to plasticizer, however, is an important factor in preparing good foams. For example, with ratios of polyvinyl chloride (Exon 654) to Santicizer B-16 of 100:100; 100:80 and 100:60, the densities of the foams were 0.62; 0.74 and 0.85, respectively. It is desirable that the density of the foamed resin be between about 0.4 gm./cc. and 0.8 gm./cc., preferably between 0.5 and 0.7 gm./cc. For this reason, the amount of plasticizer, based on the resin, should normally be between 80 parts and 125 parts per 100 parts of resin and, preferably, at least 100 parts per 100 parts of resin.

While the type of plasticizer affects the density, this effect is associated with the viscosity of the plastisol. The low viscosity plasticizers, such as dioctyl phthalate and acetyl tributyl citrate, yield foams with a density of 0.54 to 0.55 gm./cc., whereas those of higher viscosity,

resulting mixture were cured in the mold with an 0.037" x 5" x 5" cavity at the indicated temperature, time, and total pressure on the mold surfaces.

Formulation of plastisol:

Exon 654	50
Santicizer B-16	50
Dibutyl tin oxide	0.75
	100.75

	Surface active agent, g.	Blowing agent, grams	Temp., C.	Time, min.	Press., lbs.	Dens.	Size of pores	Remarks
1	None	2.5 NH ₄ HCO ₃	130	1/2	1,000	1.14	Coarse	Uneven foam.
2	Leicithin, 1	Water, 5	130	1/2	1,000			No foaming.
3	do	0.8 g. NH ₄ HCO ₃ in 5 g. H ₂ O	120	1/2	500	0.83	Coarse	Uneven.
4	do	do	120	1/2	1,000	1.18		No foaming.
5	None	do	120	1/2	500	0.84	Medium	Uneven.
6	do	do	120	1/2	100	0.88	do	Even.
7	do	do	140	1/2	100	0.89	Fine	Somewhat uneven.
8	Sodium lauryl sulfate, 0.06	do	130	1/2	1,000		do	Very uneven.
9	do	do	130	1/2	500	0.90	Medium	Even.
10	Sodium lauryl sulfate, 0.15	2.5 g. NH ₄ HCO ₃ in 12.5 ml. H ₂ O	130	1/2	200		do	Very poor tear strength.
11	Talc, 2	1.6 g. NH ₄ HCO ₃	120	1/2	100	1.13	Irregular	Nearly solid.
12	do	do	120	1/2	50	1.05	do	Do.
13	do	do	150	1/2	1,000	0.95	Coarse	Uneven.
14	Talc, 25	0.8 g. NH ₄ HCO ₃ in 5 ml. H ₂ O	120	1/2	1,000	1.86		No foaming.
15	Bentonite, 1	do	130	1/2	500	1.2		Do.
16	do	do	130	1/2	100	0.85	Coarse	Uneven.
17	Tergitol NPX, 1	do	130	1/2	500		Fine	Very uneven.
18	do	do	170	1/2	500		Medium	Do.
19	do	do	110	1/2	500		do	Even.
20	do	do	130	1/2	100	0.73	Fine	Do.
21	do	do	120	1/2	100	0.76	do	Do.
22	do	do	120	1/2	100	0.91	do	Do.
23	do	do	120	1/2	100	0.81	do	Somewhat uneven.
24	Same as 21 except	0.4 g. NH ₄ HCO ₃ in 2.5 g. H ₂ O	120	1/2	100		do	Do.
25	Tergitol NPX, 1	0.16 g. NH ₄ HCO ₃ in 5 g. H ₂ O	120	1/2	50	0.86	do	Do.
26	do	do	120	1/2	100	0.93	do	Nearly even.
27	do	0.4 g. NH ₄ HCO ₃ in 5 g. H ₂ O	130	1/2	100	0.91	Medium	Uneven.
28	do	do	120	1	100	0.85	Fine	Nearly even.
29	do	10 ml. chilled carbonated water	120	1/2	100	0.96	do	Even.
30	do	do	140	1/2	200	1.14	Coarse	Uneven.
31	None	2.4 g. NH ₄ HCO ₃ in 15 g. H ₂ O	120	1/2	100	0.69	do	Do.
32	do	Dry Ice bubbled through plasticizer 1/2 hour (Santicizer B-16)	120	1	100	1.12		Opaque sheet, very little foaming.
33	Elvanol 50-42, 0.1	0.8 g. NH ₄ HCO ₃ in 10 g. H ₂ O	120	1	100	0.55	Medium	Even.
34	Methocel 4,000 c.p.s., 0.1	do	120	1	100	0.58	do	Do.
35	None	5 g. BL-353	130	1/2	500	0.68	do	Even, yellowish.
36	do	do	170	1/2	500	1.05	do	Uneven.
37	do	do	100	5	100	1.03	Coarse	Even.
38	do	5 g. Unicef ND	170	1/2	500	0.82	Medium	Even, odor of formaldehyde.
39	do	5 g. Unicef ND, 2.5 g. urea	120	1/2	500	1.24	Fine	Even, sparse, poor.
40	do	do	150	1/2	500	0.98	Medium	Even.

