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CATALYTIC CHROMIUM PLATING PROCESS EMPLOYING BIS(ARENE)CHROMIUM

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No Drawing, Filed May 18, 1965, Ser. No. 456,805
15 Claims. (Cl. 117-107.2)

This invention relates to processes for producing a chromium plate on a solid platable substrate. More particularly, this invention relates to an improved catalytic chromium plating process wherein the chromium plate is formed by thermal decomposition of a bis(arene)chromium compound in the presence of a sulfur-containing catalyst.

Heretofore, it was known that a chromium plate could be produced on a solid platable substrate by contacting the substrate with a bis(arene)chromium compound at a temperature at or above the thermal decomposition temperature of the bis(arene)chromium compound. While various embodiments of this process are operable, they all have at least one important characteristic in common. Namely, they entail the use of a plating, i.e., contact, temperature of at least about 300° C., and preferably at least about 350° C., in order to effect the thermal decomposition of the bis(arene)chromium compound.

Unfortunately, however, the necessity for utilizing such elevated plating temperatures limits the selection of substrates which can be plated in accordance with the process. Thus, for instance, the use of many synthetic resins, such as polyethylene and poly(vinyl chloride), etc., which decompose when heated to temperatures of about 300° C. and higher, is precluded in this regard. In addition, the use of such elevated temperatures may damage the temper of many steel products, particularly tempered spring steel, on which a chromium plate is often desirable. Further, the use of such elevated temperatures may be a hazard in plating large glass objects which are ordinarily subject to strain unless heating and cooling operations are slow, the latter, in turn, being an undesirable feature from a commercial point of view. Finally such elevated temperatures are often above the stability range of common gasketing materials, such as polytetrafluoroethylene, neoprene and rubber, etc., thereby limiting the type of apparatus employed in the plating operation, or complicating the construction of such apparatus.

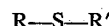
Advantageously, it has now been found that upon contacting a platable solid substrate in an inert atmosphere with a bis(arene)chromium compound in mutual contact with a sulfur-containing catalyst, the thermal decomposition of the bis(arene)chromium compound, producing a substantially pure chromium plate on the substrate, can be carried out at a temperature materially lower than that necessary in the uncatalyzed plating processes of the prior art, i.e., at temperatures as low as about 175° C., or lower. In this manner, substrates such as large glass objects, many synthetic resins, and tempered steels, etc., which are not thermally stable at the elevated temperatures employed in accordance with prior art plating techniques as indicated above, can now be plated satisfactorily through the practice of the improved process of this invention. At the same time, through the use of lower

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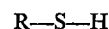
plating temperatures, a more convenient and economical plating process is made possible.

The present invention is based upon the discovery that the thermal decomposition of bis(arene)chromium compounds is catalyzed by sulfur-containing compounds which substantially lower the thermal decomposition temperature of the bis(arene)chromium compound when in contact therewith. Compounds serving as catalysts for the purposes of this invention are elemental sulfur and sulfur compounds wherein the substituents attached to the sulfur atom are composed of atoms from the group consisting of carbon, hydrogen, oxygen, nitrogen, and halogen. Sulfur-containing compounds contemplated in this regard include hydrogen sulfide, sulfur halides, carbon sulfides, dialkyl sulfides, thiols, sulfoxides, alkyl thiocyanates, alkyl isothiocyanates, and thiophenes.

Specifically illustrative of the sulfur-containing catalysts are sulfur; hydrogen sulfide; sulfur halides such as sulfur monochloride (S₂Cl₂), sulfur monobromide (S₂Br₂), sulfur dichloride (SCl₂) and sulfur tetrachloride (SCl₄); carbon sulfides such as carbon subsulfide (C₃S₂) and carbon disulfide (CS₂); dialkyl sulfides of the formula:



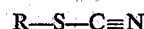
where R and R' are alkyl groups of 1 to 4 carbon atoms and may be the same or different, such as dimethyl sulfide, diethyl sulfide, di-n-propyl sulfide, di-n-butyl sulfide, and the like; thiols of the formula:



where R is as defined above, such as methyl mercaptan, ethyl mercaptan, n-butyl mercaptan, and the like; sulfoxides of the formula:



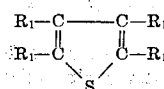
where R and R' are as defined above, such as dimethyl sulfoxide, diethyl sulfoxide, di-n-propyl sulfoxide, di-n-butyl sulfoxide, and the like; alkyl thiocyanates of the formula:



where R is as defined above, such as methyl thiocyanate, ethyl thiocyanate, n-butyl thiocyanate, and the like; alkyl isothiocyanates of the formula:



where R is as defined above, such as methyl isothiocyanate, ethyl isothiocyanate, n-propyl isothiocyanate, and the like; and thiophenes of the formula:



where each R₁ is either a hydrogen atom or a methyl group, such as thiophene, 2-methylthiophene, 2,5-dimethylthiophene, and the like.

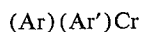
The bis(arene)chromium compounds contemplated by this invention are organometallic compounds in which the arene groups are uncharged aromatic hydrocarbons containing either an isolated benzene ring or an aryl-sub-

stituted benzene structure. As employed herein, the term "isolated benzene ring" is intended to define a benzene ring as contained in benzene itself, or in a fused ring polycyclic aromatic hydrocarbon containing a benzene ring, wherein, by the Kekule formulation, any double bond in a ring fused to such benzene ring is removed from the benzene ring carbon atom nearest to it by at least two carbon atoms. The term "isolated benzene ring" is also intended to define a benzene ring as contained in a monocyclic aromatic hydrocarbon having one or more aliphatic substituents on a benzene ring, wherein any double bond external to the benzene carbon ring is removed from the benzene ring carbon atom nearest to it by at least two carbon atoms. Thus, benzene, indane, tetrahydronaphthalene, 9,10-dihydroanthracene, 9,10-dihydrophenanthrene, alkyl-substituted benzenes such as toluene, ethylbenzene, butylbenzene, octylbenzene, etc., and alkenyl-substituted benzenes in which double bonds external to the benzene ring are separated therefrom by at least two carbon atoms, such as allylbenzene, etc., are examples of aromatic hydrocarbons containing an isolated benzene ring. By contrast, naphthalene, indene, anthracene, phenanthrene, and styrene are examples of aromatic hydrocarbons which do not contain an isolated benzene ring.

As also mentioned above, a class of aromatic hydrocarbons which do not contain an isolated benzene ring, namely aryl-substituted benzenes, also form bis(arene)-chromium compounds which are useful in the plating process of this invention. Examples of such aryl-substituted benzenes are polyphenyls, alkyl-substituted polyphenyls, such as p-isopropylidiphenyl and p,p'-dimethyldiphenyl, phenylanthracene and phenylphenanthrene.

The bis(arene)chromium compounds contemplated by this invention may, from the point of view of their organic moiety, be characterized as addition compounds in contrast to organometallic substitution compounds, wherein hydrogen or another substituent of the organic nucleus is substituted or removed in forming the organometallic compound. Thus, the bis(arene)chromium compounds are to be distinguished from the organometallic compounds formed by the chemical bonding of a cyclopentadienyl radical with an element (Fischer and Pfab, *Zeit. für Naturforschung*, 7b, page 377 (1952)), and from phenyl mercury compounds, e.g., phenyl mercuric acetate (U.S. Patent 2,502,222). Formation of such substitution compounds, it is to be noted, involves elimination of hydrogen from the cyclopentadiene or benzene nucleus. In the case of the bis(arene)chromium compounds of the present invention, the chemical union of the metal with the aromatic hydrocarbon does not involve the elimination of hydrogen or any other substituent of the organic nucleus. The bis(arene)chromium compounds may, therefore, be regarded as the addition products of chromium with aromatic hydrocarbons.

The bis(arene)chromium compounds contemplated by this invention can be represented more clearly by the formula $(Ar)_2Cr$, wherein Ar designates either an aromatic hydrocarbon containing an isolated benzene ring, or an aryl-substituted benzene, as hereinabove described. The bis(arene)chromium compounds can also have mixed Ar substituents, as more specifically represented by the formula:



wherein Ar and Ar' independently designate members of the same class of aromatic hydrocarbons. The exact nature of the bond between the aromatic hydrocarbon moiety and the metal is unknown. However, it is known that the isolated benzene ring or the benzene ring of the aryl-substituted benzene is complexed to the metal.

The bis(arene)chromium compounds contemplated by this invention include, by way of illustration, bis(benzene)chromium, bis(tetrahydronaphthalene)chromium, bis(toluene)chromium, bis(mesitylene)chromium, bis-

(hexamethylbenzene)chromium, bis(ortho-xylene)chromium, bis(meta-xylene)chromium, bis(para-xylene)chromium, bis(octylbenzene)chromium, (benzene)(tetrahydronaphthalene)chromium, bis(diphenyl)chromium, bis(cumene)chromium, and the like. The preferred bis(arene)chromium compounds are those in which the arene moiety is either benzene or a lower alkyl-substituted benzene in which the lower alkyl substituent(s) contain from 1 to about 8, and preferably from 1 to about 4 carbon atoms.

The bis(arene)chromium compounds can be prepared by reacting an anhydrous chromium salt, such as a chromium halide, with an aromatic hydrocarbon containing at least one isolated benzene ring, or with an aryl-substituted benzene, in the presence of an anhydrous aluminum halide and a reducing agent. The bis(arene)chromium compounds and methods for their production are described more fully in United States Patent 2,953,586 and such description is incorporated herein by reference.

The plating process of this invention, as hereinabove described, entails contacting a suitable substrate over the area to be plated with the bis(arene)chromium compound in mutual contact with a catalytic amount of sulfur-containing catalyst, and heating the bis(arene)chromium compound and sulfur-containing catalyst in contact with the substrate at a temperature of at least the decomposition temperature of the bis(arene)chromium compound when in contact with the catalyst. A substantially pure, ordinarily uniform chromium plate is thereby produced on the substrate. In addition, it is essential that the process of this invention be carried out in an inert atmosphere, i.e., in the absence of oxygen or oxygen-containing substances which react with the bis(arene)chromium compound, or with the resulting chromium plate itself, to form metal oxides which contaminate the plate.

The function of the sulfur-containing material employed in accordance with this invention being that of a catalyst, any amount thereof sufficient to catalyze the thermal decomposition of the bis(arene)chromium compound, resulting in the lowering of the decomposition temperature, can be utilized with satisfactory effect. Such amounts will vary to a certain extent depending upon the particular catalyst employed and the plating rate desired, and can readily be determined by one skilled in the art in light of this disclosure. Moreover, particularly good results can be obtained, for instance, employing the sulfur-containing catalyst in an amount varying in the range of from about 0.1 to about 5 weight percent, and preferably from about 0.2 to about 3 weight percent, based upon the amount of bis(arene)chromium compound employed. Within this range, an increase in the amount of catalyst ordinarily engenders a more rapid rate of plating. Greater amounts of catalyst can also be employed, although little additional advantage may accrue.

The plating temperature to be employed will vary to a certain extent, depending upon the particular bis(arene)chromium compound and catalyst employed, as well as upon the desired rate of plating. In general, however, satisfactory results can be obtained at a plating temperature of at least about 175° C. and less than about 300° C., and preferably in the range of about 175° C. to about 250° C., with more rapid plating occurring as the plating temperature is increased. Plating temperatures above 300° C. can also be employed, although the use of such higher temperatures may limit the type of substrate which can be plated, for reasons such as those described above in connection with the prior art. The maximum plating temperature is, for practical purposes, determined by the decomposition (cracking) temperature of the arene moiety of the bis(arene)chromium compound.

The heating period can also be varied broadly. Commercially acceptable plates can be obtained, for instance, by heating for a contact period of from about 10 minutes to about 3 hours, although somewhat shorter, as well as longer heating periods can also be employed. In general,

thicker plates are ordinarily produced as the heating period is extended.

Any platable solid substrate which is thermally stable at the temperature encountered can be used in the plating process of this invention in a variety of shapes or forms. By way of illustration, suitable substrates include glass, metals such as aluminum and iron, etc., thermoplastic and thermoset polymers such as poly(vinyl chloride), polyethylene, poly(ethylene terephthalate), the polyamide of isophthalic acid and metaphenylene diamine, polytetrafluoroethylene, polytrifluorochloroethylene, acrolein-pentaerythritol resins, etc., and the like. Moreover, the substrate can be in the form of single sheets, laminates, fibers, films, molded or shaped articles, etc.

The plating process of this invention can be carried out in various ways and any of the conventional vapor-phase plating techniques can be employed. In a preferred embodiment of the invention, the bis(arene)chromium compound is vaporized in a stream of inert gas and mixed, at a temperature below its decomposition temperature, with a second stream of inert gas containing the desired concentration of sulfur-containing catalyst. The mixture is then passed over the substrate, which is maintained at a temperature equal to or greater than the catalyzed decomposition temperature, whereby the bis(arene)chromium compound is decomposed on the surface of the substrate to produce a chromium plate. As will be apparent to one skilled in the plating art, the plating process can be made continuous with respect to both substrate and plating gas. In another embodiment of the invention, the substrate is initially contacted with the sulfur-containing catalyst by, for example, dipping the substrate into a solution of the catalyst in an inert solvent, such as ethanol, and subsequently evaporating the solvent, and then the bis(arene)chromium compound is vaporized in such manner that the resulting vapors are passed over and contacted with the substrate and catalyst at plating temperature.

Other means for bringing the substrate, bis(arene)chromium compound and sulfur-containing catalyst into mutual contact at a plating temperature so as to produce or deposit a chromium plate on the substrate will occur to those skilled in the art in light of this disclosure and can be employed within the contemplation of this invention.

The invention can be illustrated further by the following specific examples of its practice.

Example 1

A 1-inch by 3-inch glass microscope slide was inserted into the large end of a 32 mm. diameter glass tube, 9 inches in length, necked down to 8 mm. diameter at one end. The large end of the tube was sealed with a gas flame, the tube was purged with nitrogen through the open end, and then 0.3 cc. of dicumenechromium was introduced into the tube. Three times in succession, the tube was evacuated to 15 mm. of Hg absolute pressure and then brought back to atmospheric pressure by addition of hydrogen sulfide. The tube was then again evacuated to 15 mm. of Hg absolute pressure, sealed with a gas flame, and placed in a resistance-heated, forced-convection, thermostatically-controlled oven at 225° C. After 2 hours at this temperature, the tube was removed from the oven, cooled, and opened. Both the tube and the microscope slide were uniformly coated with a shiny and adherent chromium plate.

Example 2

A chromium plate was applied in an identical manner to that described in Example 1, except that the plating temperature was 200° C.

Example 3

A chromium plate was applied in an identical manner

to that described in Example 1, except that the plating temperature was 175° C.

Example 4

A 1-inch by 3-inch glass microscope slide was inserted into a glass tube similar to that described in Example 1, the tube was purged with nitrogen, and then 0.3 cc. of dicumenechromium and 0.03 cc. of thiophene were added to the tube. The tube was then evacuated to 0.5 mm. Hg absolute pressure, sealed with a gas flame, and placed in a resistance-heated, forced-convection, thermostatically-controlled oven at 225° C. After 2 hours at this temperature, the tube was removed from the oven, cooled, and opened. Both the tube and the microscope slide were uniformly coated with a shiny and adherent chromium plate.

Examples 5 to 10

In the same manner as that described above in Example 4, a chromium plate was applied to a glass microscope slide by decomposition of dicumenechromium employing various sulfur-containing catalysts and various plating temperatures, but with a 2-hour plating time in each case. For convenience, test conditions are summarized in the table below:

Example Number	Catalyst	Plating Temperature (° C.)
5-----	Methyl isothiocyanate-----	250
6-----	Dimethyl sulfide-----	250
7-----	Dimethyl sulfoxide-----	250
8-----	Carbon disulfide-----	225
9-----	Ethyl mercaptan-----	225
10-----	Sulfur monochloride-----	225

In each case, an adherent chromium coating was applied to the slide.

