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ELECTRODEPOSITION OF METALS

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This invention broadly relates to the electrodeposition of metals and, in some of its more specific variants, to novel compositions useful as baths for the electrodeposition of metals and to a process for electrodepositing metals therefrom.

The invention may be illustrated and described hereinafter with specific reference to the electrodeposition of aluminum on a conductive substrate employing the novel baths of the invention. However, it is understood that the invention is not limited thereto and that aluminum alloys, or still other metals or metal alloys may be electrodeposited from the novel plating baths of the invention.

A number of processes have been proposed heretofore for the electrodeposition of aluminum. For instance, aluminum may be electrodeposited from fused inorganic salt baths containing at least 75% by weight aluminum chloride and the remainder alkali metal chloride, or from prior art organic baths comprising a solution of an aluminum salt in a highly inflammable organic solvent such as ethyl ether. While satisfactory aluminum electrodeposits may be obtained from the foregoing baths, the baths have objectionable features. For instance, the inorganic bath fumes excessively at the relatively high operating temperature and some means must be provided for controlling the fuming. The organic baths of the prior art do not present a fuming problem but the organic solvent is inflammable and presents a serious fire hazard at the operating temperature. As a result, there has long been a need for a satisfactory bath for the electrodeposition of aluminum which does not present the fuming problem of the inorganic baths and the serious fire hazard of the organic baths.

It is an object of the present invention to provide a novel bath for the electrodeposition of metals or metal alloys.

It is a further object to provide additives for the baths of the invention whereby the initial resistivity may be reduced.

It is still a further object to provide a novel process for the electrodeposition of metals and metal alloys from the baths of the invention.

Still other objects and advantages of the invention will be apparent to those skilled in the art upon reference to the following detailed description.

In accordance with one variant of the present invention, novel compositions of matter are provided which consist essentially of an organic complex of an aluminum halohydride and solvent ether, with or without an organic complex of an aluminum halide. The resultant compositions are especially useful as a bath in the novel process of the invention for the electrodeposition of a metallic material on a conductive substrate. In accordance with a more specific variant of the invention, novel baths are provided for the electrodeposition of a metallic material on a conductive substrate which consist essentially of an etherate of an aluminum halohydride and solvent ether, with or without an etherate of aluminum halide. Preferably, the metallic material comprises aluminum. The solvent ether may be present in about 0.1–5% by volume and preferably 0.1–1.5% by volume.

The aluminum halohydrides suitable for practicing the present invention may include complexes of compounds of the general formula AlH_mX_n, where X is halogen, m and n each have a numerical value of at least one, and $m+n$ are equal to three. Thus, in the foregoing general formula the atomic ratio of Al to H is between 1:1 and 1:2, the atomic ratio of Al to X is between 1:2 and 1:1, and the atomic ratio of Al to H+X is 1:3. Specific examples of aluminum halohydrides include $AlHX_2$, AlH_2X, and mixtures thereof such as $Al_3H_4X_5$, which may be written as $AlH_{4/3}X_{5/3}$ for the purpose of this discussion. Chlorine and bromine are preferred over other halogens in most instances.

Preferably the foregoing aluminum halohydrides are present in the form of coordinate covalent complexes. The complexes may be prepared by reacting the aluminum halohydride with one or a mixture of compounds which are known to be complexing agents therefor and especially Lewis bases such as ethers, or suitable compounds in general containing a functional group which is capable of complexing aluminum halohydride and/or aluminum halide, such as organic compounds containing a divalent sulfur atom including the thioethers, organic compounds containing a trivalent nitrogen atom such as the amines, and organic compounds containing a trivalent phosphorus atom. An ether or a mixture of ethers is usually preferred as the complexing agent and as the free or solvent ether. A wide variety of ethers may be employed in forming the resultant etherate and as the solvent ether, such as ethyl ether, propyl ether, butyl ether, octyl ether, etc., and ethers in general wherein each of the organic groups attached to the oxygen atom contain, for example, about 1 to 8–20 carbon atoms. The ether may contain an aromatic group such as methylphenyl ether, ethylphenyl ether, diphenyl ether, etc., or a cyclohydrocarbon radical and especially those containing carbon atoms within the foregoing ranges. Ethers containing a plurality of ether linkages and organic radicals as above discussed or their equivalents also may be used, such as diethylene glycol diethyl ether, or cyclic ethers such as tetrahydrofuran. Diethyl ether or a mixture of ethers comprising diethyl ether is usually preferred.

