United States Patent Office

Patented Jan. 19, 1960

2,921,868

ALUMINUM GAS PLATING OF VARIOUS SUBSTRATES

Carl Berger, Dayton, Ohio, assignor, by mesne assignments, to Union Carbide Corporation, New York, N.Y., a corporation of New York

Application June 7, 1956, Serial No. 589,976

3 Claims. (Cl. 117—107)

This invention relates to gas plating of aluminum and to composite bodies produced thereby.

The present invention is particularly adapted for the deposition of aluminum films on substrates composed of glass, glass fiber rovings and the like non-metallic material, as well as metal such as copper, lead, iron, steel and the like.

The invention is also useful in the application of aluminum to material such as mica, quartz, graphite and organic plastics such as nylon and similar fibers or fibers. The deposition of aluminum films on natural as well as synthetic fibers or filaments may be accomplished in accordance with this invention.

The gas plating of light metal such as aluminum at relatively low temperatures and pressures, in accordance with this invention, preferably is carried out by the use of a heat-decomposable gaseous compound in the case of aluminum, making use of aluminum alkyls, for example trisnbutyl aluminum, triethyl aluminum, trimethyl aluminum, or mixtures thereof. The material to be plated with aluminum metal is placed in a chamber and the air removed and the atmosphere of the chamber filled with inert gas such as nitrogen, which is dry and free of moisture.

The article to be plated or aluminiunized is initially heated to a temperature sufficient to cause decomposition of the aluminum compound and deposition of the aluminum metal onto the material or article to be plated. Aluminum metal is thus deposited at relatively low temperatures and pressures, which distinguishes from the prior processes wherein attempts have been made to use volatile metallic compounds which require high temperatures on the order of 3272° F. to form aluminum metal vapor.

The present invention makes it possible to deposit aluminum on the surfaces of various materials, and such as will withstand the temperature used to bring about decomposition of the gaseous heat-decomposable aluminum compound. Making use of such compounds, plating of the light metal onto articles made of steel, iron, copper, magnesium, and alloy metals, as well as molded plastics, glass, wood, paper and the like, as aforementioned may be thus accomplished. Aluminum may also be plated on bearing and machine elements, hardware, cooking utensils and the like to produce products having improved resistance to corrosion.

Due to the nascent physical state of the aluminum metal, the same being deposited as it is liberated from the gaseous compound, a metal film of one molecule thickness is provided initially which may be further increased as desired. Thus a tenacious metal layer of aluminum is formed in the surface pores of the base material on which the metal is deposited.

The process of the invention permits rapid deposition of light metals, e.g., aluminum at relatively low temperatures and pressures as compared to prior processes utilizing volatilized metals.

In gas plating metal surfaces, for example the metal, after being thoroughly cleaned of foreign matter, is sub-

jected to gas plating utilizing a suitable organo-metallic compound of aluminum and which compound is heat-decomposable at temperatures substantially below the vaporization point of the light metal. The decomposition or disassociation of the gaseous metal compound is made to take place in an atmosphere which is inert to the nascent metal, being especially free of oxygen, hydrogen and water. An atmosphere in the plating chamber of dry nitrogen gas has been found suitable. The inert gas may also be used as a carrier and protecting blanket for the aluminum alkyl compound. Other gases which are inert and free of oxygen and moisture may be used in place of nitrogen, such as helium, argon, etc.

In carrying out the aluminum metal plating in accordance with the preferred practice of this invention, the material to be plated is placed in a closed chamber or container having an inlet and outlet opening. Thereafter the air and water vapor are displaced by forcing dry nitrogen through the chamber under sufficient pressure to displace the air. Aluminum alkyl is then introduced into the plating chamber using nitrogen as a carrier gas and brought in contact with the heated article to be plated with aluminum.

To bring about decomposition of the aluminum alkyl after the same is introduced into the plating chamber, suitable means, such as electrical resistance coils, are provided, to heat the material to be plated to a temperature high enough to cause the gaseous metal compound, e.g., aluminum triisobutyl, to decompose and aluminum metal to deposit on the surface of the heated material.