While carbon dioxide is much more soluble in many of the plasticizers employed than it is in water, still for good results employing carbon dioxide dissolved in the plas-

such as Santicizers B-16 and 141 yield foams with densities of 0.70 to 0.74 under identical conditions. In general, foams with densities of 0.5 to 0.7 gm./cc. can

be prepared with any of the plasticizers giving a viscosity of below 25,000 c.p.s. when employed in equal amounts, based on the resin, by adjusting the amount of blowing agent, although, preferably, the viscosity should be below 15,000, as previously indicated.

Typical formulations, using ammonium bicarbonate as a blowing agent, are given in Table VIII below. There is also included one formulation, using carbon dioxide without pressure. The formulations included:

Exon 654	100 grams.
Stayrite No. 90	2 grams.
Plasticizer	As indicated.
Surface active agent	As indicated.
Blowing agent	As indicated.

The compositions were cured as 0.0375 inch times 5 inch times 5 inch sheets in a Carver press.

polymethylsiloxane) can be employed. Alternatively, stearic acid can be incorporated into the plastisols at concentrations of 2.5% to 5%, to prevent sticking of plastisol to the hot mold without affecting adhesion of the foam to the Unichrome-coated shells adversely. Butyl stearate was similarly effected as a mold release agent and, like stearic acid, is nontoxic, but stearic acid is preferred in its overall characteristics. For example, butyl stearate served well as a mold release agent for plastisols pressured at 250 p.s.i. carbon dioxide, but was inferior to stearic acid at 500 p.s.i. Butyl stearate was less satisfactory as a replacement for the primary plasticizer in the range of 5 to 20%, as liners employing it, in some instances, leaked during the cycling test.

Mold pressure and temperature at time of cure had little effect on the density of the foam. The pressure of

TABLE VIII

Foamed PVC liners, without CO₂ pressure

	Plasticizer	Amount, grams	Surface active agent	Amount, grams	Blowing agent	Amount	Curing temp., deg.	Curing press., lbs.	Curing time, min.	Dens.	Size pores	Remarks
1	B-16	100			Cyclohexanol sat. with CO ₂ at STP.	40 g.	150	100	1		Small	Nearly solid sheet with strong odor of cyclohexanol.
2	B-16	100	Triton X-100	2	16% NH ₄ HCO ₃ aqueous solution.	10 mo.	100	110	1	0.66	Medium	Even sheet.
3	B-16	100	do.	2	do.	10 ml.	120	100	1	0.72	do.	Do.
4	B-16	100	do.	2	do.	10 ml.	130	100	1	0.83	do.	Do.
5	B-16	100	do.	2	do.	10 ml.	150	100	1	0.62	do.	Do.
6	B-16	100	do.	2	do.	10 ml.	160	100	1	0.82	do.	Somewhat sparse, uneven pores.
7	B-16	80	do.	2	do.	10 ml.	150	100	1	0.74	do.	Even sheet.
8	B-16	60	do.	2	do.	10 ml.	150	100	1	0.85	Fine	Very even pores, rather hard sheet.
9	Sant. 141	80	do.	2	do.	10 ml.	150	100	1	0.70	Medium	Nearly even sheet.
10	DOP	80	do.	2	do.	10 ml.	150	100	1	0.55	Large	Open pores, very even sheet.
11	Acetyl tri-butyl citrate.	80	do.	2	do.	10 ml.	150	100	1	0.54	Medium	Open pores, even.
12	do.	60	do.	2	do.	10 ml.	150	100	1	0.55	Large	Slightly uneven.
13	do.	60	do.	2	do.	5 ml.	150	100	1	0.72	Fine	Even sheet.