If desired, an organic complex of aluminum halide may be present in the composition and this is usually preferred. The complexing agents for the aluminum halide may be the same as discussed above for the aluminum halohydrides and, similarly, the preferred complexing agent is an ether or a mixture of ethers of the types discussed above. Preferably, the aluminum halide is aluminum chloride or aluminum bromide.

The complexes of aluminum halides or aluminum halohydrides may be prepared by a number of methods. For instance, previously prepared aluminum halohydride and/or aluminum halide may be dissolved in a solvent, the complexing agent added to the solution, and the mixture reacted to produce the desired complex, or a mixture of the two complexes when both aluminum halohydride and aluminum halide are present in the solution. The solvent may be removed subsequent to the complexing step by evaporation and/or aeration with a dry inert gas. Usually, it is more convenient to prepare an aluminum halohydride-containing complex by dissolving aluminum halide in a solvent, adding the complexing agent and an active hydrogen-containing compound to the solution in an amount to provide the desired amount of active hydrogen in the resultant composition, and reacting the mixture to produce a complex of aluminum halohydride. In instances where the aluminum halide is present in excess, a mixture of the complexes of aluminum halohydride and aluminum halide is produced. The solvent and complexing agent may be the same substance, such as when an ether is used as the solvent and complexing agent. The solvent may be

removed subsequent to the reaction as noted above and the reaction product used in preparing the baths of the invention.

When an etherate of an aluminum halohydride is prepared, preferably aluminum halide is dissolved in an excess of diethyl ether and then one or a mixture of metal hydride such as aluminum hydride, alkali metal hydrides such as sodium, potassium or lithium aluminum hydride, or alkaline earth metal hydrides such as calcium hydride, is added to the solution in the calculated quantity to provide the desired amount of active hydrogen in the resultant composition. The metal hydride may be added in the calculated amount to react with the aluminum halide and produce a desired aluminum halohydride etherate, or in a smaller amount so as to have the aluminum halohydride etherate present in solution together with aluminum chloride etherate. When metal hydride is reacted with aluminum halide, preferably the mole ratio of aluminum hydride (AlH_3) to aluminum halide (AlX_3) in the resultant aluminum halohydride-containing composition is between 1:0.5 and 1:22, and for better results between 1:2 and 1:11. In the present specification and including the claims, for convenience the mole ratio of aluminum hydride (AlH_3) to aluminum halide (AlX_3) in the aluminum halohydride-containing bath compositions of the invention is calculated by considering the aluminum halohydride content to be a mixture of AlH_3 and AlX_3, and free aluminum halide, if any, is added thereto. For example, a bath composition containing only three moles of an etherate of $AlHCl_2$ would contain one mole of AlH_3 for each two moles of $AlCl_3$ and the AlH_3 to $AlCl_3$ ratio would be 1:2. If the bath also contained one mole of an etherate of free aluminum chloride for each three moles of $AlHCl_2$, then the AlH_3 to $AlCl_3$ ratio would be 1:3 due to the presence of the excess aluminum chloride.

After reaction of the metal hydride with the ether solution of aluminum halide, the excess ether over that required to form the etherate and provide about 0.1–5% by volume of solvent ether may be evaporated by heating and/or by aeration with a dry inert gas. The ether solution often may be merely heated to its boiling point and the free or solvent ether boiled off. When this is done, the boiling point of the result composition rises slowly with evaporation of ether until the monoetherate of the aluminum halohydride and aluminum halide is formed. When diethyl ether is used as the solvent and substantially all of the solvent ether is removed, the flash point of the resultant composition will rise to about 200–215° F. and there is no further appreciable rise. When the ether is diethyl ether, preferably the solvent ether is removed by boiling the solution until the boiling point rises to about 150–160° F. Then, a dry inert gas such as nitrogen, helium, argon, etc., is passed through the composition at a lower temperature such as 90° F. for the purpose of removing an additional amount of solvent ether. This latter procedure has the advantage of reducing thermal decomposition and thermal decomposition may be further reduced by using only aeration with dry inert gas at temperatures of 70–90° F. for removing the solvent. Anhydrous conditions should be maintained throughout the reaction and during the removal of excess ether for the purpose of preventing decomposition of the aluminum halohydride.

