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COATING SURFACES WITH ALUMINUM

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9 Claims

ABSTRACT OF THE DISCLOSURE

In liquid phase plating of substrates with solutions of organoaluminum compounds by contacting the hot substrate with the solution, superior plating is obtained if the solvent for the aluminum compound has a boiling point below the decomposition temperature of said aluminum compound.

This invention relates to a method for coating surfaces with aluminum. In one of its aspects, this invention relates to a method of depositing upon a surface an adherent aluminum film from an aluminum organic compound dissolved in a low boiling solvent.

Various systems have been used to put an aluminum surface on various metallic and nonmetallic surfaces or substrates. Cladding techniques have been employed wherein an aluminum sheet is bonded to the desired surface by extensive surface treatment of the article followed by a combination of heat and pressure. High operating pressures are necessary thus limiting the type of articles which could be covered. Also, serious corrosion and operating problems are encountered.

The various well known vacuum techniques produce quite thin films and are subject to low production levels, batch production and severe size limitations.

The heat decomposition of aluminum compounds is recorded in the literature. Aluminum hydride has been decomposed into aluminum and hydrogen (Ber. 75B pages 20003-12, 1942). However, due to the explosive nature of this compound, its use as an economical source of aluminum for plating is questionable. Davis (U.S. Patent 2,599,978) and Homer (U.S. Patent 2,824,828) have shown the decomposition of aluminum compounds in the gas phase. Also, Powell (vapor plating) has described gas phase decomposition and plating. With gas phase plating, a number of practical problems are encountered. The systems must be tightly sealed against atmospheric contamination, constant pressure conditions maintained and gas flow rates controlled within narrow limits. Also, many problems exist in vaporizing decomposable materials and in almost all cases carrier gases must be provided to give direction to the flow of the decomposable gas. All additives to the gas stream, such as modifiers, must also be volatile at the operating temperature and the rates of addition carefully controlled. The article to be plated must be heated and prepared in the closed system which involves expensive process equipment.

Berger (U.S. Patent 3,041,197) makes a major breakthrough in aluminum plating with his solution plating. In his system a heat decomposable aluminum compound in a liquid or a solid solution or dispersion, said liquid or solid solution having a boiling point above the decomposition temperature of the aluminum compound, is put into contact with a heated substrate, thereby causing the formation of aluminum on the substrate. Other agents can be present, for example reducers or oxidizers. The substrate can be of any desirable material so long as said substrate can be heated to a temperature above the decomposition temperature of the aluminum compound. It is also disclosed that the solvent affects the decomposition temperature, generally lowering the same. The deposited

aluminum film can be anodized by conventional procedures.

However, the Berger process has definite limitations. For example, alkyl decomposition in the high boiling point solvents results in the bath gradually turning black. Difficulty in obtaining uniform plating is encountered, the alkyl content of the bath must be protected against oxidation and hydrolysis, the baths tend to smoke and splatter during the dipping operation, etc.

It is, therefore, an object of this invention to provide an improved method of aluminum plating a surface. Another object of this invention is to provide a method of obtaining a uniform coating of aluminum on a substrate. Still other objects and advantages will be obvious from this specification and the claims.

These and other objects of the invention are accomplished by plating the substrate with a solution of the heat decomposable aluminum compound in a liquid solvent for said aluminum compound, said solvent having a boiling point not greater than the decomposable temperature of the aluminum compound.

In one aspect of the invention, the hot substrate is dipped into a bath of the aluminum alkyl solution. In another aspect, a solution of the aluminum alkyl is sprayed onto the hot substrate.

As has been suggested, any liquid non-reactive hydrocarbon which has a boiling point no higher than the heat decomposable temperature of the aluminum compound and which can be dissolved or suspended in said aluminum compound and does not react with the aluminum compound is operable in this invention. As a practical matter, the plating bath temperature will be affected by the hot substrate being dipped therein and the property of the coated surface affected by the temperature of the bath. Suitable coatings are obtained when the bath or spray is of a temperature of at least 50° C., and preferably above 100° C. In general, we employ a bath temperature in the range 100-150° C., and, consequently, the boiling point of the solvent would be above the bath temperature, but no higher than the decomposition temperature of the aluminum compound.

Suitable solvents include liquid organic solvents having a boiling point in the range desired. Examples of such solvents include toluene, ethyl benzene, xylene, kerosene and the like.

Any aluminum-containing organic compound, capable of decomposing under heat to liberate aluminum and which can be dissolved or suspended in a solvent medium can be utilized to produce an aluminum film on a substrate in the practice of this invention. As a practical matter, due to cost, availability, safety and the temperature to which the substrates may be heated, the aluminum alkyls such as aluminum trimethyl, aluminum triethyl, aluminum diethyl hydride, aluminum tri-isopropyl and aluminum tri-isobutyl are preferred compounds for use. Other suitable compounds include di-isopropylaluminum hydride, dibutylaluminum hydride and di-isobutyl hydride. Berger, supra, indicates that aluminum triisobutyl is particularly preferred; however, we have had excellent results with aluminum triethyl, the least preferred by Berger. However, we prefer aluminum diethyl hydride. Generally operative are the higher members of the alkyl series, as well as these of the lower alkyl series, especially those members whose heat decomposition points or ranges are generally between the ranges 170 and 500° C. (preferably 300-500° C.). Examples of such compounds include aluminum tri-isopentyl, aluminum triisooctyl, aluminum tri-dodecyl and the like. Substituted aluminum alkyl, preferably wherein the substituting radical is a saturated aliphatic radical, are usually operable. Substituents tending to react with the newly deposited aluminum coatings or films would ordinarily be avoided.

Also, mono- and dialkyls of aluminum can be used, e.g. ethyl aluminum dihydride and diethylaluminum hydride can be utilized.

In general, the aluminum alkyl in solvent can vary from 10-90 weight percent aluminum compound but will preferably be employed in a 30 to 70 weight percent solution or dispersion.

As has been indicated, the use of various minor components can be employed in the solvent medium to cause modification, where desired, of the physical and chemical properties of the film deposited. Such agents as wetting agents to promote adhesion, oxidizing and reducing compounds can be employed.

The surface to be coated should be perfectly clean and free of any oxides. This cleaning can be mechanical such as by abrasion with steel wool, sand blasting, sandpaper and the like. The cleaning can also be chemical such as ammonia solution of citric acid, dilute HCl or dilute phosphoric acid and the like. The chemical cleaning agent can be removed by washing with water and drying with a drying agent such as acetone or methanol.

As disclosed by Billy J. Williams in copending application 444,392 filed Mar. 31, 1965, the substrate, particularly metal substrates, are advantageously precoated with an oil or wax prior to heating. This treatment apparently prevents even minute oxidation of the metal to be plated.

The plating can be done by any suitable method. The plating bath (aluminum compound in solvent) will be maintained at a temperature below the boiling point of the solvent and generally above room temperature. The temperature employed will be determined largely by the nature of the solvent, the aluminum compound and the aluminum finish desired. As a general rule a temperature in the range 100 to 150° C. will be employed. However, any temperature up to the boiling point of the solvent can be used. The substrate to be plated will be heated to a temperature above the decomposition temperature of the aluminum compound. The substrate can be dipped into the bath or the bath can be sprayed on the hot substrate. Since the bath is cooler than is the substrate, the substrate must be heated to a temperature above the decomposition temperature of the aluminum compound. This super temperature does not need to be great and will depend, to some extent, upon the temperature of the bath or plating solution. In general, a temperature in the range 350-1000° C. can be employed, preferably 350-700° C.

In our experiments with liquid phase plating aluminum on substrates, we expected that one needed a solvent that had a higher boiling point than the decomposition temperature of the aluminum alkyl. One would speculate that such a solvent would allow one to plate at the maximum possible temperature without boiling the solvent and thus minimize splattering. By plating at such a temperature, one would reason that a lower substrate temperature would be possible. One would also expect that a higher boiling solvent would offer greater protection from atmospheric oxidation and hydrolysis. Unexpectedly we have found just the opposite to be true.

We have found very little difference, if any, in the aluminum plate produced from a bath temperature of 50° C. or 150° C. On the other hand, there is a marked difference in the aluminum plate produced from a solution of the aluminum compound in a low boiling solvent such as kerosene and xylene and one produced from the aluminum compound in a high boiling solvent such as mineral oil or petroleum wax. The lower boiling solvent produces a more uniform plating and also allows one to operate with a much higher concentration of aluminum compound. The lower boiling solvents exert a greater vapor pressure at any given temperature than the higher boiling solvents. Therefore, they would provide a greater proportion of solvent molecules in the vapor phase directly above the surface of the aluminum compound thereby reducing the opportunity of oxidation.

Another unexpected advantage of this system is that splattering of the solvent-aluminum compound solution when contacted by high temperature substrates is greatly reduced as compared to the higher boiling solutions. One would expect that the higher boiling solutions would have less tendency to splatter, but the opposite was found to be true. It may be that this is due to the lower viscosity of the solvent which allows the vapor bubbles to escape with less disturbance.

A very important advantage in the use of the lower boiling solvent is a more efficient aluminum utilization. It has been found that with the higher boiling solvents, such as mineral oil with aluminum alkyls, the bath turns gray to black with suspended aluminum during the plating process. We have not encountered this when using the low boiling solvents, rather, the bath remains water white during the plating process.