Liners cut from cured sheets of a polyvinyl chloride plastisol foamed with ammonium bicarbonate, e.g., #5, in Table VIII, applied to shells and cycled five times between 2° C. and 75° C. showed no leakage.

Superior results were obtained by charging the plastisol 100 parts in a 750 part bomb with carbon dioxide at a pressure of 250 p.s.i. at room temperature until equilibrium was established. About 30 min. with shaking was required. The carbon dioxide saturated plastisol, in an amount of about 0.30 gram per shell, was then injected into Unichrome coated, unlacquered shells at room temperature. The shells containing the plastisol were then placed in a mold, maintained at 170° C., and shaped and cured by contact with a hot plunger for 5 seconds. Curing was almost instantaneous at 170° C. Either a stepped or regular plunger can be employed. The heating can be varied between 100° C. and 200° C. In place of carbon dioxide, other inert, non-toxic gases can be employed, but carbon dioxide is preferred, especially in preparing liners for caps for carbonated beverage containers.

Alternatively, sheets of the carbon dioxide pressurized plastisols could be prepared by injection and curing in 0.0375 inch times 5 inch times 5 inch molds and liners cut from the sheets and inserted in the caps.

To prevent sticking to the mold, conventional release agents, such as Dow Corning's silicone release fluid (a

carbon dioxide applied for saturation of the plastisols was the dominant factor regulating density of foam. Density decreased with increase in pressure up to 250 p.s.i. With little change in density or uniformity in porosity at higher pressures up to 500 p.s.i. The minimum suitable carbon dioxide pressure is 100 p.s.i. and, preferably, it should be at least 200 p.s.i. The use of 250 p.s.i. and 500 p.s.i. carbon dioxide resulted in liners having excellent cycling properties.

Little or no foaming occurs upon release of the pressurized plastisol into the cap. In normal operation foaming does not occur until the pressurized plastisol in the cap is subjected to heat. The fact that a foam does not normally result until after the plastisol is positioned in the cap is advantageous as it permits more ready control of the shaping of the liner.

The use of carbon dioxide under pressure is illustrated in Table IX below. In # 1 to 5, 19 and 20, sheets of liner 0.0375 inch times 5 inch times 5 inch were prepared, while in # 6 to 18, the composition was cured directly as a cap liner. The general formulation is:

Exon 654	100 grams.
Stayrite #90	2 grams.
Plasticizer	As indicated.
Lubricant	As indicated.
Carbon dioxide	Pressure as indicated.

TABLE IX

Foamed PVC liners with CO₂ pressure

	Plasticizer	Amount, g.	Lubricant	Amount, g.	CO ₂ Press.	Temp., deg.	Time	Press., lbs.	Dens. of sheet	Av. wt. cap liner, g.	Size of Pores	Remarks
1	B-16	100			250	130	1 min.	100	0.72		Medium	Even foam.
2	B-16	100			250	130	1 min.	50	0.69		do	Do.
3	B-16	100			250	150	1 min.	50	0.70		do	Do.
4	B-16	100			125	150	1 min.	100	0.87		do	Do.
5	B-16	100			125	170	1 min.	100	0.88		do	Do.
6	B-16	100			250	150	30 sec.	(1)		0.34	Fine	Liner very adherent to unichrome treated cap, also stuck to mold after several caps.
7	B-16	100			125	150	30 sec.	(1)	0.88	0.54	do	Do.
8	B-16	100			250	170	30 sec.	(1)	0.88	0.35	do	Do.
9	B-16	100			250	170	5 sec.	(1)		0.35	do	Weak, incomplete cure. Stuck to mold after several caps.
10	B-16	100			250	170	5-30 sec. ²	(1)		0.35	do	Apparently complete cure. Stuck to mold after several caps.
11	B-16	100	Cal. stearate.	10	250	170	5-30 sec. ²	(1)			do	Fair adhesion to cap. No adhesion to mold.
12	B-16	100	do	5	250	170	5-30 sec. ²	(1)			do	Good adhesion to cap. Stuck to mold after several caps.
13	B-16	100	Stearic acid	5	250	170	5-30 sec. ²	(1)			do	Very good adhesion to cap, no adhesion to mold.
14	B-16	100	do	3.5	250	170	5-30 sec. ²	(1)		0.36	do	Very good adhesion to cap; slight tendency to adhere to mold.
15	B-16	100	do	2.5	250	170	5-30 sec. ²	(1)			do	Adhered to mold.
16	B-16	100	Petrolite 1035.	5	250	170	5-30 sec. ²	(1)			do	Do.
17	Sant. 141	100	Stearic acid	5	250	170	5-30 sec. ²	(1)		0.25	do	Good adhesion to cap; some tendency to adhere to mold.
18	Acetyl tributyl citrate.	100	do	5	250	170	5-30 sec. ²	(1)		0.28	do	Excellent adhesion to cap; no adhesion to mold.
19	Acetyl tributyl citrate.	50	do	5	250	170	5-30 sec. ²	(1)	0.46	0.32	do	Very good adhesion to cap; no adhesion to mold.
20	Sant. B-16	50	do	5	250	170	5-30 sec. ²	(1)	0.51	0.29	do	Excellent adhesion to cap; no adhesion to mold.
	Acetyl tributyl citrate.	75	do	5	250	170	5-30 sec. ²	(1)			do	
	Sant. B-16	25	do	5	250	170	5-30 sec. ²	(1)			do	

