Jan. 2, 1968 A. W. KEHE 3,361,281

CLOSURES HAVING REMOVABLE LINERS AND TRANSFERABLE INDICIA PRINTED WITH PLASTISOL INK

Filed Oct. 15, 1964

Fig. 1

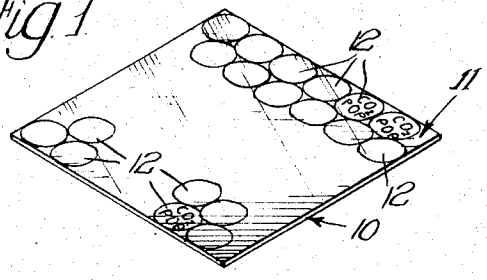


Fig. 2

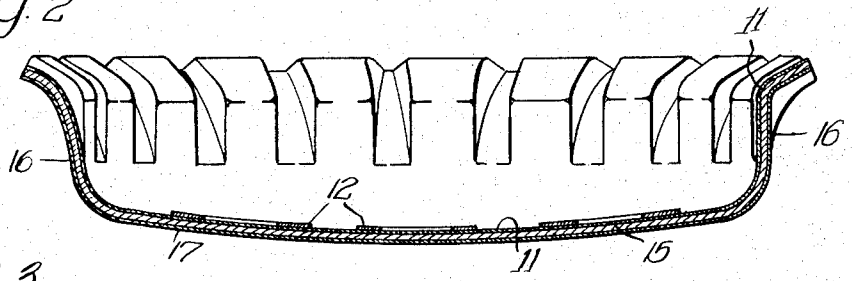


Fig. 3

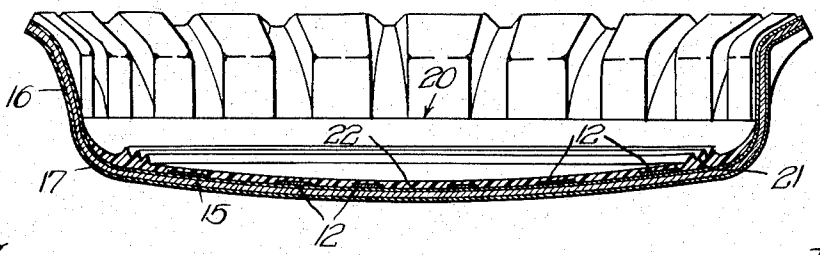


Fig. 4

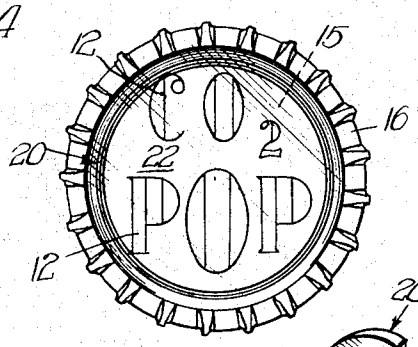


Fig. 5

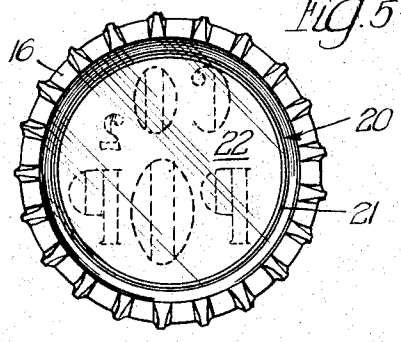


Fig. 6

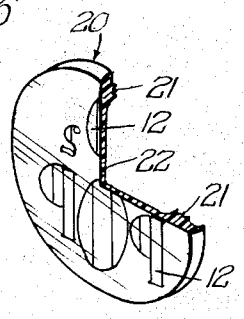
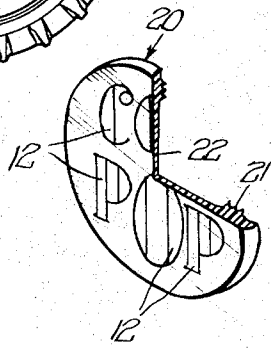


Fig. 7



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3,361,281

CLOSURES HAVING REMOVABLE LINERS AND TRANSFERABLE INDICIA PRINTED WITH PLASTISOL INK

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ABSTRACT OF THE DISCLOSURE

A plastisol-type printing ink adapted for high-speed indicia printing on a lacquered metal substrate, and for subsequent indicia transfer from the lacquered metal substrate to a removable fused plastisol liner, the ink consisting of (1) pigment, (2) a polyvinylchloride resin, (3) an epoxidized, unsaturated oil plasticizer, and (4) a methacrylate polymer tackifier.

