

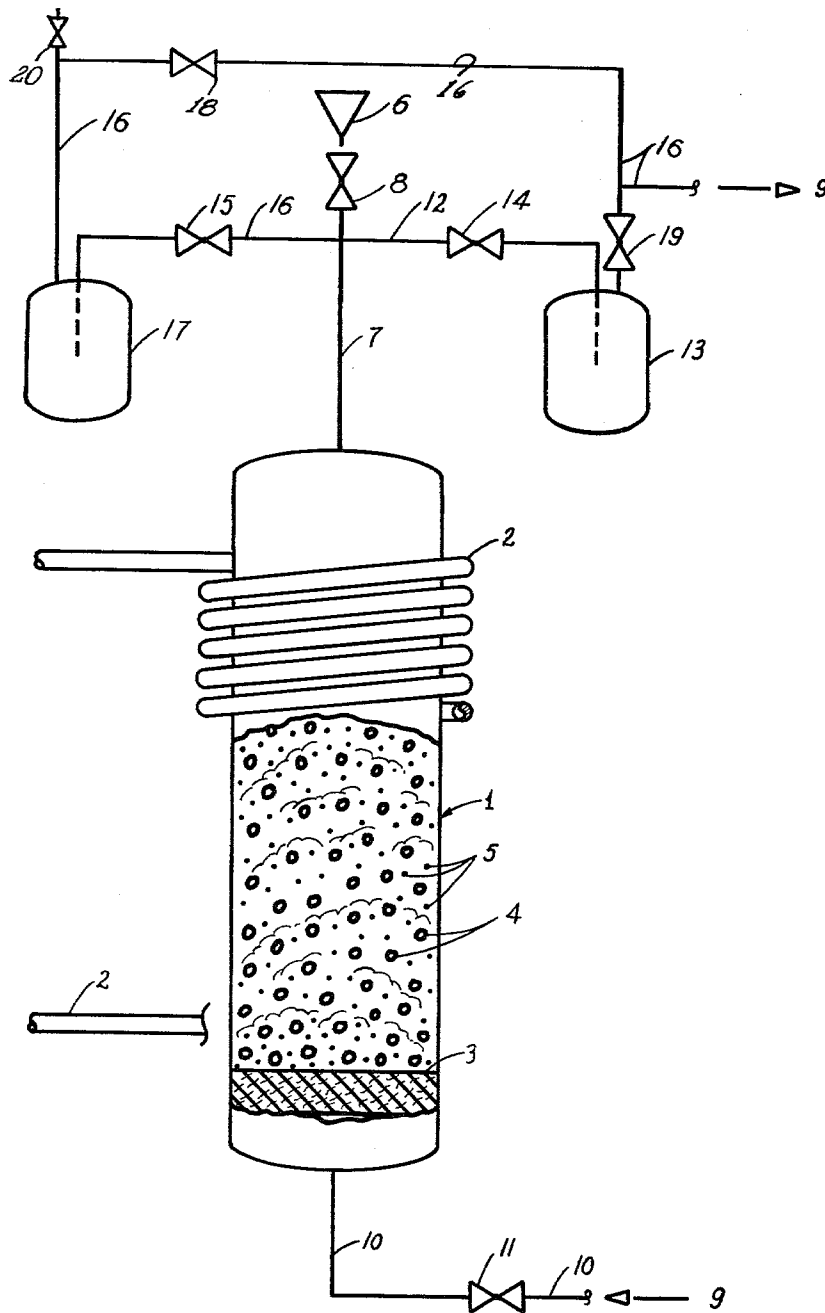
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METHOD OF METAL PLATING BY FLUIDIZED BED

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Vello Norman, Chapel Hill, N.C., and Hamilton B. Prest-
ridge, Baton Rouge, La., assignors to Ethyl Corpora-
tion, New York, N.Y., a corporation of Virginia
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This invention relates to a process for plating ap-
propriate substrates by contacting them with a solid heat-
decomposable carbon-containing metal compound in a
fluidized bed.

