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METAL PLATING PROCESS UTILIZING BIS (ARENE)METAL COMPOUNDS

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This application is a continuation-in-part of copending applications Serial No. 612,962, filed October 1, 1956, and issued on September 20, 1960, as United States Patent 2,953,586, and Serial No. 676,389, filed August 5, 1957, as a continuation-in-part of the aforesaid application Serial No. 612,962 and issued on January 25, 1966, as United States Patent 3,231,593.

This invention relates to a metal plating process. More particularly the invention relates to a process for utilizing volatile bis(arene)metal compounds as metal plating agents.

Heretofore several processes have been suggested for metal plating by means of volatile metal-containing compounds. In general, these processes have been subject to contamination of the metal plate due to oxide or carbide formation or the occlusion of undesirable solid materials in the metal plate. The nature of this contamination is discussed in more detail hereinbelow.

It is, therefore, an object of this invention to provide a process for utilizing uncharged, volatile bis(arene)metal compounds in a metal plating process.

A further object of the invention is to provide a metal plating process which is not subject to the disadvantages of the metal plating processes currently known.

A still further object of the invention is to provide a process for depositing substantially pure metal plates on a wide variety of platable solid substrates.

Other objects of the invention will be apparent from the following description and appended claims.

The bis(arene)metal compounds useful in the process of this invention are those wherein the arene organic groups are aromatic hydrocarbons containing an isolated benzene ring or are aryl-substituted benzenes. The nature of these arene organic groups is discussed in more detail hereinbelow.

The compounds useful in this invention may, from the point of view of their organic moiety, be characterized as addition compounds in contrast to organo-metallic substitution compounds wherein a hydrogen or other substituent in the organic nucleus is substituted or removed in formation of an organo-metallic compound. Thus the compounds used in the present invention are to be distinguished from those formed by the chemical bonding of a cyclopentadienyl radical with an element (Fischer and Pfab, Zeit. fur Naturforschung, 7b, page 377 (1952)), and phenyl mercury compounds, e.g., phenyl mercuric acetate (U.S. Patent 2,502,222). Formation of such substitution compounds involves elimination of one hydrogen on the cyclopentadiene or benzene nucleus. In the case of the compounds of the present invention the chemical union of the transition element with the aromatic compound does not involve elimination of hydrogen or any other substituent on the benzene nucleus. It may, therefore, be regarded as an addition product of the transition element with the aromatic organic molecule. Such addition of an aromatic compound to a transition element is an unexpected characteristic of aromatic compounds.

As employed in this application the term "isolated benzene ring system" means a benzene carbon ring per se and as contained in a fused ring compound containing a benzene carbon ring wherein, by the Kekule formulation, any

double bond in a ring fused to such benzene carbon ring is removed from the benzene ring carbon atom nearest to it by at least two carbon atoms of the ring fused to the benzene ring, and a compound having one or more aliphatic substituents on a benzene ring wherein any double bond external to the carbon ring is removed from the benzene ring carbon atom nearest to it by at least two carbon atoms external to such benzene carbon ring. Thus, benzene, aliphatic substituted benzenes, including alkyl substituted benzenes and alkenyl substituted benzenes in which double bonds external to the benzene ring are separated therefrom by at least two carbon atoms, indane, tetrahydronaphthalene, 9,10-dihydroanthracene, 9,10-dihydrophenanthrene and allyl benzene are examples of aromatic compounds containing an isolated benzene ring system. By contrast naphthalene, indene, anthracene, phenanthrene and styrene are examples of aromatic compounds which do not contain an isolated benzene ring.

