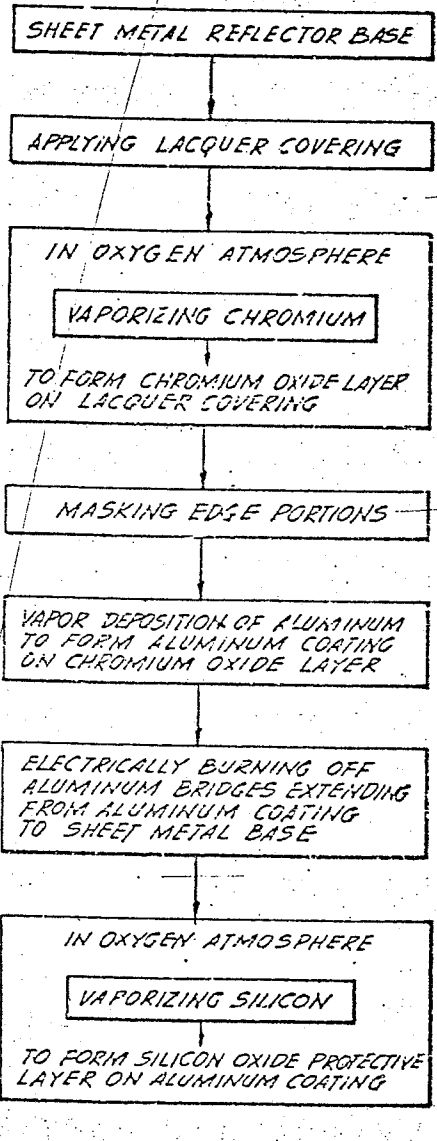
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METHOD OF FORMING CORROSION RESISTANT COATINGS

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METHOD OF FORMING CORROSION RESISTANT COATINGS

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The present invention relates to a method of forming a corrosion resistant coating and, more particularly, the present invention is concerned with a method for producing on a lacquer-covered metallic body a firmly adhering, corrosion resistant, reflecting metal coating.

Broadly, the method of the present invention is carried out by vapor deposition in a partial vacuum of an intermediate layer consisting of a metal oxide, deposition of this intermediate layer being carried out in the specific manner described further below, and thereafter vapor depositing an aluminum coating on the intermediate metal oxide layer.

The novel features which are considered as characteristic for the invention are set forth in particular in the appended claims. The invention itself, however, both as to its construction and its method of operation, together with additional objects and advantages thereof, will be best understood from the following description of specific embodiments when read in connection with the accompanying drawing, in which the drawing is a flow diagram of the present method.

It is primarily contemplated to use the method of the present invention for the forming of coatings on surfaces which will be manually contacted and which up to now usually had to be provided with galvanic coatings.

It is an object of the present invention to provide such reflecting aluminum coatings in a particularly simple and economical manner and so that the thus-formed aluminum coating will be corrosion resistant and firmly adhering to its support.

Decorative layers which up to now were formed for instance on vapor deposited neutralizing intermediate or separating layers of zinc sulfide, tin oxide, beryllium oxide, barium sulfide, chromium, or silicon oxide possess the desired permanency only when not exposed to severe conditions of wear. Thus, the adherence of the metallic layer formed on such conventional separating layers is not sufficiently firm, or even when using a chromium intermediate layer, the decorative, reflecting metallic surface layer will not withstand the severe stresses in a corrosion promoting environment to which for instance portions of automobile trim, such as the metal rings surrounding the headlights are exposed. This to a considerable extent is due to the fact that such prior art metallic surface layers cannot be completely insulated or electrically neutralized.

It is thus a further object of the present invention to provide a method for producing a metallic reflecting coating, particularly an aluminum coating which is not subject to the above discussed disadvantages of prior art coatings of this kind.

Other objects and alvantages of the present invention will become apparent from a further reading of the description and of the appended claims. With the above and other objects in view, the present invention is concerned with a method for forming on a lacquer-covered metallic body a firmly adhering, corrosion resistant, reflecting metal coating, comprising the steps of contacting the lacquer-covered body with an oxygen atmosphere maintained at subatmospheric pressure, vaporizing chromium in the atmosphere so as to deposit the same on the

lacquer-covered metallic body, the chromium being oxidized by the oxygen of the atmosphere while being deposited so as to form a layer of chromium oxide on the body, and forming by vapor deposition an aluminum coating on the layer of chromium oxide, the lacquer covering and the chromium oxide layer electrically insulating the aluminum coating from the metallic body.