The thermal stability of the bath is often improved when excess or free aluminum halide complex is present. Usually, the mole ratio of AlH_3 to $AlCl_3$ should not be higher than about 1:3, and preferably not higher than about 1:6. The bath should be at least 1 molar in active hydrogen, i.e., at least one molar in $AlHCl_2$ or the equivalent in active hydrogen content. The plating baths of the invention generally may be used at temperatures above the melting point and below the decomposition point. The optimum operating temperature for specific baths may vary somewhat, but usually temperatures about 5–20° F. above the melting point and below about 170° F. are satisfactory when the complexing agent is diethyl ether. The

current density may vary over wide ranges. For example, the lower limit is largely practical in nature and may be 0.1–1 ampere/sq. ft., while the upper limit may be 50–150 amperes/sq. ft. or higher.

Excellent plate may be produced from the above described baths but the resistivity is often high and thus the power consumption is high. It has been further discovered that the resistivity may be reduced by dissolving in the baths at least one soluble ionizable compound such as quaternary ammonium compounds, amine salts, and nonoxygen-containing mineral acids and salts thereof in an amount to lower the initial resistivity. In most instances, the ionizable compound is dissolved in the bath to the extent of its solubility, but smaller amounts may reduce the resistivity somewhat. Usually about 0.5 to 5–10% gives good results.

A wide variety of compounds of the foregoing types may be dissolved in the plating baths of the present invention. Examples of quaternary ammonium compounds include quaternary amine salts and pyridinium compounds wherein the organic radicals attached to the nitrogen atom may contain 1–8 to 20 carbon atoms. Specific examples include tetramethyl, tetraethyl, tetrapropyl, tetrabutyl, tetraamyl, tetrahexyl, tetraoctyl and higher ammonium halides or other suitable salts of nonoxygen-containing mineral acids. The organic radicals attached to the nitrogen atom may or may not be the same. For example, dodecyl trimethyl ammonium chloride and equivalent mixed quaternary ammonium salts may be used. Pyridinium compounds include methyl, propyl, amyl, octyl and higher alkyl pyridinium nonoxygen-containing mineral acid salts wherein the alkyl radical contains, for example, 1–8 to 20 carbon atoms. The nonoxygen-containing mineral acid salts of the pyridinium compounds include halides such as chlorides, bromides, etc. Inorganic salts include ammonium or alkali metal nonoxygen-containing mineral acid salts, alkaline earth metal nonoxygen-containing mineral acid salts, and nonoxygen-containing mineral acid salts in general which are soluble in an amount to reduce the resistivity of the bath. Specific examples include the halides of the foregoing groups of metals and especially the chlorides and bromides. Lithium chloride is usually preferred.

The amine salts may be derived from amines containing 1 to 3 organic radicals attached to the nitrogen atom having 1–8 to 20 carbon atoms. Preferably, the organic radicals are alkyl and the salts are formed from a nonoxygen-containing mineral acid such as hydrochloric, hydrobromic, etc. Still other ionizable compounds include nonoxygen-containing mineral acids such as the hydrogen halides and alkali or alkaline earth metal salts thereof, and especially organic derivatives wherein at least one ionizable hydrogen atom of the mineral acid has been replaced by an organic radical containing, for example, 1–8 to 20 carbon atoms. The resultant organic compound containing a mineral acid group or the alkali or alkaline earth metal salt thereof may be dissolved in the bath to some extent, and the resistivity is reduced due to the ionization of the mineral acid substituent.

In accordance with another variant of the invention, it has been discovered that the resistivity of the basic bath may be further reduced by means of a difunctional compound containing a complexing function for the aluminum halohydride and/or aluminum halide constituents of the bath and, in addition thereto, an ionizable substituent. Since the difunctional compound is both a complexing agent and an ionizable compound and complexes the aluminum halohydride and/or aluminum halide, it is soluble in the bath in large amounts and the ionizable substituent is likewise solubilized in large amounts. Due to the increase in the concentration of the ionizable substituent and the availability of additional ions for carrying the current, the initial resistivity of the basic bath may be reduced markedly.

