United States Patent Office 3,253,946 Patented May 31, 1966

3,253,946

VAPOR PLATING WITH MANGANESE, CHROMIUM, MOLYBDENUM OR TUNGSTEN EMPLOYING CYCLOPENTADIENYL METAL CARBONYL

John Kozikowski, Walled Lake, Mich., and Vello Norman and Thomas P. Whaley, Baton Rouge, La., assignors to Ethyl Corporation, New York, N.Y., a corporation of Virginia

No Drawing. Filed Aug. 11, 1960, Ser. No. 48,840
2 Claims. (Cl. 117—107.2)

This invention relates to a process for producing metallic coatings of metals of Groups VI–B, VII–B and VIII of the Periodic Chart of the Elements, Fischer Scientific Company, on appropriate substrates by decomposition of organometallic compounds of such metals.

Present techniques for plating with the elements of Groups VI–B, VII–B and VIII of the periodic chart of the elements are primarily limited to electrolytic techniques. In some cases no techniques are known for deposition of the metallic element. Moreover, these prior art techniques are limited to the preparation of the ductile metal deposit and cannot be adapted to the preparation of hard, excellently adherent commercially acceptable coatings of these metals. Furthermore, even deposition of Groups VI–B, VII–B and VIII elements has been limited to the well-known halides and pure carbonyls—that is those carbonyls wherein the carbonyl group is the only substituent on the VI–B—VIII element—and consequently the reaction conditions at which the deposition process could be carried out has also been severely limited. This lack of versatility in the prior art processes has resulted in uneconomical plating operations, oftentimes giving extremely unsatisfactory results. A process which would provide flexibility, particularly insofar as reaction conditions and availability of compounds are concerned—a process which, because of the wide range of reaction conditions available, would produce metallic coatings ranging from bright, essentially pure, excellently adhering coatings all the way to extremely hard carbide coatings of the respective metals—would provide a considerable impetus to this area of technology. It would constitute a commercially feasible process for the deposition of these elements.

It is therefore an object of this invention to provide a flexible, economical process for the preparation of metallic coatings of Groups VI–B, VII–B and VIII metals. It is a further object of this invention to provide a process which produces extremely hard, well-adhering, excellent metal carbide coatings of the aforementioned metals as well as excellent and essentially pure metal plates thereof.

These and other objects are accomplished in accordance with this invention by providing a process for plating a substrate which comprises decomposing a cyclopentadienyl transition metal coordination compound in contact with said substrate, the metal of the compound having an atomic number ranging from 8 through 12 less than that of the next higher rare gas, the compound having a cyclopentadienyl group coordinated with the metal, the compound being stabilized by additional coordination with at least one different electron donating group capable of donating from 1 through 4 electrons, and the sum of all coordinated electrons and the atomic number of the metal being equal to the atomic number of said rare gas.

By "decomposition" as used herein is meant any method feasible for decomposing said cyclopentadienyl transition metal coordination compound. Thus the term includes

decomposition by ultrasonic frequency and decomposition by ultraviolet irradiation as well as thermal decomposition. Thermal decomposition, however, is the preferred mode of carrying out this invention because of its economical simplicity.

Therefore, within the scope of this invention is a process for plating a substrate which comprises heating the substrate to be plated to a temperature above the decomposition temperature of a cyclopentadienyl transition metal coordination compound, of a metal of atomic number ranging from 8 through 12 less than that of the next higher rare gas, in contact with said substrate; said compound having said cyclopentadienyl group coordinated with said metal, the compound being stabilized by additional coordination with at least one electron donating group capable of donating from 1 through 4 electrons, the sum of all coordinated electrons and the atomic number of said metal being equal to the atomic number of said next higher rare gas.

In carrying out this latter embodiment it is preferred that the cyclopentadienyl transition metal coordination compound be a cyclopentadienyl Group VI–B carbonyl, a cyclopentadienyl manganese carbonyl or a cyclopentadienyl nickel nitrosyl. This preference is due to the ready availability of these compounds, as well as to good volatility characteristics and stability exhibited thereby which provides for ease of handling—a factor extremely important in commercial production.

