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METHOD FOR STABILIZING PALLADIUM CONTAINING SOLUTIONS

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2 Claims

ABSTRACT OF THE DISCLOSURE

An organic solvent solution of a palladium salt or complexes thereof is stabilized by the addition of a stabilizing amount of a stabilizer composition selected from copper chloride, and mixtures thereof. The resulting solution is suitable for use as a treating solution for the metal plating of plastics and related processes.

BACKGROUND OF THE INVENTION

Recently, there has developed considerable interest in the production of metal plated plastic articles. The use of such articles has become increasingly prevalent in various industries including the automotive industry, appliance industry and the like. As a result, numerous processes have been devised for the production of such metal plated articles. One such process, which represents an improvement over the heretofore known processes in terms of simplified operation and variety of plastic substrates which may be plated involves the treatment of the plastic surface with a palladium salt and complexes thereof in an organic solvent. The resulting treated surface is thereafter electroless metal plated to produce an electroless conductive coating on the plastic substrate. The resulting article can then be readily electroplated by conventional means.

In the practice of the foregoing process, particularly with respect to use of the organic solvent solution, it has been found that a scum or precipitate is formed in the solution. Presumably, the precipitate is palladium metal. The formation of the scum or precipitate is objectionable, not only from the standpoint of its deposition on the plastic surfaces being treated, but also from the fact that its formation reduces the working life of the solution thus adding to the overall cost of the process.

It is therefore, an object of the present invention to provide a stable, organic solvent solution of a palladium salt and complexes thereof. It is also the object of the present invention to provide a stable organic solvent solution which is suitable for use in a process for the metal plating of plastics. These and other objects will come apparent to those skilled in the art from the following detailed description of the invention.

SUMMARY OF THE INVENTION

This invention relates to a stable organic solvent solution of a palladium salt and complexes thereof. More particularly, this invention relates to an organic solvent solution of a palladium salt and complexes thereof which is stabilized by the addition of a stabilizing amount of a stabilizer composition selected from nickel chloride, copper chloride, copper sulfate, copper nitrate and mixtures thereof.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the present invention, there is provided an organic solvent solution of a palladium salt or complexes thereof. The anion of the palladium salt can be halide such as chloride, bromide and iodide, cyanide, nitrate, sulfate, acetylacetonates of 5 to 25 carbon atoms,

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salts of 1 to 20 carbon atoms, carboxylic acids such as acetate, and the like. The preferred salt is palladium chloride. The palladium salt can be complexed with alkali metal halides; ammonium halides; inorganic ligands; cyclic bicyclic and alicyclic olefins of 2 to 36 carbon atoms; acetylenes and cyclic acetylenes of 2 to 36 carbon atoms; phosphines of 2 to 36 carbon atoms; nitriles of 2 to 36 carbon atoms; thioethers of 2 to 36 carbon atoms and the like. Typical palladium salts and complexes are palladium chloride, palladium bromide, palladium iodide, palladium acetate, palladium butyrate, palladium acetylacetonate, palladium butyrylbutanoate, palladium cyanide, palladium nitrate, palladium sulfate, ammonium palladium chloride, lithium palladium bromide, sodium palladium iodide, potassium palladium acetate, rubidium palladium acetylacetonate, cesium palladium cyanide, dichlorodiammine palladium, tetraamine palladium bromide, diiododiammine palladium, ethylene palladium chloride, butylene-palladium chloride, styrene palladium chloride, butadiene palladium chloride, nonodecadiene palladium chloride iodide, hexadecatriene palladium chloride, β -naphthylbutylene palladium chloride, carboethoxyphenyloctene palladium chloride, aminophenylethylene palladium chloride, cyclobutene palladium chloride, diphenylcyclobutadiene palladium chloride, cyclopentene palladium bromide, cyclopentadiene palladium iodide, cyclooctatetraene palladium chloride, cyclododecatetraene palladium chloride, tetraphenylcyclobutene palladium chloride, iodophenyltriocylcyclohexene palladium chloride, phenoxyphenyltrimethylcyclooctatriene palladium chloride, [2:2:1] bicycloheptene palladium chloride, [2:2:2] bicyclooctene palladium bromide, phenyl [2:2:1] bicycloheptadiene palladium chloride, chlorobromooctyl [2:2:2] bicyclooctadiene palladium bromide, acetylene palladium chloride, phenylhexadiyne palladium iodide, cyclodecyne palladium chloride, cyclododecatetrayne palladium chloride, tris-(triphenylphosphine) palladium chloride, bis-(triethylphosphine) palladium bromide, triocylphosphine palladium iodide, bis-(benzonitrile) palladium chloride, bis-(acetoneitrile) palladium bromide, bis-(naphthonitrile) palladium iodide, phthalonitrile palladium chloride, dimethylsulfide palladium chloride, didecylsulfide palladium bromide, didecylsulfide palladium iodide, π -allyl palladium chloride, π -cycloheptadienyl palladium chloride, π -phenyldecadienyl palladium bromide, π -cyclooctatrienyl palladium chloride, and the like. The complexes can be prepared by reacting the palladium salt with the complexing agent in a ratio of at least about one mole per mole of palladium salt.