The difunctional compounds may contain the same types of complexing groups that are present in the simple complexing agents previously described and, similarly, the same types of ionizable groups that are present in the ionizable compounds previously described. Thus, the difunctional compound may be considered to be a complexing agent of the types previously described which is also an ionizable compound selected from the group consisting of quaternary ammonium compounds, amine salts, and organic compounds containing a nonoxygen-containing mineral acid group and salts thereof as defined herein.

Usually it is preferred that about 33–66 mole percent of the total amount of complexing agent contain an ionizable substituent. However, in some instances amounts as low as 15–25 mole percent and up to 75–85 mole percent may be used. Even 1 mole percent improves the conductivity.

Ethers are the preferred complexing agents and quaternary amine salts are the preferred ionizable compounds. In instances where both the ether linkage and quaternary amine group are present in the same molecule, the compounds may be of the following classes.

$$[R{-}O{-}R'{-}N{-}R_3'']^+ \ Y^-$$

or

$$Y^- \ ^+[R_3''{-}N{-}R'{-}O{-}R'{-}N{-}R_3'']^+ \ Y^-$$

where R and R'' are monovalent organic radicals containing up to about 20 carbon atoms and preferably 1–8 carbon atoms, R' is a divalent organic radical containing up to about 20 carbon atoms and preferably 1–8 carbon atoms, and Y is a nonoxygen-containing mineral acid residue such as halogen, etc. In most instances, alkyl or alkylene radicals containing 1–8 carbon atoms are preferred.

Of the above types of compounds, ethoxyethyltrimethyl ammonium chloride is preferred. Other specific ethers containing quaternary ammonium groups which may be used are methoxymethyltrimethyl ammonium halides such as the chloride, bis(2-dimethylaminoethyl) ether dimeth- halides such as the chloride, N-ethyl-N-methyl morpholinium halides such as the iodide or chloride and 2-ethoxyethyltriethyl ammonium halides such as the iodide or chloride.

In instances where the plating bath contains aluminum chloride, aluminum dichlorohydride, ethyl ether combined as the etherate, and ethoxyethyltrimethyl ammonium chloride, the following compositions are especially useful:

	Broad Range	Preferred Amount
Aluminum Chloride, moles	0–4	3.8
Aluminum Dichlorohydride, moles	6–2	2.0
Diethyl Ether (combined as the etherate), moles	2–4	3.8
Ethoxyethyltrimethyl Ammonium Chloride, moles	4–2	2.0
Diethyl Ether (solvent), percent by volume	0–1.5	1.5

The operating temperature range for the electrodeposition of aluminum or aluminum alloy from the preferred bath is above the melting point and preferably 80–90° F.

The lower limit on the current density to be employed is practical in nature, and current densities as low as 0.1 to 1 ampere/sq. ft. may be used. Current densities as high as 150–300 amperes/sq. ft. may be used with the preferred baths, and often as high as 1,000 amperes/sq. ft. in instances where the preferred additives for reducing resistivity are used. Generally, when additives for reducing resistivity are not present, current densities up to 50–150 amperes/sq.ft. will give better results. Special plating conditions may be used if desired such as pulse current, polarity reverse current, etc., or the plating may be conducted with vigorous agitation, rotating or rapidly moving cathodes, etc.

The coating metal may be supplied to the plating bath by any suitable convenient means such as by addition of a soluble salt of the coating metal, by soluble anodes, or by auxiliary anodes. In the specification and claims, it is understood that an electroplating bath of the invention contains the metal or metals to be electrodeposited on the substrate in a form that may be electroplated therefrom. When an aluminum-containing coating is electrodeposited, preferably aluminum anodes or aluminum alloy anodes are immersed in the bath in the usual manner. Other metals that may be electrodeposited include titanium, zirconium, vanadium, columbium, beryllium, molybdenum, tungsten, chromium, tantalum, magnesium, manganese, nickel, cobalt, iron, copper, and alloys thereof with or without aluminum. Preferably, in instances where aluminum is being deposited and iron is present in the bath, the concentration of iron is maintained below 0.2% by weight, and preferably between 0.01 and 0.02%.