Where the plating chamber is made of glass or plastic material which will transmit ultra-red rays, heating may be effected by the use of infra-red lamps. Utilizing resistance heater coils, Nichrome resistance wires or ribbons may be wound around the plating chamber which preferably is enclosed in asbestos felt, or the like, and connected to a source of electricity to heat the chamber and material or article therein. To bring about decomposition of the aluminum alkyl gaseous compound.

The drawing accompanying this application illustrates a flowsheet of the process and apparatus for carrying out the gas plating of aluminum.

Figure 1 is a flowsheet of the preferred method of carrying out the invention.

Refer to the drawings, and more particularly to Figure 2, a stream of dry nitrogen is introduced into the system from the tank 10 and bubbled through heptane contained in the reservoir 11, the heptane being indicated as at 12. A temperature of about 80—120° C. is maintained in the reservoir 11 by suitable heating means. The purpose of the reservoir 11 which is partially filled with normal heptane is to maintain the fluid level in the distillation container 14 constant. This requires like temperatures in the reservoir 11 and container 14 so that the evaporation rates will be substantially the same.

Nitrogen gas is bubbled through the reservoir 11 which is partially filled with heptane, and thence to a distillation container 14, the latter containing a solution of aluminum alkyl in heptane. A solution comprising aluminum triisobutyl in normal heptane is introduced as needed into the distillation container 14 through a stopper closed neck portion 15. A preferred concentration consists of 25% by volume of the aluminum triisobutyl in normal heptane. Where use is made of other alkyls such as aluminum triethyl or trimethyl, or aluminum diethyl hydride, similar concentrations are preferably used.

Aluminum triisobutyl is introduced in a liquid state
from a pressurized bottle. It begins to decompose when distilled above 90° C. at one atmosphere. The temperature of the heptane solution of aluminum trisobutyl in the distillation container 14 is kept within the range of about 90-95° C. to avoid extensive alkyl decomposition. A mixture of aluminum alkyl and nitrogen flows from the distillation container 14 and is conducted to a plating tube 16 which is heated by an electrical resistance element 17 arranged therewith to bring about decomposition of the aluminum alkyl and deposition of aluminum. Other suitable means may be used for heating the tube 16 if desired. The material or substrate 18 is heated in the tube 16 to approximately 250-500° C., depending upon the substrate and aluminum alkyl plating gas but preferably is in the neighborhood of 300° C. when using aluminum trisobutyl. This temperature produces a smooth, lustrous gas plated surface of aluminum. With use of higher temperatures there is a tendency to produce a darker colored plating. On the other hand, at lower temperatures decomposition characteristics of aluminum alkyl are not favorable.

Residual heptane and alkyl degradation products formed during the plating process are recovered by the bubbler trap 20. Nitrogen gas and other volatile compounds pass out through the exit 21 at the top of the bubbler 20 as indicated by the arrow on Figure 2. The exit velocity of the gas is maintained at approximately 0.01 to 1.0 liter per minute, the particular velocity depending upon the rate of plating desired. The plating tube 16 is encased in an oven or heating chamber 23 which is suitably heated by electrical resistance elements and controlled by a rheostat such as indicated at 24. The reservoir 11 and distillation container 14 are likewise heated by the heating elements 25 and 26, the same being controlled through a rheostat means 29.

The surface of the material to be plated with aluminum is initially cleaned of foreign matter and dried to remove moisture. Manual or chemical cleaning means or a suitable combination thereof may be employed for this purpose. Sandblasting, wire brushing or the like are suitable methods to remove solid foreign matter from metal surfaces. Where the surface is to be de-greased and cleaned, the same may be washed with petroleum solvent, such as xylol, toluol or the like, and all traces of moisture are removed by heating the material at 250 to 500° C. for a time sufficient to drive off any residual moisture.

After the article has been cleaned thoroughly and freed of all moisture and rendered chemically clean, the same, while retained-out of contact with air or moisture, is introduced into the plating chamber which is maintained filled with inert gas such as nitrogen, helium or argon, and the article heated as described. While the article is heated in the plating chamber under an atmosphere of nitrogen, an organo-aluminum compound, e.g., aluminum alkyls such as aluminum trisobutyl is introduced and the gaseous aluminum alkyl brought in contact with the surface of the heated article, the temperature of the latter being high enough to cause the gaseous aluminum alkyl compound coming into contact therewith to decompose or disassociate and deposit aluminum metal onto the surface of the article. After a desired thickness of aluminum deposit is obtained, the process is stopped and excess aluminum alkyl returned to storage.