Demand of present day high temperature technology
has brought about considerable improvement in the art
of metal plating. One of the more favorable techniques
of metal plating employed to achieve metal coats suitable
for high temperature service is the art of vapor plating.
That technique, which is a chemical process, involves
thermal decomposition of vaporous heat-decomposable
compounds. It broadly comprises the step of heating
the compound to the vapor phase after which it is trans-
ported into a plating chamber, usually by the medium of
a carrier gas. Situated in the plating chamber is the
substrate desired to be plated which is heated to a suf-
ficient temperature to decompose the plating compound.
Upon contacting the substrate with the vaporous plating
compound thermal decomposition occurs at the heated
surface of the substrate and a subsequent coating is
realized. It is apparent that one serious limitation of
vapor plating is the requirement that compounds having
appreciable volatility be employed. This physical char-
acteristic of a plating compound is necessary since the
compound must be vaporized for transportation for sub-
sequent contact with the substrate. To overcome this
inherent limitation of vapor plating other chemical pro-
cesses have been developed wherein compounds are em-
ployed whose volatility does not lend itself for use in
vapor plating. A typical such process wherein com-
pounds are employed in their solid state is commonly
referred to as a "pack technique." It broadly involves
the intimate packing of the article to be treated together
with a powdered metal-containing compound in a suit-
able container and then applying heat to decompose the
compound, the metal constituent of which contacts and
diffuses into the surface of the substrate. Coatings ef-
fected via this process are characterized by their low
purity and lack of ductility. These undesirable results
are due largely in part to the high temperature to which
the substrate is inherently subjected in the process. The
high temperature causes the metal coating and the base
metal to inter-diffuse. An intermetallic interface is pro-
duced which is quite brittle and hence limits the coating
to applications where it need not be ductile. Addition-
ally, it is apparent that the inter-diffusion between the
coating and its base metal produces an impure metal
coating. Therefore, a process allowing the use of com-
pounds heretofore unsuitable for use in vapor plating
which captures the simplicity of the "pack technique"
while simultaneously attaining ductile metal coatings of
high purity would represent a considerable contribution
to the art.

Thus an object of this invention is to provide a unique
process for plating a broad range of appropriate substrates
with compounds heretofore unsuitable for the plating of
such substrates by prior art processes. Another object
of the process of this invention is the production of
unique articles of manufacture as realized in the execu-
tion of this process and its embodiments. Another im-
portant object is to achieve the above objectives by a
process which is characterized by its ease and simplicity

of operation. A still further object is to provide a
process which particularly lends itself to the production of
high purity coatings that can be effected at relatively
high production rates. These and other objects of this
invention shall appear more fully hereinafter.

The above objectives are accomplished by the instant
process which comprises effecting contact between a heated
substrate and a body of a heat-decomposable carbon-con-
taining metal compound existing in the solid state of ag-
gregation while said substrate and said compound are in
a constant state of motion induced by a gaseous medium
in contact therewith. A preferred embodiment of the
instant invention comprises (1) conveying selected sub-
strates into a plating zone (2) exposing said substrates to
a pulverulent heat-decomposable carbon-containing metal
compound (3) fluidizing the system, preferably by an
inert gas (4) heating said substrates to a temperature suf-
ficient to decompose said metal compound (5) continually
heating said substrates until the desired thickness of coat-
ing is achieved, and (6) thereafter cooling said substrates.
The above embodiment is preferred when a relatively thick
metal coating is desired. A thick coating is attained by
continually heating the agitated substrates in the presence
of the fluidized plating compound.

Another preferred embodiment of the instant inven-
tion comprises (1) heating selected substrates to a tem-
perature sufficient to decompose a heat-decomposable
carbon-containing metal compound (2) conveying said
heated substrates into a plating zone, (3) exposing said
heated substrates to said metal compound existing in a
pulverulent state of aggregation in a constant state of
motion induced by a gaseous medium in contact there-
with (4) maintaining said substrates and said metal com-
pound in a constant state of motion until the desired
thickness of coating is achieved, and (5) thereafter
cooling said substrates. This embodiment is particularly
attractive where a thin metal coating is desired. Heating
of the substrate before contact with the plating
compound allows the use of less expensive heating
means.

A more preferred embodiment of the instant invention
comprises (1) preheating selected substrates, (2) conveying
said preheated substrates into a plating zone, (3) ex-
posing said preheated substrates to a heat-decomposable
carbon-containing metal compound existing in a pul-
verulent state of aggregation in a constant state of motion
induced by a gaseous medium in contact therewith, (4)
maintaining said substrates and said metal compound in
a constant state of motion, (5) further heating said sub-
strates to a temperature sufficient to decompose said met-
al compound until the desired thickness of coating is
achieved, (6) removing said coated substrates from said
plating zone, and (7) thereafter cooling said coated sub-
strates. The above embodiment is highly preferred since
preheating of the substrates provides for maximum pro-
duction rates. Additionally, preheating promotes more
efficient utilization of the plating compound.

The above procedure can be implemented with addi-
tional features. For instance, fluidizing gas containing
certain alloying elements can be employed to impart de-
sired properties to the coating. There are many other
variations of the instant invention which will come to
light as the discussion proceeds.

A complete understanding can be obtained from the
following detailed description and explanation of one
of the preferred embodiments of the instant invention
depicted in the accompanying drawing. In the drawing,
element 1 represents the plating chamber or zone where-
in the plating operation takes place. In this embodiment
the plating chamber comprises an elongated pressure
vessel mounted such that its longitudinal axis extends

in a vertical direction. Chamber 1 further comprises a gas permeable foraminous retainer or porous filter 3 positioned in the lower portion of the chamber and oriented in a horizontal plane. The member 3 extends over the entire cross-sectional area of the chamber 1 defining two separate compartments communicable through the foraminous retainer 3.

In this embodiment, the plating operation is initiated by charging the plating chamber 1 with selected substrates 4 and desired plating compound 5 via the funnel 6 through the conduit 7, the latter connected to the top most portion of the chamber 1. Valve means 8 is provided in conduit 7 to isolate the system from the atmosphere after charging preparatory to the plating operation. A source 9 of inert gas is then caused to flow into the chamber 1 through the conduit 10 connected to the lowermost portion of the plating chamber. Valve means 11 is provided in the conduit 10 to regulate the flow of the inert gas 9. The inert gas upon entering the chamber 1 contacts the gas permeable retainer or filter 3 over which the inert gas is distributed and through which it flows upwards toward the top portion of the chamber 1. After diffusing through the retainer 3 the inert gas impinges upon the plating compound 5 and the substrates 4 whereby they are fluidized and caused to flow upwards and remain continually suspended at a height commensurable with the volume of inert gas passing through the system as regulated by manipulation of valve 11. Positioned externally of the chamber 1 is high frequency induction heating means 2 which extends longitudinally of the plating chamber over a fixed distance to define a heating zone. Shortly before or after fluidizing the plating compound and the substrates, the heating means 2 is set into operation to heat the substrates 4 suspended in the heating zone defined by the heating means 2. During the plating operation the fluidizing inert gas exits from the plating chamber 1 by way of conduits 7 and 12. A knockout pot or separating means 13 is provided in the conduit 12 to separate entrained undecomposed plating compound from the inert gas 9. The latter can be subsequently recycled through conduit 12 back to its original source for continuous use in the system. Likewise, the undecomposed plating compound can be used further.

When the desired thickness of coating is achieved the heating means 2 is shut off and the fluidizing inert gas allowed to flow for a brief duration of time to cool the coated substrates 4. Thereafter the inert gas can be cut off by valve means 11 after which the member 1 is opened up and the coated substrates 4 removed. A more convenient manner by which to remove the coated substrates from the plating chamber after the plating operation is consummated and the heating means 2 shut off is by purging the system with a large volume of the inert gas. This is accomplished by opening the valves 15 and 18 and simultaneously closing valves 14 and 19. This will allow the coated substrates to be blown from the plating chamber 1 through conduits 7 and 16 whereby they will be trapped and separated in the knockout pot or separating means 17 from whence they can more readily be removed from the system. The inert gas by which the coated substrates are conveyed into the separating means 17 is discharged into conduit 16 for recycling back to its original source. Or, it may be discharged from the system to the atmosphere by opening valve 20 and closing valve 18.

It is understood that structural modifications can be made to the above apparatus arrangement without departing from the true spirit of the process of this invention. For example, automatic control means can be provided in conjunction with the valve 11 to automatically control the volume of the inert gas 9 entering the plating chamber 1. Additionally, this can be tied in with an overall time-sequence control of the plating operation whereby heating means 2 would also be automatically regulated. The remaining valves would like-

wise be automatically controlled from the central control means.

Further, it is apparent that the subject invention is not limited to a batch process as discussed above. Equipment conducive for a continuous plating operation can readily be employed. For example, the plating chamber can comprise a fluid conveyor having a foraminous bottom through which the fluidizing inert gas is allowed to pass whereby the plating compound and substrates contained thereon are fluidized. Heating means are provided in combination with the fluid conveyor to heat the substrate to that temperature necessary to decompose the plating compound. Modifications and changes from the specific components of the apparatus discussed above whereby the process of this invention can be practiced are within the contemplation of the present invention and are intended to be embraced within the scope of the appended claims.

To illustrate the process of this invention the following examples are presented wherein all parts and percentages are by weight.

Example I

Employing the apparatus depicted in the drawing, iron powder was coated with chromium. The plating chamber 1 was constructed of 1 inch inside diameter Pyrex pipe. Gas-permeable glass retaining means 3 was positioned in the lowermost portion of the plating chamber 1. The plating zone, that distance between the top of the retainer 3 and the top of the plating chamber, was 32 inches in length. The plating chamber was charged with powdered crystalline chromium hexacarbonyl of a quantity equivalent to 20 grams of chromium metal. The plating chamber was also charged with 200 grams of 100 mesh iron powder. The plating compound and the substrates were fluidized by means of carbon monoxide. The suspended substrates were heated to approximately 450° C. After approximately 15 minutes the plating operation was terminated. The coated substrates and the remaining plating compound removed from the chamber were then separated. The iron substrates were weighed and found to have a total weight of 209.8 grams. The quantity of plating compound recovered was 9.7 grams by weight of chromium. The chromium coating on the iron substrates had a dark silver appearance which was very adherent.

