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3,071,493

METAL PLATING PROCESS

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This invention relates to the plating of appropriate substrates using polymetallic organometallic compounds. More particularly this invention relates to the plating of alloys on appropriate substrates by the decomposition of bimetallic organometallic compounds. This invention is a continuation-in-part of our copending application, Serial No. 831,077, filed August 3, 1959, now Patent No. 3,018,194.

Heretofore, in order to deposit alloys by the decomposition of organometallic compounds, it has been necessary to employ two different mono metal containing compounds. For example, molybdenum-tungsten alloys have been prepared by pyrolysis of the mixed carbonyl vapors, i.e., a mixture of molybdenum carbonyl and tungsten carbonyl. Furthermore, alloys have been produced by hydrogen reduction of the mixed chloride vapors. Thus, titanium-tantalum alloys have been obtained by co-deposition from the respective bromides utilizing hydrogen reduction. However, in attempting alloy plating from two different chemical compounds it often happens that a marked difference exists in the chemical affinities of the two alloying constituents. In such cases deposition of only one constituent will usually occur to the entire exclusion of the other constituent. Thus, it becomes necessary to, as nearly as possible, equalize rates of deposition by proper choice of deposition temperature. In other words, it becomes necessary to choose chemically compatible compounds as plating agents. Because of this, the choice of available compounds for producing alloy plates from two different mono metal containing compounds becomes considerably narrowed. Consequently, the types of feasible alloys also are decreased. According to the present invention, these inherent disadvantages in the prior art processes for plating alloys by decomposition or reduction of different metal compounds are overcome by employing bimetallic organometallic compounds in the plating process. By virtue of this plating process, vastly improved alloy plates are provided on a wide range of substrates.

Thus, among the objects of this invention is that of providing a process for plating alloys on substrates using bimetallic organometallic compounds. Another object is to provide a decomposition process for plating substrates using these bimetallic organometallic compounds. A further object of this invention is to provide a thermal process for plating substrates by thermal decomposition of bimetallic organometallic compounds. Still another object of this invention is to provide novel and highly useful alloy plated articles made according to these processes. Other important objects of this invention will be apparent from the ensuing description.

According to this invention there is provided a process for alloy plating a substrate by the decomposition of a polymetallic organometallic compound in contact with the substrate. In their broadest aspect the bimetallic organometallic compounds of this invention contain at least two different metals. Within the scope of this invention is a process for plating a substrate comprising heating the object to be plated to a temperature above the decomposition temperature of a bimetallic organometallic compound and contacting said compound with said heated substrate. Those bimetallic organometallic compounds which contain as the exclusive constituents of

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the molecule, two different metals and unsubstituted hydrocarbon radicals are especially useful in vapor phase alloy plating operations. In carrying out these vapor phase techniques the substrate to be alloy plated is heated to a temperature above about 200° C. while maintained under an inert atmosphere such as nitrogen, the rare gases (e.g., neon, argon, krypton, xenon), etc.

Bimetallic organometallic compounds used in this invention and comprising one embodiment thereof can be represented by the general formula



wherein M is a metal selected from the group consisting of groups I, II, III-B, IV-B, V-B, VI-B, VII-B, VIII of the periodic chart of the elements and tin and aluminum; M' is a different metal selected from the group consisting of group III-A of the periodic chart of the elements and zinc and cadmium; R is a monovalent anion—i.e., group or radical; x is an integer corresponding to the valence of the metal M'; y is an integer corresponding to the valence of the metal M. It is especially preferred that the monovalent anion R be a substituent which upon the decomposition of the bimetallic organometallic plating agent forms decomposition by-products which are devoid of free hydrogen. Hydrogen by-product is particularly undesirable in those cases wherein the alloys to be plated and the substrate are susceptible to hydrogen embrittlement.

Bimetallic organometallic compounds which comprise another embodiment of the present invention may be represented by the general formula



wherein M^(a) is a metal selected from the group consisting of the group IV-A metals (silicon, germanium, tin and lead) and aluminum; M^(b) is a different metal selected from the groups consisting of IV-B, V-B, VI-B, VII-B and VIII of the periodic chart of the elements. R is an electron donating moiety individually selected from the group consisting of hydrocarbon and hydrogen, and w is an integer equaling the number of R groups bonded to the metal M^(a). The following table gives the value for x and z where the metal M^(b) contains odd and even numbers of d orbital electrons.

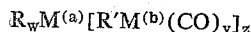
	w=1	w=2	w=3
M ^(b) is a metal having an odd number of d orbital electrons.	x=2, z=3	x=1, z=2	x=2, z=1
M ^(b) is a metal having an even number of d orbital electrons.	x=1, z=3	x=1, z=1	x=2, z=1

y is calculated from the formula

$$y = \frac{G-m-N}{2}$$

where G is the atomic number of the next rare gas of the metal M^(b); m is an integer equaling 1 when the number of d orbital electrons of the metal M^(b) is odd and 2 when the number of d orbital electrons of said metal is even. N equals the atomic number of the metal M^(b). It is preferred that the radical R be a substituent upon which the decomposition of the bimetallic organometallic plating agent forms decomposition by-products which are devoid of free hydrogen.

Other bimetallic organometallic compounds which form another embodiment of the present invention can be represented by the general formula



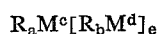
wherein M^(a) is a metal selected from the groups II-A, II-B, III-A, IV-A and V-A of the periodic chart of ele-

ments, Fisher Scientific Company, 1955; $M^{(b)}$ is a metal selected from the groups IV-B, V-B, VI-B, VII-B and VIII of the periodic chart of elements. R is an electron donating moiety individually selected from the group consisting of hydrocarbon and hydrogen, and R' is an unsaturated organo group containing up to about 20 carbon atoms. w is an integer having a value of from 0 up to the valence of the metal $M^{(a)}$ minus 1, and z is an integer having a value of 1, 2 or 3 and is dependent on the valence of the metal $M^{(a)}$ minus the value of the integer w . y is an integer, having a value of from 1 to 5, inclusive, representing the number of carbonyl groups bonded to the metal $M^{(b)}$ in accordance with the equation

$$y = \frac{G_b - n - (\beta_b + 1)}{2}$$

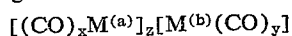
wherein G_b is an integer representing the number of electrons in the next inert gas after the metal $M^{(b)}$, and n is an integer equaling the atomic number of the metal $M^{(b)}$, while β_b is an integer equaling the number of pi electrons of the unsaturated organo group R'.

Bimetallic organometallic compounds which form a further embodiment of the present invention can be represented by the general formula



wherein M^c is a metal selected from the group consisting of boron, aluminum, gallium, indium and thallium, and M^d is a metal selected from the group consisting of selenium, tellurium, silicon, germanium, tin and lead. The groups R represent electron donating moieties individually selected from the groups consisting of hydrocarbon and hydrogen. a and b are integers having a value of from 0 to the valence of the respective metals, M^c and M^d , minus 1. e is an integer having a value of from 1 to the valence of the metal M^d minus the value of the integer a .

A further embodiment of the present invention is the bimetallic organometallic compounds which can be represented by the general formula



wherein $M^{(a)}$ is a metal selected from the group consisting of groups IV-B, V-B, VI-B, VII-B and VIII, and $M^{(b)}$ is a different transition metal selected from the groups consisting of IV-B, V-B, VI-B, VII-B and VIII of the periodic chart of the elements. x is an integer having a value of 1 to 5, inclusive, in accordance with

$$x = \frac{G - m - N}{2}$$

the equation in which G is the atomic number of the next rare gas of the metal $M^{(a)}$. m is an integer having a value of 1 where the number of d orbital electrons in the outermost shell of the metal $M^{(a)}$ is odd and 2 where the number of d orbital electrons in the outermost shell of the metal $M^{(a)}$ is even, and N is the atomic number of the metal $M^{(a)}$.

y is an integer having a value of 1 to 5, inclusive, in accordance with the equation

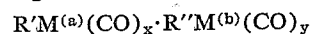
$$y = \frac{G - m - N}{2}$$

in which G is the atomic number of the next rare gas of the metal $M^{(b)}$, and m is an integer equaling 1 where the number of d orbital electrons in the metal $M^{(b)}$ is odd and 2 where the number of d orbital electrons in the metal $M^{(b)}$ is even. N is equal to the atomic number of the metal $M^{(b)}$.

z is an integer having the value of 1 when the number of d orbital electrons in the metals $M^{(a)}$ and $M^{(b)}$ is odd and a value of 2 when the number of d orbital electrons in the metals is even.

A further embodiment of the present invention is the

bimetallic organometallic compounds which can be represented by the general formula



wherein $M^{(a)}$ is a transitional metal selected from the groups consisting of groups IV-B, V-B, VI-B, VII-B and VIII; and $M^{(b)}$ is a different transitional metal selected from the groups consisting of IV-B, V-B, VI-B, VII-B and VIII; and R' and R'' are unsaturated organo groups containing up to about 25 carbon atoms. R' and R'' may be the same or different; x is an integer, having a value of from 1 to 5, inclusive, representing the number of carbonyl groups bonded to the metal $M^{(a)}$ and is calculated by the following formula

$$x = \frac{G_a - n_a - (\beta_a + 1)}{2}$$

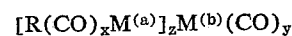
wherein G_a represents the number of electrons in the next inert gas after the metal $M^{(a)}$; n_a equals the atomic number of the metal $M^{(a)}$; and β_a equals the number of pi electrons in R'.

y is an integer, having a value of from 1 to 5, inclusive, equaling the number of carbonyl groups bonded to the metal $M^{(b)}$ and is derived by using the following formula

$$y = \frac{G_b - n_b - (\beta_b + 1)}{2}$$

wherein G_b represents the number of electrons in the next inert gas after the metal $M^{(b)}$; n_b equals the atomic number of the metal $M^{(b)}$; β_b equals the number of pi electrons in R''.

A still further embodiment of the present invention is the bimetallic organometallic compounds having the general formula



wherein $M^{(a)}$ is a metal selected from the groups consisting of groups IV-B, V-B, VI-B, VII-B and VIII of the periodic chart of the elements. $M^{(b)}$ is a different transitional metal selected from the groups consisting of the groups IV-B, V-B, VI-B, VII-B and VIII. R is an unsaturated organo group containing up to about 25 carbon atoms. x is an integer, having a value of from 1 to 5, inclusive, representing the number of carbonyl groups bonded to the metal $M^{(a)}$ and is defined by the following formula

$$x = \frac{G_a - N_a - (\beta_a + 1)}{2}$$

wherein G_a is the number of electrons in the next inert gas after $M^{(a)}$; N_a is the atomic number of the metal $M^{(a)}$; and β_a is equal to the number of pi electrons in R.