The thickness of the aluminum plate may vary over wide ranges. Usually, for strip plating thin deposits are preferred such as 15×10^{-6} to 90×10^{-6} inch. However, much heavier deposits are possible such as up to several thousandths of an inch, e.g., 5×10^{-3} to 15×10^{-3} inch, or even up to ⅛ to ½ inch. It is also possible to use the plating bath of the present invention for electroforming. When so used, preferably additives are present which tend to reduce treeing. BB' dichloroethyl ether may be used as an addition agent to improve the smoothness and hardness of the plating, regardless of whether electroplating items such as steel strip or in electroforming.

The coating metals described herein may be electrodeposited on any suitable conductive substrate. Preferably, the substrate is ferrous metal in the form of strip, wire, or other metal articles. Still other metallic substrates may be used if desired, as may normally non-conductive substrates which have been treated with a conductor to render them conductive for purposes of the present invention. Such materials are well known and the selection of a specific conductive substrate for particing the present invention is within the skill of the art.

It is preferred that metallic substrates such as ferrous metal be activated or etched prior to the electrodeposition of aluminum. This may be done by any suitable method known to the art, such by treatment with hydrogen chloride gas in a carrier gas. In one preferred method, the metal is dipped in a long chain fatty acid such as oleic, rinsed in an ether solution of aluminum halohydride, and then plated. In another preferred method, the metal is cleaned mechanically in an anhydrous atmosphere to provide a fresh, clean surface. For best results the foregoing treatments should be effected under anhydrous conditions.

The bath should be prepared under anhydrous conditions and maintained substantially anhydrous throughout its life. For instance, the bath should not contain the decomposition products of over about 1% by weight of water when such water has been deactivated by treatment of the bath with a metal hydride in an amount to provide at least about two gram atoms of active hydrogen per mole of water. Additionally, the bath should not contain over about 0.02–0.03% of water which has not been deactivated by addition of a metal hydride as at water concentrations greater than this the bath is detrimentally affected. Within the above limits, a bath containing water may be restored to its former condition and excellent plate again obtained by addition of the metal hydride in the prescribed amounts.

Where the melting point of a specific bath composition is undesirably high, a noninflammable liquid or low melting point diluent which is not detrimental to the electrodeposition of a metal therefrom may be added to reduce the melting point. Preferably, the diluent is inert with respect to the bath at the temperaures encountered.

The presence of a small amount of solvent ether in the bath results in a marked drop to practical operating levels, in the cell resistance and resistvity, and yet the fire hazard normally associated with the ether is largely overcome due to the small amount of solvent ether available as a fuel. If the ether should ignite, the flame may be quenched almost immediately and without danger to the operating personnel or substantial damage to the equipment. Also, the bath of the invention has a much longer life than prior art baths containing large amounts of solvent ether and the loss of ether from the bath may be controlled more readily.

A given bath may be used for electroplating metals and metal alloys at temperatures between its melting point and boiling point under the existing pressure. Usually a temperature of about 70–90° F. is preferred at normal atmospheric pressure, but higher temperatures may be equally satisfactory under superatmospheric pressures sufficient to maintain liquid phase conditions.

The fire and explosion hazard may be further reduced and even eliminated by maintaining a nonoxidizing atmosphere above the bath. This may be accomplished by providing a diluent gas phase above the bath, or the ether content of the vapor phase may be maintained at levels which are nonexplosive, or the vapor phase may be maintained substantially free of oxygen.

The foregoing detailed description and the following specific examples are for purposes of illustration only and are not limiting to the spirit or scope of the appended claims.

Example I

The monoetherate of $AlHCl_2$ was prepared by treating aluminum chloride in ether solution with lithium aluminum hydride in the calculated amount to form $AlHCl_2$. Excess or solvent ether was evaporated from the resultant product, and the ether content further reduced to the monoetherate of $AlHCl_2$ by aeration with dry gaseous nitrogen.

The resultant monoetherate of $AlHCl_2$ was heated to the molten condition, aluminum anodes immersed therein, and the resultant bath used for plating steel panels at 30 amperes/sq. ft. at a temperature of 100° F. Then a series of increments of diethyl ether were added to the bath and the plating procedure was repeated after adding each increment of the solvent ether.