¹ Weight of plunger.² Cap cured in mold 5 seconds, removed, kept at curing temperature 30 seconds longer.

Foamed liners were tested for bottle leakage in the five time cycling between 2° C. and 75° C. over a period of five days. No leakage was observed with any of the liners tested. The liners were prepared by charging the carbon dioxide saturated plastisol into the Unichrome coated shells and shaping and curing with a hot plunger in the manner previously indicated. Typical formulations with results are:

Liner composition:	G.
Exon 654	100
Acetyl tributyl citrate	100
Stayrite No. 90	2
Foamed at 250 p.s.i. CO ₂ .	

	Weight of liner, g.	Shoulder thickness inches	Pressure after cycling	Pressure expected, p.s.i.
1	0.28	0.046	66 p.s.i. at 30° C.	65-73
2	0.28	0.046	68 p.s.i. at 30° C.	65-73
3	0.28	0.046	67 p.s.i. at 30° C.	65-73

Note.—None leaked.

Liner composition:	G.
Exon 654	100
Plasticizer B-16	100
Stayrite No. 90	2
Foamed at 250 p.s.i. CO ₂ .	

	Weight of liner, g.	Shoulder thickness inches	Pressure after cycling	Pressure expected, p.s.i.
1	0.35	0.046	68 p.s.i. at 30° C.	65-73
2	0.35	0.046	72 p.s.i. at 30° C.	65-73
3	0.35	0.046	63 p.s.i. at 30° C.	65-73

NOTE.—None leaked.

Liners cut from Vynafoam foamed sheets of polyvinyl chloride plastisols and from talc-filled plastisols, such as those used in the cycling test, were also tested for water absorption. The liners, after weighing, were immersed in chilled bottles of Canada Dry soda water, capped and cycled five times between 2° C. and 75° C. The liners were removed, the surfaces blotted dry with filter paper and weighed. The water adsorption of the Vynafoam liners was 3.2% and that of the talc-filled liner 3.7%, both of which values are excellent.

In a further series, plastisols of polyvinyl chloride were pressurized in a bomb at 250 p.s.i. and 500 p.s.i. with carbon dioxide. Lacquered shells were primed with Unichrome 219 PX or Goodrich A 458-B and baked five minutes at 170° C. The shells were then injection filled with plastisol, molded, foamed and cured in five seconds at 170° C. in the regular crown mold. The lined crowns were removed from the mold and placed on heated platens for 30 seconds to insure uniformity of cure throughout the mass of the liner. In the following Table X, Unichrome was used as the adhesive in Nos. 1 to 5, and Goodrich A 458-B in the remaining numbers. The general formulation:

Exon 654 _____ 100 grams.
 Stayrite No. 90 _____ 2 Grams.
 Plasticizer and additives _____ as indicated.

