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COATED METAL

Frank J. Soday, Swarthmore, Pa., assignor to The United Gas Improvement Company, a corporation of Pennsylvania

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This application is a continuation-in-part of my copending applications, Serial Numbers 283,057, 283,058, and 283,059, filed July 6, 1939.

This invention pertains generally to the coating of metals and particularly to the coating of metals in sheet form.

The invention pertains more particularly to the coating of sheet metal which is to be fabricated into objects by stamping, bending, drawing, threading, turning, punching, and the like.

Machine operations, such as the foregoing, are particularly severe upon coatings or films adhering to the sheet metal, and in many instances it is extremely difficult to obtain a formed object with a coating or film system adequate for the environment to which the finished article is to be subjected when in use.

To illustrate, many types of films and particularly those made from resinous materials, crack, check, striate, silk and/or peel when subjected to the foregoing mechanical operations.

Because of the great economic advantage of coating the sheet metal prior to the various forming operations, the importance of a film or film system which will withstand the various forming operations without injury cannot be overestimated.

Another quality of extreme importance, particularly in the case of certain uses to which the finished articles are to be put, is the relative insolubility and chemical inertness of the film or film system.

An outstanding example of such a use is in the food packaging field in which metal cans and metal foil wrappings are extensively used.

The term food is employed herein to mean that which is eaten or drunk or absorbed for nourishment or otherwise, and includes not only beverages such as beer, but also substances from which food is prepared, examples of which are coffee beans, whether ground or not, and tea leaves.

In the case of cans, for example, economic considerations make it extremely advantageous to apply the film or film system to the sheet metal while in the flat. The can parts are then cut, shaped and joined all in a manner well known in the art. Severe stresses are set up during the forming operations, particularly in the case of the die-drawing of the can ends. The can ends and certain portions of the can body are again subjected to severe stresses during the can closing operation, such as by the seaming chuck, seaming rolls, and cooperating parts of the can closing machine during the well known double-seaming can sealing operation.

For instance, the die-drawing step produces in the can ends not only angles of very nearly 90° with relatively sharp bends, but also a peripheral portion which is curled back upon itself.

A film or film system to be successful must withstand such and similar metal working operations without peeling or rupturing or otherwise failing in the slightest degree.

Metal caps are used in large quantity not only on glass bottles but also on certain types of metal containers, such as those for holding beverages.

In many cases, such caps are provided with threads for engaging cooperating threads upon the bottle or other container.

The operation for forming the threads in the metal caps is extremely severe, since the metal is frequently stretched by as much as 100% during the thread-forming operation.

In the food packaging field it is, of course, absolutely essential that the film or film system be not only completely insoluble and chemically inert, but also completely incapable of imparting taste or odor to the food product.

In this connection, it is a well known fact that the ordinary tin lining is unsatisfactory in the case of certain foods of which grape juice, orange juice, and beer are outstanding examples.

Some foods develop hydrogen sulfide upon standing which, in turn, reacts chemically with the tin lining to form tin sulfide. In case any of the iron is exposed, such as through cracks, black iron sulfide is formed.

Furthermore, in the food packaging field, the packaged foodstuff, after sealing of the can, is in many cases subjected to a sterilization treatment by the application of heat. Such treatment, by reason of the increased temperatures involved, greatly accelerates any reactions capable of taking place.

Numerous attempts have been made to find a lacquer which might be applied over or substituted for the tin coating. Films made with previously known lacquers, as a rule, however, have failed to have sufficient adhesion and cohesion to resist forming operations, or they have failed to resist reaction with foods, or they have failed in that they have imparted taste or odor to the foods.

This led to the adoption of a procedure whereby a coating composition having good bonding properties was employed as a primer coat for a top coat having proper food resisting and taste and odor characteristics, of which the material known commercially as "Vinylite," a vinyl chloride-vinyl acetate copolymer, is an outstanding

example. In turn, this presented the further problem not only of finding two such coating compositions which would bond properly with each other, but also of finding a primer coat which would not impart taste and odor to the food despite the top coat.

The product known commercially as "Vinylite" though deficient as a primer coat is, nevertheless, satisfactory as a top coat provided a proper bond that will withstand not only the forming operations but also the sterilization treatment can be formed between it and the primer coat.

In this connection, many films and dual film systems develop a cloudiness during the sterilization step, such cloudiness being generally referred to as "blushing." The resulting discoloration is very undesirable from the standpoint of market appeal, since the average housewife looks with great disfavor upon any discoloration of the inside surface of a can when removing food therefrom.

It follows that any film or film system to be suitable must not only be capable of resisting "blushing," but must in itself have an acceptable appearance and preferably one suggesting utmost cleanliness.

Since films and film systems of the character under consideration are necessarily extremely thin, the primer coat is preferably one capable of direct contact with the foodstuff without chemical reaction and without imparting taste or odor hereto. Certain substances which might otherwise be satisfactory as primer coats fail because they are capable of imparting taste and odor to foodstuffs through the top coat.

In addition to the foregoing, there are certain metals which are extremely difficult to coat with satisfactorily adhering films or film systems of any character. Examples are zinc, zinc plate, magnesium and magnesium alloys, such as the material known commercially as "Dow metal." In fact, many previously known resinous coating compositions fail to form a satisfactory bond with these materials.

In accordance with my invention, single film systems and multiple film systems having all of the above desirable properties may be produced by forming (a) said single film system, or (b) the primer coat of a multiple film system provided the top coat is of a satisfactory character, or (c) the top coat of a multiple film system provided the primer coat is of a satisfactory character, with a liquid coating composition having as a base a cyclic conjugated pentadiene-aliphatic conjugated diolefin copolymer which has been prepared in a manner to impart to it certain desired properties, and then permitting such film to dry such as in a manner to be hereinafter more particularly set forth.

Generally speaking, the catalytically polymerized cyclic conjugated pentadiene-aliphatic conjugated diolefin copolymers employed herein have the following properties. They are soluble in benzene, toluene, chloroform, carbon tetrachloride and high flash naphtha, and insoluble in alcohol, acetone, ether and water. For the purpose of convenience these solubility characteristics may be defined by the term "benzene-soluble," though it is to be understood that the actual presence of benzene in the solution or in the applied films is not implied. Preferably, my liquid coating compositions have other distinctive properties. Among these properties is the ability to form a smooth, glassy, highly flexible and extensi-

ble and tenaciously adhering film upon drying with or without baking.

These cyclic conjugated pentadiene-aliphatic conjugated diolefin copolymers are prepared by the polymerization of one or more aliphatic diolefines with one or more cyclic conjugated pentadienes by the use of a suitable catalyst.

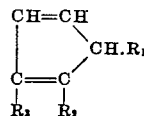
The catalysts which may be used for this purpose include metallic halides; metallic halide-organic solvent complexes; contact materials, such as clay, alumina, and silica; mineral acids, such as sulfuric acid and phosphoric acid; and mineral acid-organic solvent mixtures, such as sulfuric acid-diisopropyl ether mixtures. The use of metallic halide-organic solvent complexes, such as boron trifluoride-diethyl ether complex and aluminum chloride-diethyl ether complex, is preferred.

These copolymers also may be prepared by the separate partial polymerization of one or both of the components, followed by adding the components to each other and then completing the polymerization.

While cyclopentadiene is preferred as one component of the copolymers to be used herein, this may be replaced wholly or in part by alkyl substituted cyclopentadienes, such as methyl cyclopentadiene. In general, however, it is preferred to employ reasonably pure cyclopentadiene, or cyclopentadiene-methyl cyclopentadiene mixtures containing not more than 20% methyl cyclopentadiene. I prefer to employ a starting material in which the content of dimer and/or higher polymers of cyclic conjugated pentadiene, if present, is low, for example, never over 5% of the cyclic conjugated pentadiene content. The starting materials may be freed from such materials by any suitable means such as distillation.

Substituted cyclopentadienes other than methyl cyclopentadiene also may be employed.

The cyclic conjugated pentadiene portion of my copolymer may, therefore, be represented broadly by the alicyclic hydrocarbon of the following structure:



in which R₁, R₂, and R₃ each represents hydrogen or an alkyl group.

The aliphatic conjugated diolefines employed in the preparation of these copolymers contain less than ten carbon atoms, for example, from four to nine carbon atoms. Examples of such diolefines are butadiene, isoprene, piperylene, 1,3 hexadiene, 1-3 octadiene, and the like. Any suitable mixture of these diolefines also may be employed. For example, copolymers prepared by the polymerization of a mixture of cyclopentadiene, isoprene, and piperylene have been found to be especially suitable for coating purposes.

The aliphatic conjugated diolefines may be obtained from any suitable source, such as from synthetic processes, or from light oil obtained in the manufacture of oil gas, carburetted water gas, or from refinery products. They may be used as such, or in the form of light oil fractions of suitable concentration.

The cyclopentadiene and/or alkyl substituted cyclopentadiene which I employ may, if desired, be derived from similar sources.

Suitable methods for the preparation of these copolymers are disclosed in my said copending

applications to which reference has already been made.

Without repeating all of the details in said copending applications, they include the admixing of cyclic conjugated pentadiene and aliphatic conjugated diolefin both, for example, being in the form of light oil fractions. The addition of an organic solvent such as toluene may be made. The mixture may be added to a small amount (for example, 2% by weight) of a suitable catalyst such as a boron trifluoride-diethyl ether complex and the reaction may be stopped after a suitable reaction period by hydrolyzing the catalyst with water or other suitable agent. Drying of the resinous solution thus obtained may be effected by contact with a dehydrating agent such as lime. This is usually followed by filtering with or without the aid of a filter aid such as Celite to obtain the resin.

As disclosed in my copending application Serial No. 283,057, in the case of resins for use in coating compositions, such as spirit varnishes and lacquers suitable for use in coating metal hereunder and produced by the copolymerization of cyclopentadiene and butadiene, I prefer to employ between 50% and 99% cyclopentadiene to between 50% to 1% butadiene on the undiluted basis. 70% to 95% cyclopentadiene to 30% to 5% butadiene is very suitable. The resin obtained by polymerizing a mixture containing 90 parts cyclopentadiene to 10 parts butadiene is excellent.

In general for such spirit varnishes and lacquers an excess of cyclopentadiene is preferred.

As disclosed in my copending application Serial No. 283,058 in the case of such spirit varnishes and lacquers produced by copolymerizing cyclopentadiene and isoprene, I prefer to employ between 50% and 99% cyclopentadiene to between 50% to 1% isoprene on the undiluted basis. 70% to 95% cyclopentadiene to 30% to 5% isoprene is very suitable. The resin obtained by polymerizing a mixture containing 90 parts cyclopentadiene to 10 parts butadiene is excellent.

In general for such spirit varnishes and lacquers an excess of cyclopentadiene is preferred.

As disclosed in my copending application Serial No. 283,059 in the case of such spirit varnishes and lacquers produced by copolymerizing cyclopentadiene and piperylene, I prefer to employ between 50% and 99% cyclopentadiene to between 50% and 1% piperylene on the undiluted basis. 70% to 95% cyclopentadiene to 30% to 5% piperylene is very suitable. The resin obtained by polymerizing a mixture containing 90 parts cyclopentadiene to 10 parts butadiene is excellent.

In general for such spirit varnishes and lacquers an excess of cyclopentadiene is preferred.

As exemplifying one of a number of typical procedures which might be followed in the preparation of the resin, the following example (taken from my said copending application Serial Number 283,059) is given. It will be understood that copolymers of other cyclic conjugated pentadienes and/or other aliphatic conjugated diolefines may be prepared by generally similar methods, or otherwise.

Example 1

To a mixture of 50 parts of cyclopentadiene and 50 parts of piperylene in the form of a light oil fraction containing 78.9% piperylene and 16.9% amylenes (the resulting mixture therefore containing the following proportions of active ingredients; cyclopentadiene=45.2%, pipery-

lene=45.1%, and amylenes=9.7%) was added sufficient toluene to reduce the total diolefin concentration to 20% by weight. Approximately 2% by weight of boron trifluoride-diethyl ether complex was used as a catalyst, based on the total weight of the reaction mixture. The mixture of reactants was added to the catalyst, at a temperature of -20°C ., after which the reaction was continued for an additional period of 18 hours at this temperature. At the end of this period the catalyst was hydrolyzed with water and the reaction mixture was then allowed to come up to room temperature. The resinous solution was dried with lime and filtered. The yield of resin was 85.4% by weight of the reactants used in the process. The resin was light yellow in color.

Resinous copolymer of the foregoing character is employed in accordance with this invention for the coating of metallic surfaces such as those of food containers. This is followed by drying.

When the aliphatic diolefin is initially partially polymerized this may be accomplished by the use of a suitable catalyst such as catalysts of the metallic halide type with or without heat. After removing extraneous material the cyclic conjugated diolefin either in monomeric form or in a partially polymerized form is added, and copolymerization is effected by the use of a suitable catalyst such as a metallic halide-organic solvent complex with or without heat.

Partial polymerization of the cyclic conjugated diolefin may also be effected by the use of a suitable catalyst such as a metallic-halide-organic solvent complex with or without heat. After removing extraneous material it is ready for use for copolymerization with either monomeric aliphatic conjugated diolefin or partially polymerized aliphatic conjugated diolefin.

In the foregoing particular description of the preparation of the copolymer, it will be noted that both the reactants and the catalyst are in diluted form before use. Furthermore, the diluted reactants are preferably added to diluted catalyst rather than vice versa to afford a better control of the speed and uniformity of the reaction and of the amount of heat evolved and consequently the type of polymer produced. The reaction runs smoother and is much more easily controlled on a large scale.

The addition of water to hydrolyze the catalyst makes it possible not only to completely remove the activity of the catalyst and thus stop the reaction at any point, but also to remove the corrosive and discoloring acid constituents of the catalyst by a suitable alkali. The alkali is preferably added with the water used to hydrolyze the catalyst, although it may be added later, if desired. The failure to substantially completely remove the catalyst and its hydrolysis products may be the cause of serious discoloration. The insoluble reaction products formed during the hydrolysis and neutralization remain behind on the filter leaving a highly purified filtrate.

Examples of the formation of a single film system in accordance with my invention are as follows:

Example 2

A solution in toluene of a piperylene-cyclopentadiene co-polymer obtained in the manner generally described above was used in the coating of tin-plated steel panels, such as those used for the fabrication of food and beverage containers. The panels were dipped into the resinous solu-

tion, after which they were baked at 180° C. for a period of 15 minutes. Coating weights of 4.8 milligrams per square inch were thus obtained.

One of these panels was subjected to live steam under a pressure of fifteen pounds per square inch, after which the coating was cross-hatched in a diamond pattern, the lines extending completely through the resinous coating. The panel was sharply bent over a 1/8" mandrel through an angle of 180°, after which a piece of Scotch adhesive tape was firmly affixed to the cross-hatched section and then suddenly stripped from the surface. None of the resinous coating was removed from the panel by this procedure, which shows the unusual adhesive properties of the material.

The test was repeated after a storage period of three months, with the same results, which illustrates the excellent aging properties of my resinous material.

Sheet metal thus coated is ready for drastic forming operations, such as encountered in the manufacture of cans or other containers, bottle caps, screw caps, and the like. It will withstand extremely rough treatment without cracking, checking, striating, silking, peeling, loosening, or other injury.

When made into cans the coating is highly resistant to foods, imparts no taste or odor thereto, and is free from blushing during the sterilization treatment.

An example of the formation of a dual film system in accordance with my invention is as follows:

Example 3

Several steel panels, such as those used for the fabrication of bottle caps and closures, were dipped in a toluene solution of an isoprene-cyclopentadiene copolymer obtained in the manner generally described above, after which they were baked at a temperature of 250° F. for a period of fifteen minutes. Coating weights of 2.5 milligrams per square inch were thus obtained.

Upon cooling, a solution of "Vinylite" in a mixture of higher boiling ketones was applied to the surface of the panels by dipping. The panels were again baked at a temperature of 280° F. for a period of 12 minutes, resulting in the production of a "Vinylite" overcoating having a coating weight of approximately 2.5 milligrams per square inch.

The resulting coated product as in the case of the single film system was eminently suited to the fabrication of formed articles, not only from the standpoint of physical resistance to film breakdown during the severe forming or shaping operations, but also from the standpoint of chemical resistance to attack by foodstuffs and the like.

It will be understood, of course, that broadly speaking, the top coat is not limited to "Vinylite," which is the copolymer of vinyl acetate and vinyl chloride, but may be a polymer or copolymer of any of the vinyl compounds used as raw materials for the several vinyl resins; e. g., vinyl acetate, vinyl chloride or vinyl chloracetate. In fact, other types of resins may be adapted for use as the top coat over my catalytically polymerized cyclic conjugated pentadiene-aliphatic conjugated diolefine resin.

Vinyl resins suitable for use in forming the top coat of my invention may be formed from vinyl esters by known polymerization processes. The polymerization products of inorganic vinyl esters, such as vinyl halides, or those of organic

vinyl esters, such as vinyl esters of aliphatic acids, may be used.

I prefer to use vinyl resins resulting from the copolymerization of two or more vinyl esters. For example, vinyl resins having desirable properties may be prepared by the copolymerization of a vinyl halide and a vinyl ester of an aliphatic acid.

Products of the copolymerization of vinyl chloride and vinyl acetate in proportions ranging from about 10% to 90% by weight of the chloride are particularly desirable.

The commercial product sold under the trade name "Vinylite" falls in the latter category and contains approximately 85% vinyl chloride.

The foregoing vinyl resins are substantially water-white and transparent, and they are exceptionally resistant to acids, alkalies, and salts in the presence of moisture and may be used to form flexible top coats which adhere exceptionally well to my primer coat, such top coat (like my primer coat) being odorless and tasteless.

To a certain extent, the characteristics of the preferred vinyl resins are retained when the vinyl resin is modified by the addition of a second resin or gum, a cellulose ester, or a high boiling solvent having plasticizing or softening action on the resin. Due to this property, the vinyl resins may be modified to meet specific requirements without materially altering the chemical properties of the resins employed as the top coat.

However, in the food packaging field, the commercial product sold under the trade name "Vinylite" without modification is well suited for top coat purposes.

This product is thought to result from the copolymerization of about 85% of vinyl chloride with 15% vinyl acetate.

Since my copolymer films not only bond well to metal surfaces and the like but also are highly resistant to attack by foods, and do not impart taste or odor thereto, they may be used as top coats for primer coats of other materials, if desired. It is, of course, understood that my copolymer resin may be used for both a primer coat and a top coat or in any other number of coats.

The preparation of a dual coating system is further illustrated by the following example:

Example 4

Steel panels were dipped in a 20% solution of polycyclopentadiene in toluene prepared as described and claimed in my copending application Serial Number 204,786 filed April 28, 1938, now Patent No. 2,314,904, dated March 30, 1943. The coating resulting from said dipping was baked at a temperature of 250° F. for a period of fifteen minutes. Coating weights of 2.3 milligrams per square inch were thus obtained.

The coated panels then were dipped in a 20% solution of a cyclopentadiene-butadiene copolymer prepared generally in the manner above described, after which they were baked at a temperature of 250° F. for a period of 15 minutes. A top coat of 2.5 milligrams was thus obtained.

The coated steel panels then were fabricated in a cap-forming machine. The caps obtained were coated perfectly and showed no evidence of damage by the cap-forming die.

With respect to the temperature of baking of my cyclic conjugated pentadiene-aliphatic conjugated diolefine copolymer resin films, I prefer not to exceed about 400° F. and usually employ temperatures considerably below this point. At such top temperatures a baking time not exceed-

ing about 15 minutes is recommended to avoid any possible injury to the baked film. Thus, although my resin films may be safely subjected to higher temperatures during baking, in general, I find temperatures up to 350° F. with baking times up to 30 minutes very satisfactory. With higher temperatures the baking time may be correspondingly shortened to yield similar satisfactory results.

While I refer to drying my coatings or films by heating in the presence of air or an oxygen-containing gas, it is to be understood that the taking on of oxygen by the film need not necessarily take place simultaneously with the heating or baking. On the contrary, excellent results are obtainable by heating or baking the coating or film or the coated object in an inert atmosphere as of nitrogen, carbon dioxide, or the like, followed by exposure to the atmosphere or other oxygen-containing medium.

Additional drying or hardening of the film results from the absorption of oxygen.

Similarly, in preparing my multiple-film systems and particularly a system including my resin film and a "Vinylite" film, the drying or hardening of my copolymer resin films may be secured (a) by baking or heating in an oxygen-containing atmosphere, or (b) baking my copolymer resin films in an inert atmosphere but permitting them to stand or "season" in contact with an oxygen-containing atmosphere for a period of time (for example, a week) before applying the top coating of "Vinylite," or (c) baking or heating my copolymer resin films in an inert atmosphere, coating the baked film with a top coating of "Vinylite" and then letting the dual film stand or "season" in contact with an oxygen-containing atmosphere such as before using the coated article for its intended purpose (in the last-named case, oxygen evidently penetrates or seeps through the top coat to my copolymer resin primer coat), or (d) applying and heating my copolymer resin film in an inert atmosphere, coating with a top coat of another resin film, such as "Vinylite," still in an inert atmosphere, and heating the multiple-film system thus formed, still in an inert atmosphere, or (e) any combination of any of the foregoing.

Since the resin coating resulting from (d) wherein the entire series of operations take place in an inert atmosphere is entirely satisfactory for commercial use, it would appear that my copolymer resin films may be satisfactorily hardened either by heat, or by an oxygen-containing environment, or by a combination of both.

In fact, other drying or hardening methods may be employed.

As an illustration, my copolymer resin films may be dried or hardened by a vulcanization-like treatment, such as is accomplished by adding a vulcanization agent to the solution at the time of its application, or applying the vulcanization agent over the film after its application, or enclosing the applied film in an atmosphere of vulcanizing gas, such as H_2S , or any combination of the foregoing, or otherwise. The application of heat hastens the drying or hardening action.

Films of excellent character are obtained when the applied films are dried or hardened using H_2S with the application of heat.

For example, a solution of my resin may contain dissolved H_2S , and after its application to the metal surface, the film may be dried in an atmosphere of H_2S with the application of heat. A baking temperature of 350° F. and a baking time of 15 minutes is illustrative.

Vulcanized copolymer resin films may not be oxygen-containing, and may or may not be capable of taking up oxygen, if exposed to the atmosphere or other oxygen-containing gas, say at a greatly reduced rate.

After drying or hardening, my copolymer resin films are, generally speaking, insoluble.

While the film thicknesses mentioned are found to be extremely suitable for the purpose, and particularly for food containers, other film thicknesses may obviously be employed without departing from the spirit of the invention.

While in the above specific examples toluene is used, it is to be understood that other suitable solvents may be employed with corresponding results of which benzene, xylene, ethyl benzene, naphtha, chloroform and carbon tetrachloride are examples.

While the foregoing particular description has been concerned primarily with the application of the protective film or films to metal sheets of a gauge used in the manufacture of "tin" cans, it will be obvious that my invention is not limited thereto but may be applied to any metal surface, and in fact, to metallic objects in general whether prefabricated or not, where a tough strongly adhering film or film system is desired.

Thus, the resin film may be applied to metal foil.

As an illustration, tin foil and aluminum foil, each of which is used to package dairy products like butter and cheese, may be so coated. If desired, these materials in molten form may be poured into molds lined with foil coated in accordance with my invention.

So too, lead foil, such as is used to package tea leaves, may be coated in accordance with my invention.

Metal foil may be coated by any desired procedure. For example, the foil may be passed through a solution of the coating material and the excess removed by means of doctor blades or rolls. Or a conventional roll type coating procedure may be employed and the solvent removed and/or recovered in a drying tower. Or the coating material may be poured or sprayed onto the surface to be coated and the excess removed by means of doctor blades or rolls, or simply allowed to drain away.

If desired, metal foil may be strengthened by backing it with paper, or by laminating two or more foil layers. For example, a sheet of metal foil may be coated on one side and the coated side pressed into contact with a sheet of paper or second sheet of foil before the coating material has completely dried. This may be followed by coating the opposite side of the metal foil and drying the film for contact with foodstuffs. On the other hand, metal foil coated with my dual film system with "Vinylite" as the top coat may be hot pressed against paper or foil to effect union of the materials.

While the invention has been more particularly described in connection with the coating of sheet metal including foil in the flat, my resin film or film system may be applied during or after any forming operations for converting the initial material into the finished object. It is generally useful for coating metallic objects in general, whether fabricated from sheet metal or not, or whether pre-fabricated in whole or in part prior to application of the film or film system. Metal objects such as toys stamped or formed from sheet metal also form an important field of application for my invention.

While it is preferred to employ my resin materials without additives, the addition of other substances such as plasticizing agents, coloring agents, pigments, fillers, flattening agents, or mixtures thereof may be made with consequent modified results, provided the outstanding characteristics of the resin material are not substantially destroyed.

My copolymer resin films are an attractive light yellow in color. If desired, suitable coloring materials may be added such as dyes, pigments, and lakes. The same applies with respect to the "Vinylite" top coat. However, in the food packaging field, care should be exercised with respect to any additives so as not to lower or destroy the excellent qualities of the original material for this particular use.

Since in the food packaging field the important consideration is that the resin in contact with the food be chemically inert, insoluble in the foodstuff, incapable of imparting odor and taste thereto, and strongly adherent to the enclosing wall, outside portions of the container or foil may be left uncoated, or may be coated with other materials, particularly if suitable, or with my materials with or without additives, or otherwise.

It is to be understood that the above specific examples are by way of illustration. Therefore, changes, omissions, additions, substitutions, and/or modifications may be made within the scope of the claims without departing from the spirit of the invention.

I claim:

1. A formed film-coated article shaped by deformation of a metallic body coated with dried resinous copolymer of between 50% and 99% by weight on the undiluted basis of at least one cyclic conjugated diene selected from the group consisting of cyclopentadiene and alkyl cyclopentadiene with between 50% and 1% by weight on the undiluted basis of at least one aliphatic conjugated diolefin having less than 10 carbon atoms per molecule, said formed film adhering tenaciously to the formed metal.

2. A formed film-coated article shaped by severe deformation of metallic sheeting coated with dried resinous copolymer of between 50% and 99% by weight on the undiluted basis of at least one cyclic conjugated diene selected from the group consisting of cyclopentadiene and alkyl cyclopentadiene with between 50% and 1% by weight on the undiluted basis of at least one aliphatic conjugated diolefin having less than 6 and more than 3 carbon atoms per molecule, said formed film adhering tenaciously to the formed metal.

3. A formed film-coated food container having a portion shaped by drawing a metallic sheet coated with dried resinous copolymer of between 50% and 99% by weight on the undiluted basis of at least one cyclic conjugated diene selected from the group consisting of cyclopentadiene and alkyl cyclopentadiene, with between 50% and 1% by weight on the undiluted basis of at least one aliphatic conjugated diolefin having less than 6 and more than 3 carbon atoms per molecule, said formed film adhering tenaciously to the formed metal.

4. A formed film-coated container cap shaped by severe deformation of metallic sheeting coated with dried resinous copolymer of between 50% and 99% by weight on the undiluted basis of at least one cyclic conjugated diene selected from

the group consisting of cyclopentadiene and alkyl cyclopentadiene with between 50% and 1% by weight on the undiluted basis of at least one aliphatic conjugated diolefin having less than 6 and more than 3 carbon atoms per molecule, said formed film adhering tenaciously to the formed metal.

5. A formed film-coated article shaped by severe deformation of metallic sheeting coated with dried resinous copolymer of from 70% to 95% by weight on the undiluted basis of at least one cyclic conjugated diene selected from the group consisting of cyclopentadiene and alkyl cyclopentadiene with from 30% to 5% by weight on the undiluted basis of at least one aliphatic conjugated diolefin having less than 6 and more than 3 carbon atoms per molecule, said formed film adhering tenaciously to the formed metal.

6. A formed film-coated food container having a portion shaped by drawing a metallic sheet coated with dried resinous copolymer of from 70% to 95% by weight on the undiluted basis of at least one cyclic conjugated diene selected from the group consisting of cyclopentadiene and alkyl cyclopentadiene with from 30% to 5% by weight on the undiluted basis of at least one aliphatic conjugated diolefin having less than 6 and more than 3 carbon atoms per molecule, said formed film adhering tenaciously to the formed metal.

7. A formed film-coated container cap shaped by severe deformation of metallic sheeting coated with dried resinous copolymer of from 70% to 95% by weight on the undiluted basis of at least one cyclic conjugated diene selected from the group consisting of cyclopentadiene and alkyl cyclopentadiene with from 30% to 5% by weight of at least one aliphatic conjugated diolefin having less than 6 and more than 3 carbon atoms per molecule, said formed film adhering tenaciously to the formed metal.

8. A formed film-coated article shaped by severe deformation of metallic sheeting coated with dried resinous copolymer of between 50% and 99% by weight on the undiluted basis of cyclopentadiene with between 50% and 1% by weight on the undiluted basis of butadiene, said formed film adhering tenaciously to the formed metal.

9. A formed film-coated article shaped by severe deformation of metallic sheeting coated with dried resinous copolymer of between 50% and 99% by weight on the undiluted basis of cyclopentadiene with between 50% and 1% by weight on the undiluted basis of piperylene, said formed film adhering tenaciously to the formed metal.

10. A formed film-coated article shaped by severe deformation of metallic sheeting coated with dried resinous copolymer of between 50% and 99% by weight on the undiluted basis of cyclopentadiene with between 50% and 1% by weight on the undiluted basis of isoprene, said formed film adhering tenaciously to the formed metal.

11. A formed film-coated article shaped by severe deformation of metallic sheeting coated with dried resinous copolymer of between 50% and 1% by weight on the undiluted basis of at least one aliphatic conjugated diolefin having less than 6 and more than 3 carbon atoms per molecule with between 50% and 99% by weight on the undiluted basis of a mixture of cyclopentadiene and methyl cyclopentadiene, the methyl cyclopentadiene content of said mixture not exceeding 20%, said formed film adhering tenaciously to the formed metal.

12. A process for producing a formed article coated with a formed protective layer of synthetic resin which comprises coating metallic material from which the article is to be formed with resinous copolymer of between 50% and 99% by weight on the undiluted basis of at least one cyclic conjugated diene selected from the group consisting of cyclopentadiene and alkyl cyclopentadiene with between 50% and 1% by weight on the undiluted basis of at least one aliphatic conjugated diolefine having less than 10 carbon atoms per molecule, drying said coating, and subjecting the coated material to shaping operations to produce a formed article.

13. A method for producing a coated can cover having sharply bent portions from metallic sheeting which comprises coating said sheet from which the can cover is to be formed with resinous copolymer of between 50% and 99% by weight on the undiluted basis of at least one cyclic conjugated diene selected from the group consisting of cyclopentadiene and alkyl cyclopentadiene with between 50% and 1% by weight on the undiluted basis of at least one aliphatic conjugated diolefine having less than 6 and more than 3 carbon atoms per molecule, drying said coating, cutting a blank of the desired shape from said sheeting, and die-drawing said coated blank to the desired can cover shape having said sharply bent portions.

14. A process for producing a formed article coated with a formed protective layer of synthetic resin which comprises coating metallic material from which the article is to be formed with resinous copolymer of from 70% to 95% by weight on the undiluted basis of at least one cyclic conjugated diene selected from the group consisting of cyclopentadiene and alkyl cyclopentadiene with

from 30% to 5% by weight on the undiluted basis of at least one aliphatic conjugated diolefine having less than 6 and more than 3 carbon atoms per molecule, drying said coating, and subjecting the coated material to shaping operations to produce a formed article.

15. A method for producing a coated can cover having sharply bent portions from metallic sheeting which comprises coating said sheet from which the can cover is to be formed with resinous copolymer of from 70% to 95% by weight on the undiluted basis of at least one cyclic conjugated diene selected from the group consisting of cyclopentadiene and alkyl cyclopentadiene with from 30% to 5% by weight on the undiluted basis of at least one aliphatic conjugated diolefine having less than 6 and more than 3 carbon atoms per molecule, drying said coating, cutting a blank of the desired shape from said sheeting, and die-drawing said coated blank to the desired can cover shape having said sharply bent portion.

16. A process for producing a formed coated article having a formed protective layer of synthetic resin which comprises coating metallic sheeting from which the article is to be formed with resinous copolymer of between 50% and 1% by weight on the undiluted basis of at least one aliphatic conjugated diolefine having less than 6 and more than 3 carbon atoms per molecule with between 50% and 99% by weight on the undiluted basis of a mixture of cyclopentadiene and methyl cyclopentadiene, the content of methyl cyclopentadiene in said mixture not exceeding 20%, drying said coating, and subjecting the coated metallic sheeting to shaping operations to produce said formed article.

FRANK J. SODAY.