Example II

A similar procedure and apparatus was employed as in Example I above to coat magnesium with aluminum except that the member 1 was constructed of 2 inch inside diameter Pyrex pipe. The plating compound employed was the trimethylamine complex of aluminum hydride. A quantity of plating compound equivalent to 20 grams of aluminum was placed into the plating chamber along with 250 grams of 200 mesh magnesium powder. This system was fluidized with argon gas and the substrates heated to about 170° C. for approximately 12 minutes. A vacuum of 15 inches of mercury was maintained on the system during the plating operation. After the plating operation was terminated the coated magnesium substrates and the remaining plating compound were removed from the system. The coated magnesium substrates were then separated from the plating compound and found to weigh 263.1 grams. The quantity of plating compound remaining was 3 grams by weight of aluminum. Upon examination, the magnesium powder was found to have an aluminum coating satin silver in appearance, uniform and well adherent.

Example III

A continuous plating apparatus is provided which consists of an elongated chamber which houses a fluid conveyor. The fluid conveyor basically consists of an elongated U-shaped member having a foraminous bottom. Positioned beneath the fluid conveyor and forming an

integral part thereof is a fluid manifold arranged relative to the bottom of the fluid conveyor such that a fluidizing medium can be caused to flow through the bottom of the fluid conveyor to fluidize the material contained thereon. The fluid conveyor extends lengthwise of the plating chamber where at one end it is adapted to receive the substrates to be plated along with the plating compound to be employed. From the inlet end of the plating chamber the fluid conveyor extends lengthwise of the plating chamber at a slightly decreasing elevation. To receive the coated substrates as they are discharged from the fluid conveyor, a gravity fed screw conveyor is provided which extends from a position immediately below the discharge end of the fluid conveyor to the exterior of the plating chamber where it discharges into a totally enclosed product storage tank.

The above apparatus is employed to effect an aluminum coating of high purity on beryllium powder. Beryllium powder averaging about 200 mesh is first mixed in equal parts with a pulverulent mixture of trimethylamine and bis-trimethylamine complexes of aluminum hydride. After mixing, these materials are then conveyed under pressure into the plating chamber and discharged onto the receiving end of the fluid conveyor contained within the plating chamber. Arranged in close proximity to the fluid conveyor are high frequency induction heating means for heating the beryllium powder to approximately 190° C. Dry nitrogen is heated externally of the plating chamber to approximately 50° C. after which it is piped to the fluid conveyor manifold where it subsequently passes through the foraminous bottom of the fluid conveyor to fluidize the plating compound and substrates. The nitrogen is preheated to serve as a means of preheating the plating compound. After about 60 seconds residence time in the plating chamber, the aluminum coated beryllium powder is discharged from the end of the fluid conveyor after which it is conveyed to product storage. Upon examination, the beryllium powder is found to be coated with a very adherent aluminum coating which is quite uniform in thickness.

Example IV

The apparatus described in Example III is employed in modified form to aluminum plate $\frac{3}{16}$ inch by $\frac{1}{2}$ inch high strength alloy steel aircraft cap screw fasteners. The apparatus is modified to the extent that the cap screws are fed separately onto the fluid conveyor. They are heated to 70° C. previous to their entry into the plating chamber. The plating compound, which is a pulverulent mixture of trimethylamine and bis-trimethylamine complexes of aluminum hydride, is also separately fed onto the fluid conveyor. A residence time of approximately 3 minutes is employed to achieve a very adherent and pore-free aluminum coating on the fasteners. A high degree of uniformity of the metal coating over the threaded portion of the cap screw, existent both in the area of the top of the thread as well as the root area of the threads is noted.

Example V

The apparatus employed in Example III is employed in a modified form to plate 96 percent silicon glass pellets with chromium. The glass pellets are fed onto the fluid conveyor contained within the plating chamber. Pulverulent p-xylene chromium tricarbonyl is employed as the plating compound which is separately fed onto the fluid conveyor. The high frequency induction means is regulated to heat the glass pellets to approximately 420° C. The substrate and the plating compound are fluidized by virtue of dry nitrogen which has been previously heated to approximately 70° C. After 75 seconds residence time in the plating chamber, the chromium coated glass pellets are discharged from the end of the fluid conveyor and conveyed external of the plating chamber. Upon examination they are found to have a very adher-

ent metallic chromium coating which is dark silver in appearance.

Example VI

The apparatus employed in Example III is employed in a modified form to plate graphite flakes with tungsten. The graphite flakes are fed onto the fluid conveyor contained within the plating chamber. Pulverulent tungsten hexacarbonyl averaging about 60 mesh is employed as the plating compound. The plating agent is subsequently fed onto the fluid conveyor. Heating is provided by high frequency induction means. Shortly after entering the fluid conveyor, the graphite flakes and the tungsten hexacarbonyl are exposed to the high frequency induction heating means which is regulated to heat the graphite flakes to approximately 480° C. Argon is employed as the fluidizing medium which has been previously heated to approximately 70° C. After about 7 minutes residence time in the plating chamber, the tungsten coated graphite flakes are discharged from the end of the fluid conveyor and conveyed external of the plating chamber. The graphite flakes upon examination are found to have a very adherent tungsten coating.

Any solid heat-decomposable carbon-containing metal compound which can be thermally decomposed to deposit a metal plate can be employed as a plating agent in the process of this invention. By carbon-containing metal compound is meant a compound having at least one metal to carbon bond. However, compounds containing up to about 40 carbon atoms are preferred since they are generally more economical and are readily decomposed at convenient operating temperatures. An important physical characteristic of the plating compounds used in this process are that they have melting points above room temperature (i.e. above about 25° C.) and that they have a thermal decomposition temperature lower than the temperature at which the object to be plated would undergo thermal deterioration.

The metals which comprise the metal constituents of the metal compounds used in this invention are in general any metals of Groups IV-B through V-A of the Periodic Chart of the Elements, Fisher Scientific Company, 1955. These metals are as follows:

Group IV-B:	Group VIII—cont.
45 Titanium	Palladium
Zirconium	Platinum
Hafnium	Group I-B;
Group V-B:	Copper
Vanadium	Silver
50 Niobium	Gold
Tantalum	Group II-B:
Group VI-B:	Zinc
Chromium	Cadmium
Molybdenum	Mercury
55 Tungsten	Group III-A:
Group VII-B:	Aluminum
Manganese	Gallium
Technetium	Indium
Rhenium	Thallium
60 Group VIII:	Group IV-A:
Iron	Germanium
Ruthenium	Tin
Osmium	Lead
Cobalt	Group V-A:
65 Rhodium	Antimony
Iridium	Bismuth
Nickel	

Group VI-B metals (particularly chromium) and aluminum are preferred since plating compounds of these metals are particularly suited for use in the process of this invention. Coatings effected by use of compounds containing these metals are characterized by their high purity and adherence. Additionally, many of these compounds are readily available and hence offer economic advantages.

These solid carbon-containing metal compounds include organic metal hydrides, metal carbonyls and organometallics. A highly preferred group of compounds are the amine complexes of aluminum hydride and the metal carbonyls. This group of compounds is attractive since they possess a degree of stability desirable for use in the instant invention. Of these, the most preferred are the amine complexes of aluminum hydride, particularly the lower alkyl amine complexes of aluminum hydride such as trimethylamine, bis-trimethylamine, and dimethylethylamine complexes of aluminum hydride. By lower it is meant that the alkyl group contains 6 carbon atoms or less. The trialkylamine complexes of aluminum hydrides are preferred since coatings effected via these compounds are characterized by their high purity and adherence.

Additional examples of suitable amine complexes of aluminum hydride are: tri-n-propylamine complex of aluminum hydride, triisopropylamine complex of aluminum hydride, tetramethylethylene diamine complex of aluminum hydride, the hexyl-trimethylethylene diamine complex of aluminum hydride, dimethyl aniline complex of aluminum hydride, and the like.

Exemplary of the metal carbonyls are chromium hexacarbonyl, molybdenum hexacarbonyl, tungsten hexacarbonyl, manganese pentacarbonyl dimer, rhenium pentacarbonyl dimer, iron tetracarbonyl trimer, ruthenium tetracarbonyl trimer, cobalt tricarbonyl tetramer, rhodium tetracarbonyl dimer, iridium tetracarbonyl dimer, and the like.

Exemplary of the organometallics are the alkyls, cyclo-matics and aryls. Suitable alkyl metal compounds are dimethyl beryllium, trimethylindium, diphenylzinc, diphenylgermanium, triphenylaluminum, tetraphenyllead, diethylidiphenyltin, methylgallium dichloride, dibutyltin dichloride and the like. Of the cyclo-matics, cyclopentadienyl metal carbonyls, cyclopentadienyl metal nitrosyl and the cyclopentadienyl metal halides are preferred. Exemplary of such compounds are dicyclopentadienyl titanium, dicyclopentadienyl iron, dicyclopentadienyl vanadium, dicyclopentadienyl nickel, cyclopentadienyl manganese tricarbonyl, acetyl cyclopentadienyl manganese tricarbonyl, cyclopentadienyl rhenium tricarbonyl, cyclopentadienyl nickel carbonyl dimer, cyclopentadienyl chromium tricarbonyl dimer, cyclopentadienyl tungsten tricarbonyl dimer, cyclopentadienyl molybdenum dicarbonyl nitrosyl, dicyclopentadienyl zirconium dichloride, dicyclopentadienyl titanium dibromide, cyclopentadienyl titanium trichloride, cyclopentadienyl chromium dinitrosyl chloride, cyclopentadienyl molybdenum tricarbonyl bromide, cyclopentadienyl iron dicarbonyl bromide, dicyclopentadienyl tantalum tribromide, dicyclopentadienyl niobium tribromide. Of the aryl organometallics the most preferred are diarene metal compounds, arene metal carbonyls, arene metal nitrosyls and the arene metal halides. Typical examples of such compounds are dibenzene chromium, dibenzene molybdenum, dibenzene vanadium, bis-(diphenyl)chromium, diphenyl benzene chromium, benzene molybdenum tricarbonyl, toluene chromium tricarbonyl, p-xylene chromium tricarbonyl, m-xylene molybdenum tricarbonyl, o-xylene tungsten tricarbonyl, benzene molybdenum dinitrosyl, toluene tungsten dinitrosyl, cumene chromium dinitrosyl, diphenyl chromium iodide, dibenzene molybdenum iodide, and the like.

Exemplary of the organic metal chelates are the acetylacetonates and alkyl acetoacetates of copper, nickel, platinum, chromium, and the like.

The most outstanding and most preferred plating compounds for use in this invention are the trimethylamine complex of aluminum hydride, the bis-trimethylamine complex of aluminum hydride, and mixtures thereof. These materials provide the best coatings at the lowest cost.

The above compounds and their methods of preparation are all well known in the art.

In general, the compounds utilized in the practice of this invention can be decomposed at relatively moderate temperatures, generally no higher than about 600° C. and in some cases as low as 100° C. The metal carbonyl compounds are preferably decomposed within a temperature range of from about 400° C. to 500° C. The possibility of contamination by the by-products of the decomposition is minimized within this temperature range. The most preferred class of compounds employed in this invention, namely the trialkylamine complexes of aluminum hydride, produce the best coatings when decomposed at temperatures within the range of from 150° C. to about 200° C., particularly around 170° C. for maximum purity. As brought out above, when selecting a particular plating agent cognizance should be taken of the limitations to which the substrates can be subjected without thermal deterioration. Thus, it can be seen that the preferred class of compounds when employed in this unique process achieves additional benefits in that it is now possible to plate many substrates with an aluminum coating heretofore not realizable in the prior art.

The plating compounds used in the present invention have a particle size generally no greater than about 5 mesh nor smaller than 400 mesh. However, larger particle sizes can be employed as long as the compound is capable of being fluidized for subsequent contact with the substrate being plated. In certain instances it is desirable to have the compound exist in a much smaller size, say 50 mesh or less which can readily be achieved where appropriate by subjecting the compound to physical methods of comminution. Compounds having an average particle size less than about 400 mesh are extremely fluid and require careful control of the process variables. Generally speaking, the physical size of the plating compound desirably varies with the type of operation employed. Where production rates are maximized, it is expeditious to employ a compound existing in a fine particle size. A preferred range of particle size is from about 100 mesh to 200 mesh. Within this range maximum utilization of the plating compound is achieved when plating the preferred substrates of this invention.

The substrates or objects to be plated by the process of this invention includes those of all composition possessing sufficient structural strength under processing conditions. Substrates having a material of construction which allows prolonged heating at that temperature necessary to effect decomposition of the plating compound when contacted therewith are preferred. However, substrates that can only withstand elevated temperatures for a brief duration of time can be employed in the instant process where a thin coating is acceptable since a distinguishing feature of this process is the rapidity by which an acceptable coating can be effected. It is apparent that the substrate be of suitable size and geometry such that it can be fluidized for the plating operation. Exemplary of the substrates that can be plated by the instant invention are metals and alloys thereof, glass, ceramics, refractories, graphite, plastic resins, thermo-electric elements, and the like. A highly preferred class of substrates are metal substrates, particularly ferrous, magnesium, and beryllium metals existing in a powdered or pellet form having an average particle size in the range of from 50 to 200 mesh. These substrates are desired since coatings effected on them are characterized by their high purity, low porosity, and adherence.

There are many well known methods that can be conveniently employed to heat the substrate. For example, heating can be conducted by high frequency induction means, infrared means, and the like. The most preferred mode of heating however is by high frequency induction means. This method of heating is desirable since it allows rapid heating of the substrate and thus reduces residence time in the plating chamber.

Depending upon the end result desired, surface preparation as a preliminary step prior to employing the tech-

nique of this invention can be desirable. Exceptions are those substrates, such as glass, ceramics, and the like, which are generally suitable for plating as commercially supplied. Where it is preferred to implement this technique with a surface preparation step there are various well known methods which can be employed. Generally speaking, an initial surface preparation improves the degree of adhesion of the effected coating. Much depends upon the geometry and composition of the substrate as to the selection of the most convenient method of cleaning. For most substrates, the best metal surface preparation is achieved through degreasing with a halogenated solvent such as 1,1,2-trichloroethylene or the like followed by light sand blasting. When cleaning by sand blasting, inclusion of grains of the sand blasting material in the surface of the substrate is to be avoided. In lieu of sand blasting, cleaning by pickling with dilute acid can be employed. Where a thin unblemished coating is sought, it is highly desirable that the precleaned substrate be carefully neutralized and then rinsed.

The type of fluidizing medium employed in the preferred embodiment of the instant invention is desirably not compatible with the substrate or the plating compound. Exemplary of suitable inert fluidizing gases are carbon monoxide, nitrogen, hydrogen, helium, neon, argon, krypton, xenon, gaseous aliphatic hydrocarbons, and the like. Carbon monoxide, argon, and nitrogen are preferred since they are economical and readily available. In a variation of the instant process a fluidizing gas containing element which will be occluded by the effected coating can be employed to impart desired properties to the coating.

The pressure of the fluidizing medium is regulated to a degree sufficient to fluidize the system. Since the purpose of the fluidizing medium is to agitate and suspend the substrates and the plating compound in the heating zone, it can be seen that the process of this invention is not contingent upon definite pressures and resultant velocities. Pressures ranging from subatmospheric to superatmospheric can be employed. However, pressures from 0.01 millimeter of mercury absolute to 5 atmospheres are preferred since within this range best results are achieved when working with the preferred substrates of the instant invention. Employment of low pressures allows the use of a low pressure source of fluidizing medium. However, when working with a low pressure source of fluidizing medium, a vacuum is desirably induced on the system to insure a fairly constant velocity rate throughout a given plating operation. Nevertheless, a vacuum can be induced on the system at any pressure level to aid flow control of the fluidizing medium. The use of a vacuum with pressures above atmospheric is desirable when the fluidizing gas is recycled for subsequent use. This mode of operation is attractive since the compressor employed to recompress the recycled gas can conveniently be arranged to take suction on the system.

As can be seen in the working examples, it is possible to achieve a useful coating in a relatively short period of time. For most applications, a time range within 5 seconds to about 10 minutes is suitable to achieve desirable coatings.

There are many practical applications for articles coated by the process of this invention. Where corrosion protection is the essential objective this invention provides a rapid method for effecting pore-free coatings of corrosion resistant materials, such as chromium. This process is also attractive for effecting oxidation resistant coatings. Pursuant to this invention, metals can be deposited on desirable substrates to achieve a variety of suitable catalyst supports. For decorative purposes a very thin metal coating can be readily achieved by this process in a single step operation. This process is economically feasible for such applications because of a minimum consumption of valuable plating compounds and its adaptability to high production rates.

When employing the process of this invention for the coating of powdered or pellet substrates, it is possible to achieve unique articles of manufacture by subsequent sintering metallurgical techniques. Further, indications are that certain materials that have been heretofore difficult to handle in metal working operations can be coated with aluminum or similar metals to overcome many difficulties. A metal coating in this instance acts both as a binder and as a lubricant. In this regard, aluminum coated beryllium powder is a preferred unique article of manufacture that can economically be produced by this process. An aluminum coating on such a material allows the subsequent fabrication into other items having properties heretofore unobtainable in the art.

We have described what we believe to be the best embodiments of our invention. However, we do not wish to be confined within those embodiments set forth in the enumerated examples and depicted in the accompanying drawing which are only illustrative of our invention, but what we desire to cover by Letters Patent as set forth in the appended claims is:

1. A process for plating a substrate with a metal derived from a heat-decomposable carbon-containing metal compound comprising effecting contact between said substrate heated to a temperature sufficient to decompose said compound and a body of said compound existing in the solid state of aggregation while said substrate and said compound are in a constant state of motion induced by a gaseous medium in contact therewith.

2. The process of claim 1 further characterized in that said compound is selected from the group consisting of carbon-containing compounds having up to 40 carbon atoms.

3. The process of claim 1 further characterized in that said compound is selected from the group consisting of metal carbonyls and the amine complexes of aluminum hydride.

4. The process of claim 1 further characterized in that said compound is a trialkylamine complex of aluminum hydride.

5. The process of claim 1 further characterized in that said compound is selected from the group consisting of the trimethylamine complex of aluminum hydride, the bis-trimethylamine complex of aluminum hydride, and mixtures thereof.

6. The process of claim 1 further characterized in that said substrate is a metal.

7. The process of claim 1 further characterized in that said substrate is selected from the group consisting of ferrous, magnesium, and beryllium metals existing in a powdered or pellet form.

8. The process of claim 1 further characterized in that said substrate is a metal existing in a powdered or pellet form having an average particle size in the range of from about 50 to about 200 mesh.

9. The process of claim 1 further characterized in that said substrate is a ferrous metal and said compound is chromium hexacarbonyl.

10. The process of claim 1 further characterized in that said substrate is magnesium and said compound is the trimethylamine complex of aluminum hydride.

11. A process for plating a substrate with a metal derived from a solid heat-decomposable carbon-containing metal compound comprising (1) conveying selected substrates into a plating zone, (2) exposing said substrates to a pulverulent heat-decomposable carbon-containing metal compound, (3) fluidizing the system, by an inert gas, (4) heating said substrates to a temperature sufficient to decompose said metal compound, and (5) continuously heating said substrate until the desired thickness of coating is achieved and (6) thereafter cooling said substrate.

12. The process of claim 11 further characterized in that said compound is selected from the group consisting of amine complexes of aluminum hydride and metal carbonyls.

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13. The process of claim 11 further characterized in that said substrate is selected from the group consisting of ferrous, magnesium, and beryllium metals.

14. The process of claim 11 further characterized in that said substrate is a ferrous metal, said compound is chromium hexacarbonyl, and said substrate is heated to a temperature from about 400° C. to about 500° C.

15. The process of claim 11 further characterized in that said substrate is magnesium, said compound is the trimethylamine complex of aluminum hydride, and said substrate is heated to a temperature range of from about 150° C. to about 200° C.

16. The process of claim 11 further characterized in that said substrate is beryllium, said compound is selected from the group consisting of the trimethyl amine complex of aluminum hydride, the bis-trimethylamine complex of aluminum hydride, and mixtures thereof, and said substrate is heated to a temperature range of from about 150° C. to about 200° C.

17. A process for plating a substrate with a metal derived from a solid heat-decomposable carbon-containing metal compound comprising (1) heating selected substrates to a temperature sufficient to decompose said metal compound, (2) conveying said heated substrates into a plating zone, (3) exposing said heated substrates to said metal compound existing in a pulverulent state of aggregation in a constant state of motion induced by a gaseous medium in contact therewith, (4) maintaining said substrates and said metal compound in a constant state of motion until the desired thickness of coating is achieved, and (5) thereafter cooling said substrates.

18. A metal plating process for plating metallic substrates with aluminum comprising (1) heating said metallic substrates to a temperature above 150° C., (2) conveying said heated metallic substrates into a plating zone, (3) exposing said heated metallic substrates to a trialkylamine complex of aluminum hydride existing in a pulverulent state of aggregation in a constant state of motion induced by a gaseous medium in contact therewith, (4) maintaining said substrates and said metal compound in a constant state of motion until the desired thickness of coating is achieved and (5) thereafter cooling said substrates.

19. A process for plating substrates with a metal derived from a solid heat-decomposable carbon-containing metal compound comprising (1) preheating the selected

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substrates, (2) conveying said heated substrates into a plating zone, (3) exposing said preheated substrates to said metal compound existing in a pulverulent state of aggregation in a constant state of motion induced by a gaseous medium in contact therewith, (4) maintaining said substrates and said metal compound in a constant state of motion, (5) further heating said substrates at a constant temperature sufficient to decompose said metal compound until the desired thickness of coating is achieved, (6) removing said coated substrates from said plating zone, and (7) thereafter cooling said coated substrates.

20. A metal plating process for plating metallic substrates with aluminum comprising (1) preheating said metallic substrates, (2) conveying said heated metallic substrates into a plating zone, (3) exposing said preheated metallic substrates to a trialkylamine complex of aluminum hydride existing in a pulverulent state of aggregation in a constant state of motion induced by a gaseous medium in contact therewith, (4) maintaining said metallic substrates and said compound in a constant state of motion, (5) further heating said metallic substrates at a constant temperature above 150° C. until the desired thickness of aluminum coating is achieved, (6) removing said aluminum coated metallic substrates from said plating zone, and (7) thereafter cooling said aluminum coated metallic substrates.

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RICHARD D. NEVIUS, *Primary Examiner.*