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ELECTRODEPOSITION OF METALS FROM A FUSED BATH OF ALUMINUM HALOHYDRIDE ORGANIC COMPLEX AND COMPOSITION THEREFOR

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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 further relates to a process for preparing the baths of the invention, additives therefor, and a new chemical compound.

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, they each 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 which is noncombustible at the operating temperature.

It is an object of the present invention to provide a novel composition of matter which is especially useful as a bath for the electrodeposition of metals or metal alloys.

It is a further object to provide a novel plating bath for electroplating aluminum on a conductive substrate.

It is still 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 the new chemical compound ethoxyethyltrimethyl ammonium chloride.

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.

It is still a further object to provide a novel process for electroplating aluminum on a conductive substrate from the novel plating baths of the invention.

It is still a further object to provide a novel process for preparing the plating 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 and the specific examples.

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, with or without an organic complex of an aluminum halide. The resultant compositions are

useful for the deposition of metal on a substrate, and they 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, with or without an etherate of aluminum halide. The resultant baths are noncombustible at the operating temperature, i.e., the temperature at which the metallic material may be electrodeposited on the substrate. Preferably, the metallic material comprises aluminum.

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 includes $AlHX_2$, 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. A wide variety of ethers may be employed in forming the resultant etherate such as ethyl ether, propyl ether, butyl ether, octyl ether, etc., and ethers in general wherein 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 halodhydrides 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 to an extent to render the resultant composition noncombustible at the operating temperature of a bath prepared therefrom. 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 hydrides 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 of 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 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 resultant 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, the flash point of the resultant composition will rise to about 200–215° F. and there is no further appreciable rise. The resultant composition is noncombustible and may be decanted and used as a plating bath. 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 and raising the flash point up to about 200–215° F. 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 plating baths of the present invention preferably are treated to remove organic solvent until the vapor phase in equilibrium with the bath at the operating temperature is nonexplosive and noncombustible in air. When diethyl ether is the solvent, the ether content of the vapor phase should not be greater than about 1% by volume in most instances. The ether content that remains is largely combined chemically with the aluminum halohydride and aluminum chloride in the form of etherates. The etherates are stable at the operating temperature of the bath, and thus ether is not available in the free or uncombined form for forming a combustible or explosive mixture. The resultant noncombustible aluminum halohydride-containing compositions may be used in preparing baths for the electro-deposition of a metal such as aluminum or aluminum alloys.

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 of the order of about 1200–1300 ohm-centimeters 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. By this method, often the initial resistivity of 1200–1300 ohm-centimeters may be reduced to about 600–700 ohm-centimeters or lower. It is usually not possible to further reduce the resistivity below this level due to the relatively low solubility of such substances in the baths, which may be about 0.5% to 5–10%. 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.

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 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.

Ionizable compounds of the above types may reduce the initial resistivity of the basic bath to about 600–700 ohm-centimeters. The resultant bath may be used, as may the basic bath, for the electrodeposition of very satisfactory electrodeposits of a coating metal such as aluminum, aluminum alloys, or other metals mentioned herein. However, the power consumption is higher than ideal in commercial installations and it is usually desirable that the resistivity be reduced still lower.

In accordance with another varient of the invention, it has been discovered that the resistivity of the basic bath may be reduced a still greater extent by means of a difunctional compound having 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 to about 70 ohm-centimeters or lower. This may be accomplished without a decrease in the flash point and the bath remains noncombustible at the operating temperature.

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:

$$[R—O—R'—N—R_3'']^+Y^-$$

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

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 dimethhalides 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, and ethoxyethyltrimethyl ammonium chloride, the following compositions are especially useful:

	Broad Range (Moles)	Preferred Amount (Moles)
Aluminum Chloride	0–4	3.8
Aluminum Dichlorohydride	6–2	2.0
Diethyl Ether	2–4	3.8
Ethoxyethyltrimethyl Ammonium Chloride	4–2	2.0

The preferred bath above defined has a melting point of approximately 80–90° F. The operating temperature range for the electrodeposition of aluminum or aluminum alloy therefrom is above the melting point and preferably below about 160–170° F. Best results are usually obtained at an operating temperature of about 115–135° 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 1000 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. $\beta\beta'$ 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. This ether may be added in an amount sufficient to constitute 4–8% by volume of the bath, but smaller or larger amounts may be added in some instances.

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 nonconductive 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 practicing 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 as 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

Preferably the free solvent content of the bath is maintained at a level sufficiently low to provide an ignition point as determined by ASTM D–286–58T that is above the operating temperature of the bath and usually above 500° F. Also, 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.

As disclosed in my copending application Serial No. 159,447, filed December 14, 1961, now Patent 3,214,228 for Process for the Deposition of Metals and the Resultant Products, the halohydride-containing compositions of the invention may be used in the electroless deposition of metallic aluminum-containing material on a wide variety of bases or substrates including metals such as ferrous metal, brass, copper, etc., and nonmetallic substrates such as wood, composition board, plastics, etc. This may be conveniently accomplished by decomposing an aluminum halide-containing composition of the invention to produce metallic aluminum in intimate contact with the substrate on which the aluminum is to be deposited. The decomposition may be effected by heating a body of the composition from a lower temperature up to or above the decomposition temperature while in intimate contact with the substrate, or the substrate may be heated above the decomposition temperature and contacted with the composition.

Where the melting point of a specific bath composition is undesirably high, a noncombustible 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 temperatures encountered.

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 temperatures of 82° F. and 115° F. A thickness of about 0.03 mil of aluminum was deposited on the steel panels in the form of an adherent white mat plate which could be roll brightened.

The resistivity of the bath was determined and found to be 309 ohm-centimeters at 100° F. The bath was tested and found to be noncombustible at the plating temperatures.

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. The composition was used as a plating bath for electrodepositing aluminum on ferrous metal panels at 30 amperes/sq. ft. and at a temperature of 115° F. Aluminum anodes were immersed in the plating bath during the electrodeposition.

The aluminum plated out on the ferrous metal panels in the form of a white mat coating and was pleasing in appearance, adherent, and could be obtained in any desired thickness. The white mat plate could be roll brightened, or other forms of brightening could be used.

If desired, the corresponding aluminum bromide salt may be prepared by using aluminum bromide as the starting material. The resultant bath could be used for the electrodeposition of aluminum.

Example III

The new compound 2-ethoxyethyltrimethyl ammonium chloride was prepared by heating 54.5 grams (0.5 mole) of 2-chloroethyl ethyl ether and 120 grams (0.55 mole) of 25% triethyl amine in methanol in a steel bomb at 125° C. for 15 hours. Thereafter, the mixture was evaporated to a syrup on a rotating evaporator at 70° C., dissolved in ethyl alcohol (100 ml.) and evaporated to dryness. The product was dispersed in acetone, filtered with suction while preventing contact wtih moisture, and then dried in vacuum at 80° C. The resultant product was 70.1 grams of a white solid (83.5% of the theoretical yield) which was identified as being 2-ethoxyethyltrimethyl ammonium chloride.

The above procedure was modified somewhat by dissolving 123 grams (1.13 moles) of 2-chloroethyl ethyl ether and 307 grams (1.3 moles) of 25% trimethyl amine in methanol, and heating in a glass bottle at 70° C. for 15 hours. Thereafter, the product was evaporated to dryness using a rotating evaporator at 70° C., the product dispersed in ethyl alcohol (200 ml.) and evaporated to dryness, repeated, slurried with acetone, filtered with suction, washed with acetone and pentane, and then dried in vacuum at 80° C. overnight.

The resultant product was 152.1 grams of off-white crystalline solid (80.2% of the theoretical yield), and this likewise was identified as being 2-ethoxyethyltrimethyl ammonium chloride.

Example IV

Lithium hydride was added to a diethyl ether solution of aluminum chloride in the calculated amount to produce 2 moles of aluminum dichlorohydride for each 3.8 moles of aluminum chloride remaining in the solution. The resultant ether solution contained excess solvent or free ether, which was evaporated by heating to the boiling point of the bath.

With continued evaporation, the boiling point of the bath gradually rose until a temperature of 160° F. was reached. At this point, the bath was cooled and dry nitrogen was bubbled through the bath at about room temperature to thereby strip the remaining ether out of the bath and produce a mixture of the monoetherate of aluminum dichlorohydride and the monoetherate of aluminum chloride. At this point, the flash point of the bath was about 200–215° F., and no further rise of the flash point was noted with continued stripping with the nitrogen. The resultant bath had a melting point of about 90° F., and was used as a plating bath for the electrodeposition of aluminum.

Aluminum anodes were immersed in the bath and aluminum electrodeposited on steel panels at temperatures from slightly above the melting point up to a temperature just below the decomposition point (about 160–175° F.). The preferred temperature range was found to be 115–135° F. Current densities between 0.1 ampere/sq. ft. and 150 amperes/sq. ft., and preferably 1–100 amperes/sq. ft. could be used to produce white mat aluminum plate of good quality.

The resistivity of the above bath was about 1200–1300 ohm-centimeters and it was noncombustible at the operating temperatures.

Example V

A plating bath is prepared in accordance with the procedure of Example IV, the bath divided into a number of portions and then each of the portions is saturated with one of a number of ionizable compounds. The bath had a resistivity of about 1200–1300 ohm-centimeters. Ionizable compounds for addition to different portions of the bath include tetramethyl ammonium chloride, dodecyltrimethyl ammonium chloride, amine salts, and organic compounds containing a nonoxygen-containing mineral acid function and salts thereof.

The addition of the above compounds reduces the resistivity of the bath. The most effective are the quaternary ammonium compounds, which lowered the resistivity from about 1200–1300 ohm-centimeters to approximately 600–700 ohm–centimeters.

The resultant bath was as satisfactory as the bath of Example IV for the electrodeposition of aluminum. In addition, the power requirements were lower due to the lower resistivity.

Example VI

A plating bath was prepared from the following:

	Moles
$AlCl_3$	3.8
$AlHCl_2$	2.0
Ethyl ether	3.8
2-ethoxyethyltrimethyl ammonium chloride	2

The above composition was heated to the melting point. The resultant bath was essentially a monoetherate of aluminum chloride plus a monoetherate of aluminum chlorohydride, of which 2 moles of the ether is 2-ethoxyethyltrimethyl ammonium chloride.

The above bath was noninflammable and had a resistivity of approximately 70 ohm-centimeters. When used for the electrodeposition of aluminum on steel panels, the bath produced excellent mat aluminum plate at current densities up to 300 amperes/sq. ft. The preferred temperature of electrodeposition was 115–135° F. Aluminum deposits of any desired thickness could be produced, and the bath could be used for electroforming.

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, the bath being noncombustible at the operating temperature and substantially free of an uncombined solvent for the organic complex of the aluminum halohydride.

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 and an organic complex of an aluminum halohydride, the bath being noncombustible at the operating temperature and substantially free of an uncombined solvent for the organic complex of the aluminum halide and the organic complex of the aluminum halohydride.

3. 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, the bath being noncombustible at the operating temperature 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.

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 and an etherate of an aluminum halohydride, the etherates containing halogen selected from the group consisting of chlorine, bromine and mixtures thereof, the bath being noncombustible at the operating temperature 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.

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 and an etherate of an aluminum halohydride, the etherates containing halogen selected from the group consisting of chlorine, bromine and mixtures thereof, the bath being noncombustible at the operating temperature and substantially free of an uncombined solvent for the etherate of the aluminum halide and the etherate of the aluminum halohydride 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 a monoetherate of aluminum chloride and a monoetherate of an aluminum chlorohydride, the monoetherates being formed from at least one ether having organic radicals attached to the oxygen atom containing 1–8 inclusive carbon atoms, the bath being noncombustible at the operating temperature and having a mole ratio of AlH_3 to $AlCl_3$ between about 1:2 and 1:11.

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 a monoetherate of aluminum chloride and a monoetherate of an aluminum chlorohydride, the ether forming the etherates comprising diethyl ether, the bath having a flash point not less than about 200° F. and 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 an etherate of aluminum halide and an etherate of an aluminum halohydride, the etherates containing halogen selected from the group consisting of chlorine, bromine and mixtures therof and being formed from at least one ether having organic radicals attached to the oxygen atom containing 1–8 inclusive carbon atoms, the bath having a mole ratio of AlH_3 to $AlCl_3$ between about 1:0.5 and 1:22, the bath being noncombustible at the operating temperature 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.

9. The process of claim 8 wherein the etherates are monoetherates and the ionizable compound dissolved in the bath is an alkali metal halide.

10. 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 and a monoetherate of an aluminum chlorohydride, the ether forming the etherates comprising diethylether, the bath having a flash point not less than about 200° F. and 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.

11. 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, the bath being noncombustible at the operating temperature and the complexing agent forming the complex comprising at least one ionizable compound which is also a Lewis base selected from the group consisting of quaternary ammonium compounds, amine salts, and organic compounds containing a nonoxygen-containing mineral acid group and salts thereof.

12. 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 and an etherate of an aluminum halohydride, the etherates containing halogen selected from the group consisting of chlorine, bromine and mixtures thereof the bath being noncombustible at the operating temperature 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.

13. 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 and an etherate of an aluminum halohydride, the etherates containing halogen selected from the group consisting of chlorine, bromine and mixtures thereof, the bath having a mole ratio of AlH_3 to $AlCl_3$ between about 1:05 and 1:22, the bath being noncombustible at the operating temperature and containing an etherate formed at least in part from a quaternary ammonium compound having an ether linkage.

14. A process for electrodepositing a metallic material on 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, the bath being noncombustible at the operating temperature and the ether forming the etherate comprising ethoxyethyltrimethyl ammonium chloride.

15. 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 and an etherate of an aluminum halohydride, the etherates containing halogen selected from the group consisting of chlorine, bromine and mixtures thereof, the bath being noncombustible at the operating temperature and containing an etherate formed at least in part from ethoxyethyltrimethyl ammonium chloride.

16. 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 and an etherate of an aluminum halohydride, the etherates containing halogen selected from the group consisting of chlorine, bromine and mixtures thereof, the bath having a mole ratio of AlH_3 to $AlCl_3$ between about 1:0.5 and 1:22, the bath being noncombustible at the operating temperature and containing an etherate formed at least in part from ethoxyethyltrimethyl ammonium chloride.

17. 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 and a monoetherate of an aluminum chlorohydride, the ether forming the etherates comprising diethyl ether and ethoxyethyltrimethyl ammonium chloride, the bath having a flash point not less than about 200° F. and a mole ratio of AlH_3 to $AlCl_3$ between about 1:2 and 1:11.

18. A bath for electrodepositing a metallic material consisting essentially of an organic complex of an aluminum halohydride, the bath being noncombustible at the operating temperature 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.

19. A bath for electrodepositing a metallic material consisting essentially of an etherate of aluminum halide and an etherate of an aluminum halohydride, the etherates containing halogen selected from the group consisting of chlorine, bromine and mixtures thereof, the bath being noncombustible at the operating temperature 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.

20. A bath for electrodepositing a metallic material consisting essentially of an etherate of aluminum halide and an etherate of an aluminum halohydride, 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,

the bath having a mole ratio of AlH_3 to $AlCl_3$ between about 1:0.5 and 1:22, the bath being noncombustible at the operating temperature 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.

21. A bath for electrodepositing a metallic material consisting essentially of a monoetherate of aluminum chloride and a monoetherate of an aluminum chlorohydride, the ether forming the etherates comprising diethylether, the bath having a flash point not less than about 200° F. and 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.

22. A bath for electrodepositing a metallic material consisting essentially of an organic complex of an aluminum halohydride, the bath being noncombustible at the operating temperature and the complexing agent forming the complex comprising at least one ionizable compound which is also a Lewis base selected from the group consisting of quaternary ammonium compounds, amine salts, and organic compounds containing a mineral acid group and salts thereof.

23. A bath for electrodepositing a metallic material consisting essentially of an etherate of aluminum halide and an etherate of an aluminum halohydride, the etherates containing halogen selected from the group consisting of chlorine, bromine and mixtures thereof, the bath being noncombustible at the operating temperature 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.

24. A bath for electrodepositing a metallic material consisting essentially of an etherate of aluminum halide and an etherate of an aluminum halohydride, the etherates containing halogen selected from the group consisting of chlorine, bromine and mixtures thereof, the bath having a mole ratio of AlH_3 to $AlCl_3$ between about 1:0.5 and 1:22, the bath being noncombustible at the operating temperature and containing an etherate formed at least in part from a quaternary ammonium compound having an ether linkage.

25. A bath for electrodepositing a metallic material consisting essentially of a monoetherate of aluminum chloride and a monoetherate of an aluminum chlorohydride, the ether forming the etherates comprising diethyl ether and ethoxyethyltrimethyl ammonium chloride, the bath having a flash point not less than about 200° F. and a mole ratio of AlH_3 to $AlCl_3$ between about 1:2 and 1:11.

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