The metallic coatings produced by the process of this invention include essentially pure metal plates as well as extremely hard metal-containing coats of metal carbides. The process of this invention has the particular advantage in that through proper selection of processing conditions, the type of metal coating can conveniently and easily be "tailor-made"—varying from essentially pure, bright metal plates all the way to hard metal carbide coats. For example, when a thermal decomposition technique is employed in the process of this invention, essentially pure metal plates are produced at those temperatures approaching the decomposition temperature of the cyclopentadienyl transition metal coordination compounds of this invention, and the metal carbide coatings are increasingly produced as the temperature is raised to a maximum, generally no higher than 600° C.

Thus one of the most significant advantages of the process of this invention is that it provides a process for producing metal coatings of widely diverse properties, which divergent coatings can simply and economically be produced in the same processing equipment without the need of expensive engineering alterations. The commercial significance of this advantage is quite apparent when consideration is given to the fact that a manufacturer need only invest in the very minimum of processing equipment and yet is still able to produce a whole spectrum of metal coatings on a wide variety of substrates.

Metals of the Periodic System having an atomic number ranging from 8 through 12 less than the next higher rare gas are metals of Groups VI–B, VII–B and VIII. Examples of the foregoing coordination compounds which are employed in this invention are: cyclopentadienyl chromium tricarbonyl hydride, cyclopentadienyl manganese tricarbonyl, bis(cyclopentadienyl iron dicarbonyl), cyclo pentadienyl cobalt dicarbonyl, butylcyclopentadienyl nickel nitrosyl, methylcyclopentadienyl molybdenum tricarbonyl hydride and the like. Methylcyclopentadienyl manganese tricarbonyl and cyclopentadienyl nickel nitro-

syl are outstanding plating agents for use pursuant to this invention, especially from the cost-effectiveness standpoint.

In general, any prior art technique for metal plating an object by thermal decomposition of a metal-containing compound can be employed in the present plating process as long as a cyclopentadienyl transition metal coordination compound as described above is employed as the plating agent (i.e., the metallic source for the metal plate). For example, any technique heretofore known for the thermal decomposition and subsequent plating of metals from the corresponding metal carbonyl can be employed. Illustrative are those techniques described by Lander and Germer, American Institute of Mining and Metallurgical Engineers, Technical Publication No. 2259 (1947). Usually the technique to be employed comprises heating the object to be plated to a temperature above the decomposition temperature of the metal-containing compound and thereafter contacting the metal-containing compound with the heated object. The following examples are more fully illustrative of the process of this invention.

In Examples I–V the following technique is used:

Into a conventional heating chamber, housed in a resistance furnace and provided with means for gas inlet and outlet, is placed the object to be plated. The organometallic plating agent is placed in a standard vaporization chamber provided with heating means, said vaporization chamber being connected through an outlet port to the aforesaid combustion chamber inlet means.

For the plating operation, the object to be plated is heated to a temperature above the decomposition temperature of the plating agent, the system is evacuated and the plating agent is heated to an appropriate temperature where it possesses vapor pressure of up to about 10 millimeters. In most instances, the process is conducted at no lower than 0.01 mm. pressure. The vapors of the plating agent are pulled through the system as the vacuum pump operates, and they impinge on the heated object, decomposing and forming the metallic coating. In most instances, no carrier gas is employed; however, in certain cases, a carrier gas can be employed to increase the efficiency of the above disclosed plating system. In those cases where a carrier gas is employed, a system such as described by Lander and Germer, ibid., page 7, is utilized.

Example I

Compound	[1] $CpCr(CO)_3H$.
Compound temp.	100° C.
Substrate	Pyrex.
Substrate temp.	350° C.
Pressure	0.1 mm.
Time	3 hours.
Result	Bright metallic coating.

[1] Cyclopentadienyl chromium tricarbonyl hydride.

Example II

Compound	[1] $CpMn(CO)_3$.
Compound temp.	90° C.
Substrate	Ceramic.
Substrate temp.	400° C.
Pressure	2 mm.
Time	1 hour.
Result	Metallic coating.

[1] Cyclopentadienylmanganese tricarbonyl.