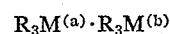
y is an integer, having a value of from 1 to 5, inclusive, equaling the number of carbonyl groups bonded to the metal $M^{(b)}$ and is defined by the formula

$$y = \frac{G_b - m_b - N}{2}$$

wherein G_b equals the atomic number of the next rare gas of the metal $M^{(b)}$; m_b is an integer having the value of 1 where the number of d orbital electrons in the metal $M^{(b)}$ is odd and a value of 2 where the number of d orbital electrons in the metal $M^{(b)}$ is even. N is an integer equaling the atomic number of the metal $M^{(b)}$.

z is an integer having a value of 1 when the number of d orbital electrons of the metal $M^{(b)}$ is odd and a value of 2 where the number of d orbital electrons in said metal is even.

A still further embodiment of the present invention is the bimetallic organometallic compounds having the general formula



wherein $M^{(a)}$ is a group III-A metal (boron, aluminum, gallium, indium and thallium); and $M^{(b)}$ is a metal selected from the group consisting of phosphorus, arsenic,

antimony and bismuth; R represents an electron donating moiety consisting of hydrogen and hydrocarbon, said hydrocarbon containing up to 20 carbon atoms.

The process of this invention presents a significant advance over the prior art in that for the first time it is possible to produce alloy plates from bimetallic organometallic compounds in a simple, safe, economical process. A further advantage of this invention is that through the employment of this process it becomes possible to produce alloy plates having exceptional purity and excellent adherence to the substrate on which the alloy is plated. Furthermore, the process of this invention provides easy control of the proportionate metallic content of the respective metal of the alloy. That is, because of the ready availability of bimetallic organometallic compounds having wide variation in the percent weight ratio of the different metals contained therein, it is, as a result of this invention, now simply a matter of choosing the compound having a metal content "tailor made" to producing the desired alloy. Thus, it becomes unnecessary to hunt for compounds having suitable mutual chemical affinity such as compatible decomposition temperatures, decomposition rates, etc., which heretofore has been such a limiting factor in applying organometallic decomposition technology to the production of alloys. Also, the process of this invention provides easy control of the alloy plate thickness. On the one hand, a micro molecular alloy film can be plated on the substrate and in other cases, if so desired, thicker alloy plates can be obtained. A particular advantage of using bimetallic organometallic compounds which upon decomposition yield by-products which are exclusive of free hydrogen and oxidizing materials is that the alloy plates are thereby obtained free of undesirable oxide impurities and are not deteriorated through hydrogen embrittlement.

In general, any prior art technique for metal plating an object by thermal decomposition of the metal containing compound can be employed in the plating process of this invention as long as a bimetallic organometallic compound is employed as the plating agent (i.e., the metallic source of the metal plate). Thus, for example, any technique heretofore known for the thermal decomposition and subsequent plating of group VI-B metals from the hexacarbonyl derivatives of those metals can be so employed. Illustrative are those techniques described by Lander and Germer, American Institute of Mining and Metallurgical Engineers, Tech. Publication No. 2259 (1957). 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 and in these and other working examples all parts and percentages are by weight.

The process employed in these examples is as follows: Into a conventional heating chamber provided with means for high frequency induction heating and gas inlet and outlet means is placed the object to be plated. The bimetallic organometallic compound 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 substrate is heated to a temperature above the decomposition temperature of the bimetallic organometallic plating agent, the system is evacuated and the organometallic compound 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 millimeter pressure. The vapors of the bimetallic organometallic compound are pulled through the system as the evacuating means operates and they impinge on the heated object decomposing and forming alloy plates. No carrier

gas need be 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 employed, a system such as described by Lander and Germer, American Institute of Mining and Metallurgical Engineers, Tech. Publication No. 2259 (1947) at page 7, can be utilized.

Example I

- 10 Compound ----- $\text{Sn}(\text{AlEt}_4)_2$ (tin bis - aluminum tetraethyl).
- Temp. of substrate --- 350°C .
- Nature of substrate --- Pyrex.
- Pressure ----- 0.5 mm.
- 15 Compound temp. ----- $90-100^\circ \text{C}$.
- Time ----- 2 hours.
- Results ----- Dull, grey, metallic coating.

Example II

- 20 Compound ----- $\text{Li}(\text{AlCp}_4)$ (lithium aluminum tetra cyclopentadienide).
- Temp. of substrate --- 350°C .
- Nature of substrate --- Mild steel.
- Pressure ----- 0.1 mm.
- 25 Compound temp. ----- 150°C .
- Time ----- 1 hour.
- Results ----- Dull metallic coating.

Example III

- 30 Compound ----- $\text{Li}(\text{Al indenide}_4)$ (lithium aluminum tetraindenide).
- Temp. of substrate --- 300°C .
- Nature of substrate --- Pyrex.
- Pressure ----- 0.5 mm.
- 35 Compound temp. ----- 130°C .
- Time ----- 1 hour.
- Results ----- Dull metallic.

Example IV

- 40 Compound ----- $\text{Li}(\text{AlEt}_3\text{H})$ (lithium aluminum triethyl hydride).
- Temp. of substrate --- 300°C .
- Nature of substrate --- Nickel.
- Pressure ----- 3-4 mm.
- Compound temp. ----- 130°C .
- 45 Time ----- 1 hour.
- Results ----- Dull metallic.

Example V

- 50 Compound ----- $\text{Cp}_2\text{TiCl}_2\text{AlEt}_2$ (dicyclopentadienyl titanium dichloride aluminum diethyl).
- Temp. of substrate --- 250°C .
- Nature of substrate --- Pyrex.
- Pressure ----- 0.1 mm.
- 55 Compound temp. ----- 120°C .
- Time ----- 2 hours.
- Results ----- Dull metallic.

Example VI

- 60 Compound ----- $\text{Fe}(\text{CO})_4\text{SnEt}_2$ (iron tetracarbonyl tin diethyl).
- Temp. of substrate --- 450°C .
- Nature of substrate --- Graphite.
- Pressure ----- 5 mm.
- 65 Compound temp. ----- 75°C .
- Time ----- $2\frac{1}{2}$ hours.
- Results ----- Dark grey, dull coating.

Example VII

- 70 Compound ----- $\text{Fe}(\text{CO})_4\text{PbEt}_2$ (iron tetracarbonyl lead diethyl).
- Temp. of substrate --- 400°C .
- Nature of substrate --- Mild steel.
- Pressure ----- 2 mm.
- 75 Compound temp. ----- 80°C .

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Time ----- 1 hour.
Results ----- Dark grey, dull coating.

Example VIII

Compound ----- $(\text{CH}_3)_2\text{SnCyFe}(\text{CO})_2$ (dimethyltin cyclopentadienyl iron dicarbonyl).

Temp. of substrate --- 250° C.
Nature of substrate --- Glass.
Pressure ----- 2 mm.
Compound temp. --- 125° C.
Time ----- 2 hours.
Results ----- Metallic grey coating.

Example IX

Compound ----- $(\text{C}_6\text{H}_5)_2\text{Pb}[\text{Mn}(\text{CO})_5]_2$ (diphenyl lead bis-manganese pentacarbonyl).

Temp. of substrate --- 500° C.
Nature of substrate --- Glass.
Pressure ----- 0.1 mm.
Compound temp. --- 95° C.
Time ----- 45 minutes.
Results ----- Metallic grey coating.

Example X

Compound ----- $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ (triphenyl tin manganese tetracarbonyl triphenyl phosphate).

Temp. of substrate --- 450° C.
Nature of substrate --- Aluminum.
Pressure ----- 0.2 mm.
Compound temp. --- 150° C.
Time ----- 30 minutes.
Results ----- Grey coating.

Example XI

Compound ----- $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5$ (triphenyl tin manganese pentacarbonyl).

Temp. of substrate --- 525° C.
Nature of substrate --- Copper.
Pressure ----- 0.5 mm.
Compound temp. --- 125° C.
Time ----- 4 hours.
Results ----- Black metallic coating.

Example XII

Compound ----- $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ (triphenyl tin manganese tetracarbonyl triphenyl phosphate).

Temp. of substrate --- 400° C.
Nature of substrate --- Glass.
Pressure ----- Atmospheric.
Compound temp. --- 150° C.
Time ----- 30 minutes.
Results ----- Grey metallic coating.

Example XIII

Compound ----- $(\text{CH}_3)_2\text{SnCyFe}(\text{CO})_2$ (dimethyltin cyclopentadienyl iron dicarbonyl).

Temp. of substrate --- 400–410° C.
Nature of substrate --- Glass.
Pressure ----- 0.5 mm.
Compound temp. --- 130° C.
Time ----- 2 hours.
Results ----- Dark grey metallic coating.

Example XIV

Compound ----- $(\text{CH}_3)_2\text{SnCyFe}(\text{CO})_2$ (dimethyltin cyclopentadienyl iron dicarbonyl).

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Temp. of substrate --- 650° C.
Nature of substrate --- Glass.
Pressure ----- 2 mm.
Compound temp. --- 175° C.
Time ----- 2½ hours.
Results ----- Grey, black metallic coating.

Example XV

Compound ----- $(\text{CH}_3)_2\text{Pb}[\text{Mn}(\text{CO})_5]_2$ (dimethyl lead bis-manganese pentacarbonyl).

Temp. of substrate --- 250° C.
Nature of substrate --- Glass.
Pressure ----- Atmospheric.
Compound temp. --- 150° C.
Time ----- 3 hours.
Results ----- Dark grey metallic coating.

Example XVI

Compound ----- $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5$ (triphenyl tin manganese pentacarbonyl).

Temp. of substrate --- 250° C.
Nature of substrate --- Iron.
Pressure ----- 0.1 mm.
Compound temp. --- 95° C.
Time ----- 45 minutes.
Results ----- Grey metallic coating.

Example XVII

Compound ----- $(\text{C}_6\text{H}_5)_3\text{SnMn}(\text{CO})_5$ (triphenyl tin manganese pentacarbonyl).

Temp. of substrate --- 400° C.
Nature of substrate --- Steel.
Pressure ----- 0.1 mm.
Compound temp. --- 150° C.
Time ----- 1 hour.
Results ----- Dark grey metallic coating.

Example XVIII

Compound ----- $(\text{CH}_3)_2\text{Pb}[\text{Mn}(\text{CO})_5]_2$ (dimethyl lead bis-manganese pentacarbonyl).

Temp. of substrate --- 400° C.
Nature of substrate --- Cobalt.
Pressure ----- 0.1 mm.
Compound temp. --- 110° C.
Time ----- 2½ hours.
Results ----- Dark grey metallic coating.