Efforts to chromium plate glass slides in an identical manner to that described in the above examples, but omitting the use of a sulfur-containing catalyst, were unsuccessful at temperatures of about 250° C. and evidence of plating was not observed under such conditions until the plating temperature reached 300° C., and then only after heating periods of several hours.

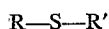
Although the invention has been illustrated by the preceding examples, it is not to be construed as limited to the materials employed therein, but rather the invention encompasses the generic area as hereinbefore disclosed. Various modifications and embodiments of this invention can be made without departing from the spirit and scope thereof.

What is claimed is:

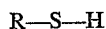
1. A process for producing a chromium plate on a platable solid substrate in an inert atmosphere, which process comprises contacting said substrate over the area to be plated with (a) a bis(arene)chromium compound of the formula $(Ar)_2Cr$ wherein Ar designates an organic hydrocarbon selected from the group consisting of aromatic hydrocarbons containing an isolated benzene ring and aryl-substituted benzenes, in mutual contact with (b) a catalytic amount of a sulfur-containing catalyst selected from the group consisting of elemental sulfur and sulfur compounds wherein the substituents attached to the sulfur atom are composed of atoms selected from the group consisting of carbon, hydrogen, oxygen, nitrogen and halogen, said catalyst being present in an amount sufficient to catalyze the thermal decomposition of said bis(arene)chromium compound, and heating said bis(arene)chromium compound and said catalyst in contact with said substrate at a temperature of at least the decomposition temperature of said bis(arene)chromium compound in contact with said catalyst and below about 330° C., thereby producing a chromium plate on said substrate.

2. A process for producing a chromium plate on a platable solid substrate in an inert atmosphere, which process comprises contacting said substrate over the area

to be plated with (a) a bis(arene)chromium compound of the formula $(Ar)_2Cr$ wherein Ar designates an organic hydrocarbon selected from the group consisting of aromatic hydrocarbons containing an isolated benzene ring and aryl-substituted benzenes, in mutual contact with (b) a catalytic amount of a sulfur-containing catalyst selected from the group consisting of elemental sulfur, hydrogen sulfide, the sulfur halides, the carbon sulfides, the dialkyl sulfides of the formula:



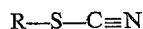
where R and R' are alkyl groups of 1 to 4 carbon atoms, the thiols of the formula:



where R is as defined above, the sulfoxides of the formula:



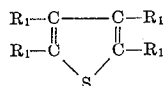
where R and R' are as defined above, the alkyl thiocyanates of the formula:



where R is as defined above, the alkyl isothiocyanates of the formula:



where R is as defined above, and the thiophenes of the formula:



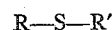
where each R_1 is independently selected from the group consisting of a hydrogen atom and a methyl group, said catalyst being present in an amount sufficient to catalyze the thermal decomposition of said bis(arene)chromium compound, and heating said bis(arene)chromium compound and said catalyst in contact with said substrate at a temperature of at least the decomposition temperature of said bis(arene)chromium compound in contact with said catalyst and below about 300° C., thereby producing a chromium plate on said substrate.

3. A process for producing a chromium plate on a platable solid substrate in an inert atmosphere, which process comprises contacting said substrate over the area to be plated with dicumenechromium in mutual contact with hydrogen sulfide, said hydrogen sulfide being present in an amount sufficient to catalyze the thermal decomposition of said dicumenechromium, and heating said dicumenechromium and said hydrogen sulfide in contact with said substrate at a temperature of from about 175° C. to about 250° C., thereby producing a chromium plate on said substrate.

4. A process for producing a chromium plate on a platable solid substrate in an inert atmosphere, which process comprises contacting said substrate over the area to be plated with sulfur monochloride, said sulfur monochloride being present in an amount sufficient to catalyze the thermal decomposition of said dicumenechromium, and heating said dicumenechromium and said sulfur monochloride in contact with said substrate at a temperature of from about 175° C. to about 250° C., thereby producing a chromium plate on said substrate.

5. A process for producing a chromium plate on a platable solid substrate in an inert atmosphere, which process comprises contacting said substrate over the area to be plated with dicumenechromium in mutual contact with carbon disulfide, said carbon disulfide being present in an amount sufficient to catalyze the thermal decomposition of said dicumenechromium, and heating said dicumenechromium and said carbon disulfide in contact with said substrate at a temperature of from about 175° C. to about 250° C., thereby producing a chromium plate on said substrate.

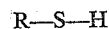
6. A process for producing a chromium plate on a platable solid substrate in an inert atmosphere, which process comprises contacting said substrate over the area to be plated with dicumenechromium in mutual contact with a dialkyl sulfide of the formula:



where R and R' are alkyl groups of 1 to 4 carbon atoms, said dialkyl sulfide being present in an amount sufficient to catalyze the thermal decomposition of said dicumenechromium, and heating said dicumenechromium and said dialkyl sulfide in contact with said substrate at a temperature of from about 175° C. to about 250° C., thereby producing a chromium plate on said substrate.

7. The process according to claim 6 wherein the dialkyl sulfide is dimethyl sulfide.

8. A process for producing a chromium plate on a platable solid substrate in an inert atmosphere, which process comprises contacting said substrate over the area to be plated with dicumenechromium in mutual contact with a thiol of the formula:



where R is an alkyl group of 1 to 4 carbon atoms, said thiol being present in an amount sufficient to catalyze the thermal decomposition of said dicumenechromium, and heating said dicumenechromium and said thiol in contact with said substrate at a temperature of from about 175° C. to about 250° C., thereby producing a chromium plate on said substrate.

9. The process according to claim 8 wherein the thiol is ethyl mercaptan.

10. A process for producing a chromium plate on a platable solid substrate in an inert atmosphere, which process comprises contacting said substrate over the area to be plated with dicumenechromium in mutual contact with a sulfoxide of the formula:



where R and R' are alkyl groups of 1 to 4 carbon atoms, said sulfoxide being present in an amount sufficient to catalyze the thermal decomposition of said dicumenechromium, and heating said dicumenechromium and said sulfoxide in contact with said substrate at a temperature of from about 175° C. to about 250° C., thereby producing a chromium plate on said substrate.

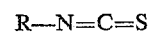
11. The process according to claim 10 wherein the sulfoxide is dimethyl sulfoxide.

12. A process for producing a chromium plate on a platable solid substrate in an inert atmosphere, which process comprises contacting said substrate over the area to be plated with dicumenechromium in mutual contact with an alkyl thiocyanate of the formula:



where R is an alkyl group of 1 to 4 carbon atoms, said alkyl thiocyanate being present in an amount sufficient to catalyze the thermal decomposition of said dicumenechromium, and heating said dicumenechromium and said alkyl thiocyanate in contact with said substrate at a temperature of from about 175° C. to about 250° C., thereby producing a chromium plate on said substrate.

13. A process for producing a chromium plate on a platable solid substrate in an inert atmosphere, which process comprises contacting said substrate over the area to be plated with dicumenechromium in mutual contact with an alkyl isothiocyanate of the formula:



where R is an alkyl group of 1 to 4 carbon atoms, said alkyl isothiocyanate being present in an amount sufficient to catalyze the thermal decomposition of said dicumenechromium, and heating said dicumenechromium and said alkyl isothiocyanate in contact with said substrate at a

temperature of from about 175° C. to about 250° C., thereby producing a chromium plate on said substrate.

14. The process according to claim 13 wherein the alkyl isothiocyanate is methyl isothiocyanate.

15. A process for producing a chromium plate on a platable solid substrate in an inert atmosphere, which process comprises contacting said substrate over the area to be plated with dicumenechromium in mutual contact with thiophene, said thiophene being present in an amount sufficient to catalyze the thermal decomposition of said dicumenechromium, and heating said dicumenechromium and said thiophene in contact with said substrate at a

temperature of from about 175° C. to about 250° C., thereby producing a chromium plate on said substrate.

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