Example III

Compound	[1] $[CpFe(CO)_2]_2$.
Compound temp.	100° C.
Substrate	Pyrex.
Substrate temp.	350° C.
Pressure	0.5 mm.
Time	2 hours.
Result	Metallic coating.

[1] Bis-cyclopentadienyl iron dicarbonyl.

Example IV

Compound	[1] $CpCo(CO)_2$.
Compound temp.	110° C.
Substrate	Pyrex.
Substrate temp.	500° C.
Pressure	0.1 mm.
Time	1 hour.
Result	Dark metallic coating, very hard.

[1] Cyclopentadienyl cobalt dicarbonyl.

Example V

Compound	[1] $CpNi(NO)$.
Compound temp.	50° C.
Substrate	Al_2O_3 pellets.
Substrate temp.	310° C.
Pressure	2 mm.
Time	1 hour.
Result	Metallic coating.

[1] Cyclopentadienyl nickel nitrosyl.

In the above examples the temperature utilized, i.e., in the vicinity of 300 to 400° C., gives excellent metallic coatings. These metallic coatings are generally very hard and exhibit excellent adherence to the substrate upon which deposited—the coats varying from bright metal plates all the way to extremely hard, dark metallic coatings, depending upon the processing conditions chosen.

The above processes employed resistance heating. The following working examples employ an induction heating method using higher temperatures. In the latter process coatings of substantial carbide content and exhibiting excellent characteristics are obtained.

The process employed in these examples is essentially the same as that employed in Examples I–V with the exception that the object to be plated is placed into a conventional heating chamber provided with means for high frequency induction heating, as opposed to the former process where the heating chamber was housed in a resistance furnace.

Example VI

Compound	[1] $MeCpMn(CO)_3$.
Compound temp.	200° C.
Substrate	Nickel coated mild steel.
Substrate temp.	600° C.
Pressure	0.2 mm.
Time	.5 hours.
Result	Hard, well-adherent coating.

[1] Methylcyclopentadienyl manganese tricarbonyl.

Example VII

Compound	[1] $CpCr(CO)_2NO$.
Compound temp.	200° C.
Substrate	Nickel coated mild steel.
Substrate temp.	600° C.
Pressure	0.5 mm.
Time	1.5 hours.
Result	Extremely hard, well-adherent coating.

[1] Cyclopentadienyl chromium dicarbonyl nitrosyl.

In addition to the thermal techniques disclosed hereinabove for decomposing the plating agents of this invention, other methods for decomposition of these materials can be employed. Thus the following working example is illustrative of the decomposition of a tungsten compound by ultrasonic frequency.

The process employed in Examples VI and VII is followed with the exception that an ultrasonic generator is proximately positioned to the plating apparatus. In this example the compound is heated to its decomposition threshold and thereafter the ultrasonic generator is ultilized to effect final decomposition.

Example VIII

Compound	[1] $[CpW(CO)_3]_2$.
Compound temp.	260° C.
Substrate	Mild steel.
Substrate temp.	400° C.
Pressure	0.1 mm.
Result	Dark metallic coating, very hard.

[1] [Bis(cyclopentadienyl tungsten tricarbonyl)].

Another method for decomposing the plating agent of this invention is by decomposition with ultraviolet irradiation. The following example is demonstrative of this technique.

The method of Example I is employed, with the exception that in place of the resistance furnace there is utilized for heating a battery of ultraviolet and infrared lamps placed circumferentially around the outside of the heating chamber. The substrate to be heated is brought to a temperature just below the decomposition temperature of the plating agent with the infrared heating and thereafter decomposition is effected with ultraviolet rays.

Example IX

Compound	[1] $[Ind.Fe(CO)_2]_2$.
Compound temp.	260° C.
Substrate	Pyrex.
Substrate temp.	450° C.
Pressure	1 mm.
Result	Hard, dark metallic coating.

[1] Di(indenyl iron dicarbonyl).

By the term cyclopentadienyl, which is a substituent in the aforementioned coordination compounds, is included substituted cyclopentadienyl groups. The cyclopentadienyl moiety therefore includes alkyl and aryl substituted cyclopentadienyl groups, as well as indenyl and fluorenyl derivatives—including substituted indenyl and fluorenyl derivatives. The term cyclopentadienyl preferably includes hydrocarbon cyclopentadienyl groups containing 5 through about 17 carbon atoms.