Example XIX

Compound ----- $(\text{C}_2\text{H}_5)_2\text{SiMo}(\text{CO})_5$ (diethyl silicon molybdenum pentacarbonyl).

Temp. of substrate --- 375° C.
Nature of substrate --- Steel.
Pressure ----- 0.1 mm.
Compound temp. --- 135° C.
Time ----- 2 hours.
Results ----- Grey metallic coating.

Example XX

Compound ----- $[(\text{CH}_3)_2\text{Al}]_2\text{Cr}(\text{CO})_5$ (bis-(dimethyl aluminum) chromium pentacarbonyl).

Temp. of substrate --- 350° C.
Nature of substrate --- Molybdenum alloy.
Pressure ----- 0.1 mm.
Compound temp. --- 145° C.
Time ----- 3½ hours.
Results ----- Light grey metallic coating.

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Example XXI

Compound ----- $(C_2H_5)_2GeNi(CO)_3$ (diethyl germanium nickel tricarbonyl).
 Temp. of substrate --- $500^\circ C$.
 Nature of substrate --- Ceramics.
 Pressure ----- 10 mm.
 Compound temp. ----- $175^\circ C$.
 Time ----- 2 hours.
 Results ----- Grey metallic coating.

Example XXII

Compound ----- $(C_6H_5)_3Sn(C_6H_5)Mn(CO)_2$ (triphenyl tin phenyl manganese dicarbonyl).
 Temp. of substrate --- $425^\circ C$.
 Nature of substrate --- Glass.
 Pressure ----- 0.1 mm.
 Compound temp. ----- $135^\circ C$.
 Time ----- $2\frac{1}{2}$ hours.
 Results ----- Grey metallic coating.

Example XXIII

Compound ----- $(C_2H_5)_2AlCyCr(CO)_3$ (diethyl aluminum cyclopentadienyl chromium tricarbonyl).
 Temp. of substrate --- $295^\circ C$.
 Nature of substrate --- Steel alloy.
 Pressure ----- 0.1 mm.
 Compound temp. ----- $110^\circ C$.
 Time ----- 3 hours.
 Results ----- Light grey metallic coating.

Example XXIV

Compound ----- $Al[CyCr(CO)_3]_3$ (aluminum tris-cyclopentadienyl chromium tricarbonyl).
 Temp. of substrate --- $375^\circ C$.
 Nature of substrate --- Chromium.
 Pressure ----- 0.1 mm.
 Compound temp. ----- $98^\circ C$.
 Time ----- 30 minutes.
 Results ----- Dark grey coating.

Example XXV

Compound ----- $(CH_3)_2Al(CH_3)_3Sn$ (dimethyl aluminum trimethyltin).
 Temp. of substrate --- $380^\circ C$.
 Nature of substrate --- Steel.
 Pressure ----- 0.1 mm.
 Compound temp. ----- $115^\circ C$.
 Time ----- $1\frac{1}{2}$ hours.
 Results ----- Grey metallic coating.

Example XXVI

Compound ----- $(C_2H_5)_2B(C_5H_{11})_3Sn$ (diethyl boron triphenyl tin).
 Temp. of substrate --- $420^\circ C$.
 Nature of substrate --- Nickel alloy.
 Pressure ----- 0.1 mm.
 Compound temp. ----- $120^\circ C$.
 Time ----- 12 hours.
 Results ----- Grey black metallic coating.

Example XXVII

Compound ----- $(C_2H_5)_2B(CH_3)_3Pb$ (diethyl boron dimethyl lead).
 Temp. of substrate --- $495^\circ C$.
 Nature of substrate --- Glass.
 Pressure ----- 0.1 mm.
 Compound temp. ----- $85^\circ C$.
 Time ----- $2\frac{1}{2}$ hours.
 Results ----- Grey black metallic coating.

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Example XXVIII

Compound ----- $Co(CO)_4Mn(CO)_5$ (cobalt tetracarbonyl manganese pentacarbonyl).
 5 Temp. of substrate --- $450^\circ C$.
 Nature of substrate --- Graphite.
 Pressure ----- 0.8 mm.
 Compound temp. ----- $130^\circ C$.
 Time ----- $6\frac{1}{2}$ hours.
 10 Results ----- Grey metallic.

Example XXIX

Compound ----- $[Co(CO)_4]_2Fe(CO)_4$ (bis-cobalt tetracarbonyl iron tetracarbonyl).
 15 Temp. of substrate --- $475^\circ C$.
 Nature of substrate --- Steel.
 Pressure ----- 0.1 mm.
 Compound temp. ----- $103^\circ C$.
 20 Time ----- $2\frac{1}{2}$ hours.
 Results ----- Light grey metallic.

Example XXX

Compound ----- $[V(CO)_6]_2Ni(CO)_3$ (vanadium hexacarbonyl nickel tricarbonyl).
 Temp. of substrate --- $510^\circ C$.
 Nature of substrate --- Steel alloy.
 Pressure ----- 0.3 mm.
 30 Compound temp. ----- $95^\circ C$.
 Time ----- 4 hours.
 Results ----- Light grey metallic.

Example XXXI

35 Compound ----- $(C_6H_6)Mn(CO)_2CyFe(CO)_2$ (benzene manganese dicarbonyl cyclopentadienyl iron dicarbonyl).
 Temp. of substrate --- $425^\circ C$.
 40 Nature of substrate --- Glass.
 Pressure ----- 1 mm.
 Compound temp. ----- $130^\circ C$.
 Time ----- $3\frac{1}{2}$ hours.
 Results ----- Metallic grey.

Example XXXII

Compound ----- $(C_4H_8)Co(CO)_2MeCyNi(CO)$ (butadiene cobalt dicarbonyl methyl cyclopentadienyl nickel monocarbonyl).
 50 Temp. of substrate --- $475^\circ C$.
 Nature of substrate --- Steel.
 Pressure ----- 0.1 mm.
 Compound temp. ----- $110^\circ C$.
 Time ----- $4\frac{1}{2}$ hours.
 55 Results ----- Grey coating.

Example XXXIII

Compound ----- $(C_6H_5)(CH_3)_3Co(CO)CyFe(CO)_2$ (cumene cobalt monocarbonyl cyclopentadiene iron dicarbonyl).
 60 Temp. of substrate --- $350^\circ C$.
 Nature of substrate --- Aluminum.
 Pressure ----- 0.1 mm.
 Compound temp. ----- $105^\circ C$.
 Time ----- 2 hours.
 Results ----- Grey coating.
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Example XXXIV

Compound ----- $[CyFe(CO)_2]_2Ni(CO)_3$ (bis-cyclopentadienyl iron dicarbonyl nickel tricarbonyl).
 75 Temp. of substrate --- $375^\circ C$.

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Nature of substrate --- Molybdenum.
 Pressure --- 0.3 mm.
 Compound temp. --- 90° C.
 Time --- 10 hours.
 Results --- Dark grey metallic coating.

Example XXXV

Compound --- $[\text{MeCyCr}(\text{CO})_3]_2\text{Ni}(\text{CO})_3$ (bis-methyl cyclopentadienyl chromium tricarbonyl nickel tricarbonyl).

Temp. of substrate --- 425° C.
 Nature of substrate --- Cobalt alloy.
 Pressure --- 0.5 mm.
 Compound temp. --- 150° C.
 Time --- 8 hours.
 Results --- Dark grey metallic coating.

Example XXXVI

Compound --- $\text{MeCyNi}(\text{CO})\text{Mn}(\text{CO})_5$ (methyl cyclopentadienyl nickel monocarbonyl manganese pentacarbonyl).

Temp. of substrate --- 480° C.
 Nature of substrate --- Steel.
 Pressure --- 0.1 mm.
 Compound temp. --- 125° C.
 Time --- 3 hours.
 Results --- Light grey metallic coating.

Example XXXVII

Compound --- $(\text{C}_2\text{H}_5)_3\text{Al}(\text{CH}_3)_3\text{Sb}$ (triethyl aluminum trimethyl antimony).

Temp. of substrate --- 290° C.
 Nature of substrate --- Steel.
 Pressure --- 0.1 mm.
 Compound temp. --- 105° C.
 Time --- 5 hours.
 Results --- Metallic grey coating.

Example XXXVIII

Compound --- $(\text{CH}_3)_3\text{In}(\text{C}_6\text{H}_5)_3\text{Sb}$ (trimethyl indium triphenyl antimony).

Temp. of substrate --- 375° C.
 Nature of substrate --- Ceramic.
 Pressure --- 0.5 mm.
 Compound temp. --- 95° C.
 Time --- 3 hours.
 Results --- Metallic grey coating.

Example XXXIX

Compound --- $(\text{C}_6\text{H}_5)_3\text{TI}(\text{C}_6\text{H}_5)_3\text{Bi}$ (triphenyl thallium triethyl bismuth).

Temp. of substrate --- 395° C.
 Nature of substrate --- Glass.
 Pressure --- 1 mm.
 Compound temp. --- 115° C.
 Time --- 6 hours.
 Results --- Grey metallic coating.

Example XL

Compound --- $(\text{C}_2\text{H}_5)_2\text{Pb}[\text{Te}(\text{CH}_3)_2]_2$ (diethyl lead bis-dimethyl telluride).

Temp. of substrate --- 495° C.
 Nature of substrate --- Ceramic.
 Pressure --- 0.5 mm.
 Compound temp. --- 105° C.
 Time --- 5½ hours.
 Results --- Grey black.

The process employed in Examples I and following is utilized with the exception that an ultrasonic generator is proximately positioned to the plating apparatus. The compound is heated to its decomposition threshold and thereafter the ultrasonic generator is utilized to effect final decomposition.

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Example XLI

Compound --- $\text{Cu}(\text{AlEt}_4)_2$ (copper bis - aluminum tetraethyl).

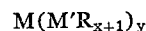
Temp. of substrate --- 200° C.
 Nature of substrate --- Glass wool.
 Pressure --- 0.1-0.2 mm.
 Compound temp. --- 110° C.
 Time --- 1 hour.
 Results --- Dull, metallic.
 Method --- Ultrasonic.

Example XLII

Compound --- $\text{Cr}(\text{BEt}_4)_3$ (chromium tris-boron tetraethyl).

Temp. of substrate --- 300° C.
 Nature of substrate --- ---
 Pressure --- 0.1 mm.
 Compound temp. --- 60° C.
 Time --- 4 hours.
 Results --- Powder—chromium boride or mixture.
 Method --- Ultrasonic.

As discussed hereinbefore the bimetallic organometallic plating agents of this invention can be represented by the general formula



wherein M is a metal selected from the group consisting of groups I, II, III-B, IV-B, V-B, VI-B, VII-B and VIII of the periodic chart of the elements and the metals tin and aluminum; M' is a metal selected from the group consisting of group III-A of the periodic chart of the elements and the metals zinc and cadmium; R represents a monovalent anion; x is an integer equal to the valence of M'; y is an integer equal to the valence of M.

The metals designated by M include lithium, sodium, potassium, rubidium, cesium, francium of group I-A. Within this group lithium is the especially preferred metal because of the desirable high temperature characteristics lithium imparts when alloyed with certain metals. The symbol M further designates the metals beryllium, magnesium, calcium, strontium, barium, radium within group II-A; scandium, indium, lanthanum, actinium (including the lanthanum and actinium series) within group III-B; titanium, zirconium, hafnium, within group IV-B; vanadium, niobium, tantalum within group V-B; chromium, molybdenum, tungsten within group VI-B; manganese, technetium, rhenium within group VII-B; and iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum of group VIII. Within the groups I-B and II-B, M designates the metals silver, copper, gold, zinc, cadmium and mercury. It of course should be recognized that because of the scarcity of certain of the above metals, their use would be reserved for those instances where their unique alloying properties are desired or needed.

The metal M' includes any of the elements of group III-A and thus includes boron, aluminum, thallium, indium and gallium. Of these aluminum is most preferred because of its wide availability and use in plating technology.

As noted above, R is a monovalent anion, preferably an unsubstituted hydrocarbon group. The hydrocarbon groups generally contain between about 1 and 20 carbon atoms each. A preferred class of bimetallic organometallic plating agent of this invention contains as one of the R groups at least one cyclopentadienyl group. By a cyclopentadienyl group is meant groups containing the five carbon atom ring found in cyclopentadiene itself. Examples are the cyclopentadienyl, indenyl and fluorenyl groups, and the corresponding groups substituted with one or more hydrocarbon radicals such as the methylcyclopentadienyl, methyl-tert-butylcyclopentadienyl, triethylindenyl, phenylcyclopentadienyl, and related groups.

R can also be other monovalent anions. These anions

Typical examples of the bimetallic organometallic plating agents of this embodiment of this invention comprise: tin tetramethylboron, chromium tetraethylboron, scandium tetraethylboron, copper tetraisopropylboron, titanium tetraoctylboron, vanadium tetraoctadecylboron, chromium tetraeicosylboron, tin tetravinylboron, iron tetra-2-2-butenylboron, cobalt 1-hexynyltriethylboron, nickel tetraethynylboron, tin tetracyclohexylboron, vanadium tetraphenylboron, copper tetrabenzyboron, titanium tetranaphthylboron, titanium tetracyclohexenylboron, vanadium tetrabutadienylboron, chromium ethyltributylboron, zirconium ethyltriocetylboron, iron ethyltriocetadecylboron, cobalt ethyltricyclohexylboron, cobalt ethyltriphenylboron, nickel ethyltri(2-phenylethyl)boron, manganese ethyltriisopropylboron, copper diethyldiisopropylboron, titanium diethyldiphenylboron, vanadium diethyldioctadecylboron, chromium octyltriocetadecylboron; molybdenum ethylborontrichloride, trifluoride, tribromide, or triiodide; iron triethylboron hydride, cobalt triocetylboron hydride; nickel ethyltrimethoxyboron, tungsten triethylethoxyboron, tin triocetylboron octanoate, copper triethylboron cyanide, titanium triphenylboron cyanide, vanadium triethylboron cyanate and thiocyanate; chromium triethylboron amide, molybdenum triethylboron mercaptide, iron triethylboron azide, cobalt triethylboron acetate, nickel triethylboron octanoate, tin triethylboron phenolate; chromium triethylboron sulfate, nitrate, nitrite, sulfite, phosphite, phosphite, arsonate, or chlorate, and the like; also similar compounds wherein other group III-A elements, zinc, or cadmium are substituted for boron as, for example, tin tetraethylaluminum, chromium tetraethylaluminum, zirconium tetraethylaluminum, copper tetraethylaluminum, tin triethylzinc, titanium triethylzinc, manganese tetraethylaluminum, and the like. It is preferable that the first metal, M, be tin, chromium, copper, vanadium, manganese, iron, cobalt, nickel, or titanium, and the second metal, M', be aluminum or boron with all of the chemical groups attached to the latter being hydrocarbon radicals having up to about 8 carbon atoms, especially the unsubstituted hydrocarbon radical, e.g., alkyl radicals. Compounds of the metals tin, chromium, and copper comprise an especially unique group of compounds of high stability and effective use. Thus, especially preferred embodiments comprise tin, chromium, or copper tetraethylaluminum or boron.

Further examples of the bimetallic organometallic plating agents of this embodiment of this invention, some of which are "tailormade" to produce the highly desirable lithium-aluminum alloys, include the following: lithium tetramethylboron, lithium tetraethylboron, lithium tetraethylaluminum, lithium triethylzinc, lithium tetraisopropylboron, lithium tetraoctylboron, lithium tetracycloaluminum, lithium trioctylzinc, lithium tetractadecylboron, lithium tetraeicosylboron, lithium tetravinylboron, lithium tetra-2-butenylboron, lithium tetra-2-butenylaluminum, lithium tri-2-butenylzinc, lithium 1-hexynyl triethylboron, lithium tetraethynylboron, lithium tetracyclohexylboron, lithium tetracyclohexylaluminum, lithium tetraphenylboron, lithium tetrabenzylboron, boron, lithium tetrabutadienylboron; lithium ethyltributylboron, lithium ethyldibutylcadmium, lithium ethyltriocetylboron, lithium ethyltriocetadecylboron, lithium ethyltricyclohexylboron, lithium ethyltriphenylboron, lithium ethyltri(2-phenylethyl)boron, lithium ethyltriisopropylboron, lithium diethyldiisopropylboron, lithium diethyl-

diphenylboron, lithium diethyldioctadecylboron, lithium octyltrioctadecylboron; lithium ethylboron trichloride, trifluoride, tribromide, or triiodide; lithium triethylboron hydride, lithium triethylaluminum hydride, lithium trioctylboron hydride; lithium ethyltrimethoxyboron, lithium triethylethoxyboron, lithium trioctylboron octanoate, lithium triethylboron or aluminum cyanide, lithium triphenylboron cyanide, lithium triethylboron cyanate and thiocyanate; lithium triethylboron amide, lithium triethylboron mercaptide, lithium triethylboron azide, lithium triethylboron acetate, lithium triethylboron octanoate, lithium triethylboron phenolate; lithium triethylboron, sulfate, nitrate, nitrite, sulfite, phosphate, phosphite, arsenate, or chlorate; potassium tetraethylboron, potassium tetraethylaluminum, lithium tetraethylboron, magnesium tetraethylaluminum, calcium tetraethylboron, magnesium tetraethylboron, strontium tetraethylboron, potassium ethyltriphenylboron, potassium triethylboron cyanide, potassium triethylboron chloride, potassium triethylboron cyanate, potassium triethylboron sulfate, and the like. It is to be understood that the hydrocarbon portions of the above and other bimetallic organometallic compounds can be further substituted with other functional groups which do not interfere with the reaction as, for example, the halogens, acid groups, both inorganic and organic, and the like. It is preferable that the R groups of the bimetallic organometallic be hydrocarbon groups, especially the lower alkyl groups having up to and including about 8 carbon atoms since these are quite suitable in the process and result in more stable and useful products.

Typical examples of plating agents which can be used in accordance with the present embodiment of this invention wherein at least one of the hydrocarbon groups is a cyclopentadienyl group are: lithium boron tetrakis- (cyclopentadienide), lithium aluminum tetrakis(cyclopentadienide), lithium aluminum tetrakis(methylcyclopentadienide), lithium gallium tetrakis(cyclopentadienide), lithium indium tetrakis(ethylcyclopentadienide), lithium boron cyclopentadienide trihydride, lithium boron tris(cyclopentadienide) hydride, lithium aluminum tris(cyclopentadienide) hydride, lithium aluminum cyclopentadienide triethyl, lithium aluminum bis(cyclopentadienide) diethyl, lithium aluminum cyclopentadienide trimethyl, sodium aluminum cyclopentadienide triisobutyl, sodium aluminum cyclopentadienide diethyl hydride, sodium aluminum cyclopentadienide trifluoride, sodium aluminum cyclopentadienide diethyl chloride, sodium aluminum cyclopentadienide ethyl dichloride, sodium aluminum cyclopentadienide ethyl dibromide, sodium aluminum cyclopentadienide ethyl difluoride, sodium aluminum cyclopentadienide ethyl diiodide, sodium aluminum tricyclopentadienide chloride, sodium aluminum tricyclopentadienide fluoride, sodium gallium tricyclopentadienide ethyl, sodium gallium tetracyclopentadienide, sodium indium tetracyclopentadienide, sodium thallium cyclopentadienide trichloride, potassium boron tetracyclopentadienide, potassium boron tricyclopentadienide hydride, potassium boron tricyclopentadienide ethyl, potassium boron tricyclopentadienide chloride, potassium boron cyclopentadienide triethyl, potassium boron cyclopentadienide trihydride, potassium boron cyclopentadienide trichloride, potassium aluminum tetracyclopentadienide, potassium aluminum tetra indenide, rubidium aluminum tetracyclopentadienide, rubidium aluminum tetraethyl cyclopentadienide, cesium boron tetracyclopentadienide, cesium aluminum tetracyclopentadienide, beryllium bis(boron cyclopentadienide triethyl), beryllium bis(aluminum tetracyclopentadienide), beryllium bis(aluminum tricyclopentadienide ethyl), beryllium bis(aluminum cyclopentadienide triethyl) magnesium bis(boron tetracyclopentadienide), magnesium bis(boron tetraphenyl cyclopentadienide), magnesium bis(aluminum tetramethyl cyclopentadienide), magnesium bis(aluminum tricyclopentadienide chloride), magnesium bis(aluminum cyclopentadienide tribromide), calcium bis(boron cyclopentadienide trichloride), calcium bis(boron cyclopentadienide trihydride), strontium bis

(gallium tetracyclopentadienide), barium bis(indium tetrafluorenone), zinc bis(boron tetracyclopentadienide), zinc bis(aluminum tetracyclopentadienide), zinc bis(aluminum cyclopentadienide triethyl), cadmium bis(aluminum tetracyclopentadienide), mercury bis(boron cyclopentadienide trihydride), mercury bis(aluminum cyclopentadienide trihydride), mercury bis(aluminum cyclopentadienide trichloride), and mercury bis(gallium tetracyclopentadienide). In addition to the compounds above, similar compounds can be made containing other cyclopentadienyl groups including the isopropyl, diisopropyl, hexyl, tolyl, xylyl, and other alkyl and aryl derivatives of cyclopentadienyl groups.