The cell resistance and resistivity of the bath were determined following addition of each increment of solvent ether. The following data were obtained:

Percent by Volume of Solvent Ether	Cell Resistance, ohms	Resistivity, ohm-cm.
None	----------	1,300
0.62	132	390
1.25	124	366
1.87	113	333
2.50	105	310
3.12	97	286

From the above data it is apparent that the presence of small amounts of solvent ether results in a marked drop in the cell resistance and resistivity.

Example II

A plating bath was prepared by dissolving aluminum chloride in diethyl ether, and then treating the solution with lithium aluminum hydride in the calculated amount to produce 2 moles of $AlHCl_2$ for each 3.8 moles of aluminum chloride remaining in the ether solution. Excess ether was evaporated from the resultant product to produce the monoetherates of the $AlHCl_2$ and $AlCl_3$.

The above prepared composition contained 2 moles of aluminum dichlorohydride etherate for each 3.8 moles of aluminum chloride etherate. Testing of the composition as a plating bath for electrodepositing aluminum on ferrous metal panels at varying levels of solvent ether gives substantially the same results as recorded in Example I.

What is claimed is:

1. A process for electrodepositing a metallic material on an electrically conductive substrate comprising

subjecting at least a portion of the substrate as a cathode to the action of an electrolyzing electric current while immersed in a bath consisting essentially of an organic complex of an aluminum halohydride and solvent ether,

the bath containing about 0.1–5% by volume of uncombined solvent ether.

2. A process for electrodepositing a metallic material on an electrically conductive substrate comprising

subjecting at least a portion of the substrate as a cathode to the action of an electrolyzing electric current while immersed in a bath consisting essentially of an organic complex of aluminum halide, an organic complex of an aluminum halohydride and solvent ether,

the bath containing about 0.1–5% by volume of uncombined solvent ether.

3. A process for electrodepositiong an aluminum-containing material on an electrically conductive substrate comprising

subjecting at least a portion of the substrate as a cathode to the action of an electrolyzing electric current while immersed in a bath consisting essentially of an etherate of an aluminum halohydride and solvent ether,

the etherate containing halogen selected from the group consisting of chlorine, bromine and mixtures thereof and the bath containing about 0.1–5% by volume of uncombined solvent ether.

4. A process for electrodepositing an aluminum-containing material on an electrically conductive substrate comprising

subjecting at least a portion of the substrate as a cathode to the action of an electrolyzing electric current while immersed in a bath consisting essentially of an etherate of aluminum halide, an etherate of an aluminum halohydride and solvent ether,

the etherates containing halogen selected from the group consisting of chlorine, bromine and mixtures thereof and the bath containing about 0.1–5% by volume of uncombined solvent ether.

5. A process for electrodepositing an aluminum-containing material on an electrically conductive substrate comprising

subjecting at least a portion of the substrate as a cathode to the action of an electrolyzing electric current while immersed in a bath consisting essentially of an etherate of aluminum halide, an etherate of an aluminum halohydride and solvent ether,

the etherates containing halogen selected from the group consisting of chlorine, bromine and mixtures thereof,

the bath containing about 0.1–5% by volume of uncombined solvent ether and having a mole ratio of AlH_3 to $AlCl_3$ between about 1:0.5 and 1:22.

6. A process for electrodepositing an aluminum-containing material on an electrically conductive substrate comprising

subjecting at least a portion of the substrate as a cathode to the action of an electrolyzing electric current while immersed in a bath consisting essentially of an etherate of aluminum halide, an etherate of an aluminum halide halohydride and solvent ether,

the etherates containing halogen selected from the group consisting of chlorine, bromine and mixtures thereof and being formed from at least one ether having organic radicals attached to the oxygen atom containing 1–8 inclusive carbon atoms per radical,

the solvent ether having organic radicals attached to the oxygen atoms having 1–8 inclusive carbon atoms per radical,

the bath containing about 0.1–5% by volume of uncombined solvent ether and having a mole ratio of AlH_3 to $AlCl_3$ between about 1:0.5 and 1:22.

7. A process for electrodepositing an aluminum-containing material on an electrically conductive substrate comprising

subjecting at least a portion of the substrate as a cathode to the action of an electrolyzing electric current while immersed in a bath consisting essentially of an etherate of aluminum chloride, an etherate of an aluminum chlorohydride and solvent ether,

the bath containing about 0.1–5% by volume of uncombined solvent ether and having a mole ratio of AlH_3 to $AlCl_3$ between about 1:2 and 1:11.

