Patented Oct. 23, 1945

2,387,626

UNITED STATES PATENT OFFICE

2,387,626

LIQUID COATING COMPOSITIONS, COATED OBJECTS, AND PROCESSES FOR MAKING SAME

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No Drawing. Application December 27, 1940, Serial No. 371,988

15 Claims. (Cl. 117—132)

This invention pertains generally to the coating of surfaces 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 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 over-estimated.

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 and 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 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" 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 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 comprising catalytically polymerized cyclopentadiene and one or more additives comprising a substance or substances of a wax-like nature with or without sulfur and/or a sulfur-containing substance. Drying of the applied film or films may be accomplished with or without the aid of 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 liquid coating composition or in the applied films is not implied. Preferably, my liquid coating composition, after admixture with a wax-like substance with or without a sulfur-containing substance and/or sulfur (referred to hereinafter and in the claims for convenience and brevity as "sulfur containing material") 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 the benzene-soluble catalytically 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 ($Ca(OH)_2$) 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.

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 cyclopentadienes 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. Other methods for making benzene-soluble catalytically polymerized cyclopentadiene obviously may be employed.

The wax-like material, which is employed according to my invention, are high molecular weight compounds or mixtures thereof such as may be found naturally in substances of animal and vegetable origin. Generally speaking, they include esters of higher acids and higher alcohols, although substances of mineral origin, for instance substances comprising one or more higher paraffin hydrocarbons likewise are included in the scope of the term. Likewise, substances of synthetic origin are included as well as those naturally occurring.

As examples of wax-like materials may be mentioned the following:

Cetyl cerotate, ($C_{16}H_{33}.OOC.C_{26}H_{53}$); cetyl acetate, ($C_{16}H_{33}.OOC.CH_3$); ethyl palmitate,

($C_2H_5.OOC.C_{15}H_{31}$)

cetyl palmitate, ($C_{16}H_{33}.OOC.C_{15}H_{31}$); lauryl laurate, ($C_{12}H_{25}.OOC.C_{11}H_{23}$); methyl stearate,

($CH_3.OOC.C_{17}H_{35}$)

glyceryl stearate, ($C_3H_5(C_{17}H_{35}COO)_3$); and spermaceti, a naturally occurring wax-like material comprising primarily cetyl palmitate.

Considering the wax-like fatty acid esters just named it may be said that especially effective additives comprise those in which the chain length of the individual molecules varies broadly from about 18 to 57 carbon atoms and particularly from about 18 to 43 carbon atoms. The esters toward the upper end of the latter range are in general preferred provided their solubility in the particular solvent containing the polycyclopentadiene is not so low as to render their practicable use less desirable. Mixtures of such esters containing molecules of 28 to 36 carbon atoms are especially satisfactory.

Excellent results are obtained when cetyl palmitate is used as the additive, particularly when in the form of the crude material known as spermaceti such as found in the head of the sperm whale.

One or more wax-like materials may be added to the benzene-soluble catalytically polymerized cyclopentadiene.

The quantity of wax-like additive may preferably be from about 15 to 25% based upon the content of polymer, although more or less may be employed with satisfactory results. Particularly desirable results are obtained when approximately 22% of wax-like additive is employed.

One or more sulfur containing substances are preferably employed as additional additive although this material may be omitted if desired.

Any suitable quantity of sulfur containing material, for example in the form of flowers of sulfur, may be employed of which from 1% to 15% and particularly 10% based upon polymer content is an example.

Usually, the addition of any sulfur-containing material is made prior to the application of the liquid coating composition to the surface or object to be coated. For example, flowers of sulfur may be added to the wax containing polycyclopentadiene prior to its application to the surface to be coated.

However, any addition of sulfur-containing material may be made after the liquid coating composition has been applied to the object to be coated. This may be accomplished for example, by drying the coated object in an atmosphere comprising hydrogen sulfide and/or other sulfur-containing material. In this case the sulfur-containing material is absorbed by the coating composition from the atmosphere.

Thus, the coated objects may be said to be coated with a dried film of a liquid coating composition comprising benzene-soluble catalytically polymerized cyclopentadiene in admixture with wax-like material with or without sulfur-containing material, and when sulfur containing material is employed the coatings may be said to be dried in admixture with sulfur-containing material irrespective of whether the sulfur containing material is first added or added by way of the drying atmosphere, or both.

The completely dried films are generally insoluble, particularly in the ordinary solvents.

I have found that by incorporating wax-like material with or without sulfur-containing material with benzene-soluble catalytically polymerized cyclopentadiene, the properties of the dried resin films are desirably modified, particularly with respect to their ability to withstand drastic metal-working operations such as the die-drawing steps employed to produce bottle caps or can ends from sheet metal.

It also appears that the addition of wax-like material with or without sulfur-containing material tends to reduce the rate of oxidation of the polycyclopentadiene film which may be desirable in some instances.

The ratio of additive employed may be varied considerably, depending upon factors such as the particular nature of the additive, the manner of drying, etc.

For example, while I have employed wax-like materials as additives in various concentrations from as low as 1% of the polycyclopentadiene content to as high as 30% and higher with satisfactory results, I find that a concentration of about from 15% to 25%, as for example 22% is particularly satisfactory, especially when combined with sulfur containing material in concentrations of from about 1% to 15% and particularly of about 10% of the polycyclopentadiene content. The maximum quantity of either material that will ordinarily be used in any given case will, of course, depend somewhat upon the solubility of the particular additive in the polymer solution, although it is conceivable that some of the additive or additives may be present in finely divided dispersed form.

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

Example 3

To a 20% solution of catalytically polymerized cyclopentadiene in toluene is added 22% spermaceti, calculated on the polymer content of the solution. The resulting liquid coating composition is applied to sheet metal, such as tin plate, in such quantities that the final resin film whether applied in one coat, or several coats with or without intermediate drying such as by baking, will have a desired thickness, for example

the equivalent of about 2 milligrams per square inch of dry film.

The coated sheet is placed in an oven and heated to a temperature of 250° F. for a period of about 8 minutes in order to insure satisfactory drying, the polycyclopentadiene adding an oxygen from the atmosphere during the baking. Alternatively, drying may take place at room temperature such as between 30 minutes and 6 hours.

Sheet metal thus coated is capable of withstanding drastic forming operations such as encountered in the manufacture of cans or other containers, container caps and the like, without injury to the film.

Example 4

To a 20% solution of catalytically polymerized cyclopentadiene in toluene is added 22% spermaceti, calculated on the polymer content of the solution. A tin plated sheet was coated with the resulting liquid coating composition in sufficient quantity to secure a desired final coating weight, for example, the equivalent of about 2 milligrams per square inch after drying such as by baking.

The coated sheet was placed in an oven and baked at a temperature rising from 86° F. (30° C.) to 266° F. (130° C.) over a period of 15 minutes while maintaining a constant flow of hydrogen sulfide through said oven and in contact with said coated sheet.

The metal sheet thus coated is able to withstand drastic metal working operations, such as are employed in the manufacture of cans, caps, and the like, without injuring the applied film.

Example 5

To a 24% solution of catalytically polymerized cyclopentadiene in toluene is added 22% spermaceti, and 10% sulfur, calculated on the polymer content of the solution. The resulting liquid coating composition is applied to sheet metal, such as tin plate, in such quantities that the final resin film whether applied in one coat, or several coats with or without intermediate drying such as by baking will have a desired thickness, for example, the equivalent of about 2 milligrams per square inch of dry film.

The coated sheet is placed in an oven and heated to a temperature of 250° F. for a period of 8 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. Baking times may be, for example, between four minutes and thirty minutes. The elevated temperatures employed favor the adding on of oxygen.

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 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.

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

Example 6

A tin plated sheet, or other metal sheet, is coated with a solution of polycyclopentadiene in toluene, say of 20% polycyclopentadiene content, to which 22% spermaceti and 10% sulfur based on polymer content have been added. The solution is applied in sufficient quantity to secure a desired final coating weight, say of approximately 1½ milligrams per square inch after drying such as by 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 5 to 10 minutes, the polycyclopentadiene adding on oxygen from the atmosphere during the baking.

Upon cooling, a solution of "Vinylite" 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 is then re-baked in the same manner as with the primer coat.

Metal sheet thus coated with the dual film may be subjected to forming operations such as those involved in the manufacture of caps, can elements and the like, without injury thereto.

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 benzene-soluble catalytically polymerized cyclopentadiene containing additives as described.

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, 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 the purpose.

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

Since my films of polycyclopentadiene plus wax-like additive, with or without sulfur containing material, 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 for primer coats of other materials, if desired. It is, of course, understood that my liquid coating composition may be used for both a primer coat and a top coat or in any other number of coats.

It will be understood that other sulfur-containing substances might be employed as sulfur containing material instead of, or together with, those already described. Examples of these are hydrogen polysulfide, H_2S_x (believed to comprise a mixture of H_2S_2 and H_2S_3), and sulfur-containing rubber vulcanization agents or accelerators, such as the product known commercially as "Tuads" (tetramethyl thiuram disulfide,

$Me_2N.CS.S.S.CS.N\ Me_2$)

or butyl zimate ($Bu_2N.CS.S.Zn.S.CS.N\ Bu_2$), either separately or insuitable admixture with each other.

With respect to the temperature and time of baking, I usually prefer to rarely if ever 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, while my resin films may be safely subjected to relatively high temperatures for brief periods 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 similarly satisfactory results.

I have found that a particularly satisfactory baking schedule is represented by a temperature of 250° F. for a period of 8 minutes. Another satisfactory baking schedule is represented by a procedure wherein the temperature during the bake is gradually raised from about room temperature to the maximum desired temperature such as about 250° F. over a period such as from 15 to 20 minutes. The advantage of a baking schedule such as the latter is that the solvent is driven off more gradually, thus minimizing or eliminating any tendency for the resin film to be ruptured by escaping solvent.

While I refer 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 may heat or bake the coating or the coated object in an atmosphere substantially devoid of oxygen such as an atmosphere of concentrated H_2S and/or in an inert atmosphere as of nitrogen, carbon dioxide, or the like.

Additional drying or hardening of the film may result from the absorption of oxygen after exposure to the atmosphere.

Thus the drying or hardening of a film of polycyclopentadiene containing a wax-like material, with or without sulfur containing material, may be secured (*a*) by baking or heating in an oxygen-containing and/or sulfur-containing atmosphere, or (*b*) baking in an atmosphere devoid of oxygen followed by exposure to an oxygen-containing atmosphere for a period of time, for example, a week before applying any top coating such as of "Vinylite," or (*c*) baking in an atmosphere devoid of oxygen, followed by application of a top coat, and then letting the dual film stand or "season" in contact with an oxygen-containing atmosphere before using the coated article for its intended purpose, (in the last-named case, oxygen evidently penetrates or seeps through the top coat to the primer coat), or (*d*) applying and drying the primer coat in an atmosphere devoid of oxygen, coating with a top coat of another resin such as "Vinylite," still in an atmosphere devoid of oxygen, and heating the multiple-film system thus formed, still in an atmosphere devoid of oxygen, or (*e*) any combination of any of the foregoing, or otherwise. It will be understood that an atmosphere devoid of oxygen may have present sulfur-containing material.

Since the resin coating resulting from (*d*) wherein the entire series of operations take place in an atmosphere devoid of oxygen is entirely satisfactory for commercial use, it would appear that my modified polycyclopentadiene films may be satisfactorily hardened either by heat, or by an oxygen-containing and/or sulfur containing environment or by any combination thereof.

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

In coating sheet metal, for instance, excellent results may be obtained by coating one side, baking that coating and then coating the other side, after which the sheet metal is again baked.

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

While the film thicknesses given are found to be extremely suitable for the purpose, and particularly for metal container elements such as food containers and caps, 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 of which benzene, xylene, ethyl benzene, naphtha, chloroform and carbon tetrachloride are examples.

For the purposes of the claims the term "highly flexible and extensible and tenaciously adhering film" or its equivalent is intended to define a film capable of withstanding the following test.

A tin panel of any convenient dimensions such as two by three inches is coated on one surface with a solution of the given resin in toluene in such quantities that the final film after baking will have a weight of from 2 to 6 milligrams per square inch. The temperature of baking is, for convenience, 270° F. After baking for one hour and cooling, the coated tin panel is bent backwardly on itself over a mandrel $\frac{1}{8}$ inch in diameter through an angle of 180° with the coated surface outward. The ends of the panel are then bent back to their original position. The film must withstand this manipulation without striation, loss of adhesion, surface cracking or checking or apparent optical change.

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 articles such as caps and "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 pre-fabricated or not, where a tough strongly adhering

film or film system is desired. The fabrication of toys from sheet metal for instance, represents another important field of application for my invention.

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 any suitable manner. Or the coating material may be poured or sprayed on the material to be coated and the excess removed by 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.

While it is preferred to employ cyclopentadiene as substantially the sole resin-forming hydrocarbon in initially preparing the catalytically polymerized polycyclopentadiene, which is then modified by additives in the manner described, the presence or addition of relatively small amounts of still other substances of a resin-forming nature with consequent modified results may be sometimes desirable, provided the outstanding characteristics of the base material are not substantially destroyed. Though in many instances I prefer to use the homopolymer of cyclopentadiene without other polymer, the presence of a homo-polymer of methyl cyclopentadiene 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 particularly for certain uses. This does not apply to resinous materials in general and extreme care should be exercised in making any additions.

The presence of up to 20% or more of methyl cyclopentadiene in the starting material from which the polycyclopentadiene resin is prepared appears to have no outstanding deleterious effect, particularly for certain uses, though I usually limit its presence or exclude it altogether. 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 for the most part highly desirable 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 new liquid coating composition has other uses than that of forming a protective surface. For example, it is an excellent adhesive or cement and serves admirably in this connection in various uses to which materials of this type are put.

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 such added substances 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 modifying agents besides those already mentioned, or otherwise.

In the specification and claims, the term "sulfur-containing" is intended to embrace elemental sulfur as well as compounds containing one or more sulfur atoms in the molecule.

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 liquid coating composition comprising benzene-soluble catalytically polymerized cyclopentadiene resin, wax-like fatty acid ester, a sulfur-containing rubber vulcanizing agent, and a volatile solvent, said resin being derived substantially entirely from said cyclopentadiene.

2. A liquid coating composition comprising benzene-soluble catalytically polymerized cyclopentadiene resin in admixture with spermaceti, said resin being derived substantially entirely from said cyclopentadiene.

3. A composition of matter comprising a wax-like material, and a benzene-soluble resinous polymer of a material having as substantially the only resin forming content thereof one of a group consisting of (*a*) cyclopentadiene and (*b*) cyclopentadiene admixed with up to 20% methyl cyclopentadiene.

4. A composition of matter comprising a wax-like fatty acid ester having between 18 and 57 carbon atoms, and a benzene-soluble resinous polymer of a material having as substantially the only resin-forming content thereof one of a group consisting of (*a*) cyclopentadiene and (*b*) cyclopentadiene admixed with up to 20% methyl cyclopentadiene.

5. A composition of matter comprising spermaceti and a benzene-soluble resinous polymer of a material having as substantially the only resin-forming content thereof one of a group consisting

of (a) cyclopentadiene and (b) cyclopentadiene admixed with up to 20% methyl cyclopentadiene.

6. A composition of matter comprising benzene-solube resinous polymer of cyclopentadiene per se, and from 15% to 25% spermaceti based upon said resinous polymer.

7. A composition of matter comprising a benzene-soluble resinous polymer of cyclopentadiene per se, from 1% to 30% spermaceti based on said resinous polymer, and from 1% to 15% sulfur-containing rubber vulcanizing agent based on said resinous polymer.

8. A formed film-coated article shaped by deformation of a metallic body coated with a dried film of a composition comprising a wax-like material and a benzene-soluble resinous polymer of a material having as substantially the only resin-forming content thereof one of a group consisting of (a) cyclopentadiene and (b) cyclopentadiene admixed with up to 20% methyl cyclopentadiene, said formed film adhering tenaciously to the formed metal.

9. A formed film-coated article shaped by drawing a metallic sheet coated with a dried film of a composition comprising a benzene-soluble resinous polymer of cyclopentadiene per se, from 1% to 30% spermaceti based on said resinous polymer, and from 1% to 15% sulfur-containing rubber vulcanizing agent based on said resinous polymer, said dried film adhering tenaciously to the drawn metal.

10. 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 spermaceti, and a benzene-soluble resinous polymer of a material having as substantially the only resin-forming content thereof one of a group consisting of (a) cyclopentadiene and (b) cyclopentadiene admixed with up to 20% methyl cyclopentadiene.

11. A formed film-coated food container shaped by deformation of metallic sheeting coated with a dried film of a composition comprising spermaceti and a benzene-soluble resinous polymer of a material having as substantially the only resin-forming content thereof one of a group consisting of (a) cyclopentadiene and (b) cyclopentadiene admixed with up to 20% methyl cyclopentadiene.

12. A food package comprising a formed film-coated metallic sheeting shaped by deformation of metallic sheeting coated with a dried film of a composition comprising spermaceti, and a benzene-soluble resinous polymer of a material having as substantially the only resin-forming content thereof one of a group consisting of (a) cyclopentadiene and (b) cyclopentadiene admixed with up to 20% methyl cyclopentadiene, 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.

13. 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 a composition comprising a wax-like material, and a benzene-soluble resinous polymer of a material having as substantially the only resin-forming content thereof one of a group consisting of (a) cyclopentadiene and (b) cyclopentadiene admixed with up to 20% methyl cyclopentadiene, drying said coating, and subjecting the coated article to shaping operations to produce a formed article.

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 a composition comprising a benzene-soluble resinous polymer of cyclopentadiene per se, and from 1% to 30% spermaceti based on said resinous polymer, drying said coating, and thereafter subjecting the coated article to shaping operations to produce a formed article.

15. 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 a composition comprising a benzene-soluble resinous polymer of cyclopentadiene per se, from 1% to 30% spermaceti based on said resinous polymer, and from 1% to 15% sulfur-containing rubber vulcanizing agent based on said resinous polymer, drying said coating, and subjecting the coated material to shaping operations to produce a formed article.

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