Suitable organic solvents include alcohols such as methanol, ethanol, isopropyl alcohol, butanol, and the like; esters such as methyl acetate, ethyl acetate, isopropyl acetate, methyl propionate, and the like; carboxylic acids such as acetic acid, propionic acid, and the like; ketones such as acetone, methyl ethyl ketone, isobutyl methyl ketone, and the like; aldehydes such as propionaldehyde, butyraldehyde, isobutyraldehyde, and the like; nitriles such as acetonitrile, propionitrile, butyronitrile, and the like; aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, and the like, and chlorinated aliphatic hydrocarbons such as methylene chloride, chloroform, trichloroethylene, perchloroethylene, and the like.

The solution concentration is generally in the range from about 0.001 weight percent of palladium salt based on the weight of the solution up to a saturated solution. Preferably, the solution concentration is in the range of about 0.005 to about 0.1 weight percent palladium salt.

In addition to the organic solvent and palladium salt or complex, the compositions of the present invention also contain a stabilizing amount of a stabilizer which is effective in minimizing the formation of scum or precipi-

tate in the solution. This stabilizer composition is selected from nickel chloride, copper chloride, copper sulfate, copper nitrate and mixtures thereof. Typically, an effective stabilizing amount of the stabilizer in the composition is an amount which is at least about 0.0001 weight percent stabilizer based on the total weight of the solution. Preferably, the stabilizer will be about 0.01 to 20 weight percent stabilizer based on the total weight of the solution containing organic solvent, palladium salt or complex and stabilizer.

The stabilized compositions of the present invention may be formulated by admixing the above-described components in amounts within the ranges which have been indicated. Although this admixing can be carried in any suitable manner, preferably the stabilizer component is first admixed with the organic solvent and thereafter the palladium salt or complex is added to the organic solvent containing the stabilizer.

The stabilized organic solvent solutions are employed in the metal plating of plastic articles. In such a process, the surface of the plastic article to be treated is contacted with the stable solution for about one second to one hour or more, preferably in the range of 1 to 10 minutes. The contacting temperature is maintained below the softening point of the plastic and the boiling point of the solvent and is generally in the range of about 10 to 135° centigrade. Preferably, the contacting is performed at ambient temperatures. It has been found that when operating in this manner, little or no precipitate is formed in the treating compositions even after they have been used for an extended period of time.

Following the treatment of the plastic articles with the stabilized activator solution, the article is subjected to a process that has become known in the art as electroless plating or chemical plating wherein the article is contacted with a solution of a metal salt so that the metallic ion of the metal salt is reduced to the metallic state and deposited on the treated plastic surface. Typical of such processes are those for the deposition of a nickel coating which employ a solution of a nickel salt in an aqueous hypophosphite or borohydride solution. The thus-treated plastic article may then be electroplated, using conventional electroplating processes, to produce a metal plated plastic article. The above-described process for the treatment of the plastic articles is set forth in detail in commonly assigned copending application Ser. No. 52,714 (Case 2372) filed of even date herewith.

The following examples serve to illustrate the invention but are not intended to limit it. Unless specified otherwise in this specification and claims, all temperatures are in degrees centigrade and parts are understood to be expressed in parts by weight.

EXAMPLE 1

A solution of lithium palladium chloride in methanol was prepared in which the lithium palladium chloride concentration was 0.125 gram per liter. A sample of a graft copolymer of polybutadiene, acrylonitrile and styrene (ABS) was immersed in the activator solution for 1 minute at 25° centigrade. The treated plastic was then dried for 1 minute at 85° centigrade and rinsed with water for 1 minute. Thereafter, the treated plastic sample was immersed in an electroless nickel solution for 7 minutes to produce an electroless conductive coating on the treated substrate. The electroless plating solution employed had been prepared by mixing 28 grams of nickel sulfate hexahydrate, 8 grams of sodium citrate dihydrate, 8 grams of sodium acetate trihydrate, 12 grams of sodium hypophosphite monohydrate, 7.8 grams of magnesium sulfate, and 800 milliliters of water. The chemical plating bath was operated at 85° centigrade. The resulting electroless plated article was electroplated to give a 0.3 mil semi-bright nickel strike and a 1.7 mil thickness of acid

copper thereon. The final electroplated product was observed to be free from pinholes.

EXAMPLE 2

The process of Example 1 was repeated continuously at a rate such that an average of about 4 ABS samples were immersed in the activator solution per hour. After 4 hours, a black precipitate could be observed in the activator solution.

EXAMPLE 3

Example 2 was repeated except that the activator solution additionally contained 0.125 gram per liter of CuCl_2 . After 4 weeks, no precipitate was observed to have been formed.

EXAMPLES 4-8

A solution was prepared containing 0.125 gram per liter of lithium palladium chloride in methanol. A black precipitate was observed to form in 4-6 hours at 25° centigrade, in 15 minutes at 40° centigrade, and within 5 minutes at reflux (65° centigrade).

A second lithium palladium chloride solution was prepared which additionally contained 0.5 gram per liter of ClCl_2 . This solution was observed to be stable, i.e., no precipitate, for several months at 25° centigrade and for 6 days at reflux (65° centigrade).

A third lithium palladium chloride solution was prepared which additionally contained 0.5 gram per liter of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. The solution was observed to be stable, i.e., no precipitate, for 3 hours at 40° centigrade.

A fourth lithium palladium chloride solution was prepared which additionally contains 0.5 gram per liter of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The solution was observed to be stable for one day at reflux temperature (65° centigrade).

A fifth lithium palladium chloride solution was prepared which additionally contained 0.5 gram per liter of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. This solution was observed to be stable for one day at reflux temperature (65° centigrade).

Similar results are obtained when various combinations of other activator compounds and organic solvents are employed in place of the lithium palladium chloride and methanol.

Various changes and modifications can be made in the process and compositions of this invention without departing from the spirit and the scope of the invention. Various embodiments of the invention disclosed herein serve to further illustrate the invention, but are not intended to limit it.

I claim:

1. A method of forming a stable activator solution which comprises mixing an organic solvent, at least one palladium salt or complex thereof selected from palladium chloride, sodium palladium chloride, lithium palladium chloride, ammonium palladium chloride, palladium chloride benzonitrile, and palladium chloride triphenylphosphine, and, as a stabilizer, copper chloride, wherein the palladium salt or complex thereof is present in an amount of at least about 0.001 weight percent of the solution and the stabilizer is present in an amount of from about 0.0001 to 20 weight percent of the solution.

2. The method as claimed in claim 1 wherein the palladium salt complex is lithium palladium chloride.

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