TABLE X

	Plasticizer	Amount, grams	Additives	Amount, grams	CO ₂ Press.	Adhesion to cap	Adhesion to mold	Wt., liner, grams	Thickness shoulder	Thickness center	Density ¹
1	B-16	80	Stearic acid	4	250	V. good	None	0.39	0.046	0.018	0.70
2	B-16	80	do	4	250	do	do	0.45	0.046	0.018	
3	B-16	80	do	4	250	do	do	0.51	0.046	0.018	
4	B-16	100	{ Stearic acid Talc	{ 5 50 }	250	do	do	0.46-0.60	0.046	0.018	0.9
5	B-16	100	Butyl stearate	5	250	do	do	0.33	0.046	0.018	0.57
6	{ B-16 Butyl stearate	{ 80 20 }			250	do	do	0.29	0.046	0.018	0.53
7	B-16	100	Butyl stearate	5	500	do	Adhered				0.61
8	B-16	100	Stearic acid	5	500	do	None	0.30	0.045	0.018	
9	Acetyl tributyl citrate	100	do	5	500	do	do	0.23	0.043	0.015	0.64
10	do	80	do	5	500	do	do	0.34	0.066	0.036	0.67
11	do	125	do	5	500	Good	do	0.22	0.046	0.018	0.59
12	Di-isobutyl adipate	100	do	5	500	do	do	0.38	0.065	0.035	0.63
13	do	150	do	5	500	Poor	do	0.22	0.046	0.018	
14	do	150	{ Stearic acid Talc	{ 5 100 }	500	Good	do	0.43	0.046	0.018	0.99

¹ Density estimated from weight and volume of cured foamed material in crown.

Liners corresponding to liners Nos. 1, 2, and 3 in Table X were cycled five times between ice water temperature (1.5 to 2° C.) and 75° C. without leakage.

The inclusion of talc, 20 to 30% by weight, in a plastisol containing equal amounts of polyvinyl chloride resin and plasticizer (Santicizer B-16) foamed without too great an increase in viscosity and without detrimental effect on the liner properties. Liners containing 20% talc (No. 4 in Table X) did not leak in the cycling test between 1.5° C. and 75° C.

Liners foamed in place by pressuring the plastisols at 500 p.s.i. did not withstand cycling nearly as well. Thus, of 8 bottles capped with liners No. 8 of Table X, six leaked; of 13 bottles capped with liner No. 9 of Table X, ten leaked; of 10 bottles capped with liner No. 10 of Table X, four leaked and of 8 bottles capped with liner No. 11 of Table X, four leaked.

With the carbon dioxide foam, the minimum weight of the liner should be 0.3 grams and the maximum weight 0.7 grams, in the conventional crowns employed today which have a bottom inside diameter of about one inch. If a liner is formed with a center depression, normally the diameter of the center depression is about $\frac{5}{8}$ inch. However, other size center depressions, e.g. $\frac{7}{8}$ inch, can be employed.

Vinyl resin modified unsaturated alkyd resins also are effective as liners. For example, a styrenated unsaturated alkyd, such as Reichhold's PolyLite Resin 8150 (the specific composition being 50% styrene, 50% alkyd resin) was catalyzed with 0.5% benzoyl peroxide, cast into a mold and polymerized 15 minutes at 130° C. Liners, 0.037 inch thick, were cut from the flexible sheets and placed in lacquered crown shells. No adhesive was employed. Bottles of Canada Dry water capped with these crowns withstood five cycles between room temperature and 75° C. without leakage.

Such ethylenically unsaturated resin modified linear alkyds should be flexible. Other examples of such resins are styrene (30 to 70%)-diethylene glycol fumarate-succinate, styrene ethylene glycol maleate, the corresponding methyl methacrylate modified resins, Vibrins (Naugatuck) unsaturated polyester resins, 35 to 75% polystyrene; Selectrons (Pittsburgh Plate Glass); Sinco resin (Synder Chemical); Stytol resin, chlorostyrene-unsaturated polyesters; and (Kappers) vinyl toluene-unsaturated polyesters.

DuPont polythene PM-1 and PM-1 cross-linked with benzoyl peroxide were molded into crown caps in the same manner as the plastisols. Irrathene (irradiated polyethylene) could not be molded directly into crown caps, because of its infusibility and high shrinkage. However, sheets of Irrathene can be produced by pressure molding (10,000 p.s.i.) at 130° C., liners cut from the sheet and the liners adhered to the cap by rubber cement.

Liners of peroxide free radical modified polyethylene

gave performance on the above cycling test, although leakage was noticed in an occasional cap. Polyethylene plasticized with natural rubber, 20 parts polyethylene to 10 parts rubber, resulted in liners which could be molded in the crown shell either with or without peroxide induced cures. The resultant liners had excellent physical properties. The range of rubber to polyethylene can be from one part to 50 parts of rubber per 100 parts of polyethylene.