Trisobutyl aluminum is supplied in steel pressure bottles, with brass valves. The pressure bottle which is fitted with a rubber dam is packed to a maximum of 60% of the free volume with trisobutyl aluminum liquid, and the remaining space is pressured to a maximum of 30 pounds/sq. in. gauge with nitrogen. To remove the contents, the bottle is provided with an adapter valve and tube outlet connection to allow the internal pressure to push out the liquid when the bottle is inverted. Fittings should be opened under a blanket of nitrogen and receiving containers should be dry and previously flushed with dry nitrogen. Storage temperatures for aluminum trisobutyl is kept below 60° C. and preferably 0° C. to 10° C.

The following examples illustrate typical runs of gas plating with aluminum using different substrates.

**Example I**

Glass rovings in the form of filaments were gas plated with aluminum and employing a solution of normal heptane containing 25% by volume of aluminum trisobutyl. The temperature and rate of flow were as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reservoir 11</td>
<td>95</td>
</tr>
<tr>
<td>Distillation container 14</td>
<td>93</td>
</tr>
<tr>
<td>Plating tube</td>
<td>300</td>
</tr>
<tr>
<td>Substrate</td>
<td>300</td>
</tr>
<tr>
<td>Flow rate</td>
<td>0.1 liter per minute</td>
</tr>
</tbody>
</table>

A plating of aluminum was deposited upon the glass filaments in the form of a thin film.

**Example II**

Aluminum plate was deposited on a copper disc using aluminum trisobutyl heptane solution as described in Example I.

**Example III**

Aluminum plate was deposited on nylon fibers using aluminum trisobutyl heptane solution is in Example I.

**Example IV**

A coating of aluminum was formed on a mica substrate as a thin film to produce an aluminum plated article and as described in Example I.

**Example V**

Aluminum plate was deposited on a copper disc using aluminum triethyl dissolved in heptane and as described in Example I.

**Example VI**

A plating of aluminum was deposited on a copper disc using aluminum diethyl hydride dissolved in heptane as in Example I.

The minimum flow rate of gas is governed by whether or not the fumes of aluminum alkyl reach and surround the hot metal or article to be plated. If the flow rate is too slow, the fumes either condense on the walls of the connecting tubes of the apparatus or else a heavy layer of white fumes accumulates in the lower half of the tube and the base metal is covered only partially. Too rapid gas flow carries undecomposed aluminum alkyl out of the plating chamber which, of course, is undesirable. Also too rapid flow rates lower the temperature inside the plating chamber and break down of the aluminum alkyl tends to occur.

The optimum rate of flow has been found to be one that will carry the aluminum alkyl into the decomposition tube or plating chamber without condensation, and which will disperse it over the whole cross section of the plating chamber so as to fill the chamber uniformly. The flow rate in each instance was maintained high enough to keep the tube filled with aluminum alkyl fumes whose flow pumped is substantially uniform even deposit of aluminum is formed on the article being plated. The rate of gas flow through the apparatus is thus adjusted whereby it is just enough to keep the tube or plating chamber filled with aluminum alkyl fumes. The flow sheet in Figure 1 illustrates the coordinated steps of the process using aluminum trisobutyl as the carrier.

The inert gas is used both as a carrier for the aluminum alkyl and to move the volatilized heat-decomposable aluminum compound through the plating chamber. Use of vacuum pumps is thus unnecessary which lowers the cost of operating the process.
The minimum temperature that will vaporize aluminum triisobutyl has been observed to be about 90°C. The density of triisobutyl aluminum at 20°C is 0.8. At temperatures of 115° to 120°C, its rate of decomposition is relatively slow so that as a result much of the aluminum alkyl vapor remains undecomposed at this temperature. It has been found by test runs, however, that temperatures between 275°C and 325°C give good decomposition of the aluminum alkyl and quality deposits of aluminum. At 350°C, the aluminum deposit on copper metal is of dark bluish color, and a clear reflecting mirror is formed on the inside of a glass tube used as a plating chamber. When the plating temperature was raised to 400°C, the mirror-like deposit formed was observed to be dark in color and not as good as where a lower temperature was used.

The plating materials when of metal substratum, if desired, may be subjected to an annealing heat treatment after the plating operation to stabilize the metal deposit. Such a heat treatment may consist of heating the plated article up to 400°C for one hour.

The invention provides a process for plating aluminum metal directly on the surface of articles whereby there is produced a composite product comprising an outer layer of aluminum or light metal intricately and tenuousciously bonded thereto.

The thickness of the light metal coating may be controlled by varying the time the metal bearing gas is in contact with the heated material to be plated. A coating of one molecule thickness up to one or more thousandths of an inch may be effected utilizing the process of the invention to thus provide a protective coating of aluminum on various metal surfaces, the like, the invention being especially useful to overcome corrosion problems.

The process further makes possible the continuous straight line production of composite products, and long length strips or sheets of material, e.g., such as used in the making of screens and the like which may be gas plated with aluminum. The invention is particularly useful in aluminumizing metals where it is desired that aluminum be deposited into the pores and interstices of the base metal surface to form a substantially integral outer shell of the corrosion resistant light metal.

Preheating and drying of the article prior to gas plating preferably is carried out in an inert atmosphere such as nitrogen gas, helium and the like to prevent oxidation. Thereafter the heated and completely dry moisture free article is subjected to gas plating with gaseous aluminum triisobutyl as described.

The aluminized metal articles, as plated, are free of oxides, but upon its removal from the plating atmosphere and subjection to the surrounding atmosphere, an outer coating of aluminum oxide is immediately formed. This, however, does not detract from the process inasmuch as this oxide film on aluminum metal functions to protect the same as is well known.

It will be understood that while there has been described and set forth certain specific embodiments of this invention, it is not intended that the invention be thus limited thereto and it is manifest that various substitutions and changes may be made by those skilled in the art and to which the invention is readily susceptible without departing from the spirit and scope of this disclosure and as more particularly set forth in the appended claims.

What is claimed is:
1. In a method of gas plating materials with aluminum metal, the improvement which comprises the steps of arranging the materials to be plated in an enclosure, removing the air from said enclosure and replacing the same with inert gas pre-washed with liquid hydrocarbon the improvement which comprises, introducing a gaseous aluminum alkyl compound into said enclosure and in contact with the material to be plated with aluminum, and heating the enclosure and material retained therein to a temperature sufficient to cause thermal decomposition of said gaseous aluminum compound and deposition of aluminum metal onto said material.
2. In a method of gas plating materials with aluminum metal, the improvement which comprises the steps of arranging the materials to be plated in an enclosure, removing the air from said enclosure and replacing the same with inert gas pre-washed with liquid hydrocarbon the improvement which comprises, introducing a gaseous aluminum alkyl compound into said enclosure and in contact with material to be plated with aluminum arranged therein, and heating the enclosure and material retained therein to a temperature sufficient to cause decomposition of said gaseous aluminum alkyl compound and deposition of aluminum onto said material, said aluminum alkyl compound being selected from the group consisting of aluminum triisobutyl, aluminum triethyl and aluminum dialdehyde hydride.
3. As an article of manufacture, an article plated with aluminum metal in accordance with the process of claim 1.

References Cited in the file of this patent

UNITED STATES PATENTS
2,516,058 Lander ........................ July 18, 1950
2,656,284 Toulmin ......................... Oct. 20, 1953
2,694,651 Pawlyk ......................... Nov. 16, 1954
2,711,973 Wainier et al. .................. June 28, 1955
2,749,255 Mack et al. ..................... June 5, 1956
2,759,855 Medcalf et al. .................. Aug. 21, 1956
2,847,320 Bulloch ......................... Aug. 12, 1958

FOREIGN PATENTS
633,701 Great Britain ..................... Dec. 19, 1949

OTHER REFERENCES