This invention is illustrated with the following examples which serve to illustrate the invention and are not to be considered limiting. It is to be understood that aluminum compounds which are decomposed to liberate the aluminum can be employed as well as solvents boiling below the decomposition temperature of the aluminum compound so long as said aluminum compound is effectively dispersed in said solvent.

Example I

The plating was carried out inside a nitrogen purged dry box. A 1½" I.D. vessel was filled with 83 grams of a 50% solution of triethylaluminum in white mineral oil. The solution was heated to 150° C. with an oil bath. A group of mild steel coupons 1 x 3 x 0.06 inch were heated to 600° C. in a muffle furnace which was also in the dry box.

When the coupons had reached the 600° C. temperature, the cover was removed from the aluminum alkyl solution and the first coupon quickly taken from the furnace and dipped into the solution. The coupon was rapidly plated with aluminum. After 3 minutes, the coupon was removed from the solution. The temperature of the solution had increased to 174° C.

The aluminum alkyl solution smoked badly during the plating process as it did at any time the cover was removed from the vessel.

Another coupon was taken from the oven and dipped into the aluminum alkyl-mineral oil solution. By this time the dry box was so filled with smoke and so clouded that the bath could not be seen and the run was discontinued. The plating solution had turned dark.

Example II

The run of Example I was repeated except the solution was 20% diethylaluminum hydride in the mineral oil. Again the run had to be discontinued due to excessive smoking.

Example III

The run was repeated; this time using 79 grams of 10% triethylaluminum in mineral oil. Although, at this concentration, the smoking was not excessive and the aluminum coating appeared to be uniform, a part of the aluminum was washed from the coupon after plating, demonstrating that not all of the decomposition to aluminum resulted in plate. The plating solution was cloudy.

Example IV

The run was repeated except that a 10% solution of diethylaluminum hydride in xylene was utilized as the plating bath. All five coupons were successively dipped. The solution did not smoke and the plate was smoother than in the preceding runs. No aluminum was washed from the plates and the solution remained water white.

Example V

In this run the furnace temperature for heating the coupons was 400° C. The plating solution was 83 grams of

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a 47.5% solution of diethylaluminum hydride in xylene. The solution did not smoke during the plating process. There was no aluminum washed from the coupons and the solution was still water white after plating all of the five coupons. The solution did not splatter during plating.

Having thus described the invention, we claim:

1. In the process of plating a substrate with aluminum, the improvement comprising suspending an aluminum alkyl capable of decomposing with heat to liberate aluminum in an organic liquid having a boiling point below the temperature required to decompose said aluminum alkyl and non-reactive therewith, heating the substrate to be plated to a temperature above said temperature required to decompose said aluminum alkyl and contacting the heated substrate with the aluminum alkyl solution.

2. In the process of plating a surface with aluminum, the improvement comprising putting an aluminum alkyl capable of decomposing under heat to deposit aluminum, in an organic solvent for said aluminum alkyl, said solvent being non-reactive with and having a boiling point lower than the decomposition temperature of the aluminum alkyl, heating the surface to be plated to a temperature above the decomposition temperature of the aluminum alkyl and contacting said surface with the aluminum alkyl-organic mixture.

3. The improvement of claim 2 wherein the aluminum alkyl is dissolved in said organic solvent.

4. The improvement of claim 3 wherein the plating is carried out in a bath and the bath temperature is maintained in the range 50 to 150° C.

5. In the process of plating a surface with aluminum, the improvement comprising preparing a solution of an aluminum alkyl compound, capable of decomposing by

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heat to liberate aluminum, in an organic solvent for said aluminum alkyl, said solvent being stable at solution temperature and having a boiling point below the decomposition temperature of the aluminum alkyl, said solution comprising 10 to 90 weight percent of said aluminum compound in said solvent, maintaining said solution in the temperature range 50 to 150° C., heating said surface to a temperature above the decomposition temperature of said aluminum alkyl and contacting said surface with said solution.

6. The improvement of claim 5 wherein said solvent is a saturated hydrocarbon.

7. The improvement of claim 6 wherein said surface is heated to a temperature in the range 350 to 1000° C.

8. The improvement of claim 7 wherein said contacting is by dipping.

9. The improvement of claim 7 wherein said contacting is by spraying.

References Cited

UNITED STATES PATENTS

2,523,461	9/1950	Young et al.	
3,041,197	6/1962	Berger.	
3,075,858	1/1963	Breining et al.	117—107.2
3,155,532	11/1964	Basile	117—50
3,305,386	2/1967	Hafner et al.	117—107.2

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