Foods such as vegetables, fruits and soups have been packed in steel or tinplate containers for many years. These containers have been made by the so-called three-piece metal can technology. That is to say, the containers are
In support of the \((\text{b})\) application made by

\[78290/81\]

(hereinafter called "applicant(s) for a patent \((c)\) for an invention entitled \((d)\) DRAWABLE SULFUR RESISTANT METAL COATING

\(\text{I/We } (e)\) Robert P. Auber, Director, Patent and Trademark Department of American Can Company, American Lane Greenwich, Connecticut 06830 United States of America

do solemnly and sincerely declare as follows:

1. Applicant(s) \(\text{are the applicant(s). (or, in the case of an application by a body corporate)}\)

2. \(\text{Robert P. Auber, Director, Patent and Trademark Department of American Can Company, American Lane Greenwich, Connecticut 06830 United States of America do solemnly and sincerely declare as follows:}\)

2. Kenneth E. Carlson of 669 Timothy Lane, Des Plains, Illinois, United States of America; Richard J. Karas 216 Baynard Road, Addison, Illinois United States of America; Kenneth R. Rentmeester, 736 S. Highland Avenue Barrington, Illinois United States of America and P.T.O. are the actual inventor(s) of the invention and the facts upon which the applicant(s) are entitled to make the application are as follows:

\(\text{Applicants are the assignees of the invention from the said actual inventors.}\)

\(\text{Note: Paragraphs 3 and 4 apply only to Convention applications}\)

3. The basic application(s) for patent or similar protection on which the application is based is/are identified by country, filing date, and basic applicant(s) as follows:

\(\text{AMERICAN CAN COMPANY}\)

United States of America
February 2, 1981
KENNETH E. CARLSON, RICHARD J. KARAS, KENNETH R. RENTMEESTER AND ROBERT C. STRAND

4. The basic application(s) referred to in paragraph 3 hereof was/were the first application(s) made in a Convention country in respect of the invention the subject of the application.

\(\text{AMERICAN CAN COMPANY}\)

Declared at \((k)\) GREENWICH, CONN

Dated \((l)\) Nov 10, 1981

To: The Commissioner of Patents

Robert P. Auber, Director
Patent & Trademark Department

PHILLIPS ORMONDE & FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne, Australia
A precoat for a metal blank which can be formed by multiple drawing into a container having said precoat on the inside surface and said precoating comprising a phenolic resin, an epoxy resin, a polyvinyl chloride acetate co-polymer and a polyvinyl chloride dispersion resin in a solvent system having saturated solvents such that low molecular weight sulfides such as sulfur containing compounds cannot react to form additional products.

2. The precoating system of claim 1 wherein said polyvinyl chloride dispersion resins is about 43% by weight of all the nonvolatiles and all other said resins are about 30% by weight of all the nonvolatiles and the rest is pigment.

3. The precoating system of claim 2 wherein said pigment is titanium dioxide.
The following statement is a full description of this invention, including the best method of performing it known to applicant(s):

DRAWABLE SULFUR RESISTANT METAL COATING

degraded due to temperatures resulting during forming but will allow passive reflow. The glass transition temperature cannot be so high that the coating will not be pliable and...
Foods such as vegetables, fruits and soups have been packed in steel or tinplate containers for many years. These containers have been made by the so-called three-piece metal can technology. That is to say, the containers are fashioned by forming a body cylinder from flat metal stock and joining the abutting edges by soldering or welding. The body cylinder is then flanged and a bottom end affixed by the process known as double seaming. The remaining end if affixed by the packer after the container is filled.

The three-piece metal containers can have protective enamels coated on them to prevent corrosion of the container particularly containers made from tin free steel (TFS). Cans are also made from tin coated steel and these may or may not have protective enamels applied to them depending on the type of food product that is to be packed.

The protective enamels used in metal cans are carefully selected to provide the required corrosion resistance and in addition contribute no flavor characteristics to the food product. Enamels that are typically used include phenolic resins, epoxide resins, amine type resins, oleoresinous materials such as China wood oil and vinyl type resins such as polyvinyl chloride or vinyl chloride vinyl acetate co-polymers. These are formulated in specific solvent mixtures such as ketones, esters, alcohols and aromatic or aliphatic hydrocarbons for ease and speed of application. The enamels are applied by well known techniques such as roller coating or spray coating. The coatings are usually of the thermosetting type and are reacted or cured in standard baking ovens.

