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COATED OBJECT AND PROCESS FOR
MAKING THE SAMENewcomb K. Chaney, Moylan, Pa., assignor to
The United Gas Improvement Company, a corporation of PennsylvaniaNo Drawing. Application August 19, 1939,
Serial No. 291,007

19 Claims. (Cl. 99—181)

This application is a continuation in part of my copending application Serial Number 174,011, filed November 11, 1937.

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 operations which result in drawing of the metal such as occurs in stamping, bending, die-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 economical 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, economical 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 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.

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 food stuff, 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" 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 food stuff without chemical reaction and without imparting taste or odor thereto. 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, practically all 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 cyclopentadiene which has been catalytically polymerized in a manner to impart to it desired properties, and then permitting such films of polymerized cyclopentadiene to dry with or without heat.

Generally speaking, the catalytically polymerized cyclopentadiene employed in my liquid coating composition has the following properties. It is soluble in benzene, toluene, chloroform, carbon tetrachloride and high flash naphtha, and insoluble in alcohol, acetone, ether and water. For the purpose of convenience in the claims, these solubility characteristics will 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 composition has other distinctive properties. Among these properties is the ability to form a smooth, glassy, highly flexible and extensible and tenaciously adhering film upon drying with or without baking.

Methods for preparing benzene-soluble cata-

lytically polymerized cyclopentadiene employed in my invention are described and claimed in copending application, Serial Number 194,523, filed March 8, 1938 by Samuel G. Trepp, and copending application Serial Number 204,786, filed April 28, 1938, by Frank J. Soday.

The following are specific examples of the preparation of the desired polymer.

Example 1

1500 pounds of toluene were charged to a small jacketed, brine cooled kettle provided with an agitator and a brine cooled reflux condenser. 3 pounds of boron trifluoride-diethyl ether complex were then charged, agitation was started, and the kettle was warmed to 35-40° C. After complete mixing, heating was discontinued and the steam in the jacket replaced with brine.

A previously prepared mixture of 525 pounds of cyclopentadiene and 500 pounds of toluene was gradually added from a mixing tank, maintained at a temperature sufficiently low to prevent the volatilization of the cyclopentadiene. The mixture is preferably below room temperature when it reaches the reaction kettle.

The rate of addition was so regulated that the contents of the reaction kettle were maintained at a temperature between 25-30° C. while circulating cooling brine through the jacket.

From 20 to 60 minutes were required for the addition of the cyclopentadiene-toluene mixture depending upon the efficiency of the cooling brine. When addition was complete, the brine flow was cut down so as to keep the temperature above 25° C. but below 50° C. and the product was agitated for an additional 1½ hours.

5 pounds of water were now added to hydrolyze the catalyst so that the fluorine might later be removed as hydrogen fluoride by the lime.

After 30 minutes further agitation, 75 pounds of milk of lime ($\text{Ca}(\text{OH})_2$) were added. The temperature was now kept between 18-30° C.

After an additional agitation of one hour 130 pounds of a good grade of filter aid, such as diatomaceous earth, was added. An additional quantity of 70 pounds of filter aid was placed on a suction filter, and the product pumped through the filter. Any type of filter, such as a plate filter press, centrifuge, etc., might be employed.

The product was a 20% solution of the desired polymer. This solution may be used as such for application to surfaces, followed by drying in an oxygen-containing atmosphere, such as with baking after suitable evaporation of solvent, or the solution may be concentrated in a vacuum still of suitable design to give a product containing any desired higher concentration of polycyclopentadiene, if desired.

In the above example, the particular temperatures chosen are more or less for expediency, but it will be noted that at no time did the temperature exceed 100° C. or even 80° C. Constant agitation and brine cooling made it possible to prevent local overheating.

Example 2

0.30 cubic centimeter of aluminum chloride-diethyl ether complex is added to 60 grams of toluene with thorough agitation to form a suspension, emulsion or solution.

A mixture of 20 grams of cyclopentadiene and 20 grams of toluene is added to the suspension during the course of 12 minutes, the temperature ranging from 26-49° C. during the addition. The mixture is then agitated for an additional

hour, after which 1 cubic centimeter of water is added. This is followed by agitation for 15 minutes.

10 grams of quicklime (CaO) are now added to the reaction mixture followed by agitation for an additional hour.

5 grams of a suitable filter aid are then added, and the mixture filtered.

A filtered solution containing 16.4 grams of polycyclopentadiene is thus obtained.

Generally speaking, any other boron trifluoride-organic solvent complex or aluminum chloride-organic solvent complex might be substituted in the above examples.

In the above specific examples it will be noted that both the cyclopentadiene and the catalyst are in diluted form before addition. Furthermore, as pointed out above diluted cyclopentadiene is 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.

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

Example A

A 24% solution of the resin in toluene is applied to sheet metal, such as tin plate, in such quantities that the final resin film whether applied to one coat, or several coats with or without intermediate baking, will have a desired thickness, such as the equivalent of from 4 to 6 milligrams per square inch of dry film after baking.

The coated sheet, after suitable evaporation of solvent, is placed in an oven and heated to a temperature of 350° F. for a period of 15 minutes in order to insure satisfactory drying during which time the film takes up oxygen from the air without loss of adhesion, flexibility or extensibility. A suitable baking time is between one-quarter of an hour and one and a half hours. The elevated temperatures employed favor the adding on of oxygen.

Sheet metal thus coated is ready for the most 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 otherwise injuring the coating.

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. In fact, the coating appears to be improved during sterilization.

An example of the formation of a dual film

system in accordance with my invention is as follows:

Example B

A tin plated sheet, or other metal sheet, is coated with a solution of my resin in toluene, say of 20% concentration, in sufficient quantity to secure a desired final coating weight, say of approximately 3 milligrams per square inch after baking.

The coated sheet after suitable evaporation of solvent is placed in an oven and baked at a temperature of say 250° F. for a period of 15 minutes, the polycyclopentadiene adding on oxygen from the atmosphere during the baking.

Upon cooling, a solution of "Vinylite" in a mixture of higher boiling ketones is applied in sufficient quantity such that the dual film system will have a desired thickness after drying of the "Vinylite" film such as with baking, say a thickness equivalent to 4 to 6 milligrams per square inch of dry dual film.

The coated sheet after suitable evaporation of solvent is then rebaked in the same manner as with the primer coat.

It will be understood, of course, that broadly speaking, the top coat is not limited to "Vinylite," which is the co-polymer of vinyl acetate and vinyl chloride, but may be a polymer 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 application as the top coat over my catalytically polymerized cyclopentadiene 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 co-polymerization of two or more vinyl esters. For example, vinyl resins having desirable properties may be prepared by the co-polymerization of a vinyl halide and a vinyl ester of an aliphatic acid.

Products of the co-polymerization 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.

The foregoing vinyl resins are substantially water-white and transparent and they are exceptionally resistant to acids, alkalis, 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 the purpose.

This product is thought to result from the co-

polymerization of about 85% of vinyl chloride with 15% vinyl acetate.

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

With respect to the temperature and time of baking my polycyclopentadiene films, I usually prefer not to exceed about 400° F. and at such temperatures a baking time not longer than about 15 minutes to avoid any possible injury to the film. However, in one experiment I was able to maintain a baking temperature of 425° F. for 70 minutes without injury to the film. Thus, although my resin films may be safely subjected to higher temperatures during baking, in general, I find temperatures up to 350° F. and 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 have referred to "baking" broadly and to "heating in the presence of air" or an "oxygen-containing gas" as a means of drying my coating or film, 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, I have obtained excellent results by heating or baking the coating 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 cyclopentadiene resin film may be secured (a) by baking or heating in an oxygen-containing atmosphere, or (b) baking my cyclopentadiene resin film in an inert atmosphere but permitting it to stand or "season" in contact with an oxygen-containing atmosphere for a period of time (e. g., a week) before applying the top coating of "Vinylite," or (c) baking or heating my cyclopentadiene resin film in an inert atmosphere, coating the baked film with the 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 resin film to my cyclopentadiene resin primer coat), or (d) applying and heating my cyclopentadiene 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 ally well to my primer coat, such top coat like commercial use, my cyclopentadiene 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 polycyclopentadiene films including those made from cyclopentadiene containing some methyl cyclopentadiene 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 H₂S, 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 H₂S with the application of heat.

For example, a solution of my resin may contain dissolved H₂S and after its application to the metal surface, the film may be dried in an atmosphere of H₂S with the application of heat. A baking temperature of 350° F. and a baking time of 15 minutes is illustrative.

Vulcanized polycyclopentadiene 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.

Similar drying procedure may be applied to the vinyl top coat, if desired.

Reference is made to my copending application Serial No. 370,138, filed December 14, 1940.

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

While the film thicknesses given 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 sheet material, 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. Reference is made to my copending application Serial No. 491,947, filed June 23, 1943.

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.

If desired, metal foil may be strengthened by

packing 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.

While it is preferred to employ it without additives, the addition of other substances may be made with consequent modified results, provided the outstanding characteristics of the material are not substantially destroyed. The presence of a polymer of methyl cyclopentadiene per se or a co-polymer of cyclopentadiene and methyl cyclopentadiene, or both, in amounts up to of the order of from 10 to 20% and possibly more, appears to have no deleterious effect. This does not apply to resinous materials in general and extreme care should be exercised in making any additions.

By the term "homo-polymer" is meant the result of the additive combination of a monomer and/or polymers of the same monomer, as distinguished from a "co-polymer" which results from the additive combination of different monomers and/or polymers of different monomers.

The presence of up to 20% or more of methyl cyclopentadiene in the starting material of Examples 1 and 2 appears to have no outstanding deleterious effect and the resulting polymerized product is defined in certain of the claims as resinous co-polymer of cyclopentadiene and methyl cyclopentadiene in which copolymer the proportion of methyl cyclopentadiene does not exceed 20%. The absence of all other materials polymerizable under the conditions employed is preferred. In fact, for the preparation of protective films giving the best results from every standpoint, it is preferred that there be present in the starting materials no substantial quantities of any other materials (besides the cyclopentadiene and methyl cyclopentadiene) which will form a resin under the polymerization conditions prevailing.

My polycyclopentadiene films are naturally colored in beautiful old gold. 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 polymer of cyclopentadiene selected from the group consisting of resinous polycyclopentadiene and resinous copolymer of cyclopentadiene and methyl cyclopentadiene in which copolymer the proportion of methyl cyclopentadiene does not exceed 20%, said formed film adhering tenaciously to the formed metal.

2. A formed film-coated article shaped by drawing a metallic sheet coated with dried resinous polymer of cyclopentadiene selected from the group consisting of resinous polycyclopentadiene and resinous copolymer of cyclopentadiene and methyl cyclopentadiene in which copolymer the proportion of methyl cyclopentadiene does not exceed 20%, said formed film adhering tenaciously to the drawn metal.

3. A formed film-coated container cap shaped by drawing film-coated metallic sheeting coated with dried resinous polymer of cyclopentadiene selected from the group consisting of resinous polycyclopentadiene and resinous copolymer of cyclopentadiene and methyl cyclopentadiene in which copolymer the proportion of methyl cyclopentadiene does not exceed 20%, said formed film adhering tenaciously to the drawn metal.

4. A formed film-coated threaded container cap shaped by drawing metallic sheeting coated with dried resinous polymer of cyclopentadiene selected from the group consisting of resinous polycyclopentadiene and resinous copolymer of cyclopentadiene and methyl cyclopentadiene in which copolymer the proportion of methyl cyclopentadiene does not exceed 20%, said formed film adhering tenaciously to the drawn metal including the threaded portion thereof.

5. A formed film-coated food container shaped by deformation of metallic sheeting coated with dried resinous polymer of cyclopentadiene selected from the group consisting of resinous polycyclopentadiene and resinous copolymer of cyclopentadiene and methyl cyclopentadiene in which copolymer the proportion of methyl cyclopentadiene does not exceed 20%, said formed film adhering tenaciously to the formed metal.

6. A food package comprising formed film-coated metallic sheeting shaped by deformation of metallic sheeting coated with a primer coat of dried resinous polymer of cyclopentadiene selected from the group consisting of resinous polycyclopentadiene and resinous copolymer of cyclopentadiene and methyl cyclopentadiene in which copolymer the proportion of methyl cyclopentadiene does not exceed 20%, and a top coat of dried resinous copolymer of vinyl chloride and vinyl acetate, said package for food having at least the surface thereof which would otherwise come in contact with the food to be packaged coated with the formed film, said formed film adhering tenaciously to the formed metal.

7. A food package comprising formed film-coated metallic sheeting shaped by deformation of metallic sheeting coated with dried resinous

polymer of cyclopentadiene selected from the group consisting of resinous polycyclopentadiene and resinous copolymer of cyclopentadiene and methyl cyclopentadiene in which copolymer the proportion of methyl cyclopentadiene does not exceed 20%, said food package having at least the surface thereof which would otherwise come in contact with the food to be packaged coated with the formed film, said formed film adhering strongly to the formed metal.

8. A formed film-coated article shaped by drawing a metallic body coated with an oxidized resinous film, said formed film adhering tenaciously to the formed metal and being comprised preponderantly of oxidized resinous polymer of material containing at least one of a group consisting of (a) cyclopentadiene and (b) cyclopentadiene in admixture with up to 20% of methyl cyclopentadiene as substantially the only resin forming content of said material.

9. A formed film-coated article shaped by drawing a metallic sheet coated with a small proportion of dried resinous polymethyl cyclopentadiene in admixture with dried resinous polycyclopentadiene, said formed film adhering tenaciously to the drawn metal, and the proportion of polymethyl cyclopentadiene in said admixture not exceeding 20%.

10. 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 polymer of cyclopentadiene selected from the group consisting of resinous polycyclopentadiene and resinous copolymer of cyclopentadiene and methyl cyclopentadiene in which copolymer the proportion of methyl cyclopentadiene does not exceed 20%, drying said coating, and subjecting the coated material to shaping operations to produce a formed article.

11. A method for producing a coated can cover having sharply bent coated portions from metallic sheeting which comprises coating said sheeting from which the can cover is to be formed with resinous polymer of cyclopentadiene selected from the group consisting of resinous polycyclopentadiene and resinous copolymer of cyclopentadiene and methyl cyclopentadiene in which copolymer the proportion of methyl cyclopentadiene does not exceed 20%, 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.

12. A process for producing a formed metallic article coated with a formed protective layer of synthetic resin which comprises coating metallic sheeting from which the article is to be formed

with resinous polymer of cyclopentadiene selected from the group consisting of resinous polycyclopentadiene and resinous copolymer of cyclopentadiene and methyl cyclopentadiene in which copolymer the proportion of methyl cyclopentadiene does not exceed 20%, drying said coating, applying over said first-mentioned coating a second coating of resinous copolymer of vinyl chloride and vinyl acetate, drying said second-mentioned coating, and subjecting the coated sheeting to shaping operations to produce said formed article.

13. A process for producing a formed coated article with a formed protective layer of synthetic resin which comprises coating metallic material from which the article is to be formed with a small proportion of resinous polymethyl cyclopentadiene in admixture with resinous polycyclopentadiene said proportion of polymethyl cyclopentadiene not exceeding 20%, drying said coating, and subjecting the coated material to shaping operations to produce a formed article.

14. A formed film-coated article shaped by deformation of a metallic body coated with a primer coat of dried resinous polymer of cyclopentadiene selected from the group consisting of resinous polycyclopentadiene and resinous copolymer of cyclopentadiene and methyl cyclopentadiene in which copolymer the proportion of methyl cyclopentadiene does not exceed 20% and a topcoat of dried resinous polymerized vinyl ester, said formed film adhering tenaciously to the formed metal.

15. A formed film-coated article shaped by drawing a metallic sheet coated with dried resinous polycyclopentadiene, said formed film adhering tenaciously to the drawn metal.

16. A formed film-coated can shaped by drawing a metallic sheet coated with dried resinous polycyclopentadiene, said formed film adhering tenaciously to the drawn metal.

17. A formed film-coated article shaped by drawing tin plate coated with dried resinous polycyclopentadiene, said formed film adhering tenaciously to the drawn metal.

18. A formed film-coated article shaped by drawing an iron sheet coated with dried resinous polycyclopentadiene, said formed film adhering tenaciously to the drawn metal.

19. A formed film-coated can shaped by drawing a metallic body coated with an oxidized resinous film, said formed film adhering tenaciously to the formed metal and being comprised preponderantly of oxidized resinous polymer of material containing cyclopentadiene as substantially the only resin forming content thereof.

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