In place of natural rubber, there can be employed an equal amount of an olefin or diolefin hydrocarbon type synthetic rubber. Either homopolymers or copolymers of these materials with each other or with other unsaturated hydrocarbons can be employed. Examples of such rubbers are butadiene-styrene copolymer (GR-S) and isoprene-isobutylene copolymer (butyl rubber). When a peroxide curing agent is employed, it is used in an amount of 0.5% to 15%, preferably 10%, based on the polyethylene.

Sheets were molded from polyethylene (PM-1), irradiated polyethylene (Irrathene) and polyethylene plasticized with low Mooney (ML 4-20) unvulcanized, natural rubber and polyethylene cross-linked with peroxide free-radicals, specifically 0.1% methyl ethyl ketone peroxide together with 0.1% colbalt octoate. Liners were cut from these sheets and placed in lacquered shells without the use of an adhesive. Bottles of Canada Dry soda water were capped with the crowns and tested through five cycles between 2° C. and 75° C. The bottles with polyethylene (PM-1) liners (39 mils) held up fairly well under the rigorous test conditions, although some slight leakage was noted in three out of eight bottles on the first cycle. Employing one part of natural rubber as a plasticizer with two parts of the polyethylene (PM-1) did not improve its performance as a liner. The peroxide cross-linked polyethylene gave excellent results in the cycling test.

Sheets of thickness 0.037 inch and 0.075 inch were molded from polyethylenes of different molecular weights and were cut into discs and cemented to shells using Bondmaster L 255 (Rubber and Asbestos Corporation) as an adhesive. Alternatively, there can be employed natural or synthetic, e.g., GR-S, rubber cement.

Surprisingly, it was found that the higher molecular weight polyethylenes gave inferior results to lower molecular weight polyethylenes. Bakelite DYNJ (mol. weight =24,000) developed many more leaks than (Du Pont) PM-1 (mol. weight=18,000 to 19,000) with the thinner liner, and the thicker liners from DYNJ were even poorer in that virtually all of them developed leaks in the 2° to 75° C. cycling test. Preferably, when uncured polyethylene is used as a liner, the molecular weight should be in the range of 8,000 to 20,000, e.g., Alathon A, mol weight 18,000 to 19,000; Alathon B, mol weight 16,000 to 17,000; Alathon C, mol weight 12,000 to 13,000; Ala-

thon D, mol weight 8,000 to 9,000. However, when cured polyethylene (cured with a peroxide, such as benzoyl peroxide, or with X-rays or ultraviolet light) is employed, considerably higher molecular weights can be used, for example, up to 100,000.

While GE Irrathene 101 gave fair results when cast into sheets of 0.0375 inch as a liner in the cycling test, considerable improvement was noted if the centers of liners made from this material were removed, the resulting rings plied against a disc of the same material, and the resultant liners molded directly into the crown caps, using Bondmaster No. L 255 as an adhesive. The products prepared were still not as good as the foamed polyvinyl chloride plastisols. Irrathenes with a different degree of irradiation from Irrathene 101 can also be employed.

As previously indicated, polyethylene cross-linked by peroxide free-radicals gives excellent results in the cycling tests. Cross-linking at too high a temperature results in occasional failure, due to polymer degradation. The use of a cross-linking temperature of 70° C., however, results in a tough, high modulus polyethylene with a softening point as high as 134° C.

Under the appropriate conditions, closed cell polyethylene foams of density 0.5 to 0.6 gram/cc. can be formed into excellent liners. Several alternative methods can be employed to form such foams.

(1) A solution of an organic blowing agent, e.g., azobis isobutyronitrile, in an amount of one gram per 200 cc. of hot benzene solution, containing 20 grams of polyethylene, is cast and the solvent evaporated to form a film. The product is then foamed in a mold under pressure, e.g., 500 p.s.i., at a temperature above the fusion point of polyethylene, e.g., 170° C., for about one minute.