8. A process for electrodepositing an aluminum-containing material on an electrically conductive substrate comprising

subjecting at least a portion of the substrate as a cathode to the action of an electrolyzing electric current while immersed in a bath consisting essentially of a monoetherate of aluminum chloride, a monoetherate of an aluminum chlorohydride and solvent ether,

the monoetherates being formed from at least one ether having organic radicals attached to the oxygen atom containing 1–8 inclusive carbon atoms per radical,

the solvent ether having organic radicals attached to the oxygen atom having 1–8 inclusive carbon atoms per radical,

the bath containing about 0.1–5% by volume of uncombined solvent ether and having a mole ratio of AlH_3 to $AlCl_3$ between about 1:2 and 1:11.

9. A process for electrodepositing an aluminum-containing material on an electrically conductive substrate comprising

subjecting at least a portion of the substrate as a cathode to the action of an electrolyzing electric current while immersed in a bath consisting essentially of a monoetherate of aluminum chloride, a monoetherate of solvent aluminum chlorohydride and solvent ether,

the ether forming the etherate and the solvent ether comprising diethyl ether,

the bath containing about 0.1–5% by volume of uncombined solvent ether and having a mole ratio of AlH_3 to $AlCl_3$ between about 1:2 and 1:11.

10. A process for electrodepositing a metallic material on an electrically conductive substrate comprising

subjecting at least a portion of the substrate as a cathode to the action of an electrolyzing electric current while immersed in a bath consisting essentially of an organic complex of an aluminum halohydride and solvent ether,

the bath containing about 0.1–5% by volume of uncombined solvent ether and having dissolved therein at least one soluble ionizable compound selected from the group consisting of quaternary ammonium compounds, amine salts and non-oxygen-containing mineral acids and salts thereof.

11. A process for electrodepositing an aluminum-containing material on an electrically conductive substrate comprising

subjecting at least a portion of the substrate as a cathode to the action of an electrolyzing electric current while immersed in a bath consisting essentially of an etherate of aluminum halide, an etherate of an aluminum halohydride and solvent ether,

the etherates containing halogen selected from the group consisting of chlorine, bromine and mixtures thereof,

the bath containing about 0.1–5% by volume of uncombined solvent ether and having dissolved therein at least one soluble ionizable compound selected from the group consisting of quaternary ammonium compounds, amine salts, and nonoxygen-containing mineral acids and salts thereof.

12. A process for electrodepositing an aluminum-containing material on an electrically conductive substrate comprising

subjecting at least a portion of the substrate as a cathode to the action of an electrolyzing electric current while immersed in a bath consisting essentially of a monoetherate of aluminum chloride, a monoetherate of an aluminum chlorohydride and solvent ether,

the ether forming the etherates comprising diethy ether,

the solvent ether comprising diethyl ether,

the bath containing about 0.1–5% by volume of uncombined solvent ether and having a mole ratio of AlH_3 to $AlCl_3$ between about 1:2 and 1:11.

and the bath having dissolved therein at least one soluble ionizable compound selected from the group consisting of quaternary ammonium compounds, amine salts, and nonoxygen-containing mineral acids and salts thereof.

13. A process for electrodepositing a metallic material on an electrically conductive substrate comprising

subjecting at least a portion of the substrate as a cathode to the action of an electrolyzing electric current while immersed in a bath consisting essentially of an etherate of aluminum halide, an etherate of an aluminum halohydride and solvent ether,

the etherates containing halogen selected from the group consisting of chlorine, bromine and mixtures thereof,

the bath containing about 0.1–5% by volume of uncombined solvent ether and containing an etherate formed at least in part from an ionizable compound selected from the group consisting of quaternary ammonium compounds containing an ether linkage, amine salts containing an ether linkage, and ethers containing a nonoxygen-containing mineral acid group and salts thereof.

14. The process of claim 13 wherein the ionizable compound is ethoxyethyltrimethyl ammonium chloride.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,355,368 November 28, 1967

Edwin J. Smith et al.

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

Column 5, line 59, for "0-1.5" read -- 0.1-5 --; column 8, line 70, strike out "halide"; column 10, line 22, for "diethy" read -- diethyl --.

Signed and sealed this 21st day of January 1969.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents