

UNITED STATES PATENT OFFICE

2,394,816

COMPOSITION OF MATTER, COATED ARTICLE, AND METHODS OF MAKING THE SAME

Frank J. Soday, Baton Rouge, La., assignor to
The United Gas Improvement Company, a corporation of Pennsylvania

No Drawing. Application May 17, 1943,
Serial No. 487,348

15 Claims. (Cl. 117-75)

This invention pertains to a new composition of matter and to the coating of surfaces such as 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, creasing, drawing, threading, turning, punching, and the like.

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 include 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 by the seaming chuck, seaming rolls, and cooperating parts of the can closing machine during the well known double-seaming can sealing operation.

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 case of metal foil wrappings, as is well known the foil is usually drastically and sharply creased in forming the food packages, as well as by the user in opening and closing the packages.

The coating on the foil therefore must be capable

of successfully withstanding very severe stresses.

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 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 accordance with my invention, single film systems and multiple film systems having 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 resinous benzene-soluble hydrogenated benzene-soluble catalytically polymerized cyclopentadiene to which is and/or has been added one or more additives comprising sulfur and/or sulfur containing substances. Drying of the applied film or films may be accomplished with or without the aid of heat.

Generally speaking, the benzene-soluble hydrogenated benzene-soluble catalytically polymerized cyclopentadiene employed in my new composition of matter has the following properties. It is soluble in benzene, toluene, chloroform, carbon tetrachloride and high flash naphtha, and insoluble in 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, nor is it implied that the hydrogenation is in the presence of benzene. Preferably, my composition containing a substance of the type described has other distinctive properties. Among these properties is the ability to form a smooth, glossy, highly flexible and extensible and tenaciously adhering film upon drying with or without baking.

The preparation of benzene-soluble hydrogenated benzene-soluble catalytically polymerized cyclopentadiene employed in my invention is described and claimed in my copending application, Serial Number 262,655, filed March 18, 1939, which will mature into Patent 2,319,271, on May 18, 1943.

As set forth in said copending application hy-

drogenation may be either partial or complete, such as substantially complete.

Hydrogenated polymers of this character, generally speaking, have an average of molecular weights above 350, and especially above 400, for example, above 450; as determined by the Rast Camphor method. Actual average molecular weights if much higher than 450, may be preferably determined by the Staudinger viscosity method, (Ind. and Engr. Chem., vol. 32, page 299, 1940) which is better adapted to the determination of high molecular weights than the Rast method. The Rast Camphor method, however, is suitable for determining whether the molecular weight is higher than any of the lower limits given.

In accordance with my present invention a sulfur-containing material (which term for brevity is to be construed as including sulfur) in suitable quantity is added to benzene-soluble hydrogenated resinous polymerized cyclopentadiene prior to the final drying (as by baking) of such hydrogenated polycyclopentadiene upon the surface to be protected.

Usually, the addition of the sulfur-containing material is made prior to the application of the benzene-soluble hydrogenated catalytically polymerized cyclopentadiene to the surface or object to be coated. Thus a sulfur-containing material, such as flowers of sulfur, may be added to said hydrogenated polycyclopentadiene prior to its application to the surface to be coated.

However, the addition of a sulfur-containing material to the hydrogenated polycyclopentadiene may be made after the latter has been applied to the object to be coated, for instance, by baking said object in an atmosphere comprising hydrogen sulfide or other sulfur-containing material in which case the sulfur-containing material is absorbed by the hydrogenated polycyclopentadiene from the atmosphere particularly when hydrogenation is partial.

Thus, the coated objects may be said to be coated with a dried film of a liquid coating composition comprising benzene-soluble hydrogenated catalytically polymerized cyclopentadiene in admixture with a sulfur-containing material and the coatings of benzene-soluble hydrogenated catalytically polymerized cyclopentadiene may therefore be said to be dried in admixture with a sulfur-containing material.

Both methods may be combined, if desired, that is the object or surface to be protected may be coated with benzene-soluble hydrogenated catalytically polymerized cyclopentadiene which already contains a sulfur-containing material, such as sulfur or hydrogen sulfide, and then the coating may be dried such as by baking in an atmosphere comprising hydrogen sulfide or the like.

By thus incorporating a sulfur-containing material with benzene-soluble hydrogenated catalytically polymerized cyclopentadiene, the properties of the finished resin film are desirably modified.

The addition of a sulfur-containing material such as sulfur will also tend to reduce the rate of oxidation of the hydrogenated polycyclopentadiene film particularly in the case of partial hydrogenation which may be desirable in some instances.

It will be understood that the optimum ratio of additives to be employed may vary somewhat, depending upon factors such as the particular additive, the manner of drying employed, etc. While

sulfur as additive may be employed in concentrations of as low as 0.1% (based upon the hydrogenated polycyclopentadiene present in the coating solution) with improved results, generally speaking concentrations in excess of 8% and particularly those lying in the range of from 10 to 16% will give very satisfactory results. The maximum quantity employed preferably depends upon the solubility of the additive in the polymer solution, which in turn depends upon the hydrogenated polycyclopentadiene concentration although it is conceivable that some of the additive may be present in a finely divided dispersion.

Higher concentrations of additives may be obtained by supersaturating or by dispersing.

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.

An example of the formation of a single film system is as follows:

Example 1

To a 20% solution of benzene-soluble hydrogenated catalytically polymerized cyclopentadiene in toluene add 3% sulfur, calculated on the polymer content of the solution. Apply the resulting liquid coating composition 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 from 4 to 6 milligrams per square inch of dry film.

Place the coated sheet in an oven and heat to a temperature, for example, of 250° F. for a period of about 15 minutes in order to insure satisfactory drying. Alternatively, drying may take place at room temperature such as between 1 hour and 6 hours or more as required.

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.

An example of the formation of a dual film system is as follows:

Example 2

Coat a tin plated sheet, or other metal sheet, with a solution of hydrogenated resinous polycyclopentadiene in toluene, say of 20% hydrogenated polycyclopentadiene content, to which 5% sulfur based on polymer content has been added. Apply the solution in sufficient quantity to secure a desired final coating weight, say of approximately 1½ milligrams per square inch after drying, such as by baking.

Place the coated sheet after suitable evaporation of solvent in an oven and bake at a temperature of say 250° F. for a period of 5 to 10 minutes.

Upon cooling, apply a solution of "Vinylite" 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.

Then rebake the coated sheet 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.

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 of any of the vinyl compounds used as raw materials for the several vinyl resins; for example, 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 hydrogenated benzene-soluble catalytically polymerized cyclopentadiene containing additives as described.

"Vinylite" is thought to result from the copolymerization of about 85% of vinyl chloride with about 15% vinyl acetate, although other proportions are possible.

Since my films of hydrogenated polycyclopentadiene plus additive 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 additives 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 other sulfur-containing rubber vulcanization agents or accelerators, such as the product known commercially as "Tuads" (tetramethyl thiuram disulfide, $Me_2N.CS.S.CS.N.Me_2$) or butyl zimate ($Bu_2N.CS.S.CS.N.Bu_2$), either separately or in suitable admixture with each other. Thus, for example, 12% hydrogen polysulfide; 0.1% to 5.0% "Tuads"; and 0.1% to 3% butyl zimate: either alone or with varying amounts such as from 1% and 3% sulfur, are among the additive combinations that may be employed with hydrogenated polycyclopentadiene to give resin films on sheet metal capable of withstanding drastic shaping and forming operations.

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, temperatures up to 350° F. with baking times up to 30 minutes will be satisfactory. With higher temperatures the baking time may be correspondingly shortened to yield similarly satisfactory results.

A particularly satisfactory baking schedule is represented by a temperature of 250° F. for a period such as from 10 to 15 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 herein 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, if this takes place at all, need not necessarily take place simultaneously with the heating or baking. On the con-

trary, 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 gas 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 depending upon the degree to which the polycyclopentadiene has been hydrogenated.

Thus the drying or hardening of a film of hydrogenated polycyclopentadiene containing 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, if applied, such as of "Vinylite," or (c) baking in an atmosphere devoid of oxygen, followed by application of a top coat, if used, 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 may penetrate or seep 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, 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, if desired.

My modified hydrogenated resinous polycyclopentadiene films may be satisfactorily hardened either by heat, or by an oxygen-containing and/or sulfur containing environment or by any combination thereof, or otherwise.

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

While the film thicknesses given are 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.

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 baking 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 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 from which the benzene-soluble hydrogenated polycyclopentadiene is made, 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, providing 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 as the material to be hydrogenated, homopolymer of methyl cyclopentadiene or copolymer of cyclopentadiene and methyl cyclopentadiene, or both, in amounts up to of the order of from 10 to 20% and possibly more may be present during hydrogenation particularly for certain uses. This does not apply to resinous materials in general and extreme care should be exercised in making any additions prior to hydrogenation.

Up to 20% or more of methyl cyclopentadiene may be present in the starting material from which the polycyclopentadiene resin which is to be hydrogenated is prepared, particularly for certain uses, though its presence may be limited or excluded altogether. The absence of all other materials polymerizable under the conditions employed is preferred.

After hydrogenation a suitable additional additive or additives, other than that to which this invention particularly relates may be also employed in regulated amount of which wax-like materials such as wax-like fatty acid esters having between 18 and 57 carbon atoms, for instance, spermaceti; vinyl resins such as vinylite; resins

extracted from petroleum oils; and inhibitors such as secondary aryl amines; are examples. Reference is made to my copending applications, Serial Nos. 487,352; 487,350; 487,349; and 487,351, all filed May 17, 1943, respectively.

While the invention has been described in considerable detail with respect to the use of hydrogenated catalytically polymerized cyclopentadiene containing an additive of the character particularly described, with or without the use of other additives, as a coating composition, it is to be understood that such compositions also may be used for other purposes for which the peculiar properties of hydrogenated polycyclopentadiene make the composition particularly applicable, such as for the preparation of plastic masses in general.

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.

The starting materials employed in this invention namely benzene soluble catalytically polymerized cyclopentadiene, benzene-soluble catalytically polymerized methyl cyclopentadiene, and benzene-soluble catalytic copolymer of cyclopentadiene and methyl cyclopentadiene may be obtained from any desired source, for example, by any of the processes described and claimed in U. S. Patents 2,314,902; 2,314,903; 2,314,904; 2,314,909; 2,314,910; and 2,314,911; all dated March 20, 1943; or in my copending applications Serial No. 414,278, filed October 9, 1941; Serial No. 415,220, filed October 16, 1941; and Serial No. 415,648, filed October 18, 1941.

These polymers, generally speaking, have molecular weights above 350, and especially above 400, for example, above 450, similarly to the hydrogenated polymers.

The hydrogenation of all these starting materials may be carried out in all respects similarly to the hydrogenation of benzene-soluble catalytically polymerized cyclopentadiene or in other words benzene-soluble resinous polycyclopentadiene as described and claimed in my above mentioned copending application Serial No. 262,655, filed March 18, 1939.

The hydrogenation of benzene-soluble catalytically polymerized methyl cyclopentadiene and of catalytic copolymer of cyclopentadiene and methyl cyclopentadiene is described and claimed in my copending application Serial No. 487,356, filed May 17, 1943.

For certain purposes, the surface active agent polymers such as the clay polymers of Serial No. 414,278 or the organic acid sulfate polymers such as the alkyl sulfuric acid polymers of Serial No. 415,220 are preferred for hydrogenation purposes.

For example, a higher degree of hydrogenation

may be attained with a given effort. This applies particularly to activated clay polymers.

It will be noted that the starting materials are polymers of monomers as distinguished from polymers of dimers.

It will be understood that monomethyl cyclopentadiene may have three isomeric forms. Of these three forms, the form in which the methyl group is attached to the carbon atom having only single bonds is generally speaking preferred.

While the invention has been described more particularly with respect to hydrogenated polymers of cyclopentadiene and hydrogenated polymers of cyclopentadiene-methyl cyclopentadiene mixtures in which the methyl cyclopentadiene is limited to 20% and with respect to mixtures of cyclopentadiene polymers and methyl cyclopentadiene polymers in which the methyl cyclopentadiene polymers are limited to 20%, this applies particularly when the polymers are to be used for the coating of metals which are to be drawn or otherwise deformed after coating in the production of a finished article such as a food container.

Since my new hydrogenated polymers may be utilized for purposes other than that of coating of metals which are to be drawn or deformed after coating and since they have utility in this field even though methyl cyclopentadiene or polymers of methyl cyclopentadiene are not restricted as suggested, it is to be understood that my new compositions of matter and their uses include the addition of my additive more particularly described to anyone or to any mixture of hydrogenated polymer of cyclopentadiene, hydrogenated polymer of methyl cyclopentadiene and/or hydrogenated polymer of cyclopentadiene-methyl cyclopentadiene mixtures without limitation as to the quantity of methyl cyclopentadiene present in such mixtures, 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.

This invention is an improvement over that of my copending application Serial No. 417,576, filed November 1, 1941.

I claim:

1. A new composition of matter comprising a benzene-soluble product resulting from the hydrogenation of at least one of a group consisting of resinous polymerized cyclopentadiene, resinous polymerized methyl cyclopentadiene, and resinous copolymer of cyclopentadiene and methyl cyclopentadiene in admixture with a sulfur containing rubber vulcanizing agent.

2. A new composition of matter comprising a benzene-soluble product having an average molecular weight above 350 and resulting from the hydrogenation of at least one of a group consisting of resinous polymerized cyclopentadiene, resinous polymerized methyl cyclopentadiene and resinous copolymer of cyclopentadiene and methyl cyclopentadiene admixed with a sulfur containing rubber vulcanizing agent.

3. A new composition of matter comprising benzene-soluble hydrogenated resinous polymerized cyclopentadiene having an average molecu-

lar weight above 400 admixed with a sulfur containing rubber vulcanizing agent.

4. A new composition of matter comprising benzene-soluble hydrogenated resinous polymerized cyclopentadiene having an average molecular weight above 450 admixed with a sulfur containing rubber vulcanizing agent.

5. A new composition of matter comprising benzene-soluble hydrogenated resinous polymerized cyclopentadiene having an average molecular weight above 350 admixed with elemental sulfur.

6. A new composition of matter comprising benzene-soluble hydrogenated resinous polymerized cyclopentadiene having an average molecular weight above 350 admixed with hydrogen sulfide.

7. A coated article having applied thereto a dried film of a benzene-soluble product having an average molecular weight above 350 and resulting from the hydrogenation of at least one of a group consisting of resinous polymerized cyclopentadiene, resinous polymerized methyl cyclopentadiene and resinous copolymer of cyclopentadiene and methyl cyclopentadiene in admixture with a sulfur containing rubber vulcanizing agent.

8. A container for food products comprising a metallic receptacle having on an interior surface thereof a dried film of hydrogenated resinous polymer of cyclopentadiene in admixture with a sulfur containing rubber vulcanizing agent.

9. A food package comprising a metallic material having at least the surface thereof which is to come in contact with the food to be packaged coated with a dried film of hydrogenated resinous polymer of cyclopentadiene having an average molecular weight of at least 350 in admixture with a sulfur containing rubber vulcanizing agent.

10. Metal foil coated with a dried film of hydrogenated resinous polymer of cyclopentadiene having an average molecular weight of at least 350 in admixture with sulfur containing rubber vulcanizing agent.

11. A method for producing a metallic food container element which comprises applying to sheet metal a coat of a benzene-soluble product resulting from the hydrogenation of at least one of a group consisting of resinous polymerized cyclopentadiene, resinous polymerized methyl cyclopentadiene, and resinous copolymer of cyclopentadiene and methyl cyclopentadiene in admixture with a sulfur containing rubber vulcanizing agent, drying said coat, cutting a blank from said sheet metal of a desired shape, and forming said blank to the finished shape of said food container element.

12. A method for producing a metal cap having sharply formed portions from sheet metal which comprises coating said sheet metal with a benzene-soluble product resulting from the hydrogenation of at least one of a group consisting of resinous polymerized cyclopentadiene, resinous polymerized methyl cyclopentadiene, and resinous copolymer of cyclopentadiene and methyl cyclopentadiene in admixture with a sulfur containing rubber vulcanizing agent, cutting a blank of desired shape from said sheet metal and die-drawing said blank to the finished shape of said cap.

13. A process for coating a metal surface with an adherent coating which comprises applying to said surface a primer coat of a benzene soluble product resulting from the hydrogenation of at least one of a group consisting of resinous polymerized cyclopentadiene, resinous polymerized methyl cyclopentadiene, and resinous copolymer of cyclopentadiene and methyl cyclopentadiene in

admixture with a sulfur containing rubber vulcanizing agent, and applying to said primer coat after drying a top coat of polymerized vinyl compound.

14. As a new composition of matter, benzene-soluble hydrogenated resinous polymer of monomeric cyclopentadiene having an average molecular weight above 450 admixed with 10 to 16% by weight thereof of elemental sulfur.

15. A formed film coated article shaped by dras-

5 tic deformation of sheet metal coated with a composition comprising benzene-soluble hydrogenated resinous polymer of monomeric cyclopentadiene having a molecular weight of at least 450 and from 10% to 16% by weight of said hydrogenated resinous polymer of elemental sulfur, said formed film adhering tenaciously to the formed metal.

FRANK J. SODAY.