(2) Finely divided polyethylene (one to 100 microns in greatest dimension) is intimately mixed with finely divided inorganic or organic blowing agents (0.2 to 100 microns in greatest dimension), such as sodium bicarbonate, ammonium carbonate, ammonium bicarbonate and/or a zobis isobutyronitrile, using 5 to 50 parts of blowing agent to 100 parts of polyethylene. The dry mixture is poured into a mold, the mold closed under moderate to high pressure, e.g., 10 to 500 p.s.i., and the mixture is foamed by heating at a temperature above the fusion point of the polyethylene and the decomposition point of the blowing agent, e.g., 140° to 170° C., for a period of time from 10 seconds to 2 minutes.

Centrifuged natural rubber latex of 60% solids preserved with ammonia was measured into lacquered shells to give liners having a shoulder thickness of (a) 19 mils and (b) 28 mils. The latex was evaporated to dryness in the shells at 70° C. Bottles of Canada Dry soda water were capped with these crowns and cycled as above. The bottles with caps containing 0.4 gram of latex, resulting in a liner weight of 0.24 gram (19 mils), all leaked badly, while bottles with the caps containing 0.6 gram of latex, resulting in a liner weight of 0.36 gram and a thickness of 28 mils, did not leak. Adhesion to the crowns was excellent. However, water absorption was quite high, due to the non-rubber solids present in the latex.

The distribution of the injected plastisol is an important feature of the present invention, as can now be appreciated. In some cases, the plastisol, after injection into the center area of the cap, does not spread radially and uniformly over the interior surface thereof in reaching out to meet the circumferential wall of said cap. The surface concavity of the cap (5½ in. radius) serves as a gravity barrier preventing complete lateral movement of the plastisol so that, in effect, the fluid deposit may be irregularly shaped and of gibbous definition which is influenced by the high speed forward travel of the shells in the machine. Under these conditions, after the cap has passed into the curing and molding dial, the plastisol, being controlled to an exact volume, frequently does not assume the full contour of the plunger, leaving a strip

void in the peripheral area of the cured liner on one side and squeezing upward by reason of localized excess into the fluted skirt on the side directly opposite thereto. Whenever this condition arises, the crowns must be scrapped.

To overcome these defects provision was made to cause the plastisol, while being injected into the cap at or near its center, to be centrifugally impelled toward the circumferential wall of said cap, uniformly of distribution being controlled by the speed of rotation, e.g., about 600 to 2000 r.p.m., preferably, 1000 r.p.m. The r.p.m. is preferably increased in proportion to the increase in viscosity. The spreading time required by this centrifugal distribution can be between about 0.05 and 0.2 second, and is dependent upon the speed of the liner-forming machine, i.e., the longer time being used with the slower speed of the machine. The complete fluid coverage over the entire interior horizontal surface of the cap facilitates and insures quality molding of the material at high speed. Scrap is virtually eliminated thereby.

Experience teaches that the greater the speed of operation, the more delicate the control must be. Control is commensurate with speed. In order, therefore, to make the operation practical and economical sound, the finest points of control are embodied in the plastic liner molding assembly unit. It is also preferably that the various steps in the process be incorporated into a single machine, for separate and distinct operations develop costs proportionately. The method of this application is, therefore, a continuous one embodying in sequence the several steps of manufacture in one composite unit.

As described above, partial or complete precuring of the plastisol before molding is advantageous. The injected plastisol, having been laterally dispersed in all directions over the concave interior surface of the cap, is subjected to radiant heat which impinges merely on the exposed plastisol surface thereby forming a tack-free surface film, leaving the under-portion still in a tacky condition. The exposure time to the radiant heat is between about 2 and 4 second, depending upon the speed of the machine. This procedure is necessary to offset any tendency of the material to stick to the molding punch and to permit low molding pressures. Pinpoint deposits, left on the molding punch, act as foci for further build-up of material. Since the thermal life for a vinyl chloride plastisol, for example, is extremely short, these deposits decompose on the punch and redeposit on subsequent liners during molding or adhere tenaciously thereto, resulting in said liners being forcibly pulled out of the shell when the punch is retracted at the ejector station.

An alternate method we have found for eliminating the above-mentioned sticking tendency, is to effect full cure of the plastisol in the cap under radiant heat prior to molding under heat and pressure. Full cure is attained in a few seconds, the speed of cure depending on the intensity of the heat source. Higher pressures, however, are usually required for molding a fully cured plastisol than is demanded for one that is but partially cured. After hot molding of the fully cured plastisol, adhesion thereof to the lacquered shell is of substantially the same order of magnitude as that after hot molding of the totally uncured or partially cured plastisol.

