

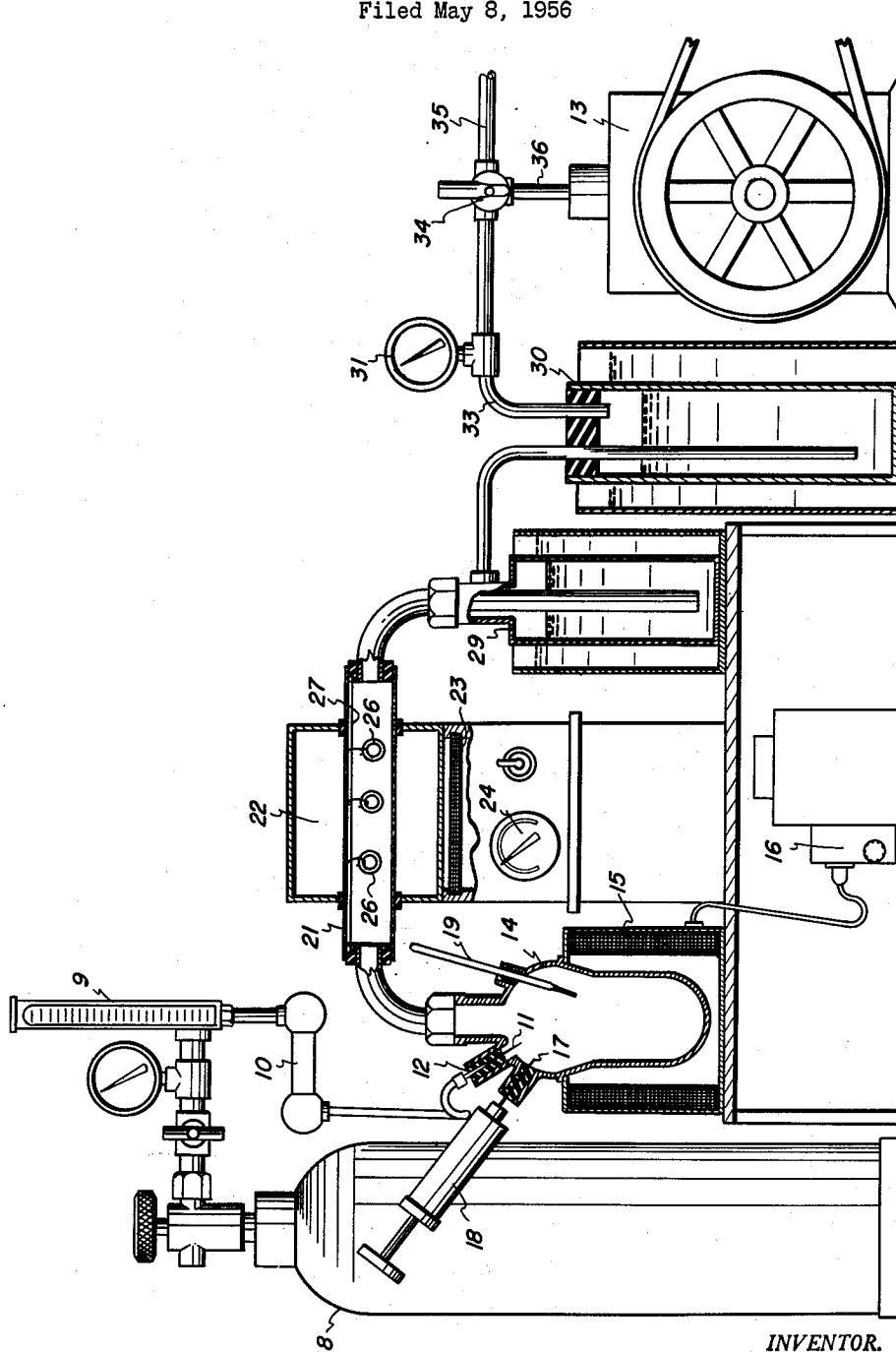
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METHOD FOR GAS PLATING WITH ALUMINUM ORGANO COMPOUNDS

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METHOD FOR GAS PLATING WITH ALUMINUM ORGANO COMPOUNDS

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4 Claims. (Cl. 117—47)

This invention relates to gas plating with organo-aluminum compounds to deposit aluminum metal, and more particularly to an improved apparatus and method for carrying this out.

The problem of depositing aluminum metal by volatilization of the metal and condensing the same onto a surface to form a coating of the metal thereon has been difficult to achieve, heretofore, and of little commercial value. This is principally because of the high temperatures necessitated.

In vacuum metallizing, utilizing aluminum as the metallizing agent, aluminum is heated above its melting point and the plating is carried out under sub-atmospheric pressure conditions. Vacuum metallizing, however, has many disadvantages. Principally among the disadvantages is that only surfaces perpendicular to the linear vapor propagation are metallized. The process also is not adapted for metallizing complex shapes. Also the vacuum deposition of metals has poor adhesion and often has to be lacquered in order to produce a satisfactory adherent coating. These poor adhesion properties are apparently due to the relative difference in the temperature of the plating surfaces as employed in vacuum metallizing processes. Further, the vacuum metallizing process is a very slow one.