Alternatively the cyclopentadienyl substituent of the transition metal coordination compounds of this invention can be defined as a hydrocarbon cyclomatic group. The term cyclomatic hydrocarbon includes cyclomatic hydrocarbon radicals having from about 5 through about 17, or more, carbon atoms and embodying a group of 5 carbons having the configuration found in cyclopentadiene. The cyclomatic hydrocarbon Group VI–B, VII–B and VIII metal coordination compounds of this invention are further characterized in that the cyclomatic hydrocarbon radical is bonded to the transition metal by carbon to metal bonds, through the carbons of the cyclopentadienyl group contained therein. Thus the cyclopentadienyl transition metal coordination compound can be represented by the illustrative formula

$$(R_aMQ_b)_x$$

wherein R represents a cyclopentadienyl moiety containing a 5 carbon ring (similar to that contained in cyclopentadiene itself) coordinated to the Group VI–B, VII–B or VII transition metal, M, through the carbon atoms of the cyclopentadienyl ring; Q represents an electron donor group, or a combination of separate electron donor groups, which can be the same or different from each other, involved in covalent or coordinate covalent bonding with the metal atom and which donor groups are each capable of donating from 1 through 4 electrons to the metal atom through said bonding; *a* has a value of 1 or 2 and *b* has a value of up to 7—preferably 1–4; and *x* has a value of 1 or 2. In most cases the cyclopentadienyl moiety, R, contains from 5 to about 15 carbon atoms. Illustrative of these cyclopentadienyl moieties are cyclopentadienyl, methylcyclopentadienyl, methyl - tert - butylcyclopentadienyl, (o-tolyl)-cyclopentadienyl, indenyl, 2-methylindenyl, 3-phenyl-indenyl, fluorenyl, 2-m-tolyl-fluorenyl, and the like cyclopentadienyl-

containing moieties. The cyclopentadienyl radicals can alternatively be considered as a cyclomatic radical such as 4,5,6,7 - tetrahydroindenyl, 1,2,3,4,5,6,7,8 - octahydrofluorenyl; 3-methyl - 4,5,6,7 - tetrahydroindenyl, and 2-ethyl-3-phenyl-3,4,5,6,7-tetrahydroindenyl.

The constituents represented by Q in the above formula are electron donating groups capable of coordinating with the Groups VI–B, VII–B and VIII metal atoms of the compounds which are employed as plating agents in the process of this invention. These groups are capable of sharing from 1 through 4 electrons with the metal atom so that the metal achieves a more stable structure by virtue of such added electrons. These electron donating groups in coordination with the metal are, generally, either organic radicals or molecular species which contain labile electrons. These electrons assume a more stable configuration in the molecule when associated with the metal. The electron donating group represented by Q may also be inorganic entities which are capable of existing as ions, such as hydrogen, the cyanide group, and the various halogens. The halogens are representative of electron donating groups donating one electron and carbonyl illustrative of an entity donating two electrons. An entity donating three electrons is represented by the nitrosyl group and aliphatic diolefins are illustrative of entities capable of donating four electrons. In those compounds which are preferred plating agents in the process of this invention, Q represents carbonyl and nitrosyl electron donating entities which are capable of donating 2 and 3 electrons respectively.

The Group VI–B, VII–B and VIII metals which form the metallic constituent of a coordination compound of this invention include the metals chromium, molybdenum, tungsten, manganese, technetium, rhenium, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium and platinum. Chromium, manganese, molybdenum, tungsten and nickel are preferred because of their greater availability and excellent chemical and refractory properties. Of these chromium and nickel are especially preferred because of their availability and excellent chemical and wear resistance properties. Furthermore, these last mentioned elements have extremely wide adaptability to a multitude of uses.

The following compounds further illustrate the types of Groups VI–B, VII–B and VIII transition metal coordination compounds which can be employed as plating agents in this invention. These compounds are cyclopentadienyl chromium tricarbonyl hydride, cyclopentadienyl chromium dicarbonyl methyl, cyclopentadienyl chromium dicarbonyl nitrosyl, cyclopentadienyl chromium dinitrosyl chloride, octylcyclopentadienyl molybdenum tricarbonyl hydride, cyclopentadienyl molybdenum tricarbonyl methyl, cyclopentadienyl molybdenum tricarbonyl chloride, methylcyclopentadienyl molybdenum tricarbonyl methyl, cyclopentadienyl molybdenum tricarbonyl isopropyl, cyclopentadienyl molybdenum dicarbonyl nitrosyl, bis(cyclopentadienyl molybdenum tricarbonyl), bis-[(methylcyclopentadienyl)molybdenum tricarbonyl], cyclopentadienyl molybdenum tricarbonyl hydride, cyclopentadienyl tungsten tricarbonyl hydride, cyclopentadienyl tungsten tricarbonyl ethyl, cyclopentadienyl tungsten dicarbonyl nitrosyl, cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, acetylcyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese benzene, dicyclopentadienyl rhenium hydride, cyclopentadienyl rhenium tricarbonyl, cyclopentadienyl iron dicarbonyl bromide, bis(cyclopentadienyl iron dicarbonyl), bis(methylcyclopentadienyl iron dicarbonyl), bis(ethylcyclopentadienyl iron dicarbonyl), bis(indenyl iron dicarbonyl), bis(tetrahydroindenyl iron dicarbonyl), cyclopentadienyl cobalt dicarbonyl, cyclopentadienyl cobalt cyclopentadiene, cyclopentadienyl rhodium cyclopentadiene, cyclopentadienyl rhodium cyclo-

1,5-octadiene, cyclopentadienyl nickel nitrosyl, cyclopentadienyl nickel carbonyl iodide, bis(cyclopentadienyl nickel carbonyl) and the corresponding Groups VI–B, VII–B and VIII metal compounds containing ethyl cyclopentadienyl, butyl cyclopentadienyl, octyl cyclopentadienyl, dimethyl cyclopentadienyl, dihexyl cyclopentadienyl, vinyl cyclopentadienyl, ethynyl cyclopentadienyl, phenyl cyclopentadienyl, methylphenyl cyclopentadienyl, acetyl cyclopentadienyl, allyl cyclopentadienyl, benzyl cyclopentadienyl, tolyl cyclopentadienyl, and other like radicals.

Any of the above compounds can be employed to plate their respective metallic constituent upon a multitude of substrates—employing any of the techniques described hereinbefore—by controlling the temperature of the plating operation, so that temperatures above the decomposition temperature of the particular cyclopentadienyl coordination compound are employed.

The term substrate as employed herein can be defined further as the object to be plated and includes any material stable at the temperature necessary for the decomposition of the Groups VI–B, VII–B and VIII transition metal coordination plating agents employed in this invention. Illustrative of various substrates are Pyrex glass and spun glass; various synthetic fibers and plastics such as polytetrafluoroethylene, polychlorotrifluoroethylene, rayon, nylon, Delrin (polyformaldehyde resin) and the like; steel, such as nickel plated steel, mild steel, nickel plated mild steel; metallic turnings such as copper, zinc and the like; cellulose materials such as cotton, paper and the like—in short, any material stable under the plating conditions employed. Thus, further demonstrative of the substrates of this invention are carbonaceous materials, such as graphite; other refractory substrates, such as Carborundum, ceramics, cermets and the like; other metallic substrates such as aluminum, titanium, vanadium, yttrium, copper, zinc, cadmium and the like; nuclear reactor fuel elements such as uranium 235, uranium 233, thorium and other fissionable materials.

It should be noted that when employing the novel organo-metallic plating agents of this invention it is important to maintain enough vapor pressure below the decomposition temperature of the organometallic plating agent to enable the process to be conducted at an appreciable rate of plating. Too high vapor pressure results in somewhat inferior substrate adherence. Thus, it is preferred to employ up to about 10 mm. pressure during the plating operation—preferably 0.01 to 10 mm. pressure.

As has already been pointed out, temperatures are very important in obtaining the desired plated product. Thus, although temperatures above the decomposition temperature of the cyclopentadienyl transition metal coordination compound of this invention can, in general, be employed in the plating process, best results are attained within certain preferred temperature ranges. For example, temperatures ranging from about 50° C. to about 250° C. above the decomposition temperature of the plating agent produce very hard carbide containing products. Lower temperatures—generally very near the decomposition temperature of the plating agent—are employed in the preparation of essentially pure metal plates.