This invention relates to printing inks for lacquered metal substrates, to methods of printing therewith, and to printed articles obtained thereby. More particularly, this invention is concerned with non-volatile homogeneous plastisol-type printing inks adapted for initial high speed indicia printing on lacquered metal substrates and for subsequent indicia transfer to fused vinyl chloride polymer plastisols.

It is sometimes desirable to provide printed metal substrates with a temporary protective elastomeric covering which is semi-adherent to and removable from the metal substrate and which, by its removal, will effect a transfer of the printed indicia from the face of the metal substrate to the surface of the elastomeric covering which has been in separable adherence with the metal substrate. A particularly useful application of such scheme of temporary indicia protection and subsequent indicia transfer can be found in the closure field. For example, in a metal crown closure having indicia printed on the internal face of its shell and containing a plastisol cushion sealing liner over the indicia, the liner, besides providing a seal when in engagement with the container lip, also acts as a protective covering to prevent the contents of the container from coming in contact with the ink substances forming the indicia. If the closure is made in such a manner so as to provide a low order of adhesion between the closure shell and the liner so that the two are in separable adherence, and further if the printing ink providing the indicia is selected so as to exhibit a higher degree of adhesion to the liner than to the closure shell, then the removal of the liner from the shell will effect a transfer of the printed indicia from the shell to the liner. Closures of this type, which are described in copending application Ser. No. 285,315, filed June 4, 1963, and issued as U.S. Patent No. 3,257,021, are useful in cases where the bottler or seller has a promotional campaign depending upon proof of use of a product, and also where attention to a complaint as to the product requires knowledge of lot number, date or other identification of the goods. In such cases, the liners with the indicia adhered to them can be readily peeled from the shells by the customer and shipped as thin flexible bodies which can be handled in ordinary envelopes. This overcomes the disadvantages of the former practice of shipping the entire closure assembly which is bulky and difficult to mail and which in the past has caused damage to mail cancelling machines when enclosed in ordinary envelopes.

In attempting to form structures of the type described above, one of the primary considerations is the proper selection of the printing ink for providing the indicia. A desirable printing ink for such purpose must be one which, in its cured state, exhibits adhesion to the metal substrate, either directly or through a primer coating on the metal, and also exhibits preferential adhesion to the protective elastomeric covering, which, in closure applications, is typically a fused vinyl chloride polymer plastisol. Moreover, the residual tack of the ink must be sufficiently slight so as to permit its ready separation with the protective elastomeric covering from the metal substrate. For economic reasons, the ink should be capable of being used in high speed offset lithography operations and should therefore have the proper body and tack necessary for adequate transfer properties on the printing rolls. Since a lithographic ink comes into intimate and continuous contact with water during printing, it also must have low water absorption properties. Furthermore, any additives present in the ink for providing any of the foregoing necessary properties should not impart any undesirable offcolor to the ink and should be compatible with the other components of the ink so as to insure indicia which has clarity, sharpness and uniformity. Additionally, if the metal substrate is to be primed with a lacquer, which is generally the case in closure applications in order to effect adhesion of the plastisol liner, the ink should be nonvolatile so as to prevent the possibility of attack of the lacquer primer by solvent vapors.

In prior attempts to formulate printing inks of this nature, the printing inks heretofore developed have been found to be lacking in one or more of the foregoing desired properties. Thus, for example, where the metal substrate has been primed with a lacquer and the protective elastomeric covering is a fused vinyl chloride polymer plastisol, which is the typical situation in closure applications, it has been found that a printing ink based on a vinyl chloride polymer plastisol vehicle has the proper degree of adhesion to both the lacquered metal substrate and the plastisol covering layer. However, the primary plasticizers conventionally used in formulating vinyl chloride polymer plastisols, such as the alkyl phthalates, the alkyl phthalyl alkyl glycolates, the dicarboxylic acid esters, the triaryl phosphates and the higher fatty acid esters, have all been found to have relatively poor pigment wetting properties and also to render the resulting ink deficient in roll transfer properties in the lithography operation because of excessively high vinyl resin solvation, excessively high water absorption and excessive pseudoplasticity. The only class of vinyl resin plasticizers found not to possess these defects is the epoxidized unsaturated oils, but even with these plasticizers, the ink does not exhibit the proper body and tack necessary for adequate roll transfer properties without the addition of a tackifier. Various tackifiers have been proposed, such as high molecular weight epoxy resins, rosin esters, cellulose acetate butyrate, low molecular weight styrenated hydrocarbons and several acrylic resins, but all of these have been objectionable because of incompatibility with the other ink components, undesirable color and/or excessive residual tack.

It is an object of this invention to provide a non-volatile homogeneous and compatible plastisol-type printing ink having acceptable color and being adapted for initial high speed indicia printing on lacquered metal substrates and for subsequent indicia transfer to fused vinyl chloride polymer plastisols.

Another object of this invention is to provide a lacquered metal substrate having clear, sharp, uniform, acceptably colored indicia economically printed thereon and overlaid with a continuous outermost layer of a fused vinyl chloride polymer plastisol which is semi-adherent to and removable from said lacquered metal substrate and which, by its removal from the lacquered metal sub-

strate, will effect a transfer of the printed indicia from the face of the lacquered metal substrate to the surface of the plastisol which has been in separable adherence with the lacquered metal substrate.

A further object of this invention is to provide an internally lacquered crown closure shell having clear, sharp, uniform, acceptably colored indicia economically printed on its lacquered internal face and further containing over the indicia a plastisol cushion sealing liner which is semi-adherent to and removable from the shell and which, by its removal from the shell, will effect a transfer of the printed indicia from the lacquered face of the shell to the surface of the liner which has been in separable adherence with the shell.

Other and additional objects of this invention will become apparent hereinafter.

The foregoing objects are achieved by means of the novel printing ink of the present invention which is non-volatile, homogeneous and compatible and which consists essentially of (A) pigment, (B) a vinyl chloride polymer, (C) as the sole plasticizer for said vinyl chloride polymer, an epoxidized unsaturated oil, and (D) a resinous tackifier selected from low to medium molecular weight homopolymers of either n-butyl methacrylate or isobutyl methacrylate or copolymers thereof with up to about 70 weight percent methyl methacrylate.

The vinyl chloride polymer components of the ink may be polyvinyl chloride or copolymers of vinyl chloride with a minor amount of copolymerizable ethylenically unsaturated material. Generally, the copolymerizable material is used in an amount of 20% or less and preferably 10% or less. As illustrative copolymerizable materials, there can be used vinyl acetate, vinylidene chloride, acrylonitrile, trichloroethylene, maleic anhydride, diethyl maleate, dibutyl maleate, and other alkyl maleates. The molecular weight of the polymer should be a minimum of about 50,000, and generally up to about 200,000. The polymer should be an emulsion type resin capable of forming a plastisol type dispersion, i.e., paste-forming with a normally liquid plasticizer at a temperature below the fluxing temperature of the resin-plasticizer mixture and capable, upon being heated to the fluxing temperature of the resin-plasticizer mixture, of forming a permanent rubbery gel. The particle size range of the resin is preferably very narrow with an average size of approximately 2 microns to insure proper rheology of the link. The emulsifier content of the polymer preferably should not exceed 1% methanol extractables and should exhibit a high degree of water resistance.

As the sole plasticizer for the vinyl chloride polymer in the ink, there is employed an epoxidized unsaturated oil, such as epoxidized linseed oil, epoxidized safflower oil or epoxidized soybean oil. These epoxidized oils have several oxirane groups in an internal open chain portion of the molecule and are substantially free of terminal oxirane groups. The oxirane group is introduced by well-known methods into the fatty alkyl portion of the unsaturated fatty alkyl molecule across carbon to carbon linkages formerly occupied by unsaturated bonds. For example, the oils may be epoxidized by any of the conventional methods involving percarboxylic acids. Epoxidized linseed oil has a maximum oxirane content of about 9%, epoxidized safflower oil about 7.5%, and epoxidized soybean oil about 7%. Because of their high oxirane contents, these epoxidized oils exhibit excellent compatibility with both the vinyl chloride polymer and the methacrylate polymer resinous tackifier, and also exhibit excellent pigment wetting properties which is highly desirable in inks which generally employ high pigment loadings. It is extremely important that the epoxidized unsaturated oils be used as the sole plasticizer for the vinyl chloride polymer in the ink, since, as explained above, the presence in the ink of conventional primary vinyl resin plasticizers renders the ink deficient in roll transfer properties in lithography operation because of excessively high vinyl resin solvation, excessively high water absorption and excessive pseudoplasticity, none of which defects are possessed by the epoxidized unsaturated oils.

The resinous tackifier employed in the ink is selected from a rather narrow group of methacrylate polymers which in addition to imparting the necessary amount of tack and body to the ink, are, at the same time, completely compatible with both the vinyl chloride polymer and the epoxidized unsaturated oil. Furthermore, their inherent water-white color imparts no undesirable offcolor to the ink. The limited class of polymers possessing these particularly desirable properties consists of low to medium molecular weight polymers of n-butyl methacrylate and isobutyl methacrylate, including their homopolymers and also copolymers of either one with up to about 70 weight percent methyl methacrylate. With anymore than about 70 weight percent methyl methacrylate, the polymer loses its compatibility with the epoxidized unsaturated oil plasticizer. The expression "low to medium molecular weight polymers," as used in the description of the invention and in the claims to describe the resinous tackifier, is meant to include polymers having an inherent viscosity within the range of from 0.20 to 0.38, measured with a No. 50 Cannon-Fenske viscometer at 20° C. in chloroform solution containing 0.25 gram of polymer per 50 ml. of chloroform.

In selecting the pigment to be employed in the ink, the use of large quantities of organic pigments is generally to be avoided. The reason for this is that the printing ink vehicle is highly thixotropic, and the use of organic pigments in large amounts tends to increase the thixotropic condition to the point where the transfer and flow properties of the ink are deleteriously affected. Thus the selection of pigments is confined principally to those of the inorganic type, such as molybdate orange, iron oxide, cadmium sulfide, chrome oxide and titanium dioxide. The use of organic pigments, such as carbon black, the phthalocyanines and the quinacridones, is permissible in minor amounts, e.g., up to about 10 weight percent of the total pigment content, for the purpose of providing proper color range modification.

Preferably, the ink contains a stabilizer for the vinyl chloride polymer. Vinyl chloride resin stabilizers, which improve the resistance of vinyl chloride resins to the deleterious effects of light, oxygen, heat and the like, are the so-called "acid acceptor" compounds which are capable of reacting with and neutralizing any hydrogen chloride which might split off from the vinyl chloride resin. Examples of stabilizers which can be employed are calcium stearate, zinc stearate, magnesium stearate, aluminum stearate, calcium ricinoleate, zinc ricinoleate, cadmium laurate, barium laurate, and other fatty acid soaps of these metals.

Suitable proportion ranges for the various components of the printing ink are illustrated in the following table:

Table 1

Component:	Parts by weight
Vinyl chloride polymer	60 to 80
Epoxidized unsaturated oil	70 to 100
Resinous tackifier	5 to 20
Pigment	50 to 70
Stabilizer	1 to 2

The printing ink of the present invention is preferably compounded by first forming a homogeneous solution of the resinous tackifier in the epoxidized unsaturated oil, then incorporating the pigment and milling the mixture to a homogeneous dispersion, and finally adding the vinyl chloride polymer, along with any stabilizers, and again milling the mixture to a homogeneous dispersion. The initial mixing of the resinous tackifier with the epoxidized unsaturated oil is carried out at elevated temperatures, preferably in excess of about 250° F. The resulting homogeneous solution is then allowed to cool to a temperature

below about 120° F. before adding the pigment. The pigment is added with suitable agitation to wet it down, and then the mixture is milled to a North Standard fineness of grind of about 5½ to 6. The final milling operation, after the vinyl chloride polymer addition, is carried out until the dispersion has a North Standard fineness of grind of about 6 to 7. This mixing procedure insures the formulation of a compatible and homogeneous printing ink.

The resulting printing ink can be applied to a lacquered metal substrate by silk screening, rotogravure, offset lithography, or other printing methods, and subsequently fused at temperatures of from 300 to 375° F. for a period of from 2 to 10 minutes. The metal substrate can be tinplate, steel, aluminum, iron, magnesium, nickel or any alloy thereof. The laquer employed should be one which, in its baked condition, exhibits separable adhesion to a fused vinyl chloride polymer plastisol outer layer. An example of a suitable lacquer for this purpose is a solvent solution containing a vinyl chloride-vinyl acetate-maleic anhydride interpolymer and also a phenolic resin modifier. Such a lacquer applied to metal and baked at 350° F. for 10 minutes provides good adhesion to a fused vinyl chloride polymer plastisol layer, but the adhesion of the plastisol is markedly reduced, to the point desired for the indicia transfer applications of the present invention, if the lacquer is over-baked on the metal substrate, e.g., at a temperature of about 400° F. for about 10 minutes.

The printed lacquered metal substrate, after cooling, is then overlaid with a vinyl chloride polymer plastisol and subsequently heated to a temperature of from 300 to 375° F. to completely fuse the plastisol into a continuous outermost layer which is adherent to the printed indicia and semi-adherent to and removable from the lacquered metal substrate. Useful plastisols for the outer layer comprise fine granules of a vinyl chloride polymer, such as polyvinyl chloride or copolymers of vinyl chloride with up to about 20 weight percent of a copolymerizable ethylenically unsaturated material such as vinyl acetate vinylidene chloride, maleic anhydride, dibutyl meleate, etc., said polymer granules being suspended in a conventional primary vinyl resin plasticizer such as an alkyl phthalate, an alkyl phthalyl alkyl glycolate, a dicarboxylic acid ester, a triaryl phosphate, a higher fatty acid ester, etc. The plastisol may be applied to the printed lacquered metal substrate by any suitable procedure designed to give a layer of the thickness and shape desired. For example, in closure applications, a measured quantity of plastisol is deposited in the formed shell over the printed lacquered internal face and then hot-molded to provide a cushion sealing liner in the shell.

To illustrate the manner in which the invention may be carried out, the following examples are given. It is to be understood that the examples are for the purpose of illustration and the invention is not to be regarded as limited to any of the specific compounds or conditions recited therein, except as defined in the appended claims. Unless otherwise specified, parts disclosed in the examples are parts by weight.

EXAMPLE I

15 parts of a low molecular weight copolymer of 70 weight percent methyl methacrylate and 30 weight percent n-butyl methacrylate was dissolved in 90 parts of an epoxidized linseed oil having an oxirane content of 9%, by heating the mixture in a stainless steel container at a temperature of approximately 280° F. with agitation until a homogeneous solution was obtained. The solution was then allowed to cool to about 120° F. A pigment consisting of 55 parts of molybdate orange and 2 parts of quinacridone violet was then added to the solution with stirring in order to wet down the pigment. The mixture was then passed through a water-cooled 3 roll-mill two times. The resulting homogeneous dispersion had a North Standard fineness of grind of 6. Thereafter, 65 parts of polyvinyl chloride and 1 part of a stabilizer consisting of a mixture of calcium and zinc stearates, were added simultaneously with stirring to the pigmented product which, in turn, was passed through a water-cooled 3 roll-mill an additional pass. The resulting homogeneous and compatible printing ink had a North Standard fineness of grind of 7.

EXAMPLE II

15 parts of a medium molecular weight homopolymer of isobutyl methacrylate was dissolved in 90 parts of an epoxidized soybean oil having an oxirane content of 7%, by heating the mixture in a Pyrex glass container at a temperature of approximately 280° F. with agitation until a homogeneous solution was obtained. The solution was then allowed to cool to about 120° F. A pigment consisting of 53 parts of chrome yellow and 4 parts of phthalocyanine blue was then added to the solution with stirring in order to wet down the pigment. The mixture was then passed through a water-cooled 3 roll-mill two times. The resulting homogeneous dispersion had a North Standard fineness of grind of 6. Thereafter, 65 parts of polyvinyl chloride and 1 part of a stabilizer consisting of a mixture of calcium and zinc sterates, were added simultaneously with stirring to the pigmented product which, in turn, was passed through a water-cooled 3 roll-mill an additional pass. The resulting homogeneous and compatible printing ink had a North Standard fineness of grind of 7.

EXAMPLE III

A sheet of tinplate was coated with a lacquer comprising an organic solvent solution of a vinyl chloride-vinyl acetate-maleic anhydride interpolymer containing a tung oil-modified phenol-formaldehyde resin, and subsequently baked at a temperature of about 400° F. for 10 minutes. The lacquered tinplate was then printed on an offset lithographic press with the printing ink of Example I and thereafter baked at 375° F. for 5 minutes to fuse the ink into clear, sharp and uniform indicia which was adherent to the lacquered tinplate. A vinyl chloride polymer plastisol, comprising polyvinyl chloride suspended in a dioctyl phthalate plasticizer, was then applied over the indicia-bearing face of the lacquered tinplate and baked at 375° F. for 5 minutes to completely fuse the plastisol into a continuous outer layer which was adherent to both the indicia and the lacquered tinplate. The outer plastisol layer could, however, be readily peeled from the lacquered tinplate. When the plastisol layer was removed from the lacquered tinplate in this manner, it was found that such removal effected a transfer of the printed indicia from the face of the lacquered tinplate to the surface of the plastisol layer which had been in separable adherence with the lacquered tinplate. The transferred indicia was clear, sharp and uniform, and was completely adherent to the plastisol surface.

Similar results were obtained when the above procedure was carried out employing the printing ink of Example II.

A specific embodiment of this invention, in closure applications, is illustrated in the accompanying drawings, in which:

FIGURE 1 is a perspective view showing how multiple patterns of indicia can be printed upon the sheet stock prior to the blanking and forming of the shells;

FIGURE 2 is a diametrical section view through a lacquered crown shell according to this invention;

FIGURE 3 is a like view, with a formed liner in the shell;

FIGURE 4 is a plan view into the open face of a crown shell as in FIG. 3, with a transparent liner in place;

FIGURE 5 is a plan view like FIGURE 4, with a liner present as in FIGURE 3, with an opaque liner;

FIGURE 6 is a perspective view of a transparent liner according to this invention, after removal from its shell, and with a sector cut away to show the thickness of the liner; and

FIGURE 7 is a like view of an opaque liner.

In the illustrative practice of the invention, a metal sheet **10**, FIG. 1, has an all-over lacquer coating **11** on its upper face, portions of which will provide the inner surfaces of the crown shells, and a plurality of printed indicia **12** are printed thereon; e.g. by use of a silk screen, by offset lithography, by rotogravure, or by other means. The other or bottom face of the sheet **10** can be printed for the indicia which are to appear on the other surface of the crown shells. It is preferred to apply the two lacquer or enamel coatings and then cure the same by baking before printing thereon; and to bake the sheet again to set the printed indicia. The printed sheet, after cooling, can be punched into crown sheets and then made into caps as shown is FIGURES 2–5.

The individual areas of FIG. 1 provide shells as in FIGS. 2 and 4, with the metal shell having a bottom or dome **15** and the corrugated skirt **16**. The internal lacquer layer **11** covers the metal, and has local cured applications **12** of ink constituting the indicia .The outer enamel is a layer **17**. The shells are then provided with liners or cushions **20** as in FIGURES 3, 6 and 7, which may have a thicker annular portion **21** for engagement with the container lip and a thin central portion **22**. Such liners may be formed by depositing a measured quantity of plastisol in the shell and forming the same by shaping punch while heating to cure or effect inter-dissolution of the plasicizer liquid and the resin particles into one another. Useful plastisols comprise fine granules of polyvinyl chloride suspended in a plasticizer such as diotyl phthalate: such plastisol is a viscous liquid or paste at room temperature and up to about 110° F., but quickly fuses at an elevated temperature such as 325 to 375° F. Such a plastisol can form a transparent elastic cushion upon curing and therewith the indicia **12** will be visible therethrough; and the appearance of the indicia, upon looking into the closure cap, will remain as shown in FIG. 4. When the plastisol contains a coloring or opaqing agent so that the indicia are not visible therethrough as in FIG. 4, it is preferred to print the indicia in reverse, as shown in FIG. 5. In each case, the cured plastisol forming the exposed surface of the liner **22** acts to prevent contents of the container from coming in contact with the ink substances forming the indicia **12**. When the liner **22** is of transparent material, and is removed, the lettering etc. appears in reverse when viewed from the back, that is, at the surface which has been in separable adherence with the metal shell; such is shown in FIG. 6, and it will be understood that when viewed from the opposite side, the indicia are clearly visible in normal order. When an opaque liner **22** is provided, over indicia printed in reverse as in FIG. 5, the removed liner has the indicia readable in normal order, as shown in FIG. 7. In each instance, the customer and the company employees can read the indicia without difficulty.

