

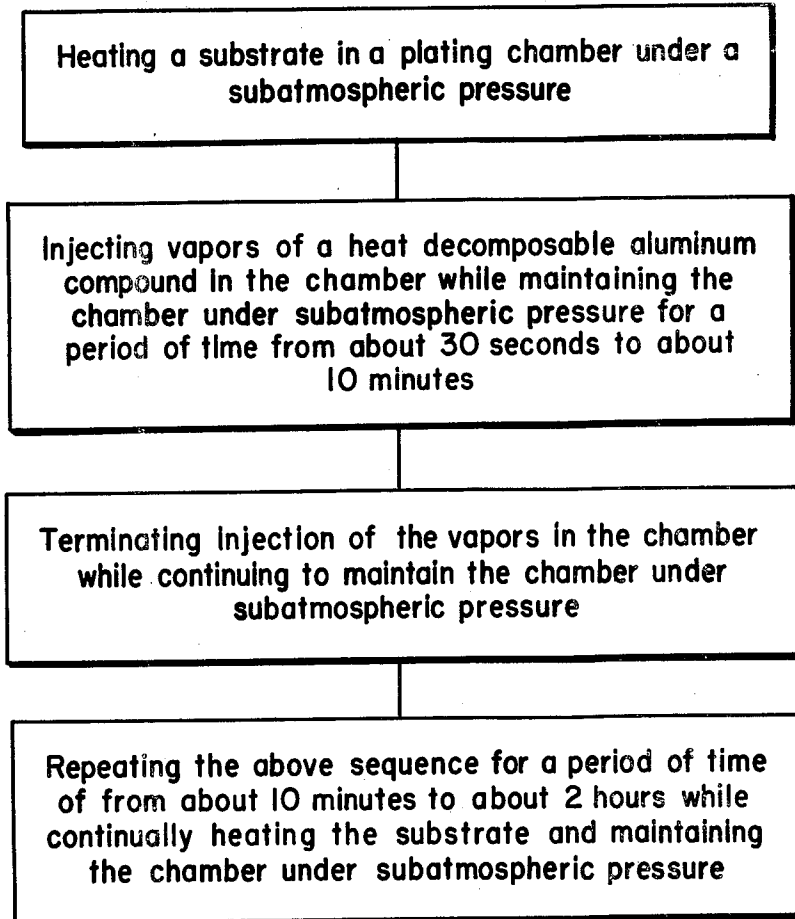
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ALUMINUM INTERMITTENT PLATING PROCESS

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ALUMINUM INTERMITTENT PLATING PROCESS

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This invention relates to an improved process of vapor plating. This invention further relates to a process of vapor plating aluminum wherein the plates produced are relatively free from discoloration and impurities.

Heretofore, it has been well known that metal plates may be obtained by the decomposition of metal containing compounds. For example, articles have been published and patents issued concerning the plating of molybdenum, chromium and tungsten from the hexacarbonyl compounds wherein carrier gases and high vacuum were employed in order to obtain plates. Narrow temperature ranges were also considered to be very critical in the plating process. After all of these critical features were employed, the product obtained generally had a high percentage of carbide and oxide, which caused much discoloration of the plate. Thus, the plates obtained, although useful in some instances, were not attractive commercially.

The impurities found in the plate also caused other defects. For example, plates high in carbide content were found to be extremely brittle. In some instances there was no mechanical interlocking between plate and base, ultimately attributed to the impurities. This lack of mechanical interlocking was demonstrated by flaking and welts on the plate.

In some instances the decomposition by-products caused a change in the nature of the base being plated. For example, when hydrogen is emitted as a by-product, it sometimes causes embrittlement of the substrate. This weakens the metal substrate causing it to become less useful commercially.

Many attempts have been made to overcome these undesirable effects which were caused by the harmful decomposition by-products of the plating compound, in many instances reacting with the deposited metal. As stated hereinabove, temperatures were varied, high vacuums employed and carrier gases used to eliminate the harmful adulteration of the metal plate by the decomposition by-products, but all of no avail.

It is therefore an object of this invention to provide an improved process of vapor plating aluminum. It is a further object to provide a process wherein harmful decomposition by-products are not allowed to accumulate in the plating zone and thus do not harm the aluminum plate or the substrate. It is still a further object of this invention to provide an aluminum plating process whereby the plates obtained are adherent to the substrate and are bright.

The drawing depicts a schematic arrangement of the main steps of the instant invention.

The above and other objects of this invention are accomplished by providing a marked improvement over the conventional vapor plating procedures which involve thermally decomposing the vapor of a heat decomposable aluminum containing compound in contact with a heated substrate. The improvement comprises contacting said substrate with the vapor of a heat decomposable alumi-

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num containing compound, thereafter terminating contact, causing withdrawal of undesirable by-products, and then re-establishing contact. This cycle of contacting and terminating contact of vapor of the heat decomposable aluminum containing compound with the heated substrate may be continued as long as is deemed necessary in order to obtain the desired thickness of plate. The preferred compounds which are employed in this invention are the aluminum hydride trimethyl amine complex, $\text{AlH}_3 \cdot (\text{CH}_3)_3\text{N}$, the aluminum hydride bis-trimethyl amine complex, $\text{AlH}_3[(\text{CH}_3)_3\text{N}]_2$, and the like.

In the process of this invention the object to be plated is maintained at a temperature sufficient to decompose the heat decomposable aluminum containing compound. This temperature is substantially maintained throughout all of the plating cycles.

The advantages of the process of this invention are numerous. The cycle of contacting and terminating contact of the vapor with the object to be plated causes the prompt elimination or withdrawal from the plating zone of the undesirable decomposition by-products of the aluminum containing compound, thereby inhibiting and largely preventing a reaction of said by-products with the aluminum plate and substrate. As stated hereinabove, high percentages of carbide and oxide tend to cause much discoloration of plate. This undesirable characteristic is hereby eliminated by the contacting and termination of contact cycle. Other undesirable properties experienced in vapor plating hereinbefore, i.e., brittleness and embrittlement of substrate, are likewise eliminated or at least largely reduced since the decomposition by-products are removed from the area of the plate by the contact and termination of contact cycles. Thus, the plates obtained by the process of this invention are shiny, bright, less brittle, and possess good mechanical interlocking between the plate and substrate with a minimum of embrittlement of the substrate being plated.

The term "contact" as used in the process of this invention contemplates contacting a heated substrate with the vapor of a heat decomposable aluminum containing compound. The phrase "termination of contact" as used herein may be defined as the cessation of contact of the vapors of the heat decomposable aluminum containing compound. Thus, one cycle includes contacting the heated substrate with the vapor of the heat decomposable aluminum containing compound after which contact is terminated by stopping the flow of vapor, permitting the plating chamber to clear of plating material and by-products. This cycle may be repeated as many times as is necessary in order to obtain the desired thickness of plate which is a shiny metallic, relatively carbide-free plate and which is well bonded to the substrate.

Generally, the equipment employed in the process of this invention may be any prior art plating equipment for plating from heat decomposable metal containing compounds. Illustrative of the equipment which may be employed is set forth in Lander and Germer, American Institute of Mining and Metallurgical Engineers, Technical Publication No. 2259 (1947). In other words, a conventional heating chamber which is provided with a means of heating the substrate equipped with a gas inlet and outlet means may be employed. The heat decomposable aluminum containing compound is placed in a vaporization chamber provided with a heating means and connected through an outlet port equipped with a cutoff valve to the inlet means of the combustion chamber.

For the plating operation, the object to be plated is

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heated to a temperature above the decomposition temperature of the heat decomposable aluminum containing compound of the system is evacuated to a sub-atmospheric pressure of from 500 mm. to about 0.001 mm. pressure. The preferred pressure ranges from about 10 mm. to about 0.01 mm. of mercury. The metal containing vapors are pulled through the system as the vacuum pump operates, said vapors impinging on the heated object, decomposing and forming the aluminum coating. After the vapors are permitted to impinge on the heated substrate for a period of time, ranging from about one minute to about five hours, the aluminum containing vapor is shut off, permitting the plating chamber to clear of all undesirable by-products. The preferred contact time generally ranges from about 10 minutes to about 2 hours. The termination of contact time generally ranges from about 15 seconds to about 30 minutes, but the preferred time ranges from about 30 seconds to about 10 minutes. The cycle of contacting the substrate with the aluminum containing vapors is repeated after which the chamber is cleared again of undesirable by-products. In order to avoid further contamination of the plates obtained, it is generally desirable not to employ a carrier gas since it is known that carrier gases contain impurities such as oxygen which contaminate the substrate. However, in some instances, in the use of particular plating agents a carrier gas may be employed. It should be noted that the precise times of the cycle are ultimately controlled by the geometry of the plating chamber, size of the substrate, plating temperature, nature of the plating compound, and pressure employed during the plating process.

The process of this invention is a simple continuous sequence of operations, i.e., placing the object to be plated in the plating chamber, heating said object to a temperature sufficient to decompose the heat decomposable aluminum containing compound, contacting said heated object with the vapors of the heat decomposable aluminum containing compound, terminating contact and clearing the system of all vapors. **The cycle, contact and termination of contact may be repeated as many times as is necessary.**

Thus, the process of this invention is a controlled, continuous decomposition process wherein the rate of decomposition is carefully controlled and the undesirable decomposition by-products are eliminated from the scene, thus preventing contamination of the plate.

The following working examples more adequately demonstrate the products obtained by the unique process of this invention.

Example I

Plating compound	Aluminum hydride trimethyl amine complex, $\text{AlH}_3 \cdot (\text{CH}_3)_3\text{N}$.
Substrate	Titanium alloy.
Temperature of substrate	180° C.
Temperature of compound	40° C.
Duration of initial contact between vapors and substrate	10 minutes.
Duration of contact termination	10 minutes.
Duration of re-establishment contact (2nd cycle)	10 minutes.
Duration of contact termination	10 minutes.
Duration of re-establishment contact (3rd cycle)	10 minutes.
Duration of contact termination	5 minutes.
Duration of re-establishment contact (4th cycle)	10 minutes.
Plate obtained	Silvery white uniform aluminum coating.

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Example II

Plating compound	Aluminum hydride bis-trimethyl amine complex $\text{AlH}_3 \cdot 2[(\text{CH}_3)_3\text{N}]$.
Substrate	Steel.
Temperature of substrate	175° C.
Temperature of compound	50° C.
Duration of initial contact between vapors and substrate	5 minutes.
Duration of contact termination	5 minutes.
Duration of re-establishment contact (2nd cycle)	5 minutes.
Duration of contact termination	5 minutes.
Plate obtained	Silvery white uniform, well adhering aluminum coating.

It is noted from the working examples above that by employing the novel process of this invention well-adherent shiny aluminum coatings are obtained with a minimum of undesirable side effects caused by the decomposition by-products of the plating compounds.

The temperature employed in decomposing the heat decomposable metal containing compounds of this invention is directly dependent on the plating agent being used and the pressures employed. However, temperatures ranging between about 125° C. up to about 550° C. may be used. The temperature does not constitute a critical feature of this invention except that it be high enough to decompose the aluminum containing compound to liberate the free metal since this unique process inhibits the reaction of the metal with the undesirable by-products of the decomposed compound whereas generally in the prior art high temperatures would cause a reaction or interaction between the metal plate and the decomposition by-products.

The pressures generally employed may range from about 500 mm. of mercury down to about 0.001 mm. However, the range generally used as a matter of practice ranges from about 10 mm. down to about 0.01 mm. of mercury since better plates are obtained within this range and the plating compound is more volatile.

As stated hereinabove, it is not desirable to use a carrier gas since carrier gases often contain impurities which tend to combine with the substrate, forming oxides and other undesirable combinations with the metal. However, in some instances, a carrier gas may be employed where the plating agent so demands. In those instances, carrier gases which generally may be used are the inert gases such as purified helium, neon, argon, krypton, xenon, and the like. Purified nitrogen in some instances may also be employed as a carrier gas if it does not react with either substrate or liberated metal.

The substrates which may be plated in the process of this invention are any substrates, e.g., metals, metalloids, minerals, etc., which can withstand the temperature and pressure within a plating chamber. In some instances with certain plating agents, substrates such as fibrous polyesters, cotton, wool, and the like may be used. Other substrates which may be employed include glass, wood, ceramics, plastics, paper, and the like.

The practical purposes of vapor deposition on a given substrate according to the novel process of this invention generally fall into one of the following categories: abrasion protection, corrosion protection, oxidation protection, catalytic uses and decorative purposes.

Having thus described this invention and all its embodiments, it is not intended that this invention be limited except as within the spirit and scope of the attendant claims.

We claim:

1. A vapor plating process comprising:

- (1) heating a substrate in a plating chamber to a temperature within the range of from about 125° C. to about 550° C. and under a subatmospheric pressure of from about 0.01 millimeter to about 10 millimeters mercury absolute, 5
 - (2) injecting vapors of an aluminum hydride trimethylamine complex in said chamber while maintaining said chamber under subatmospheric pressure, said vapors being at a temperature less than that of said heated substrate such that upon contact therewith said vapors are decomposed and an aluminum coating is effected upon said substrate, said vapors being injected in said chamber for a period of time of from about 30 seconds to 10 minutes. 15
 - (3) terminating injection of said vapors in said chamber while continuing to maintain said chamber under subatmospheric pressure, and
 - (4) repeating the above sequence for a period of time of from about 10 minutes to about 2 hours while continually heating said substrate and maintaining said chamber under subatmospheric pressure. 20
2. A vapor plating process comprising:
- (1) heating a substrate in a plating chamber to a temperature within the range of from about 125° C. to 550° C. and under a subatmospheric pressure of from about 0.01 millimeter to about 10 millimeters mercury absolute, 25
 - (2) injecting vapors of an aluminum hydride bis-trimethylamine complex in said chamber while maintaining said chamber under subatmospheric pres-

- sure, said vapors being at a temperature less than that of said heated substrate such that upon contact therewith said vapors are decomposed and an aluminum coating is effected upon said substrate, said vapors being injected in said chamber for a period of time of from about 30 seconds to about 10 minutes,
- (3) terminating injection of said vapors in said chamber while continuing to maintain said chamber under subatmospheric pressure, and
 - (4) repeating the above sequence for a period of time of from about 10 minutes to about 2 hours while continually heating said substrate and maintaining said chamber under subatmospheric pressure.

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