In accordance with the present invention, the difficulties as encountered with the use of volatilized aluminum metal is avoided by employing heat-decomposable organo-aluminum compounds. Gas plating of this light metal is carried out at relatively low temperatures and pressures, as compared to the vaporized metal. The material to be plated with aluminum metal is placed in an enclosure free of air and the plating carried out in the presence of an inert atmosphere. Deposition of aluminum metal is accomplished by heating the article or substrate to be plated to a temperature sufficient to cause decomposition of the organo-aluminum compound brought in contact therewith, thus releasing aluminum metal which is deposited onto the surface of the substrate.

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 aluminum alkyl. Plating of the light metal may be made on various metal surfaces, e. g., steel, iron, copper, magnesium, or metal alloys as well as non-metal materials, e. g., glass, molded plastics, wood, paper and the like. Gas plating of aluminum on bearing and machine elements, and hardware, utensils and the like also may be readily accomplished utilizing the invention.

The metallized aluminum coating produced in accordance with this process provides a film of metal which is built up by one molecular thickness at a time so that a tenacious adherent metal layer of aluminum is formed on the surface of the material being coated. The tenacity of the layer is believed to be partly due to the heat effect

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and boundary inter-diffusion of the particles of metal as deposited during the gas plating process.

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

In gas plating metal surfaces, for example the metal, after being thoroughly cleaned of foreign matter, is subjected 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. This inert gas also may 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.

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 300° 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 alkyl such as aluminum triisobutyl 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 in 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.

Triisobutyl 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 triisobutylaluminum 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 triisobutyl are kept below 60° C. and preferably 0° to 10° C.

Other organo-aluminum compounds which may be used

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to produce aluminum metal deposits in accordance with this invention are listed in the following table along with their decomposition plating chamber temperatures and pressures:

Table I

Compound	Pressure, mm.	Decomposition Chamber Temperature, °C.
Isobutylaluminum	2	300-500
Trimethylaluminum	2	300-500
Trimethylaluminum 75% and Triethylaluminum 25%	2	300-500
Triethylaluminum	3	500-800
Dimethylaluminum chloride	3	800-500
Diethylaluminum chloride	8	300-500
Diethylaluminum hydride	6-7	300-500
Diethylaluminum bromide	4	300-500
Dipropylaluminum chloride	5	300-500
Triisobutylaluminum	760	250-300

In carrying out the gas plating using each of the above compounds the organo-aluminum compound was provided as a 25% solution of the aluminum compound in normal heptane and the plating chamber was filled with dry nitrogen.

The best results were obtained using the following aluminum alkyls:

Table II

Compound	Formula
Trimethylaluminum	$(\text{CH}_3)_3\text{Al}$
Dimethylaluminum chloride	$(\text{CH}_3)_2\text{AlCl}$
Triethylaluminum	$(\text{C}_2\text{H}_5)_3\text{Al}$
Diethylaluminum chloride	$(\text{C}_2\text{H}_5)_2\text{AlCl}$
Diethylaluminum bromide	$(\text{C}_2\text{H}_5)_2\text{AlBr}$
Diethylaluminum hydride	$(\text{C}_2\text{H}_5)_2\text{AlH}$
Diisopropylaluminum chloride	$(\text{C}_3\text{H}_7)_2\text{AlCl}$
Dibromaluminum hydride	AlHBr_2
Chloroaluminum dihydride	ClAlH_2
Aluminum tripropyl	$(\text{C}_3\text{H}_7)_3\text{Al}$
Aluminum triisobutyl	$(\text{C}_4\text{H}_9)_3\text{Al}$

While the aluminum alkyls are required to be kept free of uncontrolled amounts of oxygen and water vapor during the plating operation, the organo-aluminum heptane or other alkanes and, in such solvents, can be handled readily, even in the open air at ordinary room temperatures. Preferably the aluminum alkyls are dissolved in heptane or the like solvent and stored in self-sealing containers, being retained under positive pressure of inert gas.

One embodiment of an apparatus suitable for carrying out the gas plating of aluminum metal by the use of decomposable organo-aluminum compounds is illustrated in the accompanying drawing and forming a part of this application.

In the drawing there is shown in elevation a schematic layout of an apparatus for depositing aluminum metal as described. As illustrated, there is provided a tank for supplying nitrogen under pressure, designated generally at 8, the same being connected through a flow meter 9 to a drying tube 10, and injection needle 11 inserted into a self-sealing rubber closure 12. The system is connected through a vacuum pump 13 to maintain the proper pressure in the system. The injection needle 11 is connected to an evaporation container 14 which is heated by an electrical resistance coil 15, the latter being controlled by a rheostat 16.

Aluminum organo compound is introduced through a hypodermic needle 17, the compound being contained in solution in the cylinder 18 and injected into the system in small increments by a plunger of the cylinder 18. A thermometer 19 is suitably inserted into the container 14 as illustrated in the drawing. The material admitted to the evaporation container 14 is flash evaporated and conducted to the plating tube 21 which is surrounded by a heating oven 22, the temperature of the latter being controlled by a suitable resistance coil or rheostat 23.

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The tube 21 comprises an elongated pipe preferably made of transparent material such as glass or plastic, and is heated by the oven 22. Control of the temperature of the oven is set by operation of the temperature dial 24 on the oven.

Residual aluminum organic compound and waste products and organic solvents such as heptane are condensed in the water cooled bubble traps 29 and 30, the latter being preferably surrounded by cooling water, as shown in the drawings.

A manometer 31 is connected to the conduit 33 leading from the bubble trap 30 and conduit 33 is connected through a 3-way valve 34 to the discharge line 35. The vacuum pump 13 is suitably connected through the three-way valve 34 by line 36 whereby the same may be connected to the line 33 to evacuate the system during the plating operation.

Articles to be plated with aluminum, such as illustrated at 26, are suspended in the tube 21 by means of a wire 27. Other means may be used to support the articles or where long continuous lengths of articles are to be plated the same may be moved continuously there-through while the plating chamber is maintained under a sub-atmospheric pressure at the inlet and outlet to prevent the surrounding atmosphere from entering the plating tube.

In the operation of the apparatus the equipment is first flushed with oil pumped nitrogen delivered from the tank 8 through the flow meter 9 and drying tube 10 and hence into the system. After flushing the system with nitrogen for about 15 minutes the injection needle 11 is withdrawn and the system is evacuated by operation of the vacuum pump 13. A pressure in the system of slightly below atmospheric pressure is maintained, as indicated by the manometer 31.

At the proper temperature and pressure corresponding to that required for evaporating the aluminum organo compound used and which is placed in the hypodermic needle cylinder 18, the aluminum compound is injected through the hypodermic needle 17 into the evaporation container. Increments of the aluminum compound are injected, of about one milliliter fractions. The time intervals for injection are approximately from one to one and one-half minute intervals. The organo aluminum compound after being injected into the evaporation container 14 is flashed vaporized and passed to the plating chamber 21, the same being drawn through the system by operation of the vacuum pump 13.

To insure the maintenance of the proper temperature in the plating tube the same is warmed for about 30 minutes at the required temperature to cause decomposition of the aluminum organo vapor compound and to accomplish this the temperature dial 24 is set at the proper point so that this temperature is maintained in the plating tube 21. Residual aluminum alkyl, degradation products and heptane as drawn through the system and discharged from the plating tube are caught and condensed in the water cooled bubble bottles or traps 29 and 30 as described. The nitrogen is introduced into the system in a continuous flow similar as during flushing of the apparatus. After diluting the residual material in the evaporation container with heptane and blanketing it with nitrogen the system may be disassembled and cleaned in preparation for another plating operation.

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. A method of gas plating aluminum metal onto substrate by decomposition of an organo aluminum halide

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compound which comprises the steps of cleaning the substrate to remove foreign matter and moisture from the surface, heating the cleaned substrate in an unoxidizing atmosphere which is free of water vapor, subjecting the thus heated substrate to an atmosphere containing a heat-decomposable organo metallic alkyl halide compound of aluminum, the temperature of the substrate being high enough to cause thermal decomposition of the organo metallic halide aluminum compound and deposition of aluminum metal onto said substrate.

2. A method of gas plating aluminum metal onto substrate by decomposition of an organo aluminum halide compound which comprises the steps of cleaning the substrate to remove foreign matter and moisture from the surface, heating the cleaned substrate in an unoxidizing atmosphere which is free of water vapor, subjecting the thus heated substrate to an atmosphere containing a heat-decomposable organo halide metallic compound of aluminum under reduced atmospheric pressure conditions, the temperature of the substrate being high enough to cause thermal decomposition of the organo metallic halide aluminum compound and deposition of aluminum metal onto said substrate, said metallic organo compound being selected from a group consisting of diethyl aluminum chloride, diethyl aluminum bromide, dimethyl aluminum chloride, dipropyl aluminum chloride, di-isopropyl aluminum chloride, and mixtures thereof.

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3. A method of gas plating aluminum metal onto substrate by decomposition of an organo alkyl aluminum halide compound which comprises the steps of cleaning the substrate to remove foreign matter and moisture from the surface, heating the cleaned substrate in an atmosphere comprising inert gas which is free of air and water vapor, said atmosphere being under reduced atmospheric pressure, subjecting the thus heated substrate to an atmosphere containing a heat-decomposable organo metallic halide compound of aluminum, the temperature of the substrate being high enough to cause thermal decomposition of the organo metallic aluminum halide compound and deposition of aluminum metal onto said substrate.

4. The method of gas plating aluminum metal onto a substrate, as set forth in claim 3, wherein the substrate is magnesium metal.

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