Another embodiment of the bimetallic organometallic plating agents is represented by the general formula



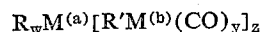
wherein R represents any alkyl or cycloalkyl group generally containing up to about 20 carbon atoms. The R groups which are bonded to the metal $M^{(a)}$ are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, and the like. The cycloalkyl groups which may be bonded to the metal may also be substituted alkyl groups. Thus, cyclohexane is a typical example of the cycloalkyl group which may be bonded to the metal, and ethyl cyclohexane is a typical example of a substituted cycloalkyl group.

The metal $M^{(a)}$ in the above formula may be any group IV-A metal, i.e., silicon, germanium, tin and lead, and aluminum found in group III-A. $M^{(b)}$ in the formula represents a different metal which may be selected from the groups IV-B, V-B, VI-B, VII-B and VIII of the periodic chart of the elements, Fisher Scientific Company, 1955. Thus, typical examples of the metal represented by $M^{(b)}$ are titanium, zirconium, hafnium, vanadium, tantalum, chromium, molybdenum, tungsten, manganese, technetium, iron, rhenium, ruthenium, osmium, cobalt, iridium, nickel, platinum, palladium, and the like.

Typical examples of the compounds of the above formula are: diethyllead iron tetracarbonyl, dibutyllead iron tetracarbonyl, methylethyllead iron tetracarbonyl, di-2-ethylhexylgermanium iron tetracarbonyl, dimethylgermanium iron tetracarbonyl, diethylgermanium iron tetracarbonyl, dipropylgermanium iron tetracarbonyl, di-n-decylsilicon iron tetracarbonyl, diundecylsilicon iron tetracarbonyl, diethylsilicon iron tetracarbonyl, dimethylsilicon iron tetracarbonyl, dimethyltin iron tetracarbonyl, diethyltin iron tetracarbonyl, hexyldecyltin iron tetracarbonyl, dimethylaluminum manganese pentacarbonyl, diethylaluminum manganese pentacarbonyl, diisobutylaluminum manganese pentacarbonyl, diisoamylaluminum manganese pentacarbonyl, bis(dimethyl)aluminum chromium pentacarbonyl, bis(diethyl)aluminum chromium pentacarbonyl, bis(di-n-hexyl)aluminum chromium pentacarbonyl, bis(diisobutyl)aluminum chromium pentacarbonyl, dihexadecyllead chromium pentacarbonyl, diheptyllead chromium pentacarbonyl, diethyllead chromium pentacarbonyl, dimethyllead chromium pentacarbonyl, methylethyllead chromium pentacarbonyl, diethylgermanium chromium pentacarbonyl, dioctadecylgermanium chromium pentacarbonyl, dipropylgermanium chromium pentacarbonyl, di-n-hexylgermanium chromium pentacarbonyl, dimethylsilicon chromium pentacarbonyl, diethylsilicon chromium pentacarbonyl, dipropylsilicon chromium pentacarbonyl, dinonylsilicon chromium pentacarbonyl, diethyltin chromium pentacarbonyl, dimethyltin chromium pentacarbonyl, dibutyltin chromium pentacarbonyl, diisobutyltin chromium pentacarbonyl, bis(dimethylaluminum)iron tetracarbonyl, bis(diethylaluminum)iron tetracarbonyl, bis(diisobutylaluminum)iron tetracarbonyl, bis(diisopropylaluminum)iron tetracarbonyl, diisobutylaluminum cobalt tetracarbonyl, diethylaluminum cobalt tetracarbonyl, dimethylaluminum cobalt tetracarbonyl, dipropylaluminum cobalt tetracar-

bonyl, bis(diethylaluminum)chromium pentacarbonyl, bis(dipropylaluminum)molybdenum pentacarbonyl, bis(diisobutylaluminum)molybdenum pentacarbonyl, bis(didodecylaluminum)molybdenum pentacarbonyl, bis(dimethylaluminum)tungsten pentacarbonyl, bis(diisobutylaluminum)tungsten pentacarbonyl, bis(diisoamylaluminum)tungsten pentacarbonyl, dimethyllead nickel tricarbonyl, diethyllead nickel tricarbonyl, dipropyllead nickel tricarbonyl, diisobutyllead nickel tricarbonyl, methylethyllead nickel tricarbonyl, dimethylgermanium nickel tricarbonyl, diethylgermanium nickel tricarbonyl, diisobutylgermanium nickel tricarbonyl, diisoamylgermanium nickel tricarbonyl, dipropylgermanium nickel tricarbonyl, dimethylsilicon nickel tricarbonyl, diethylsilicon nickel tricarbonyl, dipropylsilicon nickel tricarbonyl, dibutylsilicon nickel tricarbonyl, diisobutylsilicon nickel tricarbonyl, dimethyltin nickel tricarbonyl, diethyltin nickel tricarbonyl, dipropyltin nickel tricarbonyl, dibutyltin nickel tricarbonyl, diisopropyltin nickel tricarbonyl, diisobutyltin nickel tricarbonyl, dioctadecyltin nickel tricarbonyl, bis(dimethylaluminum)nickel tricarbonyl, bis(diethylaluminum)nickel tricarbonyl, bis(dipropylaluminum)nickel tricarbonyl, bis(dibutylaluminum)nickel tricarbonyl, bis(diisobutylaluminum)nickel tricarbonyl, bis(di-2-ethylhexylaluminum)nickel tricarbonyl, and the like.

A further embodiment of the bimetallic organometallic plating agents of this invention is represented by the general formula



wherein R represents any electron donating moiety bonded to the metal $M^{(a)}$. Typical of the electron donating moieties which are bonded to said metal are organo groups such as alkyl, aryl, cycloalkyl, alkaryl, and the like. Another electron donating moiety which may be bonded to the metal $M^{(a)}$ is hydrogen. Thus, typical examples of R in the above formula are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, and the like. Some examples of cycloalkyl groups which are sigma bonded to the metal are cyclohexane and cyclopentane. These cycloalkyl groups may also be substituted cycloalkyls. The metal $M^{(a)}$ may be any metal such as zinc, cadmium, mercury, beryllium, magnesium, strontium, barium, boron, aluminum, gallium, indium, thallium, silicon, germanium, tin, lead, phosphorus, arsenic, antimony, and bismuth. R' is an unsaturated organic group pi bonded to the metal $M^{(b)}$. Thus, typical examples of unsaturated organo groups are the arenes, alkenes, cycloalkenes, alkarenes, and the like. Typical examples of the unsaturated organo groups are cyclopentadiene, phenyl, butadiene, cyclohexadiene, methylcyclopentadiene, toluene, xylene, cumene, and the like. $M^{(b)}$ can be any metal found in the groups IV-B, V-B, VI-B, VII-B and VIII of the periodic chart of elements which include titanium, vanadium, chromium, molybdenum, tungsten, manganese, technetium, rhenium, iron, ruthenium, osmium, cobalt, iridium, nickel, palladium, platinum, and the like. CO in the above formula represents carbonyl groups bonded to the metal $M^{(b)}$.

Typical examples of the compounds which correspond to the formula above are: triphenyltin cyclopentadienyl iron dicarbonyl, triphenyltin cyclopentadienyl nickel monocarbonyl, triphenyltin cyclopentadienyl chromium tricarbonyl, triphenyltin cyclopentadienyl molybdenum tricarbonyl, triphenyltin butadiene manganese tricarbonyl, triphenyltin phenyl cobalt monocarbonyl, triphenyltin butadiene cobalt dicarbonyl, triphenyltin phenyl manganese dicarbonyl, diethyl aluminum cyclopentadienyl iron dicarbonyl, diethyl aluminum cyclopentadienyl nickel monocarbonyl, diethyl aluminum cyclopentadienyl chromium tricarbonyl, diethyl aluminum butadiene manganese tricarbonyl, diethyl aluminum phenyl cobalt monocarbonyl, diethyl aluminum butadiene cobalt dicarbonyl, di-

ethyl aluminum phenyl manganese dicarbonyl, tri-n-propyl lead cyclopentadienyl iron dicarbonyl, triisopropyl cyclopentadienyl nickel monocarbonyl, triisopropyl lead cyclopentadienyl chromium tricarbonyl, triisopropyl lead cyclopentadienyl molybdenum tricarbonyl, tri-n-propyllead butadiene manganese tricarbonyl, tri-n-propyllead phenyl cobalt monocarbonyl, tri-n-propyllead butadiene cobalt dicarbonyl, tri-n-propyllead benzene manganese dicarbonyl, trixylyl germanium cyclopentadienyl iron dicarbonyl, trixylyl germanium cyclopentadienyl nickel monocarbonyl, trixylyl germanium cyclopentadienyl chromium tricarbonyl, trixylyl germanium cyclopentadienyl molybdenum tricarbonyl, trixylyl germanium cyclopentadienyl tungsten tricarbonyl, trixylyl germanium butadiene manganese tricarbonyl, trixylyl germanium phenyl cobalt monocarbonyl, trixylyl germanium butadiene cobalt dicarbonyl, trixylyl germanium phenyl manganese dicarbonyl, dimethyllead bis-cyclopentadienyl iron dicarbonyl, dimethyllead bis-cyclopentadienyl nickel monocarbonyl, dimethyllead bis-cyclopentadienyl chromium tricarbonyl, dimethyllead bis-cyclopentadienyl molybdenum tricarbonyl, dimethyllead bis-butadiene manganese tricarbonyl, dimethyllead bis-phenyl cobalt monocarbonyl, dimethyllead bis-butadiene cobalt dicarbonyl, dimethyllead bis-benzene manganese dicarbonyl, dibutyl germanium bis-cyclopentadienyl iron dicarbonyl, dibutyl germanium bis-cyclopentadienyl nickel monocarbonyl, dibutyl germanium bis-cyclopentadienyl chromium tricarbonyl, dibutyl germanium bis-cyclopentadienyl tungsten tricarbonyl, dibutyl germanium bis-methyl cyclopentadienyl molybdenum tricarbonyl, dibutyl germanium bis-2-ethyl butadiene manganese tricarbonyl, dibutyl germanium bis-phenyl cobalt monocarbonyl, dibutyl germanium bis-butadiene cobalt dicarbonyl, dibutyl germanium bis-phenyl manganese dicarbonyl, beryllium bis-cyclopentadienyl iron dicarbonyl, beryllium bis-cyclopentadienyl chromium tricarbonyl, beryllium bis-butadiene cobalt dicarbonyl, aluminum tris-cyclopentadienyl iron dicarbonyl, aluminum tris-cyclopentadienyl chromium tricarbonyl, aluminum tris-cyclopentadienyl molybdenum tricarbonyl, aluminum tris-methyl cyclopentadienyl tungsten tricarbonyl, aluminum tris-phenyl manganese dicarbonyl, phenyl silicon tris-cyclopentadienyl iron dicarbonyl, phenyl silicon tris-cyclopentadienyl chromium tricarbonyl, phenyl silicon tris-methyl cyclopentadienyl molybdenum tricarbonyl, phenyl silicon tris-ethyl cyclopentadienyl tungsten tricarbonyl, phenyl silicon tris-butadiene manganese tricarbonyl, phenyl silicon tris-phenyl cobalt monocarbonyl, phenyl silicon tris-butadiene cobalt dicarbonyl, phenyl silicon tris-phenyl manganese dicarbonyl, and the like.

A still further embodiment of the bimetallic organometallic plating agents of this invention is represented by the formula



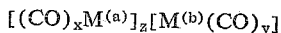
wherein R represents an electron donating moiety which may be an alkyl, cycloalkyl group or hydrogen. The organo groups generally contain up to about 20 carbon atoms. Thus, typical examples of an alkyl group in the formula above would be methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, eicosyl, nonadecyl, heptadecyl, hexadecyl, pentadecyl, and the like. The cycloalkyl groups represented by R in the above formula may be substituted cycloalkyl groups. Thus, a typical example of a cycloalkyl group is cyclohexane, while a typical example of an alkyl substituted cycloalkyl is 1-ethyl cyclohexane. Since there are three electron donating groups bonded to the metal, the electron donating groups in each instance may be the same or different.

M^c represents a metal selected from the group consisting of boron, gallium, indium and thallium, while M^d is a metal selected from the group consisting of selenium, tellurium, silicon, germanium, tin, lead, and the like.

Typical examples of compounds which correspond to

the above formula are: diethyl boron trimethyl silicate, diethyl boron triethyl silicate, diethyl boron trimethyl silicate, aluminum hydride trimethyl silicate, dimethyl aluminum trimethyl silicate, diethyl aluminum trimethyl silicate, dipropyl aluminum triethyl silicate, diisopropyl aluminum triethyl silicate, diisobutyl aluminum triisopropyl silicate, diethyl gallium trimethyl silicate, dipropyl gallium trimethyl silicate, dipropyl gallium triethyl silicate, dimethyl indium triethyl silicate, diethyl indium triethyl silicate, diisobutyl indium trimethyl silicate, dimethyl thallium triethyl silicate, dimethyl thallium trimethyl silicate, dipropyl thallium trimethyl silicate, dipropyl thallium tripropyl silicate, diisopropyl thallium trimethyl silicate, diundecyl thallium triundecyl silicate, diethyl boron trimethyl germanium, dipropyl boron tributyl germanium, dimethyl boron trimethyltin, diethyl boron tributyltin, dipropyl boron tripropyltin, diethyl boron triethyllead, dimethyl boron methyl diethyllead, dibutyl boron ethyl dimethyllead, diethyl aluminum triethyl germanium, ethylpropyl aluminum, methylethylpropyl germanium, dibutyl aluminum trimethyl germanium, diisobutyl aluminum tributyl germanium, diethyl aluminum triethyltin, diethyl aluminum trimethyltin, methylethyl aluminum dipropyl ethyltin, diisobutyl aluminum tributyltin, diethyl aluminum triethyllead, dimethyl aluminum triethyllead, diisobutyl aluminum methyl diethyllead, diisobutyl aluminum triethyllead, aluminum trihydride triethyllead, dimethyl gallium trimethyl germanium, dipropyl gallium trimethyl germanium, diundecyl gallium tripropyl germanium, dimethyl gallium trimethyltin, dipropyl gallium tripropyltin, diisobutyl gallium tributyltin, dimethyl gallium trimethyllead, dipropyl gallium triethyllead, dimethyl gallium ethyldimethyllead, dimethyl indium trimethyl germanium, dibutyl indium trimethyl germanium, dimethyl indium tributyltin, diethyl indium methyl diethyltin, diundecyl indium triheptyltin, dimethyl tantalum triethyllead, dimethyl tantalum triethyllead, diethyl tantalum methyl diethyllead, and the like.

Another embodiment of the bimetallic organometallic plating agents of this invention is represented by the formula

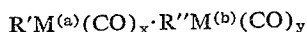


in which M^(a) and M^(b) represent different metals from the transitional metal series of the periodic chart of the elements, Fisher Scientific Company, 1955. Thus, typical examples of the metals represented in the above formula are titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, technetium, rhenium, iron, ruthenium, osmium, cobalt, iridium, nickel, platinum, palladium, and the like. It should be noted that the compounds as described above have a unique metal to metal bond. In other words, the metals are bonded by free electrons, each metal having less than the adequate number of carbonyl groups on each to satisfy the electronic structure. Thus, the above formula does not represent a mere mixture of metal carbonyls but an actual metal to metal bond wherein each metal contains carbonyl groups bonded to it respectively.

Typical examples of organometallic compounds which represent the above formula are: cobalt tetracarbonyl manganese pentacarbonyl, vanadium hexacarbonyl manganese pentacarbonyl, vanadium hexacarbonyl cobalt tetracarbonyl, bis(cobalt tetracarbonyl)iron tetracarbonyl, bis(manganese pentacarbonyl)iron tetracarbonyl, vanadium hexacarbonyl iron tetracarbonyl, bis(cobalt tetracarbonyl)nickel tricarbonyl, bis(manganese pentacarbonyl)nickel tricarbonyl, vanadium hexacarbonyl nickel tricarbonyl, bis(cobalt tetracarbonyl)chromium pentacarbonyl, bis(manganese pentacarbonyl)chromium pentacarbonyl, vanadium hexacarbonyl chromium pentacarbonyl, bis(cobalt tetracarbonyl)molybdenum pentacarbonyl, bis(manganese pentacarbonyl)molybdenum pentacarbonyl, vanadium hexacarbonyl molybdenum pen-

tacarbonyl, bis(cobalt tetracarbonyl)tungsten pentacarbonyl, bis(manganese pentacarbonyl)tungsten pentacarbonyl, vanadium hexacarbonyl tungsten pentacarbonyl, and the like.

A still further embodiment of the present invention is the bimetallic organometallic plating agents represented by the formula

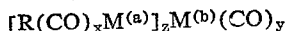


wherein R' and R'' represent unsaturated organo groups containing up to about 25 carbon atoms. Typical examples of these groups are arenes, cycloalkenes, alkadienes, cycloalkadienes, and the like. In each instance, R' and R'' may be the same or different. Typical examples of the organo groups which are bonded to the metals are butadiene, 2-methylbutadiene, benzene, naphthalene, toluene, xylene, cumene, cyclopentadienyl, methylcyclopentadienyl, p-isopropyl benzene, tertiary butyl benzene, fluorenyl, and the like. Other cyclopentadienyl groups which may be employed are the isopropyl, diisopropyl, tolyl and xylyl derivatives of the cyclopentadienyl groups.

The metals represented by M^(a) and M^(b) are different transitional metals. The transitional metals include titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, technetium, rhenium, ruthenium, iron, osmium, cobalt, iridium, nickel, and the like.

Typical examples of the compounds represented by the formula above are: butadiene manganese tricarbonyl cyclopentadiene iron dicarbonyl, benzene manganese dicarbonyl cyclopentadiene iron dicarbonyl, benzene manganese dicarbonyl cyclopentadiene nickel monocarbonyl, benzene manganese dicarbonyl cyclopentadiene chromium tricarbonyl, benzene manganese dicarbonyl cyclopentadiene tungsten tricarbonyl, benzene manganese dicarbonyl cyclopentadiene molybdenum tricarbonyl, butadiene manganese tricarbonyl cyclopentadiene nickel monocarbonyl, butadiene manganese tricarbonyl cyclopentadiene chromium tricarbonyl, butadiene manganese tricarbonyl cyclopentadiene tungsten tricarbonyl, butadiene cobalt dicarbonyl cyclopentadiene iron dicarbonyl, butadiene cobalt dicarbonyl methyl cyclopentadiene iron dicarbonyl, butadiene cobalt dicarbonyl ethyl cyclopentadiene nickel monocarbonyl, butadiene cobalt dicarbonyl dimethyl cyclopentadiene chromium tricarbonyl, butadiene cobalt dicarbonyl cyclopentadiene molybdenum tricarbonyl, benzene cobalt monocarbonyl cyclopentadiene iron dicarbonyl, toluene cobalt monocarbonyl cyclopentadiene iron dicarbonyl, cumene cobalt monocarbonyl cyclopentadiene iron dicarbonyl, mesitylene cobalt monocarbonyl cyclopentadiene nickel monocarbonyl, naphthalene cobalt monocarbonyl cyclopentadiene nickel monocarbonyl, cycloheptatriene cobalt monocarbonyl cyclopentadiene chromium tricarbonyl, cycloheptatriene cobalt monocarbonyl cyclopentadiene tungsten tricarbonyl, and the like.

Still another embodiment of the present invention is the bimetallic organometallic plating agents represented by the formula



wherein R represents any unsaturated organo group containing up to about 25 carbon atoms. Thus, R may represent cyclopentadienyl groups, substituted aryl and alkyl cyclopentadienyl groups, aryl groups, alkyl substituted aryl groups, and the like. Typical examples of the unsaturated organo groups are cyclopentadienyl, methylcyclopentadienyl, fluorenyl, benzene, toluene, cumene, butadiene, naphthalene, acenaphthene, and the like. The metals M^(a) and M^(b) represent different transitional metals selected from the groups IV-B, V-B, VI-B, VII-B and VIII of the periodic chart of the elements, Fisher Scientific Company, 1955. These groups generally include the metals nickel, palladium, platinum, cobalt, iron, iridium, ruthenium, rhenium, osmium, manganese, chro-

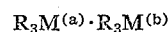
mium, molybdenum, tantalum, vanadium, niobium, titanium, zirconium, hafnium, and the like.

Typical examples of the compounds represented by the above formula are:

- 5 bis(cyclopentadienyl iron dicarbonyl)nickel tricarbonyl, bis(cyclopentadienyl iron dicarbonyl)chromium pentacarbonyl, bis(cyclopentadienyl iron dicarbonyl)molybdenum pentacarbonyl,
- 10 bis(cyclopentadienyl iron dicarbonyl)tungsten pentacarbonyl, bis(cyclopentadienyl chromium tricarbonyl)nickel tricarbonyl, bis(cyclopentadienyl chromium tricarbonyl)iron tetracarbonyl,
- 15 bis(cyclopentadienyl molybdenum tricarbonyl)nickel tricarbonyl, bis(cyclopentadienyl tungsten tricarbonyl)nickel tricarbonyl,
- 20 bis(cyclopentadienyl molybdenum tricarbonyl)iron tetracarbonyl, bis(cyclopentadienyl tungsten tricarbonyl)iron tetracarbonyl, bis(methylcyclopentadienyl chromium tricarbonyl)nickel tricarbonyl,
- 25 bis(ethylcyclopentadienyl molybdenum tricarbonyl)iron tetracarbonyl, bis(cyclopentadienyl nickel monocarbonyl)iron tetracarbonyl,
- 30 bis(cyclopentadienyl nickel monocarbonyl)chromium pentacarbonyl, bis(butylcyclopentadienyl nickel monocarbonyl)molybdenum pentacarbonyl, bis(methylcyclopentadienyl nickel monocarbonyl)tungsten pentacarbonyl,
- 35 methylcyclopentadienyl nickel monocarbonyl manganese pentacarbonyl, cyclopentadienyl nickel monocarbonyl cobalt tetracarbonyl,
- 40 cyclopentadienyl nickel monocarbonyl vanadium hexacarbonyl, cyclopentadienyl iron dicarbonyl manganese pentacarbonyl, cyclopentadienyl iron dicarbonyl cobalt tetracarbonyl,
- 45 cyclopentadienyl iron dicarbonyl vanadium hexacarbonyl, cyclopentadienyl chromium tricarbonyl cobalt tetracarbonyl, methylcyclopentadienyl molybdenum tricarbonyl vanadium hexacarbonyl,
- 50 ethylcyclopentadienyl tungsten tricarbonyl manganese pentacarbonyl, bis(butadiene manganese tricarbonyl)iron tetracarbonyl, bis(butadiene cobalt dicarbonyl)iron tetracarbonyl, bis(cyclohexadiene manganese tricarbonyl)iron tetracarbonyl,
- 55 bis(cumene manganese dicarbonyl)chromium pentacarbonyl, bis(toluene manganese dicarbonyl)molybdenum pentacarbonyl,
- 60 bis(naphthalene manganese dicarbonyl)tungsten pentacarbonyl,

and the like.

A further embodiment of the present invention is the bimetallic organometallic plating agents represented by the formula



- 70 wherein the R groups represent any organo group containing up to about 20 carbon atoms. These groups are generally the alkyl, aryl, cycloalkyl and aralkyl groups. Thus, typical examples of the organo groups in the above formula are methyl, ethyl, propyl, butyl, pentyl, hexyl,
- 75 heptyl, octyl, decyl, nonyl, undecyl, eicosyl, phenyl,

cumene, pseudocumene, naphthalene, cyclopentane, cyclohexane, and the like. $M^{(a)}$ in the formula above can be any metal such as boron, aluminum, gallium, indium, and thallium, while $M^{(b)}$ is a metal or metalloid representing phosphorus, arsenic, antimony, and bismuth.

Typical examples of compounds represented by the formula above are:

triethyl boron trimethyl arsenic,
tributyl boron trimethyl antimony,
trioctyl boron tridecyl bismuth,
triethyl aluminum triphenyl arsenic,
triisobutyl aluminum tricumene arsenic,
tripropyl aluminum tricumene arsenic,
triethyl aluminum trimethyl antimony,
triisobutyl aluminum tripropyl antimony,
triisoamyl aluminum trimethyl bismuth,
triphenyl gallium trimethyl arsenic,
trimethyl gallium tributyl antimony,
tripropyl gallium triphenyl bismuth,
trimethyl indium trimethyl arsenic,
tripropyl indium tributyl arsenic,
triphenyl indium triisoamyl arsenic,
trimethyl indium trimethyl antimony,
tributyl indium triphenyl antimony,
triisopropyl indium trimethyl antimony,
tributyl indium tributyl bismuth,
triphenyl indium triphenyl bismuth,
triethyl thallium triethyl arsenic,
trimethyl thallium trimethyl arsenic,
triphenyl thallium triphenyl arsenic,
triisobutyl thallium trimethyl arsenic,
trimethyl thallium trimethyl antimony,
triethyl thallium triethyl antimony,
triphenyl thallium trimethyl antimony,
trimethyl thallium trimethyl bismuth,
triethylthallium trimethyl bismuth,
triphenyl thallium tributyl bismuth,
tricumene thallium tributyl bismuth,

and the like.

When employing the bimetallic organometallic plating agents of this invention in the absence of a carrier gas, it is desirable to maintain enough vapor pressure below the decomposition temperature of the organometallic to enable the process to be conducted at an appreciable rate of plating. Too high vapor pressure results in poor substrate adherence. Thus, it is preferred to employ up to about 10 mm. pressure during the plating operation, preferably 0.01 to 10 mm. of pressure. When an inert carrier gas such as argon or other carrier gases such as hydrogen and carbon dioxide are employed in the process, it is desirable to employ a higher vapor pressure, e.g., between about 10 to 20 mm. of pressure. In this connection, however, it is to be noted that the partial pressure of the bimetallic organometallic is about 0.01 to about 10 mm. pressure during the plating operation.

Although temperatures above the decomposition temperature of the organometallic plating agent are generally employed (usually temperatures no higher than about 700° C. are used), a preferred temperature exists for each organometallic plating agent. When this temperature is employed, better plating results can be obtained. At these temperatures exceptionally brighter, better adhering coatings are obtained.

By the term alloy as employed herein is meant "a mixture of two or more metallic elements (or non-metals, such as—Te, P) which have a metallic appearance and which are either: (1) A molecular mixture, microscopically homogeneous; . . . (2) a colloidal mixture, microscopically heterogeneous"; . . . Hack's Chemical Dictionary, 3rd edition (1944), McGraw-Hill Book Co., Inc., page 34.

In some cases more uniform coating can be obtained through the employment of pack metalizing techniques. The plating agent when employed in such pack metalizing

technique is a solid such as chromium tris(aluminum tetraethyl). One of the advantages of employing such pack metalizing technique is that very uniform plating temperatures can be achieved because of the solid materials employed in this type of process. Pack metalizing involves packing the substrate to be plated into a metal or glass reaction vessel provided with a gas outlet means. (Usually a metal substrate is used.) With the plating agent is employed an inert filler material such as sand, refractory powders or any other material inert under the application conditions. Thus, the reaction vessel contains the object to be plated surrounded by the solid plating agent, the remaining space of the reaction vessel being filled with the aforesaid inert filler. The reaction container is thereafter placed in an induction heating furnace and the temperature of the furnace raised to a point above the decomposition temperature of the plating agent. The following example illustrates this technique more fully.

Example XLIII

20	Compound	Cr(AlEt ₄) ₃ (chromium tris - aluminum tetraethyl).
	Temp. of substrate	400° C.
25	Nature of substrate	Mild steel.
	Pressure	0.1 mm.
	Compound Temp.	—
	Time	1½ hours.
	Results	Dull, metallic.
30	Method	Pack metalizing.

In addition to the thermal and ultrasonic techniques discussed hereinabove, other methods for decomposition of the bimetallic organometallic plating agents of the instant invention can also be employed. These other methods encompass other techniques such as decomposition of the bimetallic organometallic plating agent with ultraviolet irradiation. In employing such a technique an apparatus substantially the same as employed in Example I is used with the exception that in place of the high frequency induction heating means a source of ultraviolet irradiation is employed. This ultraviolet technique is particularly applicable to those bimetallic organometallic compounds of this invention having good volatility characteristics.

Another decomposition technique which can be employed in achieving alloy plates from the plating agents of this invention involves chemical decomposition. Illustrative of such chemical decomposition is the decomposition of copper tetraethylaluminum by treating with acid (50 percent HCl) to produce a colloidal alloy decomposition.

In general, any substrate which is stable to decomposition at the temperatures employed in the plating process utilized are suitable substrates for this invention. Exemplary of the wide diversity of substrates which can be employed in the instant invention are metallic substrates such as ferrous metal substrates (particularly steel), aluminum, copper, yttrium, molybdenum, beryllium, and the like. Alloy substrates can also be employed which result in the deposition of an alloy upon an alloy material. Glass substrates such as Pyrex can be used. Other substrates which can be employed are ceramics, cermets, refractories such as alumina, graphite, and the like; plastics such as "Teflon" (e.g., polyfluoro hydrocarbons), and a multitude of cellulose materials such as wood, cloth, paper, etc.

Other bimetallic organometallic plating agents can be employed in the above working examples to produce similar alloy plating on the substrate to be plated. Thus, when tin tetramethylboron, scandium, tetraethylboron, tin triethylzinc, titanium triethylzinc, potassium triethylboron chloride, sodium indium tetracyclopentadienide, beryllium bis(boron cyclopentadienide) triethyl, strontium bis(gallium tetracyclopentadienide), zinc bis(aluminum tetracyclopentadienide) are employed in the examples de-

scribed above, alloy plates of the corresponding metals contained in each of these compounds are deposited upon the substrate plated.

The decomposition techniques of this invention can be varied so that, in some instances, substrates can be plated with one or both of the metals from the bimetallic organometallic compound while concurrently depositing therefrom metal powders. By such techniques it is possible to produce two useful materials from one plating agent, i.e., the plated article of manufacture and the concurrently deposited metallic powders.

The alloy depositions produced from bimetallic organometallic compounds according to the processes of this invention have many applications in the metallurgical and related arts. In the following working example the application of the processes of this invention to plating aircraft landing gear fabrication materials is illustrated.

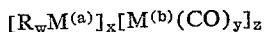
Example XLIV

A high performance steel aircraft landing gear structural member is placed in a conventional heating chamber provided with means for high frequency induction heating and gas inlet and outlet means. Lithium aluminum tetracyclopentadienide 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. The member is heated to a temperature of approximately 350° C. and the system is evacuated. The lithium aluminum tetracyclopentadienide is heated to a temperature (about 150° C.) where it possesses vapor pressure of up to about 10 mm. The lithium aluminum tetracyclopentadienide vapors are pulled through the system by a vacuum pump and they impinge on the heated aircraft landing gear structural member decomposing and forming a well adherent lithium-aluminum alloy coating over the entire surface of the structural member. In such a manner the structural member is coated with a high performance corrosion resistant lithium-aluminum alloy coating having high tensile strength for application to the extreme requirements of modern age aircraft. The compounds above may be used to plate substrates such as ceramics in order to obtain semi-conductors of great value in the electronics industry.

Having thus described the process of this invention, it is not intended that it be limited except as set forth in the following claims.

We claim:

1. A process for plating a substrate comprising heating the object to be plated to a temperature above the decomposition temperature of the bimetallic organometallic compound and contacting said bimetallic compound with said heated object, said bi-metallic organometallic compound being further defined as having the general formula



wherein

- (1) $M^{(a)}$ is a metal selected from the group consisting of the group IV-A metals and aluminum;
- (2) $M^{(b)}$ is a different metal selected from the groups consisting of groups IV-B, V-B, VI-B, VII-B and VIII;
- (3) R is an electron donating moiety individually selected from the group consisting of hydrocarbon and hydrogen;
- (4) w is an integer having a value of from 1 to 3, inclusive;
- (5) x and z are integers having a value from 1 to 2 and from 1 to 3, respectively, x and z being dependent

upon the identity of the metal $M^{(b)}$ in accordance with the following tabulated relationships:

	$w=1$	$w=2$	$w=3$
$M^{(b)}$ is a metal having an odd number of d orbital electrons.	$x=2, z=3$	$x=1, z=2$	$x=2, z=1$
$M^{(b)}$ is a metal having an even number of d orbital electrons.	$x=1, z=3$	$x=1, z=1$	$x=2, z=1$

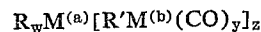
and

- (6) y is an integer from 1 to 5, inclusive, in accordance with the equation

$$y = \frac{G - m - N}{2}$$

in which G is the atomic number of the next rare gas of the metal $M^{(b)}$; m is an integer from 1 to 2 and is 1 when $M^{(b)}$ is a metal having an odd number of d orbital electrons and is 2 when $M^{(b)}$ is a metal having an even number of d orbital electrons; N is the atomic number of the metal $M^{(b)}$.

2. A process for plating a substrate comprising heating the object to be plated to a temperature above the decomposition temperature of the bimetallic organometallic compound and contacting said bimetallic compound with said heated object, said bi-metallic organometallic compound being further defined as having the formula



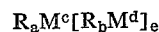
wherein

- (1) $M^{(a)}$ is a metal selected from the groups consisting of groups II-A, II-B, III-A, IV-A and V-A;
- (2) $M^{(b)}$ is a different metal selected from the groups consisting of the groups IV-B, V-B, VI-B, VII-B and VIII;
- (3) R is an electron donating moiety selected from the groups consisting of hydrocarbon and hydrogen;
- (4) R' is an unsaturated organo group containing up to 20 carbon atoms;
- (5) w is an integer having a value of from 0 to the valence of the metal $M^{(a)}$ minus 1;
- (6) z is an integer having a value of 1, 2 and 3 and is dependent on the valence of the metal $M^{(a)}$ minus the value of the integer w ;
- (7) y is an integer having a value of from 1 to 5, inclusive, in accordance with the equation

$$y = \frac{G_b - n - (\beta_b + 1)}{2}$$

in which G_b is an integer representing the number of electrons in the next inert gas after the metal $M^{(b)}$; n is an integer representing the atomic number of the metal $M^{(b)}$; and β_b is an integer representing the number of pi electrons of R' .

3. A process for plating a substrate comprising heating the object to be plated to a temperature above the decomposition temperature of the bimetallic organometallic compound and contacting said bimetallic compound with said heated object, said bimetallic organometallic compound being further defined as having the general formula



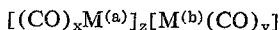
wherein

- (1) M^c is a metal selected from the group consisting of boron, aluminum, gallium, indium, and thallium;
- (2) M^d is a metal selected from the group consisting of selenium, tellurium, silicon, germanium, tin and lead;
- (3) The groups R represent electron donating moieties individually selected from the groups consisting of hydrocarbon and hydrogen;
- (4) a and b are integers having a value of from 0 to the valence of the respective metal minus 1;
- (5) e is an integer having a value of from 1 to the

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valence of the metal $M^{(a)}$ minus the value of the integer α .

4. A process for plating a substrate comprising heating the object to be plated to a temperature above the decomposition temperature of the bimetallic organometallic compound and contacting said bimetallic compound with said heated object, said bimetallic organometallic compound being further defined as having the general formula



wherein

- (1) $M^{(a)}$ is a metal selected from the groups consisting of the groups IV-B, V-B, VI-B, VII-B and VIII;
- (2) $M^{(b)}$ is a different transition metal selected from the groups consisting of IV-B, V-B, VII-B and VIII of the periodic chart of the elements;
- (3) x is an integer having a value of 1 to 5, inclusive, in accordance with the equation

$$x = \frac{G - m - N}{2}$$

in which G is the atomic number of the next rare gas of the metal $M^{(a)}$; m is an integer having a value of 1 where the number of d orbital electrons in the outermost shell of the metal $M^{(a)}$ is odd and 2 where the number of d orbital electrons in the outermost shell of the metal $M^{(a)}$ is even; N is the atomic number of the metal $M^{(a)}$;

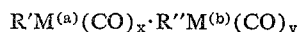
- (4) y is an integer having a value of 1 to 5, inclusive, in accordance with the equation

$$y = \frac{G - m - N}{2}$$

in which G is the atomic number of the next rare gas of the metal $M^{(b)}$; m is an integer equaling 1 where the number of d orbital electrons in the metal $M^{(b)}$ is odd and 2 where the number of d orbital electrons in the metal $M^{(b)}$ is even; N is equal to the atomic number of the metal $M^{(b)}$;

- (5) z is an integer having the value of 1 when the number of d orbital electrons in the metals $M^{(a)}$ and $M^{(b)}$ is odd and a value of 2 when the number of d orbital electrons in the metals $M^{(a)}$ and $M^{(b)}$ is even.

5. A process for plating a substrate comprising heating the object to be plated to a temperature above the decomposition temperature of the bimetallic organometallic compound and contacting said bimetallic compound with said heated object, said bimetallic organometallic compound being further defined as having the general formula



wherein

- (1) $M^{(a)}$ is a transition metal selected from the groups consisting of the groups IV-B, V-B, VI-B, VII-B, and VIII;
- (2) $M^{(b)}$ is a different transition metal selected from the groups consisting of IV-B, V-B, VI-B, VII-B and VIII;
- (3) R' and R'' are unsaturated organo groups containing up to about 25 carbon atoms;
- (4) x is an integer having a value of from 1 to 5, inclusive, in accordance with the following equation:

$$x = \frac{G_a - n_a - (\beta_a + 1)}{2}$$

in which G_a represents the number of electrons in the next inert gas after the metal $M^{(a)}$; n_a equals the atomic number of the metal $M^{(a)}$; and β_a represents the number of pi electrons in R' ;

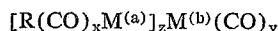
- (5) y is an integer having a value of from 1 to 5, inclusive, in accordance with the following equation:

$$y = \frac{G_b - n_b - (\beta_b + 1)}{2}$$

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wherein G_b represents the number of electrons in the next inert gas after the metal $M^{(b)}$; n_b equals the atomic number of the metal $M^{(b)}$; and β_b represents the number of pi electrons in R'' .

6. A process for plating a substrate comprising heating the object to be plated to a temperature above the decomposition temperature of the bimetallic organometallic compound and contacting said bimetallic compound with said heated object, said bimetallic organometallic compound being further defined as having the general formula



wherein

- 15 X (1) $M^{(a)}$ is a metal selected from the groups consisting of groups IV-B, V-B, VI-B, VII-B and VIII;
- (2) $M^{(b)}$ is a different transition metal selected from the groups consisting of groups IV-B, V-B, VI-B, VII-B and VIII;
- 20 (3) R is an unsaturated organo compound containing up to about 25 carbon atoms;
- (4) x is an integer having a value of from 1 to 5, inclusive, in accordance with the following equation:

$$x = \frac{G_a - N_a - (\beta_a + 1)}{2}$$

in which G_a is the number of electrons in the next inert gas after the metal $M^{(a)}$; N_a is the atomic number of the metal $M^{(a)}$; and β_a is equal to the number of pi electrons in the group R ;

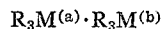
- (5) y is an integer having a value of from 1 to 5, inclusive, in accordance with the following equation:

$$y = \frac{G_b - m_b - N}{2}$$

in which G_b represents the atomic number of the next rare gas of the metal $M^{(b)}$; m_b is an integer having the value of 1 where the number of d orbital electrons in the metal $M^{(b)}$ is odd and a value of 2 where the number of d orbital electrons of the metal $M^{(b)}$ is even; and N equals the atomic number of the metal $M^{(b)}$;

- (6) z is an integer having the value of 1 when the number of d orbital electrons of the metal $M^{(b)}$ is odd and 2 when the number of d orbital electrons in said metal is even.

7. A process for plating a substrate comprising heating the object to be plated to a temperature above the decomposition temperature of the bimetallic organometallic compound and contacting said bimetallic compound with said heated object, said bimetallic organometallic compound being further defined as having the general formula



wherein

- (1) $M^{(a)}$ is a metal selected from the group consisting of boron, aluminum, gallium, indium and thallium;
- (2) $M^{(b)}$ is a metal selected from the group consisting of phosphorus, arsenic, antimony and bismuth;
- (3) R is an electron donating moiety selected from the groups consisting of hydrogen and hydrocarbon.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,071,493

January 1, 1963

Thomas P. Whaley et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 41, strike out "V-B," first occurrence; column 5, line 48, for "(1957)" read -- (1947) --; column 13, line 68, after "tetracyclohexylaluminum" insert a comma; line 70, strike out "boron, lithium tetrabutadienylboron; lithium ethyltributyl-" and insert instead -- lithium tetra-naphthylboron, lithium tetracyclohexenylboron, lithium tetrabutadienylboron; lithium ethyltributyl- --; column 25, line 14, after "V-B," insert -- VI-B, --; column 26, line 15, for "X (1)" read -- (1) --.

Signed and sealed this 3rd day of September 1963.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents

**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,071,493

January 1, 1963

Thomas P. Whaley et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 41, strike out "V-B," first occurrence; column 5, line 48, for "(1957)" read -- (1947) --; column 13, line 68, after "tetracyclohexylaluminum" insert a comma; line 70, strike out "boron, lithium tetrabutadienylboron; lithium ethyltributyl-" and insert instead -- lithium tetra-naphthylboron, lithium tetracyclohexenylboron, lithium tetrabutadienylboron; lithium ethyltributyl- --; column 25, line 14, after "V-B," insert -- VI-B, --; column 26, line 15, for "X (1)" read -- (1) --.

Signed and sealed this 3rd day of September 1963.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents