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ALUMINUM PLATING PROCESS

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13 Claims

ABSTRACT OF THE DISCLOSURE

A process for providing at least two distinct superimposed coatings on a substrate material, one coating comprising a film of metallic aluminum adjacent to said substrate and the other comprising a protective resin overcoat for said aluminum. The process comprises depositing an aluminum hydride decomposition metal catalyst on said substrate; depositing an aluminum hydride material on said substrate in contact with said catalyst; immersing the substrate in a heated inert liquid bath containing a dissolved resin overcoating material thereby decomposing said aluminum hydride material and providing a metallic aluminum coating on said substrate; removing said aluminum coated substrate from said bath and removing the inert liquid to provide a resin overcoat on said metallic aluminum coating.

BACKGROUND

It is known that metallic aluminum may be plated from aluminum hydrides by contacting such hydrides with a substrate at or above the decomposition temperature of the aluminum hydride. Such a process usually requires relatively high temperatures to cause decomposition of the aluminum hydride and therefore cannot be used to plate aluminum onto many heat sensitive substrates. Necessary heat is usually applied to these reaction systems by such means as convection ovens, heat guns, radiant heat and the like. It is difficult to maintain critical temperature control when employing such heating means. Consequently the plates thus formed are not consistently of a uniform adherent nature. It would be highly desirable, therefore, to have a process which would permit the uniform plating of aluminum at relatively low temperatures.

Also, since many aluminum hydride compounds are unstable in the presence of water, it is desirable to plate the hydrides in a substantially anhydrous inert atmosphere. A further desideratum of the art, therefore, is to provide a method allowing the use of water-unstable hydrides.

A substrate which has been coated with a thin aluminum film is usually also coated with a resin overcoating, e.g., lacquer, to protect the soft aluminum from scratches, tarnishing and to preserve the mirror-like surface. Previously, it has taken at least two distinct process steps to provide these coatings; an aluminum plating step and an overcoating step. It would be desirable, therefore, to provide a process which would permit the uniform plating of metallic aluminum at relatively low temperatures, and overcoat in one operation. This would allow the plating of heat sensitive substrates and reduce the number of stations in the process and the amount of time involved in preparing the finished product. The present invention allows

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for the deposition of both an aluminum and a protection overcoat at lower temperatures, with more precise control over the reaction conditions than heretofore possible and also decreases the number of operational steps usually required.

SUMMARY

The present invention comprises depositing on a substrate a transition metal catalyst capable of decomposing aluminum hydrides to form metallic aluminum coatings at a relatively low temperature; depositing on said substrate in the presence of the catalyst an aluminum hydride compound; immersing said catalyst and aluminum hydride coated substrate in a heated inert liquid bath containing a dissolved overcoating substance; maintaining the substrate in the bath to decompose the aluminum hydride compound, thereby forming a metallic aluminum coating on the substrate; removing the aluminum coated substrate from the bath and removing the inert liquid to deposit an overcoat consisting of the resin overcoating substance.

PREFERRED EMBODIMENT

In the practice of the present invention, substantially any solid material is suitable as a substrate. For example, metals such as iron, magnesium, brass and copper, polymers such as polyolefins, polyamides, polyesters and polymeric fluorocarbons, glass, paper, cloth, carbon and graphite, wood, ceramics and the like can all be plated with aluminum and overcoated by the process of this invention. The nature of the surface being plated determines to a large extent the brightness of the aluminum plate. In general, the use of a smooth, nonporous surface such as found on most metals and some polymer films produces a brighter plate than a relatively porous surface such as those encountered with paper or cloth. On the surfaces of some polymers such as polyethylene, polytetrafluoroethylene, acrylonitrile-butadiene-styrene terpolymers and polypropylene, it has been found that even better adhesion of the aluminum plate is achieved if the surface has been made more polar, e.g., by sulfonation, corona discharge and the like, prior to plating with the aluminum. Various shaped objects may also be plated by the process such as, for example, whisker materials, reflectors, automobile trim and other decorative objects.

The term "aluminum hydride" is used herein in its broad sense and is meant to include any hydride compound which contains at least one aluminum atom to which at least one hydrogen atom is directly bonded and includes both the solvated and non-solvated forms of those aluminum hydrides occurring in both forms. Included, therefore, are aluminum trihydride, the substituted aluminum hydrides such as those having the empirical formula AlH_nX_{3-n} wherein X is a halogen, an —OR group or an —R group (wherein R is an alkyl, substituted alkyl, aryl or substituted aryl group) and n has a numerical value equal to or less than 3. Also included are the complex aluminum hydrides such as $LiAlH_4$, $NaAlH_4$, $Mg(AIH_4)_2$ and the like and complex substituted aluminum hydrides such as those having the empirical formula $M(AIH_mX_{4-m})_a$ wherein X has the definition given above, m has a numerical value equal to or less than 4 and M is a metal or mixture of metals, preferably an alkali or alkaline earth metal and "a" has a numerical value equal to the valence of M. Of particular utility are the relatively simple aluminum hydrides containing at

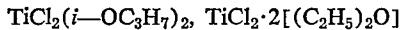
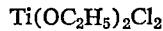
least two hydrogen atoms attached to the aluminum, e.g., AlH_3 , AlH_2Br , LiAlH_4 , and the like. Mixtures of the various aluminum hydrides may also be employed.

It is usually desirable for ease of application to employ the aluminum hydride in solvated form. Compounds known to solvate or form complexes with the aluminum hydrides include ethers and other oxygen-containing organic compounds, and compounds containing a functional group such as divalent sulfur atom, or trivalent nitrogen or trivalent phosphorous atom which is capable of allowing the solvation of an aluminum hydride with such compound. It is usually preferred that the solvate be an etherate and a wide variety of ethers containing from about 2 to about 20 carbon atoms are suitable. Usually the lower aliphatic ethers such as ethyl, propyl, or butyl ethers are employed but those containing an aromatic group such as methylphenyl ether, ethylphenyl ethers, propylphenyl ether or the alicyclic ethers such as tetrahydrofuran and the like may be employed.

In general, to achieve ease and uniformity of application of the aluminum hydride compound, any solvent or mixture of solvents or suspending agents for the aluminum hydride may be employed which will not react with the aluminum hydride beyond the formation of a complex or solvate. Suitable solvents include aromatic hydrocarbons such as benzene, toluene and xylene, aliphatic hydrocarbons such as hexane, ethers, tertiary amines and the like.

If desired, such aluminum hydrides may be prepared in situ simultaneously with the plating step by employing aluminum hydride-forming reactants such as mixtures of lithium aluminum hydride and aluminum chloride, or sodium aluminum hydride and aluminum bromide, or the like. The presence of a metal halide such as LiCl , MgCl_2 or AlCl_3 together with the aluminum hydride is not detrimental to the plating reaction.

In order to produce decomposition of the aluminum hydrides below their normal decomposition temperatures and to cause the aluminum thus produced to form a coating or plate on the substrate, it is necessary to contact the aluminum hydride with certain transition metal decomposition catalysts. Transition metal decomposition catalysts useful herein are compounds of the metals occurring in Groups IVb and Vb of the periodic table. In instances where the catalyst is applied to the substrate in a solvent, is preferable that the metal be in the form of a compound which is soluble to the extent of at least 1×10^{-6} weight percent of the solvent employed. For example, such compounds as ZrCl_4 , NbCl_5 , VOCl_2 , VOCl_3 , $\text{TiCl}_4 \cdot 2[(\text{C}_2\text{H}_5)_2\text{O}]$, TiCl_4 , TiBr_4 , VCl_4 ,



$\text{Ti}(\text{BH}_4)_3 \cdot 2[(\text{C}_2\text{H}_5)_2\text{O}]$ have proved effective. Some of the transition metal catalysts defined herein have a more pronounced effect than others in lowering the decomposition temperature of the aluminum hydride. The chlorides, bromides and oxychlorides of titanium, niobium, vanadium and zirconium generally seem to be more effective than the other compounds of Group IVb and Vb transition metals and TiCl_4 has been found particularly effective in achieving lower temperature decomposition of the aluminum hydrides and plating of the aluminum thus produced. If the defined catalysts are not employed, undesirably high temperatures are required to produce decomposition of the aluminum hydride. At such elevated temperatures, even when decomposition is achieved, there is usually no aluminum coating or plate formed thereby.

The transition metal decomposition catalyst is preferably applied to the substrate prior to contact with the aluminum hydride. Such decomposition catalyst may be applied to the substrate directly as a finely divided solid, as a liquid solution or suspension or, where the nature of the catalyst and the substrate permit, deposited by

5 vapor deposition. Preferably, however, the substrate is contacted with a sufficient quantity of a relatively dilute solution of the catalyst to wet the surface of the substrate. The solvent for the catalyst is then removed, e.g., by evaporation, leaving the catalyst substantially uniformly dispersed over the surface to be plated. Catalyst solutions at least about 1×10^{-6} weight percent in decomposition catalyst, and preferably in concentrations of from about 5×10^{-5} to about 100 weight percent of catalyst when applied to the substrate provide sufficient catalyst to achieve plating of aluminum from an aluminum hydride at a significantly lower temperature than is possible where no catalyst is employed. It has been found that uniformity of distribution of the catalyst on the 10 substrate has a significant effect on both the uniformity and thickness of the aluminum plate. It is, therefore, desirable to apply the catalyst to the substrate in a manner which will assure relatively uniform distribution.

15 For substrates, such as magnesium metal and some solid polymers, having surface characteristics making uniform distribution of a catalyst solution or aluminum hydride difficult to achieve, it has been found advantageous to add to such solution a small amount, e.g., from about 0.0001 to about 5.0 weight percent, of a wetting agent. Suitable wetting agents include, for example, stearates such as sodium or aluminum stearate or aluminum alkoxides such as aluminum isopropoxide.

20 Solvents for the transition metal decomposition catalysts are those normally liquid materials in which the catalyst is soluble to at least the extent of 1×10^{-6} weight percent, which will not adversely effect the substrate and which will not change the anion of the catalyst sufficiently to render it insoluble. Suitable solvents include non-reactive solvents such as benzene, hexane, and halogenated 25 hydrocarbons, reactive solvents such as alcohols, aldehydes, ketones, mercaptans, carboxylic acids and mineral acids, and coordinating solvents such as ethers, nitriles, amides and amines.

20 By application of the transition metal decomposition catalyst to only selected areas of the substrate, it is possible to form an aluminum plate only on such selected areas. In this manner, ornamental designs, outlines, printed circuits and the like may be produced. Likewise, all or a portion of a selected substrate may be coated or plated with 35 aluminum to enhance the ability of such surface to adhere to other materials. Of particular utility is the aluminum coating of glass, ceramic, metal or polymer surfaces to enhance their bonding to adhesive polymers and copolymers such as the copolymers of ethylene and acrylic acid.

35 Once the desired form and quantity of decomposition catalyst is applied to the substrate, the catalyzed substrate surface is contacted with a suitable form of aluminum hydride. In general, it is desirable to apply the aluminum hydride as a solution or suspension from 0.1 molar to 1.0 molar or more in aluminum hydride which may be applied by dipping, spraying or other suitable means. However, 45 good results are also achieved by contacting the catalyzed substrate surface with a finely divided solid aluminum hydride.

40 The solvent for the aluminum hydride compound is usually evaporated and the so-treated substrate is then immersed in a hot inert liquid bath containing a dissolved over-coating material.

45 The inert liquid bath can consist of any substance which is a liquid at elevated temperatures, usually at temperatures of from 50 to about 200° C. and which is substantially inert to a aluminum hydride and the particular substrate employed. The bath should be substantially anhydrous i.e., usually containing less than about 20 parts per 50 million of water, due to the sensitivity of most aluminum hydride to moisture. Likewise, the application of the aluminum hydride compound to the substrate material should be conducted in a substantially anhydrous inert atmosphere for best results. Suitable materials for preparing the bath consist of, for example, naphtha, ethylbutylbenzene,

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ethylbenzene, diphenyl ether, octadecane, xylene and other like materials. Other inert aliphatic, aromatic and ether compounds which are liquid at the indicated temperature range can be employed. The bath however, should not be prepared from compounds which contain active species such as alcohols, ketones, aldehydes, esters, acids and unsaturated aliphatics since the aluminum plate which develops will be dark, uneven and the substrate will contain unplated areas. It has also been found convenient, although not essential to employ materials which boil in the range of about 100° to about 140° C. Such a bath will allow the application of adequate heat for producing the aluminum plate, yet will evaporate quickly to provide an even overcoat having a minimum of run marks. Higher boiling inert liquids can be removed after the overcoat has been deposited for example, by wiping or draining the coated substrate material.

The overcoating material can be any substance which is substantially unreactive with aluminum hydride compounds, which will provide a clear, flexible and adherent film and which will dissolve or form a liquid dispersion in a heated inert liquid as defined hereinbefore. Coating materials usually consists of an organic material and include for example, insoluble resins such as polyethylene, polypropylene, polyvinylidene fluoride, hexafluoroacetone, polyformaldehyde, polyparaxylene, polyethers, e.g., polyethylene oxide and polypropylene oxide, copolymers of epoxide and other like materials which dry to a non-tacky finish. The actual overcoating material chosen will depend on the desired toughness and other characteristics of the coating to be formed. The concentration of the overcoating material in the liquid dispersion will depend to some extent on the thickness of the final overcoating desired.

As indicated previously the bath should usually be maintained at a temperature of about 50 to about 200° C. A temperature of from about 100 to about 150° C. is usually preferred. The actual deposition temperature of aluminum hydried compounds catalyzed by the transition metal catalysts defined herein will vary depending on the particular aluminum hydride employed, upon the catalyst used and to some extent, upon the catalyst concentration. Such deposition temperatures will, however, be substantially lower than those required where no catalyst is present.

The present process can be run as a continuous operation for the coating of various shaped objects such as films, webs, paper and the like. Also it may be employed to coat various other objects such as whisker materials, beads, powders, various irregularly shaped forms of reflectors for lights, piping and the like.

The following example will facilitate a more complete understanding of the present invention.

EXAMPLE

A sample of a Mylar brand polyester film was first coated with a metal catalyst consisting of $TiCl_4$ dissolved in an inert solvent consisting of ethyl ether and the solvent evaporated. Next an AlH_3 solution consisting of 0.25 molar AlH_3 in diethyl ether was applied to the sample and the solvent again evaporated.

An organic bath, inert to the aluminum hydride, was then prepared consisting of xylene containing about 5 percent weight of polystyrene as the overcoating substance. The solvent bath was heated to about 130° C., and the sample film was submerged in the bath for about 5 seconds, whereupon an aluminum plate formed on the film. The sample was removed from the bath and the xylene allowed to evaporate from the surface thereof. A polystyrene overcoat was deposited onto the metallic aluminum coating. The overcoat was very adherent, lending a good degree of toughness to the coated film.

In a manner similar to that described in the foregoing example other substrate materials of magnesium, aluminum, cloth, glass, ceramic, paper are treated as described

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hereinbefore to provide a glossy, uniform aluminum film and a protective overcoat of a resinous material such as polyethylene, polypropylene, polytetrafluoroethylene and the like.

Various modifications may be made in the present invention without departing from the spirit or scope thereof for it is understood that we are limited only as defined in the appended claims.

What is claimed is:

1. A process which comprises:
 - (a) coating a substrate with an aluminum hydride compound and an aluminum hydride decomposition catalyst, in the presence of each other, said aluminum hydride decomposition catalyst comprising a compound selected from the group consisting of compounds of the metals selected from the group consisting of V, Nb, Ta, Ti, Zr and Hf;
 - (b) contacting said coated substrate with an inert liquid bath maintained at a sufficient temperature to decompose said aluminum hydride compound, thereby depositing metallic aluminum onto said substrate, said bath comprising a solvent which is substantially unreactive with the said substrate, aluminum hydride, aluminum metal, and overcoating material and a resin overcoating material dissolved in said solvent;
 - (c) removing the aluminum coated substrate from said bath; and
 - (d) removing excess inert solvent from said substrate, thereby depositing said overcoat material onto said aluminum plated substrate.
2. The process as defined in claim 1 wherein said aluminum hydride compound is a solvated aluminum hydride compound.
3. The process as defined in claim 1 wherein said decomposition catalyst comprises a member selected from the group consisting of bromide, chloride, oxychloride and oxybromide compounds of the metals selected from the group consisting of V, Nb, Ta, Ti, Zr, and Hf.
4. The process as defined in claim 1 wherein said overcoating material is an oil soluble resin which dries to a non-tacky finish.
5. The process as defined in claim 1 wherein said solvent consists of a substantially anhydrous material which is a liquid at a temperature of from about 50 to 200° C.
6. The process as defined in claim 1 wherein said solvent consists of a substantially anhydrous material which is a liquid at a temperature of from about 100 to 140° C.
7. The process as defined in claim 1 wherein said inert bath is maintained at a temperature of from about 50 to 200° C.
8. The process as defined in claim 1 wherein said decomposition catalyst is applied to the substrate as a solution containing at least 1×10^{-6} weight percent catalyst and the aluminum hydride compound is applied to the catalyst-treated substrate in liquid dispersion containing at least 0.0001 weight percent of said aluminum hydride compound.
9. The process as defined in claim 1 wherein said substrate is a shaped object of a material selected from organic polymers, glasses, ceramics, metals and cellulose fibers.
10. The process as defined in claim 1 wherein said overcoating material is a soluble resin selected from the group consisting of polyethylene, polypropylene, polyvinylidene fluoride, polyhexafluoroacetone, formaldehyde copolymers, polyparaxylene, polyepoxides and polyethers.
11. The process as defined in claim 1 wherein said decomposition catalyst is applied to only a portion of the substrate to thereby produce a metallic aluminum design.
12. The process as defined in claim 1 wherein said decomposition catalyst and said aluminum hydride compound are separately applied to said substrate material

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as separate liquid dispersions containing said decomposition catalyst and said aluminum hydride compound.

13. The process as defined in claim 12 wherein said liquid dispersions contain a surface wetting agent.

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