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FORMATION OF REFLECTING COATINGS

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This invention relates generally to improvements in articles comprising a base material having a lustrous, light reflecting coating thereon and to methods of producing these articles.

The formation of mirror-like films by chemical deposition of a metal or of a metallic salt, such as a sulfide, has been well known for many years. By this method, non-metallic articles not directly susceptible to having a metallic coating formed thereon by electrodeposition can be provided with films of silver, copper or other metals which can readily be deposited by reducing agents from solutions of one or more of their salts. Glass, for example, may be provided with mirror-like coatings of silver. Other non-metallic bases, such as various synthetic resinous materials, have also been subjected to chemical deposition of mirror-like coatings with generally less satisfactory results. Examples of resinous materials which have been provided with mirror-like coatings are cellulose acetate, cellulose nitrate and polymethyl methacrylate. Processes of coating these latter materials have, however, been open to several serious disadvantages. Unless treated with a sensitizing agent, cellulose derivatives usually take an imperfect metallic coating with many blemishes and discolorations. Also, coatings, which are heavy enough and of sufficient reflectivity when first deposited, discolor badly upon ageing.

These defects have been found to be virtually eliminated and otherwise improved films of various metallic substances have been produced by the process of the present invention. Briefly, this invention comprises forming a film of any one of a number of non-polar, non-saponifiable hydrocarbon resins on any suitable base material and then depositing a light-reflecting film of a metallic substance by chemical deposition on the resin film. By metallic substance is meant either a metal or metallic salt. It is necessary to form the resin film by dissolving the resinous material in a solution of a volatile solvent, applying the solution to the article which is to be coated and then evaporating the solvent.

One object of the present invention is to provide improved articles having mirror-like surface coatings thereon.

Another object of the invention is to provide an improved process of preparing a material to receive a mirror-like coating.

Another object of the invention is to provide an improved process of providing a base material with a mirror-like coating.

Another object of the invention is to provide an improved process of preparing a base material to have chemically deposited thereon a lustrous coating of a metallic substance.

Still another object of the invention is to provide an improved method of depositing a metallic coating on synthetic resinous objects formed by extrusion or compression molding or by calendering.

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These and other objects will be more apparent and the invention will be more readily understood when considered in connection with the following specification.

In general, the method of the present invention comprises making up a solution of a non-saponifiable resin from the group consisting of hydrocarbon resins and chlorinated hydrocarbon waxes, in a convenient organic solvent, applying the solution to the surface of the article to be coated either by dipping, brushing, spraying, etc., permitting the solvent to evaporate, leaving a resinous or waxy film and then chemically depositing a metallic coating thereon. The surface of the resinous film may first be sensitized by treatment with a sensitizing solution such as stannous chloride, although this is not absolutely necessary.

Example I

A glass plate was dipped into a solution comprising 100 g. of toluol and 5 g. of a cyclized rubber resin ("Pliolite"). The solvent was permitted to evaporate, thus forming a film of the resinous material on the glass. The coated plate was then immersed in a 2 per cent solution of stannous chloride for one minute, then rinsed thoroughly with water. The thus treated surface was then silvered, using the well known Rochelle salt formula. The silvering solution was composed of equal volumes of "A" and "B" solution. The "A" solution comprised 20 g. of silver nitrate per liter of solution and enough ammonium hydroxide to just dissolve the precipitate, due to the presence of the ammonia. The "B" solution was made up of 2 g. of silver nitrate and 1.7 g. Rochelle salt per liter. After 10 minutes at room temperature the plate was removed from the silvering solution, washed and dried. A good mirror coating of silver was deposited on the surface of the resinous film.

As a comparison test, a thin sheet of similar cyclized rubber prepared by calendering was silvered as described above. The resulting silver coating was non-uniform and had much lower reflectivity and luster than the coating applied as first described.

As a further comparison test, a sheet of similar cyclized rubber prepared by calendering was brushed with a solution of toluol which was then permitted to evaporate. The thus treated sheet was then silvered as described above. Besides having a lower luster than the coating made as first described, the surface showed undesirable distortion and wrinkling known as "alligatoring."

Example II

A panel of polished wood was dipped into a solution containing a 5 per cent by weight solution of a chlorinated paraffin wax (Chlorafine 70). The solvent was permitted to evaporate and the surface was then treated and silvered as in Example I. A silver coating having high reflectivity and luster was produced.

A similar attempt to deposit a silver coating on a sheet of the same chlorinated paraffin wax produced by calendering resulted in the formation of a lusterless coating having low reflectivity.

Example III

A sheet of ethyl cellulose was partly dipped into a 5 per cent solution of a chlorinated rubber ("Parlon") in toluol. The solvent was allowed to evaporate after which the sheet was cleaned in a 2 per cent aqueous solution of trisodium phosphate, which was later rinsed off with water. The entire sheet was then submitted to a silvering operation, as described in Example I. The area coated with the chlorinated rubber showed much greater brilliance of the silver mirror than the uncoated ethyl cellulose area. After several months of ageing, the relative brilliance of the two areas remained substantially unchanged.

Example IV

A sheet of vinyl plastic consisting of a copolymer of vinyl chloride-vinyl acetate was partly dipped into a 10 per cent solution of a polyindene resin (Nevindene LX–509) in toluol. After evaporation of the solvent, the sheet was cleaned and sensitized as in Example I, but the silvering in this case was according to the Brashear formula. A reducing solution was prepared by dissolving 90 g. of cane sugar and 4 cc. of concentrated nitric acid in 1 liter of water. A silver solution was prepared by dissolving 20 g. of silver nitrate in 400 cc. of water, adding 10 g. of potassium hydroxide and enough ammonia to dissolve the precipitate. One part by volume of the reducing solution and 5 parts by volume of the silver solution were mixed and the sheet immersed therein. After 10 minutes, the sheet was removed, washed and dried. The area coated with the polyindene resin showed much greater brilliance of the silver mirror than the uncoated area of the vinyl sheet.

Example V

A sheet of cellulose nitrate was partly dipped in a 5 per cent solution of a chlorinated naphthalene wax ("Halowax") in tetrachloroethane. After evaporation of the solvent and washing in warm water, the sheet, without sensitization, was silvered according to the "Formaldehyde" formula. A reducing solution was prepared by dissolving 40 cc. concentrated formaldehyde solution in 200 cc. of water. A silver solution was prepared by dissolving 20 g. of silver nitrate in 1 liter of water and adding just enough ammonia to dissolve the precipitate first formed. Five parts by volume of the silver solution and 1 part by volume of the reducing solution were mixed and the sheet immersed. After 10 minutes, the sheet was removed, washed and dried. The area coated with the chlorinated naphthalene wax had taken a silver mirror of much greater brilliance than that produced on the part of the sheet not resin-coated.

Solutions of various other synthetic hydrocarbon resins in volatile solvents were made up and films were applied to various bases which were sufficiently non-porous to take a smooth surfaced film. Two examples of additional synthetic hydrocarbon resins on which excellent results were observed are "Clarite" and "Nypene" (produced by the Neville Company, Pittsburgh, Pennsylvania). "Clarite" resin is a cycloparaffin or naphthene polymer. "Nypene" resin is a terpene polymer hydrocarbon. Chlorinated diphenyls and chlorinated cymenes were also successfully silvered as described in the examples above, as were coumarone resins, polymerized vinyl naphthalenes and others.

The type of silvering solution used is not critical in the process. Any of those described in the above examples can be used interchangeably. These and others have been more fully described in Circular No. 389, the U. S. Bureau of Standards, entitled "The Making of Mirrors by the Deposition of Metals on Glass" by Gardner and Case.

It has been found further that the process of the present invention is also applicable to the chemical deposition of films of metal other than silver and of mirrorlike films of metallic salts. Mirror-like films of copper can be formed, for example, which have physical and optical properties superior to those found in films deposited by other methods.

Example VI

A sheet of cellulose acetate was partly dipped in a 10 per cent solution of cyclized rubber resin (Pliolite) in toluol. A copper-depositing solution was then made up according to the directions given in U. S. Bureau of Standards Circular No. 389, January 6, 1931, page 12. In this example, the mixture comprised 50 cc. of a 10 per cent solution of ammoniacal copper sulfate, 40 cc. of a 5 per cent solution of hydrazine sulfate and 30 cc. of a 10 per cent solution of sodium hydroxide. The mixture was used at about 160° F. After evaporation of the solvent, the sheets were immersed in the above described copper solution. A copper mirror was deposited on both the coated and uncoated parts of the sheet but the metal film on the resin-coated portion had superior optical properties to that deposited on the uncoated portion. Similar results were observed on sheets coated with polystyrene deposited from a 5 per cent toluol solution.

Example VII

The present process can also be used for the chemical deposition of nickel films. A sheet of ethyl cellulose was coated over part of its area with a film of cyclized rubber deposited from a 10 per cent toluol solution. A nickel depositing solution was prepared which contained:

70 cc. of a 1 per cent solution of nickel formate
7 cc. of a 50 per cent solution of sodium hypophosphite
7 cc. of an 85 per cent solution of hydrazine hydrate
28 drops of a 0.1 per cent solution of palladium chloride

Previous to the making of the above solution, the nickel formate solution had been cooled to about 10° C. The partially coated sheet of ethyl cellulose was immersed in the above mixture and the palladium chloride added to initiate the reaction. After 10 minutes, the sheet was removed from the bath, washed and dried. The nickel film deposited on the part coated with cyclized rubber showed reflectivity decidedly superior to that deposited on the uncoated ethyl cellu-

lose. Similar results were obtained on a film of polystyrene coated from a 5 per cent toluol solution on ethyl cellulose.

Example VIII

As an example of the deposition of a mirror-like film of a metallic salt, a film of lead sulfide was deposited. Sheets of ethyl cellulose partially coated with cyclized rubber or polystyrene were prepared as in Example VII. A deposition solution of lead sulfide was then made up according to the instructions given in U. S. Bureau of Standards Circular No. 389, page 13. 50 cc. of a 2 per cent solution of thiourea in water were mixed with 25 cc. of a 10 per cent sodium hydroxide solution and heated to about 140° F. The resin-coated sheets were immersed in the solution and 50 cc. of a 10 per cent solution of lead acetate added with stirring. A film of lead sulfide developed very rapidly on the sheets. After 5 minutes, they were removed, washed and dried. The mirror properties of the lead sulfide film formed on the resin-coated surfaces were far superior to those of the film formed on the ethyl cellulose surfaces.

The improvement in mirror-like films obtained by forming them as in the above described examples has been found to be obtained generally using solvent-deposited resin films of any non-saponifiable resin of the group consisting of hydrocarbon resins and chlorinated hydrocarbon waxes. The observed difference in brilliance appears to be due to the difference in grain size and grain alignment of the metallic crystals obtained on the respective surfaces. In some cases, the grain size of the silver crystals, for example, formed on the solvent-deposited resin films appears to be about one-fifth of that obtained on the surfaces which have not been coated with the resin. This difference, together with more uniform alignment, seems to account for the greater brilliance.

The difference in grain size and alignment, in turn, appears to be greatly influenced by the type of surface upon which the metallic layer is deposited. It has been found that, generally, resins of the polymerized hydrocarbon type; i. e., free of acidic groups and therefore non-saponifiable, have the tendency to promote the growth of a metallic layer of extremely fine grain size and therefore of high brilliance. Moreover, when these resins are deposited as a film from solvent solution, their surface characteristics are different from those of formed bodies of the same resins produced by other methods, such as extrusion, calendering or compression molding. Local strain differentiations in the plastic base, which are unavoidable in a calendered, extruded, molded or cast sheet, are absent in a film produced by solvent evaporation.

In resinous bodies produced by casting, calendering, extrusion, etc., the alignment of the surface molecules is disturbed in such a manner as to affect the physical nature of the subsequently deposited metal or metallic salt. Thus, while two hydrocarbon resin bodies, one of which is produced by extrusion and the other produced by solvent evaporation, may be chemically identical, it has been found that there is marked difference in the optical characteristics of a metallic coating deposited on their respective surfaces. In addition, the absence of polar groups in the non-saponifiable hydrocarbon resin is thought to affect the initial formation of metallic nuclei in such a manner that they

are smaller, more uniform and numerous than in the presence of polar groups in other types of resins. The chlorine atoms in the chlorinated hydrocarbon waxes may be polar in themselves, but by balancing each other in the molecule itself, may be considered non-polar. This explains the excellent results obtained with chlorinated hydrocarbon waxes.

It has been found that neither the thickness of the resin film nor its aging time, either at room temperature or at elevated temperatures, affects the characteristics of the metallic deposit. Nor is there any effect due to differences in the solvent. The particular base material upon which the resinous film is deposited also does not affect the character of the metallic film subsequently deposited although, of course, it is preferable to start with a smooth, non-porous surface.

The manner in which chemical deposition is accomplished is also subject to various modifications. Reduction of the metal or metallic salt can be brought about by a spray process instead of immersing the coated object in a solution. That is, the resin-coated base may be sprayed simultaneously with solutions of metal salt and reducing agent as is commonly done in silvering large pieces of plate glass.

I claim as my invention:

1. A process of depositing a mirror-like coating on a surface of a solid object comprising applying to said surface a solution consisting essentially of a coating material selected from the group consisting of non-saponifiable hydrocarbon resins and chlorinated hydrocarbon waxes in a volatile organic solvent, permitting said solvent to evaporate thereby depositing on said surface a film consisting essentially of said coating material, and then applying a metallic film over said first-mentioned film by the process of chemical deposition comprising reducing a solution of a metal salt with a solution of a reducing agent.

2. A process according to claim 1 in which said coating material is a cyclized rubber.

3. A process according to claim 1 in which said coating material is a chlorinated paraffine.

4. A process according to claim 1 in which said coating material is a polyindene resin.

5. A process according to claim 1 in which said metallic film is silver.

6. A process according to claim 1 in which said metallic film is copper.

7. A process according to claim 1 in which said metallic film is lead sulfide.

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