The coatings applied to three-piece containers are not subjected to any extensive mechanical deformation in the can making process. For this reason the type of enamels for three-piece containers can be formulated from a broad range of resinous components such that when baked in an oven they cure to highly cross-linked structures. This cross-linking allows a maximum degree of corrosion prevention and chemical resistance to be achieved thus affording protection for the food product packaged in the cans.

In making two-piece metal containers by the drawing

Examples of these kinds of foods are kidney beans or whole kernel corn. Frequently, a coating is formulated in a
and redrawing of flat metal blanks, different criteria must be applied to the selection of enamels. For reasons of economy, it is preferred that the metal be precoated with the enamel and the precoated blank be then formed into the container by forming the blank in a suitable die. The forming operation places severe and extensive mechanical stresses on the enamel with respect to its adhesion to the metal substrate testing its extensibility or ability to flow without fracturing. For this reason, enamels for drawn cans are difficult to formulate and attention to the blends of resins and solvents used is required so that on baking they form strongly adhering films with the proper degree of cross-linking to provide good corrosion and chemical resistance but retaining a higher level of flexibility than comparable three-piece can enamels in order to go through the forming operation without fracturing.

To properly control the cross-linking in these drawn can enamels, cross-linking resins may be adjusted or baking temperatures may be slightly lower than those used for three-piece can enamels. The resultant effect is to produce enamel coatings which are somewhat more soluble in organic solvents after baking than their three-piece can enamel counterparts. That is to say, the drawn can enamels can retain small (ppm) quantities of some solvents after the baking steps. These solvents residues can then be released after the can is packed and cause undesirable flavor properties in the food product. Sometimes the solvent is relatively innocuous if it is present inside the packed can. A solvent by itself may be relatively innocuous but it can react with the food product to produce highly objectionable flavor characteristics.

Metal containers made by multiple drawing of precoated tin free steel can be coated with various types of thermosetting organic coatings formulated with phenolic resins, epoxy resins, acrylic resins amine type resins, polyvinyl chloride resins and co-polymers thereof, polyester resins. The inside and the outside of each sheet of plate or blank is coated; the inside is that which becomes the inside of the container and the outside is the outside.
In the manufacture of 3-piece food or meat containers, sheet plate, either tin free steel or electrolytic tin plate, is coated in a separate coating operation. Since three-piece food cans may require coating on both the inside and outside surfaces several passes are usually required to provide adequate corrosion protection for the finished can. For example, the outside coating is put on in one pass and the inside coating which may consist of one or two coats requires a separate operation for each inside coating. As a result three passes through a coater can be required to manufacture 3-piece can stock. The coated plate must then be slit into body blanks in an operation following the slitting operation. The body blanks must be transferred to a body maker where the cylindrical shape is formed and either soldered or welded at the side seam. In a final operation, a can end is doubleseamed on a bottom of a body cylinder. These numerous operations add considerable time and cost to the manufacture of 3-piece containers.

Food containers made by the newer 2-piece process of multiple drawing from precoated plate offers considerable cost savings in that a number of the previously described 3-piece manufacturing operations are either consolidated or eliminated. The metal stock for forming 2-piece containers in a multiple drawing process can be coil coated. In this kind of coating operation, both the inside and the outside coating can be applied to the can making metal in a single operation thus offering manufacturing economy.

Multiple drawn cans can be made from either tin free steel or electrolytic tinplate. For reasons of economy, most containers are manufactured from tin free steel. The tin free steel can be of any number of plate thicknesses, but, the usually preferred material is 75# per base box, T-4, continuously cast stock or 65# DR9. A base box is a can maker's measure of 31,360 square inches of surface (on one side) for a given weight of metal. T-4 and DR9 are steel mill designations for the hardness of the material and by inference the rolling process used to make the sheet.

In forming cans by multiple drawing operations from precoated stock, careful selection of the organic coating materials is required. Since the stock is precoated, the can
forming operation subjects the coating to the same mechanical stretching and forming operations that the metal is subjected to. This requires that the coating have good adhesion to the metal substrate and possess the necessary mechanical properties to withstand stretching and forming without fracturing it from or forcibly removing it from the substrate metal.

In comparison with 3-piece technology, the multiple drawn containers have an integral bottom and no side seam. This offers manufacturing economies in that the side seam soldering or welding operation is eliminated, side seam stripe coating is eliminated and bottom end doubleseaming is eliminated. In addition, the drawn can process operates in a continuous manner. That is to say that, precoated sheet is fed to a multiple forming press. Finished shells leave the press passing in a continuous manner through a flanger, beader and air tester and are finally palletized. The continuous nature of the multiple forming operation eliminates considerable labor within the manufacturing process thus affording additional economies.

The severe mechanical forces imposed on the coating during multiple drawing operations would suggest rubbery or highly flexible polymeric materials should be more suitable for precoated multiple drawn containers. While rubbery materials may stretch adequately during forming multiple drawn containers their chemical resistance and adhesion properties are generally inferior to thermosetting coatings. Consequently, there is the paradox of flexibility necessary for multiple forming operations working against the chemical protection necessary to protect the metal from the food packed in the container. Another problem with rubber is the flavor characteristics imparted by the vulcanizing chemicals can be absorbed by the food stuffs packed in metal containers which have been precoated with rubbers. For this reason, these materials cannot be used in metal container coatings.

Coatings having good flux properties when applied to the metal surface can provide an essentially eye-hole, blister free or continuous covering over the metal. This is particularly important when packing food stuffs because any uncoated portions of the can will serve as sites for corrosion.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A precoat for a metal blank which can be formed...
can nearest the flange since it is well known that the maximum metal working in terms of axial stretching and circumferential compression occurs about the flange area. A frequently used method to test the coverage of the coating over the metal is the enamel rater or quick test. This test is carried out with a special testing instrument and essentially measures the electrical conductivity of the interior of the can when it is filled with an electrolyte.

In order to perform a quick test a specified piece of equipment is required. More particularly, a Model 1071 WACO Enamel Rater with a 0 to 1 milliamp attachment is used. The apparatus has an electrode which is adapted to move vertically in and out along the axis of a can positioned beneath it. The electrode is positioned about 1" from the bottom of the can. The can is held in position by a vise-like device which clamps it about the bottom holding it so that the open end of the can faces up toward the electrode. The can is filled with 2% solution of sodium sulfate and allowed to soak for at least 30 seconds before the electrode is dropped into the can. The solution temperature should be maintained between 72 to 78°F, and the can should be filled so that when the electrode is lowered into the test position the solution will reach approximately 1/8" below the top flange radius of the can. Care should be taken to avoid wetting the flange since that will result in a false high reading. The milliamp meter of the tester is connected to the vise-like device which holds the bottom of the can. The electrode is connected to another lead of the milliamp meter. A zeroing of the instrument is required and the operator adjusts the milliamp to read "0" on the scale. Shortly after zeroing the meter a warning light comes on and the reading should be taken immediately. When this procedure was applied to properly precoated cans readings in the range of 0 to 8 milliamps should be obtained and such data is indicative of an acceptable container.

Consequently, a coating system for a metal substrate which will withstand the severity of multiple forming operation
without destruction has been sought. A coating system which functions to protect the metal substrate and prevent corrosion and off flavor is the thrust of this invention.

It is an object of this invention to provide a means of fabricating by multiple draws an essentially flavor free enamel coated metal can.

It is a further object of this invention to fabricate such a drawn can from precoated sheet metal such as tin free steel (TFS) or tin coated steel (ETP).

Another object of this invention is to provide the coating system which functions to protect the metal substrate and prevent corrosion and off flavor is the thrust of this invention.

It is an object of this invention to provide a means of fabricating by multiple draws an essentially flavor free enamel coated metal can.

It is a further object of this invention to fabricate such a drawn can from precoated sheet metal such as tin free steel (TFS) or tin coated steel (ETP).

Another object of this invention is to provide the most economical coating process for the sheet metal by using coatings formulated so as to be applied by direct roll coating or reverse roll coating.

Still another object of this invention is to provide an intermediate thermosetting coating formulation that has the proper solvent release properties to allow application to the sheet metal by the lower temperature sheet coating process or the higher temperature coil coating process.

Another object of this invention is to describe a precoatable resinous coating mixture that provides a good corrosion barrier for the metal can when it is packed with a variety of different food products.

A further object of this invention is to describe a resinous coating mixture that will withstand the mechanical stretching and deformation of the multiple drawing process without fracturing or loss of adhesion.

Still another object of this invention is to provide a solvent system for the enamel that incorporates the desirable properties of coating application to the sheet metal yet contains no chemicals that confer undesirable flavor characteristics to the food product or that contains solvents which can react with chemical products such as hydrogen sulfide given off by the food product, such chemical reaction products forming unpalatable or noxious by-products in the food.

A final object of the invention is to describe a resinous enamel and solvent mixture that incorporates the desired application properties to the sheet metal and releases essentially all of the solvent during the baking process so that when the precoated metal is exposed to passive reheating during the multiple drawing operation residual traces of solvent would plasticize the enamel and off flavor would be imparted to the can.

It is the object of the present invention to provide a metal can which can be fabricated by multiple draws from precoated metal sheet such as tin free steel (TFS) or tin coated steel (ETP) and which can be effectively coated with a high solvent release properties to allow application by direct roll coating or reverse roll coating.

Another object of the invention is to provide a precoatable resinous coating mixture that provides a good corrosion barrier for the metal can when it is packed with a variety of different food products.

A further object of this invention is to describe a resinous coating mixture that will withstand the mechanical stretching and deformation of the multiple drawing process without fracturing or loss of adhesion.

Still another object of this invention is to provide a solvent system for the enamel that incorporates the desirable properties of coating application to the sheet metal yet contains no chemicals that confer undesirable flavor characteristics to the food product or that contains solvents which can react with chemical products such as hydrogen sulfide given off by the food product, such chemical reaction products forming unpalatable or noxious by-products in the food.

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solvent or other small molecules from catalyst residues or plasticizers are not outgassed by the enamel to contribute off flavors to the packed food product.

To overcome problems in the prior art of can manufacturing and in accordance with obtaining the desired objects of this invention, the present disclosure provides a unique combination of materials which operate to permit precoated stock to be multiply drawn into a useful and successful finished container.

Because of the mechanical stretching and forming operations used in manufacturing multiple drawn containers, the coatings on the metal substrate require unique properties. A system of inside and outside coatings is required that is compatible with the multiple drawing process. An outside coating is applied by roller coating or coil coating and cured in an oven. For sheet coating operations, this coating is baked in a temperature range of 300 to 400°F for about 6 to 10 minutes. It is usually applied to the metal substrate at a film weight of 8 to 15 mg per 4 square inches of plate area. This coating can be of several chemical types such as vinyl organosol, an epoxy resin, an amine resin, a phenolic resin or suitably formulated blends of these resins. The outside coating is generally applied at lower film weights than the inside coating for reasons of economy and less severe corrosion requirements.

The inside coating is generally applied at a film weight of 15 to 35 mg per 4 square inches of plate area. The coating can be either sheet coated or coil coated. A baking temperature of 300 to 400°F for 8 to 10 minutes is generally used in sheet coating. In addition, sheet coatings can be applied in more than one pass. For example with a single drawn container, a base coating such as an epoxy type can be applied first. In a second pass, a different chemical type of coating can be applied such as an oleoresinous enamel. This kind of versatility allows the can maker to apply the best inside enamel system with regard to adhesion to the metal and corrosion resistance to the packed food product.

The inside coating can also be applied to the metal substrate by coil coating. In coil coating, both the inside
and outside coating are applied at the same time. This process offers economies of manufacture because the entire coating operation is carried out in one pass. Baking temperatures in coil coating are in the range of 500 to 600°F for about 20 seconds, just enough time to remove every last trace of solvent as either the inner or outer coating has about 75% solvent in its formulation.

Because of the severe mechanical deformation the multiply drawn can coatings are subjected to, they will have special requirements for adhesion and mechanical strength. Preferred inside coatings for multiply drawn cans are the organosol type. These coatings contain mixtures of phenolic resin, epoxy resin, vinyl solution resins of the vinyl acetate-vinyl chloride copolymer type and high molecular weight polyvinyl chloride dispersion resins. The molecular weight range of the polyvinyl chloride has been found to be a critical aspect in making successful multiple draw inside coatings. If the resin is not above a certain molecular weight, the coating exhibits adhesion loss or fracturing about the top third of the can during the drawing operation resulting in unsatisfactory packed container performance. It has been found that a weight average molecular weight greater than 110,000 is required with a preferred molecular weight greater than 150,000. The molecular weight is defined by measurements made on a gel permeation chromatograph using polystyrene gel packings of known pore diameter.

The mechanical working of the precoated metal in the dies of the press causes a rise in temperature in the metal container as it is formed. Temperatures in the press tooling and consequently in the can rise to 150°F in the first redraw station but can go as high as 200°F in the second redraw station. The increased temperature softens the coating on the can causing the coating to reflow. The range of Tg of the coatings is important. A Tg is required that is neither too high so as to cause brittle coating fracture nor so low that softening and coating breakthrough occurs. Heating occurs passively in the forming operation and more with the severity of the process of multiple drawing. The beneficial effects of heating on coating performance have been shown in prior U.S. Patent #3,206,848. Coating reflow is evident by the
increased gloss on the outside coating during drawing. This is due to the higher temperatures and pressures.

Lubrication applied to the coating is another critical aspect for forming multiple drawn containers. The lubricant provides the needed slip properties when precoated plate is formed in the press tooling. Without proper lubrication, the coatings will be scraped off by the press tools resulting in unsatisfactory containers and possible damage to the tools and dies in the press. Lubricants such as Boler wax, lanolin or petrolatum can be used. For multiply drawn containers, petrolatum is the best with regard to tool lubrication and good flavor performance. The lubricant is applied by spraying from standard spray guns or fogging over the coated plate by special electrostatic waxing machines.

The integrity properties of the coatings are important not only from a corrosion resistance standpoint but also from a flavor characteristic viewpoint. That is to say, residual solvents or small molecules that are present in the film because of incomplete elimination during the coating bake operation must be minimized as they impart undesirable flavor characteristics to the food product. Particularly, in connection with a drawn can where the process will squeeze residual solvent from the coating. Materials and solvents left in the coatings must be chosen so as to eliminate off-flavor properties but, in addition, they must be selected to have the right amount of cross linking and to avoid interaction with small molecules which emanate from the food product through secondary reactions with solvent residues to form undesirable off-flavor properties.

A well known property of food products such as peas, corn, beans, etc., is the liberation of small molecules such as cystine and hydrogen sulfide after packing. These chemical compounds arise from the breakdown of proteins in the food and they can react with the residual solvents and oligomers in the coating film to form reactive products which introduce undesirable flavor properties in the food product. More particularly, the flavor characteristic from the reaction of mesityl oxide, a contaminant in certain coating solvents...
such as diacetone alcohol, with hydrogen sulfide can give rise to a catty odor. The reaction product, 4-methylmercaptoketone, has been identified with off-flavor properties in certain canned meat and vegetable products. This mercapto ketone has been associated with a catty off-flavor. Therefore, elimination of mesityl oxide, for example, from the coating systems of drawn food cans is highly important in maintaining the desired flavor free properties in these containers.

In the drawings Fig. 1 is a partial side cross-sectional view showing a container drawn from precoated metal stock. 2- Fig. 2 is a sectional view taken along lines 2-2 in Fig. 1. Fig. 3 is a partial side cross-sectional view of a container side wall and bottom doubleseamed end as fabricated by rolling a flat blank of material into a hollow cylinder with a welded side seam and then flanging the cylinder and doubleseaming a flat circular end thereto; and Fig. 4 is a cross-sectional view taken along lines 2-2 in Fig. 3 and showing in particular the section through the side seam shown in Fig. 3.

In Figs. 1 through 4 the contrast of the 2-piece container formed by multiply drawing precoated metal stock with the 3-piece container formed by rolling and side seaming container system and, in particular, in Fig. 1 the multiply drawn can 10 has the precoated inside 11 and outside 12 layers which adhere to the base metal 13 of the free steel or electrolytically deposited tin plate. Now insulating the forming operation required to draw the flat precoated material into a cup shape having a diameter which is usually less than its height, in contrast, the 3-piece container 14, shown in Fig. 3, is precoated with two inside 15 and 16 and one outside coating 17. This container is formed from material 18 cut into blanks which can be rolled onto a hollow cylindrical container and side seamed along its meeting longitudinal edges by means of welding (as in Figs. 3 and 4),
bonding or can seaming and soldering. Notwithstanding the side seam technique selected it is necessary to repair coat and cure the inside with a stripe 20 of side seam coating material to prevent the subsequently packed comestibles from attacking the side seam or the adjacent metal. It is required that an end 21 be doubleseamed 22 onto the hollow cylindrical container and consequently sealing compound 23 must be used to hermetically seal that end. The additional side seam stripe 20 and doubleseaming of the bottom end 21 would be an expense to the manufacturer of the 3-piece container as compared to the multiply drawn 2-piece container. For many applications, the outside of the container at the side seam 24 must also be protectively coated and cured. It can be appreciated that the proper coating systems for the inside 11 and outside 12 of a multiply drawn 2-piece containers are essential to achieving a safe and low cost container which will not corrode or affect the flavor of the comestibles packed therein.

The preferred outside coating 12 is primarily an epoxy resin and a slight amount lubricant in combination applied as explained with a film weight of 9 to 12 mg per 4 square inches. The particular epoxy coating is Mobil Chemical MC9372 and more than half the weight of material consists of epoxy resin. About 75% epoxy resin has been used successfully in the combination. The preferred inside coating 11 is composed of polyvinyl chloride dispersion resin, epoxy, phenolic, vinyl chloride acetate copolymers as the solution resins, lanolin as a lubricating aid during forming and titanium dioxide as a pigment. The above resins, pigment and lubricants are dispersed or dissolved in appropriate solvents to give a viscosity of 160 seconds in a number four Ford viscosity cup. Typically the solvents are slightly more than one half the total by weight. The composition of polyvinyl chloride, epoxy, phenolic, vinyl chloride acetate copolymers, lanolin, solvents and titanium dioxide can be purchased from Midland-Dexter as MM478A. A similar formulation of the dispersion and solution resins, lubricant and pigment can be made as follows:
All Resins Except PVC 30% by weight of non volatiles
PVC Dispersion Resin 43% by weight of non volatiles
Pigment 27% by weight of non volatiles

It has been found that the molecular weight of the polyvinyl chloride dispersion resin is particularly important in producing a satisfactory multiple draw container precoate. If the molecular weight of the polyvinyl chloride dispersion resin is below a critical value as defined by the intrinsic viscosity, the coating will lose adhesion or rupture near the top of the can because of the mechanical stretching and axial compression during severe multiple drawing operations.

The coating failure is reflected in the enamel rater reading measured for the coating. Organosol coatings formulated with three different molecular weight ranges of polyvinyl chloride dispersion resin, sheet coated at 37 mg per 4 square inches and baked at 380°F for 10 minutes show the following enamel rater readings after being drawn and redrawn to form a can of 3 3/16" diameter by 4 3/8" height.

Enamel Rater Readings of Multiple Drawn Cans
Precoated with an Inside Organosol Coating

<table>
<thead>
<tr>
<th>PVC Resin</th>
<th>Viscosity</th>
<th>Enamel Rater</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.02</td>
<td>50</td>
</tr>
<tr>
<td>B</td>
<td>1.00</td>
<td>45</td>
</tr>
<tr>
<td>C</td>
<td>1.40</td>
<td>2</td>
</tr>
</tbody>
</table>

As can be seen, the organosol coating with PVC resin C having the highest intrinsic viscosity has the lowest enamel rater reading thus showing superior performance with respect to its formability with the metal substrate.

Flavor test packs are an important step in evaluating the performance of inside coatings in multiple drawn cans. Initial screening tests are generally carried out with three test pack media. Water is used as one media because of the high water content of many foods such as corn, peas, or tomatoes. Water will quickly generate corrosion and coating adhesion will be lost if the inside coating is discontinuous, eyeholed or fractured. Chicken soup is used to test for most soups because of its fat content. These fats have a softening action on the coating. If a coating is in-
sufficiently baked, or is not formulated properly to obtain an adequate degree of crosslinking, the fat in chicken soup will soften the coating causing loss of adhesion or swelling and subsequent rupture of this coating film. Apple juice is used primarily as a flavor test medium and also as a material that will aggressively promote corrosion at discontinuities in the coating film. Apple juice is an important test media in characterizing the flavor properties of an inside container coating. The following table illustrates the coating adhesion performance of multiple drawn cans when precoated with inside organosol coatings and test packed with three media.

<table>
<thead>
<tr>
<th>PVC Resin Viscosity</th>
<th>Intrinsic Water Pack</th>
<th>Chicken Soup</th>
<th>Apple Juice</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 1.02</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td>B 1.00</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td>C 1.40</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
</tbody>
</table>

As can be seen, the organosol coating with the highest intrinsic viscosity has the best test pack performance. The following data was all taken from cans coated with an organosol inside coating and baked at a temperature of 380°F for 10 minutes. Drawn cans made from a precoated organosol coating, but baked at a cell coating bake schedule of 550°F for 20 seconds showed similar enamel rater readings and test pack results.

The glass transition temperature of the inside coating must be properly adjusted during formulation so that the coating neither scuffs nor becomes brittle under the heat and pressure of the forming operations. Similarly, the composition of the resin is essential to obtaining a suitable composition which is also resistant to chemical attack of packed products. That is to say, that if the glass transition is too low, it will soften and swell when subjected to fats and it will hydrolyze with acid products. Some products will also leach out part of the coating and combine therewith to give off-flavors. The glass transition temperature must be selected to not permit the inside or outside coatings to
degrade due to temperatures resulting during forming but will allow passive reflow. The glass transition temperature cannot be so high that the coating will not be pliable and reflow to a certain degree during forming. Consequently, the formulation as discussed with the proper ratios of materials, particularly solution resins, will give the right amount of cross linking and therefore the appropriate glass transition temperature.

Measurements made of the apparent glass transition temperature of the inside and outside coating show the following results.

**APPARENT GLASS TRANSITION TEMPERATURES OF DRAWN CAN COATINGS**

| Inside Coating | 136 |
| Outside Coating | 189 |

In forming metal containers by the draw and redraw process, precoated metal is frequently used to avoid more expensive post forming coating operations. The forming operation results in considerable stretching and extension of the coating. The forming operation also increases the temperature of the metal substrate and hence the coating applied to it. If the coating film contains resins below a critical molecular weight, the draw and redraw operation will open the coating film and make it less resistant to the migration of chemical species in the packed product into the film and the migration out of the film of any retained solvents, resin oligomers, etc., present in the coating film.

A well-known property of food products such as peas, corn, beans, etc., is the liberation of small molecules such as cystine and hydrogen sulfide after packing. These chemical compounds arise from the breakdown of proteins in the food and they can react with the residual solvents and oligomers in the coating film to form reactive products which introduce undesirable flavor properties in the food product.

It has been found that certain solvents, when added to organosol coatings can lead to the formation of off-flavors in certain packed foods, in particular, foods that are known to release sulfides such as hydrogen sulfide.
Examples of these kinds of foods are kidney beans or whole kernel corn. Frequently, a coating is formulated in a solvent system of esters and alcohols that by themselves contain no sulfide interacting compounds. When the coatings are diluted in the manufacturing plant to achieve proper coating viscosity, certain solvents are used for reasons of exonomy as the diluents. An example of this is a diluent which is a mixture of xylene and diacetone alcohol or xylene and isophorone. Diacetone alcohol or isophorone are condensation products of acetone that are frequently used in metal coatings as diluents because they are low in cost or have excellent solvent properties for many industrial or container coatings.