This difference in the isolated and not isolated benzene ring systems may be explained in terms of the characteristics of the two types of compounds with respect to their aromatic nature. The fusion of a benzene ring to another aromatic ring in conjugated relation thereto, or linkage of a ring carbon atom of a benzene ring to an unsaturated aliphatic radical wherein the ring carbon is linked to an aliphatic carbon atom which in turn is linked by a double bond to another aliphatic carbon atom, may be considered as orienting the double bonds in the benzene ring, thus producing a ring structure of less reactivity than is characteristic of an isolated benzene ring and rendering the electrons in the double bonds of the benzene ring unavailable for reaction with the transition element halides. This essential characteristic may also be explained upon energy considerations. The fusion of an aromatic ring to the benzene ring in conjugated relation and the inclusion of an unsaturated aliphatic radical on the benzene ring with the unsaturation in the aliphatic constituent being in conjugated relation with double bonds in the benzene ring may be considered as decreasing the energy and concomitantly increasing the stability of the ring to such a point that the compounds useful in this invention cannot be prepared.

A class of arene hydrocarbons which do not contain an isolated benzene ring, namely aryl-substituted benzenes, also form organo-metallic compounds useful in the present invention. Examples of such aryl-substituted benzenes are polyphenyls, alkyl-substituted polyphenyls such as p-isopropyldiphenyl and p-p'-dimethyldiphenyl, phenylanthracene and phenylphenanthrene.

The compounds useful in the process of this invention may be represented by the formula

$$(Ar)_2M$$

wherein Ar represents an organic hydrocarbon compound which may be an aromatic hydrocarbon containing an isolated benzene ring or an aryl-substituted benzene, the organic compound being bound to a transition element M, and M is vanadium, niobium, tantalum, chromium, molybdenum or tungsten.

Moreover the metal complexes may have mixed Ar substituents and consequently may have the formula

$$(Ar)(Ar')M$$

wherein the symbols are the same as above except that Ar' is different from Ar.

The exact nature of the bond between the Ar portion of the molecule and the transition element is unknown; however, it is known that the isolated benzene ring or the benzene ring of the aryl-substituted benzene is complexed to the transition element.

A method by which compounds useful in the present invention may be produced involves reacting an anhydrous transition element salt, preferably a transition element halide, with an aromatic compound having at least one isolated benzene ring system or with an aryl-substituted benzene in the presence of an anhydrous aluminum halide and a reducing agent.

This method is described in the aforementioned United States Patents 2,953,586 and 3,231,593. In particular, detailed examples are given showing the preparation of bis(benzene)chromium, bis(benzene)molybdenum, bis(tetrahydronaphthalene)chromium, bis(benzene)vanadium, bis(toluene)chromium, bis(mesitylene)chromium, bis(hexamethylbenzene)chromium, bis(ortho - xylene)chromium, bis(meta-xylene)chromium, bis(para-xylene)chromium, bis(benzene)tungsten, (benzene)(tetrahydronaphthalene)chromium, and bis(diphenyl)chromium. Other compounds useful in this invention and included in the formula $(Ar)_2M$, such as bis(benzene)niobium, bis(benzene)tantalum, bis(diphenyl)molybdenum and bis(cumene)chromium are also prepared by this process.

Broadly stated the process of the present invention comprises contacting an uncharged, volatile bis(arene) metal compound with a platable solid substrate at a temperature above the decomposition temperature of the bis(arene)metal compound. In general this temperature will be above about 150° C. Temperatures considerably above the decomposition temperature of the diarene metal compound may be used and temperatures up to about 600° C. are operable. The upper limit of operable temperatures for the process of this invention is determined by the properties of the arene organic group. If the operating temperature is too high, the arene organic group will decompose to give carbon or polymerizable hydrocarbons such as ethylene and acetylene which may cause contamination of the metal plating. Thus, the lower operable temperature for the process is set by the decomposition temperature of the bis(arene)metal compound and the upper operable temperature limit is determined by the decomposition (cracking) temperature of the arene organic moiety.

The process of this invention must be carried out in substantially oxygen free surroundings. Oxygen may react with the diarene organic compound or other metal plate itself to form metal oxides which contaminate the metal plate. Also, oxygen-containing substances which will react with the plating compound or metal plate at the operating temperature must also be substantially excluded.

As pointed out hereinabove the process of the present invention applies to the bis(arene)metal compounds of vanadium, niobium, tantalum, chromium, molybdenum and tungsten wherein the arene group is an aromatic hydrocarbon compound containing an isolated benzene ring, or an aryl-substituted benzene. These are the transition elements which form neutral diarene metal compounds as opposed to those transition metal elements which form only salt-like compounds containing a diarene metal cation, for example, dimesitylene iron dibromide. The decomposition of the latter compounds may give a metal plate contaminated by occlusion of or reaction with elements or moieties present in the anionic portion of the compound.

Any platable solid substrate which is thermally stable at the plating temperature may be used in the process of the present invention. Platable substrates include glass, glass cloth, ceramics, plastics such as nylon and Bakelite, and a variety of metals such as copper, aluminum, stainless steel and silver.

The process of the present invention, which employs volatile bis(arene)metal compounds, is to be distinguished from processes employing other volatile metal-containing compounds. The compounds useful in the process of the present invention have the unique and important property of decomposing to give a substantially pure metal and a stable, volatile organic compound. It is the stable nature of the organic compound which makes possible the substantially pure and uncontaminated metal plates obtained by the process of this invention. In general, the volatile metal-containing compounds heretofore known contain some element or moiety which can cause contamination of the metal plate. For example, metal carbonyls such as chromium hexacarbonyl are volatile. When the metal carbonyl is decomposed, however, carbon and oxygen derived from the carbon monoxide which is released may react with the metal plate to form metal oxides or metal carbides. As another example, dicyclopentadienyl compounds such as dicyclopentadienyl iron are volatile. However, the cyclopentadienyl group which results from the decomposition of such compounds is not a stable entity. The cyclopentadienyl group polymerizes readily to form solid residues or decomposes to give carbon and polymerizable hydrocarbons. The resulting carbon and organic polymers cause contamination of the metal plate.

The contact between the bis(arene)metal compound and the platable substrate may be brought about by any convenient method. For example, vapors of the diarene metal compound may be passed over the heated substrate under subatmospheric pressure. Another suitable method is to pass the vapors of the diarene metal compound over the substrate by means of a carrier gas which is oxygen-free and which does not otherwise react with the metal plate or the diarene metal compound. Examples of suitable carrier gases are argon, nitrogen, helium and hydrogen. Atmospheric pressure is most convenient when a carrier gas is employed but higher or lower pressures may be used if desired. Still another suitable method is to dissolve the bis(arene)metal compound in a solvent and thereafter contact the resulting solution with a heated substrate. Other methods will occur to those skilled in the metal plating art. The contacting of the diarene metal compound with the platable substrate may be continued until a plate of the desired thickness is obtained.

The organo-metallic compounds of this invention may vary in heat stability but they may all be decomposed by the employment of temperatures in excess of 400° C. Such thermal decomposition of the compounds results in formation of metallic mirrors comprising a coating or film of the particular transition element. Such metallic coatings and films exhibit desirable and useful electrical conductance properties, furnish corrosion protection when applied to corrodible base materials and result also in striking decorative effects. Compounds of this invention may thus be deposited on glass, glass cloth, resin and other insulating substrates, and the resulting metal-coated material may be employed as strip conductors and resistors for electrical purposes. The metals may be deposited by thermal decomposition in desired portions of the substrate to provide the so-called printed electrical circuits. Similarly the metals may be plated on metal substrates to enhance corrosion resistance and on glass cloth or asbestos to provide decorative metallic surfaces and designs thereon.

In a preferred embodiment of the present invention bis(arene)metal compounds are used in which the arene organic group is benzene or a lower alkyl-substituted benzene. Such preferred compounds may be represented by the formulae R_2Cr, R_2Mo, R_2W, R_2V, R_2Nb and R_2Ta wherein R is benzene or a lower alkyl-substituted benzene. Examples of the preferred compounds are bis(benzene)vanadium, bis(toluene)vanadium, bis(benzene)chromium, bis(toluene)chromium, bis(cumene)chromium, bis(mesitylene)chromium, bis(benzene)molybdenum, bis(toluene)molybdenum, bis(mesitylene)molybdenum, bis(cumene)molybdenum, bis(benzene)tungsten and bis(toluene)tungsten.

A particularly useful mixture of compounds for chromium plating according to the process of this invention is a mixture of bis(xylene)chromium compounds. The pure compounds are all solids at room temperature, bis

(orthoxylene)chromium melting at about 142° C., bis (meta-xylene)chromium melting at about 34–36° C., and bis(para-xylene)chromium melting at about 110° C. However, a mixture of these three isomers is a liquid at room temperature. Thus it is possible to carry out the plating process in the liquid phase without employing an additional solvent for the bis(arene)chromium compound.

A preferred temperature for the process of this invention is a temperature about 75° C. above the decomposition temperature of the bis(arene)metal compound. This preferred temperature will vary from about 200° C. for bis(arene)molybdenum compounds up to about 350 to 400° C. for bis(arene)chromium and bis(arene)vanadium compounds.

When the substrate to be plated has relatively low thermal stability, another preferred embodiment of this invention involves the use of bis(polyphenyl)metal compounds which may be represented by the formula D_2M wherein D is diphenyl or a lower alkyl-substituted diphenyl and M is vanadium, niobium, tantalum, chromium, molybdenum or tungsten. Examples of such compounds are bis(diphenyl)chromium, bis(diphenyl)molybdenum, bis(diphenyl)tungsten, bis(diphenyl)vanadium, bis(p-isopropyldiphenyl)chromium, and bis(p,p'-dimethyldiphenyl)molybdenum. In general, such bis(diphenyl)metal compounds and bis(lower alkyl-substituted diphenyl) metal compounds decompose at lower temperatures than do the bis(benzene)metal compounds of bis(alkyl-substituted benzene)metal compounds. Thus, the use of compounds such as bis(diphenyl)chromium is particularly advantageous when the substrate has relatively low thermal stability and the plating process must be carried out at the lowest possible temperatures.

The following examples are illustrative of the plating process of the present invention.

Example I

Two strips of glass cloth were dried in an oven at 150° C. for one hour, after which they weighed 0.8503 and 0.8915 gram. Then, together with 0.2 gram of bis(benzene)chromium, they were sealed in an evacuated glass tube and heated at 400° C. for one hour. The tube was cooled and opened, and the cloth had a uniform metallic gray appearance. Gains in weight of the glass cloth were 0.0180 and 0.0189 gram. The cloth had a resistivity of approximately 2 ohms per centimeter. Each individual fiber was found to be conducting. Application of voltage across the cloth gave a rise in temperature as would be expected. Thus a conducting cloth has been prepared. This may be used for reduction of static charge, for decoration, reflective thermal insulation, protection and to provide a heating element.

Example II

The following were placed in a glass tube; 1.5 grams of bis(benzene)chromium, small glass rings, small pieces of copper and a stainless steel wrench. The tube was evacuated and sealed. It was then heated at 380° C. for 30 minutes, after which it was cooled and opened. The inner surface of the glass tube and the surface of the glass rings were coated with an adhering plate of chromium metal. The copper objects were similarly plated with an adhering coat as was the stainless steel wrench.

Example III

A small strip of glass cloth was placed in a Pyrex glass tube, which was sealed on one end. The tube and contents were dried in an oven for one hour. Bis(benzene)chromium (0.4 gram) was placed in the tube, which was then evacuated and sealed. The tube and contents were heated to 400° C. for one hour. During this period of time the inside of the glass tube and the glass cloth were plated with chromium metal. After cooling, the tube was opened. The glass cloth was shiny and metallic-appearing. The resistance was measured from one end to the other and was practically nil. The glass was parted down to an individual fiber. Even the individual fiber was metallic in appearance.

Example IV

Bis(toluene)vanadium is used according to the method of Example III to deposit vanadium metal plates on Pyrex glass tubing and glass fibers.

Example V

Bis(benzene)tungsten is used following the procedure of Example III to deposit tungsten metal plates on Pyrex glass tubing and glass fibers.

Example VI

A three foot length of Pyrex glass tubing 25 millimeters in diameter was fitted with an inlet tube and an exit tube and argon was passed through the system. In the upstream end of the 25 millimeter tube was placed a quartz boat containing one gram of bis(toluene)molybdenum. The downstream end of the tube was enclosed in a tube furnace and heated to 250° C. The portion of the tube near the quartz boat was then heated to about 100° C. to vaporize the bis(toluene)molybdenum into the argon stream. As the stream of bis(toluene)molybdenum in argon entered the zone heated to 250° C., rapid decomposition occurred and a shiny molybdenum metal plate formed on the inner walls of the glass tubing.

Example VII

Bis(diphenyl)molybdenum is used to deposit a molybdenum plate on glass according to the procedure of Example VI except that a temperature of only 200° C. is required to bring about rapid decomposition of the plating compound.

Example VIII

A three-foot section of Pyrex glass tubing one inch in diameter was fitted with an inlet tube and an exit tube. In the upstream end of the one-inch tube was placed a porcelain boat containing one gram of bis(benzene)chromium. In the downstream end was placed a graphite rod 2 inches long and ¾ inch in diameter. The downstream end was enclosed in a tube furnace and heated for one hour at 400° C. Then the porcelain boat was moved into the heated zone. The bis(benzene)chromium sublimed into the argon stream and decomposed on the surface of the boat and on the graphite rod. Both the porcelain and graphite surfaces were coated with a shiny chromium metal plate.

Example IX

Following the procedure of Example VIII, bis(cumene) chromium is used to deposit a chromium metal plate on porcelain and graphite.

What is claimed is:

1. A process for depositing a substantially pure metal plate on a platable solid substrate which comprises contacting a bis(arene)metal compound represented by the formula $(Ar)_2M$, wherein Ar is an organic hydrocarbon compound selected from the group consisting of aromatic hydrocarbons containing an isolated benzene ring and aryl-substituted benzenes and M is selected from the group consisting of vanadium, niobium, tantalum, chromium, molybdenum and tungsten, with a platable solid substrate at a temperature above the decomposition temperature of said bis(arene)metal compound but below the decomposition temperature of the arene moiety of said bis(arene) metal compound while excluding oxygen and reactive oxygen-containing substances.

2. Process in accordance with claim 1 wherein vapors of said bis(arene)metal compound are contacted with said substrate under reduced pressure.

3. Process in accordance with claim 1 wherein vapors of said bis(arene)metal compound are brought into con-

tact with said substrate by means of an inert, oxygen-free carrier gas.

4. Process in accordance with claim 1 wherein said bis(arene)metal compound is dissolved in a solvent and the resulting solution is brought into contact with said substrate.

5. Process in accordance with claim 1 wherein said temperature is about 75° C. higher than the decomposition temperature of said bis(arene)metal compound.

6. A process for depositing a substantially pure vanadium metal plate on a platable solid substrate which comprises contacting a bis(arene)vanadium compound represented by the formula R_2V, wherein R is selected from the group consisting of benzene and lower alkyl-substituted benzenes, with a platable solid substrate at a temperature above the decomposition temperature of said bis(arene)vanadium compound but below the decomposition temperature of the arene moiety of said bis(arene)chromium compound while excluding oxygen and reactive oxygen-containing substances.

7. A process for depositing a substantially pure chromium metal plate on a platable solid substrate which comprises contacting a bis(arene)chromium compound represented by the formula R_2Cr, wherein R is selected from the group consisting of benzene and lower alkyl-substituted benzenes, with a platable solid substrate at a temperature above the decomposition temperature of said bis(arene)chromium compound but below the decomposition temperature of the arene moiety of said bis(arene)chromium compound while excluding oxygen and reactive oxygen-containing substances.

8. Process in accordance with claim 7, wherein said bis(arene)chromium compound is bis(cumene)chromium.

9. Process in accordance with claim 7 wherein said bis(arene)chromium compound is a mixture comprising bis(ortho-xylene)chromium, bis(meta-xylene)chromium and bis(para-xylene)chromium.

10. A process for depositing a substantially pure molybdenum metal plate on a platable solid substrate which comprises contacting a bis(arene)molybdenum compound represented by the formula R_2Mo, wherein R is selected from the group consisting of benzene and lower alkyl-substituted benzenes, with a platable solid substrate at a temperature above the decomposition temperature of said bis(arene)molybdenum compound but below the decomposition temperature of the arene moiety of said bis(arene)molybdenum compound while excluding oxygen and reactive oxygen-containing substances.

11. A process for depositing a susbtantially pure tungsten metal plate on a platable solid substrate which comprises contacting a bis(arene)tungsten compound represented by the formula R_2W, wherein R is selected from the group consisting of benzene and lower alkyl-substituted benzenes, with a platable solid substrate at a temperature above the decomposition temperature of said bis(arene)tungsten compound but below the decomposition temperature of the arene moiety of said bis(arene)tungsten compound while excluding oxygen and reactive oxygen-containing substances.

12. A process for depositing a substantially pure metal plate on a platable solid substrate which comprises contacting a bis(arene)metal compound represented by the formula D_2M, wherein D is selected from the group consisting of diphenyl and lower alkyl-substituted diphenyls and M is selected from the group consisting of vanadium, niobium, tantalum, chromium, molybdenum and tungsten with a platable solid substrate at a temperature above the decomposition temperature of said bis(arene)metal compound but below the decomposition temperature of the arene moiety of said bis(arene)metal compound while excluding oxygen and reactive oxygen-containing substances.

13. In a process for metal plating a ferrous metal substrate by thermal decomposition of a chromium containing compound, the improvement which comprises depositing a substantially pure chromium plate on the ferrous metal substrate with a bis(aromatic)chromium penetration complex wherein each aromatic group is an uncharged aromatic nucleus complexed with the chromium atom, at a temperature above the decomposition temperature of said aromatic chromium complex but below the decomposition temperature of the aromatic moiety of said complex.

14. In a process for metal plating a platable solid substrate by the thermal decomposition of a chromium-containing compound, the improvement which comprises employing as said chromium-containing compound a bis(aromatic)chromium complex wherein each aromatic group is an uncharged aromatic nucleus complexed with the chromium atom.

15. In a process for metal plating a platable solid substrate by the thermal decomposition of a chromium-containing compound, the improvement which comprises depositing a substantially pure chromium plate on the substate with a bis(aromatic)chromium complex wherein each aromatic group is an uncharged aromatic nucleus complexed with the chromium atom at a temperature above the decomposition temperature of said complex but below the decomposition temperature of the aromatic moiety of said complex.

16. A process for depositing a substantially pure metallic mirror coating on a platable solid substrate which comprises contacting a bis(arene)metal compound represented by the formula $(Ar)_2M$, wherein Ar is an organic hydrocarbon compound selected from the group consisting of aromatic hydrocarbons containing an isolated benzene ring and aryl-substituted benzenes and M is selected from the group consisting of vanadium, niobium, tantalum, chromium, molybdenum and tungsten, with a platable solid substrate at a temperature above the decomposition temperature of said bis(arene)metal compound but below the decomposition temperature of the arene moiety of said bis(arene)metal compound while excluding oxygen and reactive oxygen-containing substances.

17. A process for plating with metal a solid substrate by thermal decomposition, which comprises heating a surface of the solid substrate to a temperature above the decomposition temperature of bis(benzene)chromium and contacting the heated surface with bis(benzene)chromium.

18. A process for plating a solid substrate with a metal plate which comprises contacting said solid substrate in an inert atmosphere with a bis(arene)metal compound of the formula R_2M, where R is selected from the group consisting of benzene and lower alkyl-substituted benzenes and M is selected from the group consisting of chromium, molybdenum and tungsten, at a temperature above the decomposition temperature of said bis(arene)metal compound.

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