A preferred manner of carrying out the method of the present invention comprises the steps of contacting the lacquer-covered body with an oxygen atmosphere maintained at subatmospheric pressure of about 10^{-3} mm. Hg, vaporizing chromium in the atmospheres so as to deposit the same on the lacquer-covered metallic body, the chromium being oxidized by the oxygen of the atmosphere while being deposited so as to form a layer of chromium oxide on the body, forming by vapor deposition in an inert argon atmosphere maintained at subatmospheric pressure of about 10^{-3} mm. Hg, the atmosphere being ionized by glow discharge, an aluminum coating on the layer of chromium oxide, the lacquer covering and the chromium oxide layer substantially but not completely electrically insulating the aluminum coating from the metallic body without, however, completely eliminating the formation of small aluminum bridges extending transversely through the chromium oxide layer and the lacquer covering from the aluminum coating to the metallic body, electrically burning off the aluminum bridges so as to completely insulate the aluminum coating from the metallic body, and forming by vapor deposition of silicon in an oxygen atmosphere maintained at a subatmospheric pressure of about 10^{-4} mm. Hg a protective layer of silicon oxides on the aluminum coating.

According to the present invention, aluminum coatings are produced by forming a chromium oxide covering or layer on the lacquer-covered metallic body by vapor deposition of chromium in a diluted oxygen atmosphere. Thereby it is accomplished that the vaporized chromium, while being deposited, will be transformed into chromium oxide. Thereafter, an aluminum coating is vapor deposited on the thus formed chromium oxide layer. When only portions of the metallic body are to be thus treated and, consequently only portions of the metallic body are lacquer covered, then it is essential to prevent the formation of aluminum bridges at the edges of the lacquer covering, since such aluminum edges would form an electrical contact between the aluminum coating and the only partially lacquer-covered metallic body. For this reason, in cases where not the entire metallic body is covered with lacquer, it is contemplated according to the present invention to mask the edge portions of the lacquer covering prior to vapor deposition of the aluminum coating so that, after removal of the masking, the edge portion of the lacquer covering will extend outwardly beyond the aluminum coating and consequently lateral contact between the aluminum coating and the metallic body will not occur.

It is frequently unavoidable that cracks or fissures occur or are formed in the lacquer covering and in the chromium oxide layer. Upon vapor deposition of the aluminum coating, aluminum will penetrate such cracks or fissures and small bridges will be formed, electrically connecting the aluminum coating with the metallic body. It is important according to the present invention that in such cases, these small bridges are destroyed, i.e., electrically burned off, as will be described in more detail further below, in order to maintain the aluminum coating safely insulated from the metallic body.

Basically, corrosion is prevented by avoiding any possibility for the localized formation of galvanic elements. However, even by taking the greatest possible care in applying the intermediate layers, it is still possible as

discussed above, that conductive bridges will be formed between the outer decorative metallic coating and the metallic base body. In order to reduce this possibility as much as possible, the present invention proposes first of all to replace a current conducting chromium layer—although the same would possess the desired high degree of adherence to the underlying lacquer layer as well as to the superposed vapor deposited aluminum coating—with an electrically insulating chromium oxide layer. The chromium oxide layer is formed by vapor deposition of chromium in a diluted oxygen atmosphere so that oxidation of the chromium will take place after the same has been vaporized. Thus, the electrically conductive intermediate chromium layer which requires careful insulation, is replaced with a non-conductive chromium oxide layer so that neither between the aluminum coating and the intermediate layer, nor between the intermediate layer and the metallic base body a corrosion causing galvanic element will be formed.

The aluminum coating is preferably applied by vapor deposition in an argon atmosphere which is ionized by glow discharge.

In order to assure complete electrical insulation of the aluminum coating from the metallic base body, any small metallic, electrically conductive bridges which may connect the aluminum coating with the metallic base body are then burned off electrically. By thus burning off any conductive bridges which may have been formed due to the inadvertent presence of conductive particles in the intermediate and lacquer layers, or due to penetration of cracks and pin holes by aluminum, complete electric insulation of the aluminum coating from the metallic base body is assured. The electrical burning off of such small bridges can be carried out in various ways, for instance by discharge of a condenser, or by application of either direct or alternating current. Preferably, the thus treated bodies are then subjected to appropriate testing in order to assure that complete insulation of the aluminum layer has been achieved.

In some cases it is difficult to prevent corrosion at the edges of the body which is to be aluminum coated. This may be due to the fact that the lacquer layer on such edge portions usually is very thin, of poor adherence, or may have torn during drying. Sometimes, particularly when the metallic base body is formed with sharp edges, the lacquer layer has receded and the metal's sharp edges are exposed. For all these reasons, the insulation of the aluminum coating in the vicinity of such edge portions required particular attention. In order to assure electric insulation between the aluminum coating and the metallic support in the region of these edge portions, it is preferred to mask the edge portions during the vapor deposition steps, particularly during the vapor deposition of the aluminum coating.

As a further safeguard against corrosion and for additional protection of the reflecting or mirror-like aluminum coating against mechanical attacks, it is also contemplated according to the present invention to form on the aluminum coating a protective layer of silicon oxides formed by vapor deposition in an oxygen atmosphere at reduced pressure of between about 5×10^{-5} and 5×10^{-3} mm. Hg under simultaneous ionization by glow discharge. The degree of partial vacuum which is applied depends in each case primarily on the conditions which are required in order to maintain the glow discharge and on the distance between the body which is to be coated and the source of the vapors which are to be deposited.

The chromium, aluminum and silicon which are used for vapor deposition should have a purity of at least 99%, and in the case of aluminum preferably of 99.9%. Instead of aluminum, also aluminum alloys containing small quantities of chromium and/or magnesium may be vaporized.

Vaporization of chromium and silicon in the oxygen atmosphere, as described above, will result in oxidation of the vapors of these elements so that the respective oxide layers will be formed.

The metallic base body may be covered by any suitable lacquer known in the art. Such lacquers may be based on synthetic resins, for instance alkyd-melamine resins, urea resins or epoxy resins, however, it is also possible to use natural resin lacquers and it is furthermore also within the scope of the present invention to cover the aluminum coating or the protective layer of silicon oxides thereon with a suitable transparent lacquer.

The following example is given as illustrative only of the present invention, without, however, limiting the invention to the specific details of the example.

The lacquer-covered metallic body which is to be coated is placed into the vapor deposition chamber which also contains the chromium which is to be vaporized. The chamber is then evacuated at room temperature to a pressure not exceeding 5×10^{-4} mm. Hg. Thereafter, oxygen gas is introduced into the chamber until the pressure has risen to about 10^{-3} mm. Hg. The chromium is then vaporized by electric heating and the thus formed chromium vapors, after reacting with the oxygen atmosphere, will precipitate on the relatively cold lacquer-covered metallic body. Thereafter, aluminum is introduced into the chamber and pressure therein is again reduced to below 5×10^{-4} mm. Hg.

At this very low residual pressure, the aluminum is vaporized by being heated electrically to about 1000° C., which may be carried out with a current of a few volts and about 100 amperes.

The vaporization and deposition of aluminum can also be carried out in a different manner, namely by introducing, after evacuation of the chamber to 5×10^{-4} mm. Hg, argon until the pressure rises to about 10^{-3}. During subsequent vaporization of the aluminum, a potential of several thousand volts is applied to an electrode located in the chamber, for instance about 10,000 volts until glow discharge starts and about 1000 volts thereafter. Thus produced glow discharge will increase the kinetic energy of the aluminum vapor so that the same will become hotter and this will improve the adherence of the aluminum coating formed by the deposition of the aluminum vapors. For instance, as described in U.S. Patent No. 1,710,747, one terminal may be attached to an electrode located within the vaporization chamber or vessel, and the terminal of opposite polarity may be attached to the metal wall of the vaporization vessel. Upon application of the above described potential to the two terminals, glow discharge will then take place between the electrode and the wall of the vaporization vessel.

The thus formed aluminum coating may still include aluminum bridges cross-secting the chromium oxide and lacquer layers and electrically connecting the aluminum coating with the metallic base body. In order to burn off these aluminum bridges, an electrode of large area is electrically connected with the aluminum layer and the opposite pole is connected with the metallic base body. Parallel thereto, a condenser of between 4 to 40 μf. is arranged in the circuit, which condenser is first charged and will then be discharged by connecting the circuit including the metallic body. This discharge will pass through the above discussed electrically conductive bridges and will destroy the same. Preferably, burning off of the bridges is started with relatively low voltage and a small condenser and voltage and condenser capacity are then increased until all bridges are destroyed. Good results were obtained with a series of condensers ranging in capacity from 4 to 40 μf. and from 20 to 150 volts. However, these values are not necessarily limiting.

After the aluminum coating has been applied as described above and the conductive bridges have been burned off, the thus coated body is lacquered, or a protective layer of silicon oxides is applied by vapor deposition in a manner similar to the formation of the intermediate chromium oxide layer described above, except that, of

course, the chromium as starting material is replaced by silicon.

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can by applying current knowledge readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention and, therefore, such adaptations should and are intended to be comprehended within the meaning and range of equivalence of the following claims.

What is claimed as new and desired to be secured by Letters Patent is:

1. A method for forming on a lacquer-covered metallic body a firmly adhering, corrosion resistant, reflecting metal coating, comprising the steps of contacting said lacquer-covered body with an oxygen atmosphere maintained at subatmospheric pressure; vaporizing chromium in said atmosphere so as to oxidize vaporized chromium and to form a layer of chromium oxide on said lacquer-covered metallic body; and forming by vapor deposition an aluminum coating on said layer of chromium oxide, the lacquer covering and said chromium oxide layer electrically insulating said aluminum coating from said metallic body.

2. A method for forming on a lacquer-covered metallic body a firmly adhering, corrosion resistant, reflecting metal coating, comprising the steps of contacting said lacquer-covered body with an oxygen atmosphere maintained at subatmospheric pressure of about 10^{-3} mm. Hg; vaporizing chromium in said atmosphere so as to oxidize vaporized chromium and to form a layer of cromium oxide on said lacquer-covered metallic body; and forming by vapor deposition an aluminum coating on said layer of chromium oxide, the lacquer covering and said chromium oxide layer electrically insulating said aluminum coating from said metallic body.

3. A method for forming on a lacquer-covered metallic body a firmly adhering, corrosion resistant, reflecting metal coating, comprising the steps of contacting said lacquer-covered body with an oxygen atmosphere maintained at subatmospheric pressure; vaporizing chromium in said atmosphere so as to oxidize vaporized chromium and to form a layer of chromium oxide on said lacquer-covered metallic body; and forming by vapor deposition in an inert atmosphere maintained at subatmospheric pressure an aluminum coating on said layer of chromium oxide, the lacquer covering and said chromium oxide layer electrically insulating said aluminum coating from said metallic body.

4. A method for forming on a lacquer-covered metallic body a firmly adhering, corrosion resistant, reflecting metal coating, comprising the steps of contacting said lacquer-covered body with an oxygen atmosphere maintained at subatmospheric pressure; vaporizing chromium in said atmosphere so as to oxidize vaporized chromium and to form a layer of chromium oxide on said lacquer-covered metallic body; and forming by vapor deposition in an inert atmosphere maintained at subatmospheric pressure, said atmosphere being ionized by glow discharge, an aluminum coating on said layer of chromium oxide, the lacquer covering and said chromium oxide layer electrically insulating said aluminum coating from said metallic body.

5. A method for forming on a lacquer-covered metallic body a firmly adhering, corrosion resistant, reflecting metal coating, comprising the steps of contacting said lacquer-covered body with an oxygen atmosphere maintained at subatmospheric pressure; vaporizing chromium in said atmosphere so as to oxidize vaporized chromium and to form a layer of chromium oxide on said lacquer-covered metallic body; and forming by vapor deposition in an inert argon atmosphere maintained at subatmospheric pressure of about 10^{-3} mm. Hg an aluminum coating on said layer of chromium oxide, the lacquer covering and said chromium oxide layer electrically insulating said aluminum coating from said metallic body.

6. A method for forming on a lacquer-covered metallic body a firmly adhering, corrosion resistant, reflecting metal coating, comprising the steps of contacting said lacquer-covered body with an oxygen atmosphere maintained at subatmospheric pressure; vaporizing chromium in said atmosphere so as to oxidize vaporized chromium and to form a layer of chromium oxide on said lacquer-covered metallic body; forming by vapor deposition an aluminum coating on said layer of chromium oxide, the lacquer covering and said chromium oxide layer substantially but not completely electrically insulating said aluminum coating from said metallic body; and electrically burning off aluminum bridges extending transversely through said chromium oxide layer and said lacquer covering from said aluminum coating to said metallic body so as to completely insulate said aluminum coating from said metallic body.

7. A method for forming on a lacquer-covered metallic body a firmly adhering, corrosion resistant, reflecting metal coating, comprising the steps of contacting said lacquer-covered body with an oxygen atmosphere maintained at subatmospheric pressure of about 10^{-3} mm. Hg; vaporizing chromium in said atmosphere so as to oxidize vaporized chromium and to form a layer of chromium oxide on said lacquer-covered metallic body; forming by vapor deposition in an inert argon atmosphere maintained at subatmospheric pressure of about 10^{-3} mm. Hg, said atmosphere being ionized by glow discharge, an aluminum coating on said layer of chromium oxide, the lacquer covering and said chromium oxide layer substantially but not completely electrically insulating said aluminum coating from said metallic body; and electrically burning off aluminum bridges extending transversely through said chromium oxide layer and said lacquer covering from said aluminum coating to said metallic body so as to completely insulate said aluminum coating from said metallic body.

8. A method for forming on a lacquer-covered portion of a metallic body a firmly adhering, corrosion resistant, reflecting metal coating, comprising the steps of masking the peripheral portion of said lacquer covering; contacting said lacquer-covered portion of said body with an oxygen atmosphere maintained at subatmospheric pressure; vaporizing chromium in said atmosphere so as to oxidize vaporized chromium and to form a layer of chromium oxide on said lacquer-covered metallic body; and forming by vapor deposition on aluminum coating on said layer of chromium oxide, the lacquer covering, the masking of the peripheral portion thereof and said chromium oxide layer electrically insulating said aluminum coating from said metallic body.

9. A method for forming on a lacquer-covered portion of a metallic body a firmly adhering, corrosion resistant, reflecting metal coating, comprising the steps of contacting said lacquer-covered body with an oxygen atmosphere maintained at subatmospheric pressure; vaporizing chromium in said atmosphere so as to oxidize vaporized chromium and to form a layer of chromium oxide on said lacquer-covered metallic body, masking the peripheral portion of said lacquer covering; and forming by vapor deposition an aluminum coating on said layer of chromium oxide, the lacquer covering, the masking of the peripheral portion thereof and said chromium oxide layer electrically insulating said aluminum coating from said metallic body.

10. A method for forming on a lacquer-covered metallic body a firmly adhering, corrosion resistant, reflecting metal coating, comprising the steps of contacting said lacquer-covered body with an oxygen atmosphere maintained at subatmospheric pressure; vaporizing chromium in said atmosphere so as to oxidixe vaporized chromium and to form a layer of chromium oxide on said lacquer-covered metallic body; forming by vapor deposition an

aluminum coating on said layer of chromium oxide, the lacquer covering and said chromium oxide layer electrically insulating said aluminum coating from said metallic body; and forming by vapor deposition of silicon in an oxygen atmosphere maintained at subatmospheric pressure a protective layer of silicon oxides on said aluminum coating.

11. A method for forming on a lacquer-covered metallic body a firmly adhering, corrosion resistant, reflecting metal coating, comprising the steps of contacting said lacquer-covered body with an oxygen atmosphere maintained at subatmospheric pressure; vaporizing chromium in said atmosphere so as to oxidize vaporized chromium and to form a layer of chromium oxide on said lacquer-covered metallic body; forming by vapor deposition an aluminum coating on said layer of chromium oxide, the lacquer covering and said chromium oxide layer electrically insulating said aluminum coating from said metallic body; and forming by vapor deposition of silicon in an oxygen atmosphere maintained at subatmospheric pressure of about 10^{-4} mm. Hg a protective layer of silicon oxides on said aluminum coating.

12. A method for forming on a lacquer-covered metallic body a firmly adhering, corrosion resistant, reflecting metal coating, comprising the steps of contacting said lacquer-covered body with an oxygen atmosphere maintained at subatmospheric pressure of about 10^{-3} mm. Hg; vaporizing chromium in said atmosphere so as to oxidize vaporized chromium and to form a layer of chromium oxide on said lacquer-covered metallic body; forming by vapor deposition in an inert argon atmosphere maintained at subatmospheric pressure of about 10^{-3} mm. Hg, said atmosphere being ionized by glow discharge, an aluminum coating on said layer of chromium oxide, the lacquer covering and said chromium oxide layer substantially but not completely electrically insulating said aluminum coating from said metallic body; electrically burning off aluminum bridges extending transversely through said chromium oxide layer and said lacquer covering from said aluminum coating to said metallic body so as to completely insulate said aluminum coating from said metallic body; and forming by vapor deposition of silicon in an oxygen atmosphere maintained at a subatmospheric pressure of about 10^{-4} mm. Hg a protective layer of silicon oxides on said aluminum coating.

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