While these solvents possess technically useful properties for use in coating, both isophorone and diacetone alcohol usually contain trace quantities of mesityl oxide. Mesityl oxide is highly reactive unsaturated ketonic compound which easily adds sulfides such as hydrogen sulfide to produce noxious odors or off-flavors in food or meat products. In the example of hydrogen sulfide released in the presence of mesityl oxide, the reaction product was identified as 4-methyl-4-mercaptopentane-2-one. The following table compares flavor characteristics with residual solvent content in the multiply formed cans having a height greater than the diameter.

<table>
<thead>
<tr>
<th>No.</th>
<th>Can</th>
<th>Residual Solvent Index (T.I)</th>
<th>Diacetone Alcohol Index</th>
<th>Mesityl Oxide Index</th>
<th>Flavor Test Score Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Control</td>
<td>213</td>
<td>0</td>
<td>0</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>- 3 piece ETP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Multiple</td>
<td>34.0</td>
<td>0</td>
<td>0</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>Drawn</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Organosol 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Multiple</td>
<td>38.0</td>
<td>2.6</td>
<td>4.8 greater than 9</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Drawn</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Organosol 2</td>
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</tr>
</tbody>
</table>
flavor properties in the corn. Other food products such as kidney beans show similar trends in flavor properties.

**FLAVOR TEST WITH KIDNEY BEANS**

<table>
<thead>
<tr>
<th>No.</th>
<th>Can</th>
<th>Coating Diluent Solvent Mixture</th>
<th>Taste Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Control</td>
<td>Xylene-Butyl Cellosolve</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>3-Piece</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ETP</td>
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<td></td>
</tr>
<tr>
<td>2</td>
<td>Organosol 1</td>
<td>Xylene-Butyl Cellosolve</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>Organosol 1</td>
<td>Xylene-diacetone alcohol</td>
<td>3.4</td>
</tr>
</tbody>
</table>

The results show that the coating diluted with the xylene-diacetone alcohol mixture in which diacetone alcohol was shown to contain mesityl oxide in the 1-2 ppm range produced higher taste scores than coatings diluted with xylene-butyl cellosolve.

Similar results have been found with organosol coatings diluted with xylene-isophorone mixture.

While specifics have been disclosed in connection with the preferred coatings for the inside and the outside of a metal substrate to be multiply formed into a container, the discoveries sought to be protected by the claims which follow should be considered in their broadest context. More specifically, an inside coating formulation which when applied can be multiply formed without degradation because the resins are sufficiently pliable due to molecular weight. Similarly, a coating for the inside which will not react unfavorably with the food packed in the container and produce off-flavors or odors.
materials is required. Since the stock is precoated, the can
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A precoat for a metal blank which can be formed by multiple drawing into a container having said precoat on the inside surface and said precoating comprising a phenolic resin, an epoxy resin a polyvinyl chloride acetate co-polymer and a polyvinyl chloride dispersion resin in a solvent system having saturated solvents such that low molecular weight sulfides such as sulfur containing compounds cannot react to form additional products.

2. The precoating system of claim 1 wherein said polyvinyl chloride dispersion resins is about 43% by weight of all the nonvolatiles and all other said resins are about 30% by weight of all the nonvolatiles and the rest is pigment.

3. The precoating system of claim 2 wherein said pigment is titanium dioxide.

4. The precoating system of claim 2 wherein said saturated solvent is either of the ester, ether, aliphatic or aromatic type.

5. The precoating system of claim 4 wherein said metal blank includes another precoat for the outside of the container, said outside precoat being primarily an epoxy resin and a slight amount of lubricant.

6. The precoating system of claim 5 wherein said epoxy resin is 75% by weight of the coating.

7. The precoating system of claim 6 wherein said outside precoat is applied to a film by weight of 9 to 12 mg per 4 square inches.

8. The precoating system of claim 5 wherein said inside precoat is applied to a film weight of about 33 mg per 4 square inches.

9. The precoating system of claim 4 wherein said solvent system is between 5% to 25% aromatic by hydrocarbons, 10% to 15% ketones, up to 60% ether esters or other alcohols by weight.
that when the precoated metal is exposed to passive reheating during the multiple drawing operation residual traces of...
substrate by coil coating. In coil coating, both the inside
severity of the process or multiple drawing. The beneficial effects of heating on coating performance have been shown in prior U.S. Patent #3,206,848. Coating reflow is evident by the