For purposes of illustration, the cap shells may be at room temperature but preferably are heated somewhat above room temperature to reduce viscosity of the plastisol when the latter is injected into the same. The plastisol is injected into the heated caps while the caps are rotating in their plane of travel and is centrifugally dispersed from the area of material introduction to extend circumferentially and engage the shell wall, thereby covering substantially the entire interior surface of the shell. The shells are rotated at a speed from 600 to 2000 r.p.m., which speed is variable and correlated with the viscosity of the plastisol, a preferred speed of rotation being about

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1000 r.p.m. The particular plastisol used had the following composition:

A

Exon 654 -----	56.00
Geon 202 -----	4.00
Diocetyl phthalate -----	40.00
Paraplex G-62 -----	3.00
Staybelite No. 10 (Glycerol ester of hydrogenated rosin) -----	3.00

The rotating of the shell to centrifugally distribute the plastisol as a coating on the interior of the shell will usually take from 0.05 to 0.2 second, depending upon the r.p.m. and viscosity of the plastisol, the higher the speed, the shorter the time period required to produce the liner. Thereupon the shell, with the liner therein, is heated, preferably by the use of any suitable radiant heating means, being exposed thereto from about 2 to 4 seconds, and until the temperature of the metal shell and the liner material reaches a temperature from about 150° to 275° F., preferably about 180° F. Thereupon, the liner, having a substantially tack-free surface produced by the aforesaid exposure to radiant heating, is subjected to a curing and molding under pressure, as above-described. Preferably, the curing and molding time will be from 6 to 12 seconds, and the pressure will vary from 5 to 150 p.s.i., depending upon the extent of the pre-curing, the curing and molding being conducted under a temperature of from about 325° to 380° F.

The following composition:

B

Exon 654 -----	56.00
Geon 202 -----	4.00
Diocetyl phthalate -----	50.00
G-62 -----	5.00
Staybelite No. 10 -----	5.00

was formed as a liner, as just above-described, except that the radiant heat was conducted to give the shell and liner material a temperature of 300° to 375° F., preferably 350° F., and the molding and curing time was less, namely, 4 to 10 seconds, since the radiant heating produced a substantially complete pre-curing. The pressure employed to form the liner varied from 150 to 350 p.s.i. and the temperature varied from 325° to 380° F.

In addition to the compositions above referred to, the following compositions were also operated with satisfactory results:

C

Vinylite QYNV (high molecular weight polyvinyl chloride) -----	56.00
Geon 202 -----	4.00
DOP-20 (dioctyl phthalate) -----	30.00
G-62 -----	3.00
Goodrite 261 -----	10.00

D

Geon 121 -----	60.00
DOP-20 -----	40.00
G-62 -----	3.00
Staybelite No. 10 -----	3.00

E

Geon 121 -----	60.00
Diocetyl phthalate -----	40.00
Calcium stearate -----	3.00
Staybelite No. 10 -----	3.00

Geon 202, as indicated previously in the specification, has a molecular weight much lower than that of Exon 654. The use of such a low molecular weight polyvinyl chloride, e.g., 50,000 or less, together with a higher molecular weight polyvinyl chloride, is especially advantageous as the lower molecular weight polymer aids in

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plasticizing the high molecular weight polymer, increases the shelf life of the plasticol, and improves the adhesion of the higher molecular weight polymer to the shell. This is true whether or not the shell has a lacquer coating on it.

We claim:

1. A container closure comprising a shell having a cushion liner comprising a foamed vinyl chloride polymer plastisol, including a mold lubricant in the liner.

2. The container closure of claim 1, including stearic acid as a mold lubricant.

3. A container closure comprising a shell having a cushion liner comprising a vinyl chloride polymer plastisol containing a plasticizer and including the glycerol ester of hydrogenated rosin to reduce migration of the plasticizer.

4. A container closure comprising a shell having a cushion liner including a high molecular weight vinyl chloride resin and a low molecular weight vinyl chloride resin in an amount sufficient to increase the adhesiveness of the composition to the shell.

5. A container closure comprising a shell having a cushion liner comprising a vinyl chloride polymer plastisol and also including a mold lubricant in the liner.

6. A container closure according to claim 5 wherein said cushion liner also includes a plasticizer and the glycerol ester of hydrogenated rosin to reduce migration of the plasticizer.

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