The plating compounds of the present invention vary somewhat insofar as their thermal stability is concerned but generally all of them can be decomposed at a temperature above 400° C. Although temperatures as high as 700°–750° C. can be employed the maximum temperatures utilized herein are generally no higher than about 600° C.

In one embodiment of the instant invention mixtures of plating agents, each containing a different metal, are employed in the plating process to produce alloys of the respective metals upon appropriate substrates. An example is the utilization of cyclopentadienyl manganese tricarbonyl and dicyclopentadienyl iron as plating agents in a process similar to that used in Examples I–V to produce an iron-manganese alloy deposit upon various substrates.

The metal plates produced by the process of this invention find a multitude of uses in the aircraft, missile and chemical processing industries. Thus aircraft and missile components which require ultra high quality performance characteristics such as resistance to high temperatures, wear resistance and resistance to chemical attack can satisfactorily meet these requirements when coated with a Group VI–B, VII–B and VIII metal produced according to the process of the instant invention.

The metal carbide coatings which are so conveniently prepared by the process of this invention find particular applicability in utilities where their excellent high temperature and wear resistance properties come into play. Such applications are as coatings for dies, such as when automotive die is coated with nickel to produce a hard nickel metallic coating by the process of the instant invention.

Having thus described and demonstrated the instant invention it is not intended that the scope thereof be limited in any way except as set forth in the following claims.

We claim:

1. A process for plating a substrate which process comprises:
   (1) heating said substrate in an enclosed system to a temperature maintained within the range of from about 400° C. to about 750° C.,
   (2) heating a cyclopentadienyl carbonyl compound of a metal selected from the class consisting of manganese, chromium, molybdenum and tungsten, which compound is capable of being decomposed within said temperature range and contains in the molecule only one cyclopentadienyl hydrocarbon group per metal atom, said heating being to a temperature less than its decomposition temperature but sufficient to generate vapors thereof,
   (3) contacting said heated substrate with said vapors in said enclosed system while maintaining a pressure therein of from about 0.01 mm. to about 10 mm. mercury, and
   (4) continually contacting said heated substrate with said vapors until the desired thickness of coating is realized.

2. A process for effecting a manganese coating upon a substrate which process comprises:
   (1) heating said substrate in an enclosed system to a temperature maintained within the range of from about 400° C. to about 750° C.,
   (2) heating a cyclopentadienyl manganese tricarbonyl compound capable of being decomposed within said temperature range and containing in the molecule only one cyclopentadienyl hydrocarbon group per metal atom, to a temperature less than its decomposition temperature, but sufficient to generate vapors thereof,
   (3) contacting said heated substrate with said vapors in said enclosed system while maintaining a pressure therein of from about 0.01 mm. to about 10 mm. mercury, and
   (4) continually contacting said heated substrate with said vapors until the desired thickness of manganese coating is realized.

References Cited by the Examiner

UNITED STATES PATENTS

2,818,416	12/1957	Brown et al.	260—429
2,868,697	1/1959	Bingeman et al.	260—429
2,930,767	3/1960	Novak	117—107
2,955,958	10/1960	Brown	117—113
3,031,338	4/1962	Bourdeau	117—107.2 X

(Other references on following page)

9

UNITED STATES PATENTS

3,032,572 5/1962 Fischer et al.
3,061,464 10/1962 Norman et al. ---- 117—107.2

FOREIGN PATENTS

1,060,399 7/1959 Germany.

OTHER REFERENCES

Lander et al.: "Plating Molybdenum, Tungsten and Chromium by Thermal Decomposition of Their Carbonyls," A.I.M.M.E. Technical Publication No. 2259, September 1947; pp. 6 and 7 relied on.

Powell et al.: "Vapor Plating" (1955), John Wiley and Sons Inc. (N.Y.); pp. 1–4 relied on.

10

RICHARD D. NEVIUS, *Primary Examiner.*

R. E. HOWARD, A. GOLIAN, *Assistant Examiners.*