

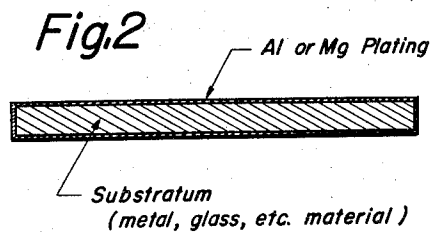
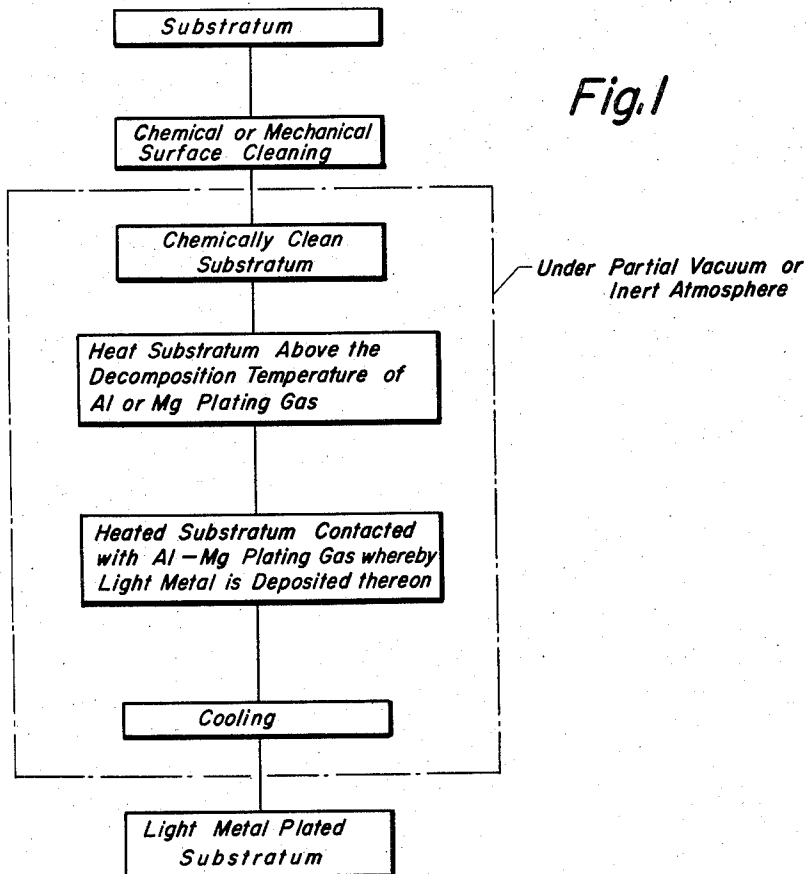
March 31, 1959

F. E. DRUMMOND

2,880,115

METHOD OF GAS PLATING LIGHT METALS

Filed July 13, 1955



INVENTOR.

FOLSOM E. DRUMMOND

BY

Taulmin & Taulmin

Attorneys

1

2,880,115

METHOD OF GAS PLATING LIGHT METALS

Folsom E. Drummond, Washington, D.C., assignor to
The Commonwealth Engineering Company of Ohio,
Dayton, Ohio, a corporation of Ohio

Application July 13, 1955, Serial No. 521,921

2 Claims. (Cl. 117—50)

This invention relates to gas plating of light metal such as aluminum, magnesium or the like, and to composite metal bodies produced thereby.

Attempts to produce coatings of light metals such as aluminum and magnesium have been difficult and of little value commercially because of the necessity of volatilizing the metals. Aluminum metal vaporizes at a temperature of 1800° C. (3272° F.) and magnesium at 1110° C. (2030° F.). The high temperature requirements for volatilizing these light metals, together with the difficulty of handling such hot metal vapor, has mitigated against their use in conventional plating processes.

In accordance with the present invention heat decomposable compounds of the light metals are utilized to deposit the pure metal by gaseous deposition. The process overcomes the difficulties of working with ultra high temperature gases as when using volatilized metals.

In accordance with the present invention, aluminum or magnesium metal, or suitable mixtures thereof are deposited directly upon a substratum such as steel, iron, copper, magnesium, aluminum or alloy metals to provide a tenaciously bonded metal layer or coating of light metal. The process permits gas plating of light metals at relatively low temperatures, as compared to that of the volatilized metals, and wherein the light metal is deposited directly on the substratum without the need of utilizing an intermediate bonding layer.

The principal object of the present invention is to gas plate such light metals as aluminum or magnesium directly onto a supporting or base surface which may comprise a ferrous or non-ferrous metal or suitable alloy metal whereby the base surface portion is provided with an outer shell of substantially pure aluminum or magnesium metal as desired.

Another object of the invention is to provide a composite metal article consisting of a substratum of light metal, e.g. magnesium, which is protected by an outer coating or layer of aluminum metal deposited thereon by gas plating.

Another object of the invention is to provide a composite metal article and made of either light or heavy metals as described, which comprises a gas plated layer of aluminum metal or magnesium metal.

Another object of the invention is to provide a method whereby light metal, such as magnesium and aluminum, may be plated onto metal castings, sheets, strips or the like and fabricated into a wide variety of products and shapes, and where it is desirable that the article have an outer portion composed of light metal.

Another object of the invention is to provide a method whereby metals such as steel, iron, copper and the like may be suitably protected with a layer of aluminum metal, the same being deposited directly onto the substratum.

Another object of the invention is to provide a method of tenaciously uniting aluminum or magnesium metal to a supporting base metal without the necessity of em-

2

playing an intermediate bonding layer or alloy as has been the practice heretofore.

Another object of the invention is to provide an improved method of gaseous metal plating the light metals of groups II and III of the periodic system onto the surface of articles.

Another object of this invention is to provide an improved process for plating light metals such as aluminum and/or magnesium, or other light metals of groups II and III in the periodic system, and wherein organo-metal compounds of these light metals are utilized which are heat-decomposable at relatively low temperatures, as compared with the vaporized metal, and whereby deposition of these light metals in the form of a thin film or plate is accomplished under conditions which are commercially practical.

It is still another object of the invention to provide a method for producing aluminum coated articles whereby aluminum metal is deposited onto the surface of the substratum and into the pores and interstices of the surface to provide an interlocked substantially integral layer or coating of aluminum metal thereon.

These and other objects and advantages will become apparent as the description proceeds.

In accordance with the present invention, metal surfaces such as magnesium, aluminum, steel, iron, copper and the like, and alloy metals are cleaned to remove foreign matter and then subjected to gas plating utilizing a suitable heat-decomposable organo-metallic compound of aluminum or magnesium, or suitable mixtures thereof, to provide a finished composite metal product. The process may be carried out using an inert atmosphere such as helium, argon, or nitrogen or the operation may be carried out in a vacuum.

The present invention comprises subjecting a clean metal surface to gas plating utilizing suitable organo-metallic compounds of aluminum or magnesium, and wherein the light metal compounds employed are heat-decomposable at temperatures substantially below the vaporization point of the light metals and decomposition or disassociation of the compound takes place in an atmosphere which is inert and free of oxygen to bring about deposition of the light metal without encountering oxidation reactions.

In carrying out the gaseous metal plating in accordance with this invention, in the production of light metal plated products organo-metallic compounds of aluminum, magnesium, etc., in either liquid or gaseous state, are preferably admixed with dry inert gas such as helium, argon, nitrogen, etc., and brought in contact with the heated previously cleaned metal surface upon which the light metal is to be plated, the temperature of the metal on which the plating is to be deposited is high enough to bring about decomposition or disassociation of the light metal organo-metallic compound and deposition of the metal constituent onto the metal substratum.

Cleaning of the metal surface to be plated may be effected by employing mechanical or chemical means, or suitable combinations thereof. Sandblasting, wire brushing, or the like, may be used to remove solid foreign particles. Where the metal surface is to be degreased and cleaned, the same may be washed with petroleum solvents such as xylol, toluene, or the like, and use may be made of aqueous alkaline washes. A suitable treatment consists of immersing the metal article in a solution containing 10% sodium hydroxide, the temperature of the solution being approximately 100° C. and allowing the metal to soak thereon for from ten to thirty minutes. Thereafter the article is removed, thoroughly rinsed with clean water and dried at a temperature around 300° C. for a sufficient time to remove all mois-

3

ture and provide a thoroughly dry chemically clean metal surface for gas plating with light metal compounds. The thus cleaned metal surface which is retained out of contact with air, and preferably in an inert atmosphere such as nitrogen or helium, is subjected to gaseous metal plating by bringing the same while heated in contact with a heat-decomposable organo-metallic compound. Following the gaseous metal plating the metal may again be heated if desired to stabilize the coating, as for example heat annealing the same by subjecting to a heat of approximately 250–300° C. for from one to two hours. This annealing step, however, may be omitted where the same is not required, or the use of the article thus plated does not necessitate it.

The accompanying drawing illustrates a preferred method of carrying out the process and the article produced thereby.

Figure 1 is a flow sheet illustrating the process; and Figure 2 illustrates a sectional view taken through a substratum plated with light metal by decomposition of a gaseous metal compound of aluminum or magnesium, in accordance with this invention.

The following organo-metallic compounds of aluminum and magnesium are useful in gas plating these light metals in accordance with this invention. Such compounds which are suitable may have the general formula: $Me(R)_n$, wherein Me represents aluminum or magnesium, n the valency of the metal, and R is hydrogen, or a hydrocarbon radical. Typical examples of such aluminum and magnesium compounds are listed as follows:

ALUMINUM

Alkyl and aryl compounds

$Al(C_nH_{2n+1})_3$ and aromatic derivatives
Aluminum trimethyl
Aluminum triethyl
Aluminum triphenyls
Aluminum benzyl lithium

Hydrides

Aluminum tri-hydride
Aluminum dimethyl hydride
Aluminum diethyl hydride
Aluminum boro-hydride

Nitrides and benzoates

Aluminum nitride
Aluminum nitro-benzoate

Esters

Aluminum alcoholates of lower and higher alcohols, e.g.:
Ethyl aluminate
Lauryl aluminate

MAGNESIUM

$Mg(C_nH_{2n+1})_2$ and aromatic derivatives
Magnesium di-ethyl
Magnesium di-methyl
Magnesium di-phenyl
Magnesium diphenyl ethyl or methyl (substituted)
Magnesium benzyl lithium

Halides

Magnesium alkyl halides and alkylmagnesium salts

Nitrides

Magnesium nitride and benzoates
Magnesium nitro-benzoate

Hydrides

Magnesium di-hydride
Magnesium methyl hydride
Magnesium ethyl hydride

Sulfur compounds

Magnesium ethyl sulfide

4

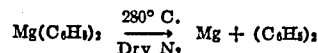
In accordance with the process of the present invention, gas plating of these light metals on various substrata may be carried out utilizing volatile or gaseous compounds of aluminum or magnesium which are heat-decomposable. Metallic compounds of aluminum or magnesium, such as listed above, and which may be in a solid or liquid state and volatilized to a gaseous state are used. The gaseous compound of the metal is brought in contact with the surface which is to be plated with the light metal and caused to decompose or disassociate and deposit the light metal constituent onto the surface.

The process of the invention thus differs from other suggested coating methods wherein special electrolytic baths are required and high or low voltage power means are employed. Further, while it is known that metal halides, particularly the chloride of aluminum, may be reacted with hydrogen to produce aluminum and hydrochloric acid, it has not been known to plate out aluminum, magnesium and such light metals by employing heat-decomposable gaseous compounds of these metals, the same being brought in contact with the article to be plated under controlled temperature and atmospheric conditions to cause decomposition or disassociation of the gaseous metal compound and deposition of the metal constituent onto the surface of the article.

The following examples are illustrative of the method of gas plating these light metals but it is understood that the examples are not limitative of this invention.

EXAMPLE I

Magnesium metal casting sand blasted to provide a clean surface is heated to about 350° C.–400° C. in an atmosphere of dry helium containing magnesium diphenyl. This magnesium organo-metallic compound decomposes at about 280° C. disassociating into magnesium and diphenyl. The process is carried out under atmospheric pressure conditions and in the absence of moisture to avoid fire hazard. In this instance the deposition of magnesium may be according to the equation:



EXAMPLE II

In this instance magnesium casting which is freed of foreign matter is heated to 300–400° C. and contacted with an atmosphere of dry helium containing aluminum trimethyl, and employing vacuum pressure conditions e.g. 15–20" mercury. Aluminum trimethyl starts to disassociate at about 250° C. whereupon the aluminum metal is deposited onto the surface of magnesium.

EXAMPLE III

Magnesium sheet metal is gas plated with magnesium metal similarly as in Example I, but under sub-atmospheric pressure conditions of from 18–25" mercury, and using dry nitrogen as the inert gas carrier for magnesium diphenyl.

EXAMPLE IV

In this instance steel strip material previously freed of foreign matter is heated to 350° C. and contacted with an atmosphere of dry helium containing magnesium diethyl, and under sub-atmospheric pressure conditions as in Example III. Upon decomposition of the magnesium alkyl compound magnesium is deposited onto the surface of the steel.

EXAMPLE V

Iron castings are gas plated with magnesium as in Example IV employing methylmagnesium iodide which thermally decomposes at about 250° C.

EXAMPLE VI

Magnesium metal is gas plated on steel as in Example IV using triarylmethylmagnesium iodide and at plating temperatures to bring about thermal decomposition of the iodide in an atmosphere of dry inert gas, e.g., nitrogen.

5

EXAMPLE VII

In this instance a 50-50 weight mixture of aluminum triethyl and magnesium diethyl was used and the gas plating being carried out on steel strip as in Example IV. In this case an alloy coating of magnesium and aluminum is plated onto the steel strip, the temperature being raised to bring about disassociation of the mixture of organo-metallic compounds and deposition of the metal constituent.

EXAMPLE VIII

Copper plate is cleaned and heated in an atmosphere of helium at a temperature of about 385° C. and in which is introduced approximately 10% of aluminum trimethyl. This compound boils at about 135° C. and is caused to disassociate to deposit the metal.

EXAMPLE IX

One mol of aluminum alcoholate and 0.1 mol of chlorine is heated to approximately 400-500° C. to bring about disassociation of the alcoholate and drive off the alcohol under vacuum of 18-20" Hg. The chlorine is used as a catalyst to assist the operation. Iodine or bromine may be substituted for chlorine where desired, and the temperature increased as necessary to bring about disassociation of the metal alcoholate and release of aluminum which may be deposited on a moisture-free surface heated to 350-450° C. and retained under the vacuum pressure conditions.

These light metals such as aluminum and magnesium are thus plated directly onto a substrate metal which may be an alloy metal such as steel, copper, iron, etc., whereby there is produced a composite product comprising the light metal integrally and tenaciously bonded to the metal or metal alloy which is of the heavy metal type.

Other organo-metallic compounds which may be used to gas plate magnesium or aluminum as described are magnesium dimethyl; aluminum trimethyl; triarylmethylmagnesium halides; diphenylethynylmagnesium, aluminum hydride magnesium and aluminum nitrides and such as will decompose under temperature, pressure and inert atmosphere conditions imposed. The light metal halide compounds such as bromides, iodides or chlorides may be obtained from sea water or formed as by-products during the recovery or process of making various chemical compounds and products utilizing brine-containing waters.

Coatings of these light metals may be of various thickness as desired depending upon the use to which the article is to be put. A coating of 0.001 to 0.0025 inch is adequate for providing protection against corrosion in most instances.

The process makes possible continuous straightline production of composite magnesium-aluminum products, such as wire, cable, metal plate, strip, sheet material or screen. The thickness of the coating may be controlled by limiting the duration of the gas plating or time the article remains in the plating enclosure. The invention is particularly useful in aluminizing metals where it is desirable that the metal be deposited into the pores and interstices of the base metal surface to form a substantially integral outer shell of aluminum metal. Aluminum metal thus deposited on steel, for example, provides a corrosion resistant product.

The material being gas plated with the light metals may be composed of various metals or alloys and in the various shapes and forms described. To clean the metal preparatory to gas plating, use may be made of conventional methods, such as washing or immersing the material in alkali or acid solutions, and rinsing the same with clear hot water and heating to 150 to 200° C. for sufficient time to drive off all moisture and produce a perfectly dry surface. Electro-chemical cleaning methods as commonly used also may be employed if desired

6

as well as mechanical cleaning methods, e.g. wire brushing and sandblasting.

Pre-heating and drying of the article prior to gas plating is preferably carried out in an inert atmosphere such as nitrogen, helium or the like to prevent oxidation. Thereafter the heated and completely dry metal surface is subjected to gas plating.

By employing gas plating in accordance with this invention, it is possible to envelope the material or article by a metal film or plate of any desired thickness, and which consists of substantially pure metal. A protective film is thus provided which film or plating does not have occluded foreign matter such as undesirable metals, salts, anode particles, bubbles and the like, which are inevitably plated out on the cathode along with the desired metal during ordinary electroplating methods.

Gas plating on the contrary, avoids these difficulties with respect to the impurities occluded by way of the electrolyte during electroplating, inasmuch as the gas plating works best, in most cases, in the absence of moisture or water vapor. Oxygen and oxidizable materials are also absent. The plating deposited by such gas plating method has been observed to produce a metal deposit which penetrates into the pores and interstices of the substrate metal but does not produce the undesirable brittle alloy effects as observed when such plating is applied by wet processes or molten metal plating methods.

It is not known the exact reason for this, but it is believed that these beneficial effects are accounted for by reason of the freedom of the metal deposit from impurities, particularly metal impurities which produce the brittle alloy characteristic property. The metal deposit at the interstices of the substratum by gas plating produces a tenacious intermediate portion which remains ductile and tough so that the metal thus plated can be worked as desired. Any desired thickness of plating may be deposited by gas plating, for example, so thin that the metal area is actually transparent and when deposited on a transparent substratum, such as glass, produces a smoked glass. The metal plating may also be increased so as to provide a coating thickness such as $\frac{1}{1000}$ to $\frac{1}{32}$ " if desired, or greater.

In the use of conduit, pipe and the like conveying corrosive material, it is desirable to coat or plate the interior of the pipe so that it will resist corrosion. This may be done by gas plating so that the inner wall is resistant to corrosion. Metal plating done in this manner is very superior to wet plating methods because it has been difficult to bring about uniform plating on the interior of hollow objects, especially conduits. Furthermore, employing conventional wet electroplating methods there is always a certain amount, even though minor, of entrapment of electrolyte. While this may be imperceptible under ideal conditions, there is generally enough impurities plated out with the metal to ultimately cause deterioration of the plated article. Gas plating eliminates these difficulties because no electrolyte is present or required in order to carry out the process and as is a prerequisite element in performing the wet electrolytic plating process.

Further, gas plating makes it possible to bring nascent pure metal in direct contact with chemically clean substrate surfaces on which the metal is to be plated, and due to the deposition of the metal from a gaseous state, the penetration of the same deeply into the pores and interstices of the metal is accomplished without the inclusion of impurities and such as will alter the physical characteristics of the metal so that the interstitial plate portions function to actually enhance the physical characteristics of the base metal or substrate.

What is claimed is:

1. A method of gas plating light metal selected from the group consisting of aluminum and magnesium on the surface of an article, which comprises heating said article in an inert atmosphere, and contacting said heated article

with a gaseous heat-decomposable compound selected from the group consisting of alkyl and aryl compounds of said light metals, said article being heated to a temperature to cause thermal decomposition of said compound and deposition of the light metal constituent onto the surface of the article whereby the same is coated with said light metal.

2. A product made in accordance with the method of claim 1.

References Cited in the file of this patent

UNITED STATES PATENTS

1,497,417	Weber	June 10, 1924
1,675,120	Marden et al.	June 26, 1928
1,732,326	Copper	Oct. 22, 1929
2,114,665	Loewe	Apr. 19, 1938
2,643,959	Fischer	June 30, 1953
2,656,283	Fink et al.	Oct. 20, 1953