Such crown closures may be applied to and their corrugated skirts crimped upon containers in the usual way. The liner with the indicia adhering to it can be readily peeled from the lacquered shell so that the liner is identified.

When proof of the consumer's acquisition or use of the contents is required, the liner **20** can be peeled from the shell as an integral article having the indicia at the face thereof which was in contact with the lacquer. Such a removed cushion or liner is shown in FIGURE 6, where a sector has been cut away to show the section of the article: noting that in practice the diameter can be about one inch, the center thickness 2 to 10 mils, and the thickness at the annulus **20** around 30 to 40 mils. Such an article is highly flexible, and approximately of the thickness of a cardboard which can be mailed in an ordinary envelope without the aforesaid difficulties.

With the employment of transparent liner materials, the preference is to have letters and numbers appear in normal arrangement for viewing through the liner, as shown in FIGURE 4: and hence in reversed arrangement when the bottom of the liner is viewed as in FIGURE 6. This is not compulsory; and with opaque liner materials, it is preferred to print in reverse upon the interal lacquer coating as shown by dotted lines in FIGURE 5, so that the letters etc. appear for direct reading on the bottom of the liner when removed from the shell, as in FIGURE 7.

Although the invention has been illustrated by a specific embodiment in closure applications, it is to be understood that such illustrative embodiment is not restrictive, and that the invention can be employed in many ways within the scope of the appended claims.

I claim:

1. A lacquered metal substrate having indicia printed thereon and overlaid with a continuous outermost layer of a fused vinyl chloride polymer plastisol which is semi-adherent to and removable from said lacquered metal substrate, said indicia being disposed between the lacquer and the outermost plastisol layer and adherent to both of the same but capable of exhibiting preferential adhesion to said outermost plastisol layer when the latter may be peeled from said lacquered metal substrate, said indicia being provided by a fused plastisol-type printing ink consisting essentially of (A) about 50 to 70 parts by weight pigment, (B) about 60 to 80 parts by weight of a vinyl chloride polymer having a molecular weight of at least 50,000, (C) as the sole plasticizer for said vinyl chloride polymer about 70 to 100 parts by weight of an epoxidized unsaturated fatty oil, and (D) about 5 to 20 parts by weight of a resinous tackifier consisting of a low to medium molecular weight polymer of from about 70 to 0 weight percent methyl methacrylate and from about 30 to 100 weight percent of a methacrylate monomer selected from the group consisting of n-butyl methacrylate and isobutyl methacrylate.

2. The plastisol-overlaid printed lacquered metal substrate of claim **1** wherein the epoxidized unsaturated oil of the printing ink is selected from the group consisting of epoxidized linseed oil, epoxidized safflower oil and epoxidized soybean oil.

3. The plastisol-overlaid printed lacquered metal substrate o f claim **2** wherein the resinous tackifier of the printing ink is an isobutyl methacrylate homopolymer.

4. The plastisol-overlaid printed lacquered metal substrate of claim **3** wherein the epoxidized unsaturated oil is epoxidized soybean oil.

5. The plastisol-overlaid printed lacquered metal substrate of claim **2** wherein the resinous tackifier of the printing ink is a copolymer of 70 weight percent methyl methacrylate and 30 weight percent n-butyl methacrylate.

6. The plastisol-overlaid printed lacquered metal substrate of claim **5** wherein the epoxidized unsaturated oil is epoxidized linseed oil.

7. The plastisol-overlaid printed lacquered metal substrate of claim **1** wherein the lacquered metal substrate is an internally lacquered crown closure shell, and the outermost plastisol layer is a cushion sealing liner within the shell.

8. The crown closure described in claim **7** wherein the plastisol liner is transparent so that the indicia may be viewed therethrough.

9. The method of forming the plastisol-overlaid printed lacquered metal substrate of claim **1** which comprises the steps of (1) applying a lacquer to one face of a metal substrate and then overbaking the same, (2) providing indicia on the lacquered metal substrate by printing thereon with a non-volatile homogeneous and compatible plastisol-type printing ink and thereafter heating to completely fuse the same, said printing ink consisting essentially of (A) about 50 to 70 parts by weight pigment, (B) about 60 to 80 parts by weight of a vinyl chloride polymer having a molecular weight of at least 50,000 and an average particle size of approximately 2 microns, (C) as the sole plasticizer for said vinyl chloride polymer about 70 to 100 parts by weight of an epoxidized unsaturated fatty oil,

(D) about 5 to 20 parts by weight of a resinous tackifier consisting of a low to medium molecular weight polymer of from about 70 to 0 weight percent methyl methacrylate and from about 30 to 100 weight percent of a methacrylate monomer selected from the group consisting of n-butyl methacrylate and isobutyl methacrylate, and (3) applying a vinyl chloride polymer plastisol over the printed lacquered metal substrate and thereafter heating to completely fuse the same into a continuous outermost layer which is adherent to said indicia and semi-adherent to and removable from said lacquered metal substrate.

10. The method of claim **9** wherein the epoxized unsaturated oil of the printing ink is selected from the group consisting of epoxidized linseed oil, epoxidized safflower oil and epoxidized soybean oil.

11. The method of claim **10** wherein the resinous tackifier of the printing ink is an isobutyl methacrylate homopolymer.

12. The method of claim **11** wherein the epoxidized unsatruated oil is epoxidized soybean oil.

13. The method of claim **10** wherein the resinous tackifier of the printing ink is a copolymer of 70 weight percent methyl methacrylate and 30 weight percent n-butyl methacrylate.

14. The method of claim **13** wherein the epoxidized unsaturated oil is epoxidized linseed oil.

15. The method of making the crown closure described in claim **7** which comprises the steps of (1) applying a lacquer to one face of a metal sheet and then overbaking the same, (2) providing indicia on the lacquered face of the sheet by printing thereon with a non-volatile homogeneous and compatible plastisol-type printing ink and thereafter heating to completely fuse the same, said printing ink consisting essentially of (A) about 50 to 70 parts by weight pigment, (B) about 60 to 80 parts by weight of a vinyl chloride polymer having a molecular weight of at least 50,000 and an average particle size of approximately 2 microns, (C) as the sole plasticizer for said vinyl chloride polymer about 70 to 100 parts by weight of an epoxidized unsaturated fatty oil, and (D) about 5 to 20 parts by weight of a resinous tackifier consisting of a low to medium molecular weight polymer of from about 70 to 0 weight percent methyl methacrylate and from about 30 to 100 weight percent of a methacrylate monomer selected from the group consisting of n-butyl methacrylate and isobutyl methacrylate, (3) forming the sheet into a crown shell with the printed lacquered face inside the same, and (4) depositing a vinyl chloride polymer plastisol in the shell and molding under pressure and heat to completely fuse and shape the same into a cushion sealing liner which is adherent to said indicia and semi-adherent to and removable from the shell.

16. A non-volatile homogenous and compatible plastisol-type printing ink adapted for initial high speed indicia printing on a lacquered metal substrate and subsequent indicia transfer to a fused vinyl chloride polymer plastisol, said printing ink consisting essentially of (A) about 50 to 70 parts by weight pigment, (B) about 60 to 80 parts by weight of a vinyl chloride polymer having a molecular weight of at least 50,000 and an average particle size of approximately two microns, (C) as the sole plasticizer for said vinyl chloride polymer about 70 to 100 parts by weight of an epoxidized unsaturated fatty oil and (D) about 5 to 20 parts by weight of a resinous tackifier consisting of a low to medium molecular weight polymer of from about 70 to 0 weight percent methyl methacrylate and from about 30 to 100 weight percent of a methacrylate monomer selected from the group consisting of n-butyl methacrylate and isobutyl methacrylate.

17. The printing ink of claim **16** wherein the epoxidized unsaturated oil is selected from the group consisting of epoxidized linseed oil, epoxidized safflower oil and epoxidized soybean oil.

18. The printing ink of claim **17** wherein the resinous tackifier is an isobutyl methacrylate homopolymer.

19. The printing ink of claim **18** wherein the epoxidized unsaturated oil is epoxidized soybean oil.

20. The printing ink of claim **17** wherein the resinous tackifier is a copolymer of 70 weight percent methyl methacrylate and 30 weight percent n-butyl methacrylate.

21. The printing ink of claim **20** wherein the epoxidized unsaturated oil is epoxidized linseed oil.

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