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3,216,845

METAL DEPOSITIONS FROM ALKOXIDES

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17 Claims. (Cl. 117—35)

The present invention relates to methods of depositing an elemental metal from an alkoxide of the metal and an alcohol.

While the gradual heating of a metal salt of an organic acid or a metal alkoxide, when the metal is more electropositive than hydrogen, generally leads to thermal decomposition, with the formation of the metal oxide or carbonate, the present invention provides for a method for obtaining directly in elemental form such metals as nickel or cobalt, from suitably chosen alkoxides, by moderate heating, without apparent formation of the metal oxide or carbonate.

It is an object of the present invention to provide a method of depositing a metal from an alkoxide thereof.

It is an object of the present invention to provide a method of obtaining a metal in elemental form from a compound thereof by splitting the metal-oxygen bond of a metal alkoxide in which the metal is one of the electromotive series that is above hydrogen and below iron.

It is an object of the present invention to provide a method of depositing a metal such as nickel in the form of a continuous metal mirror on a substrate such as glass by heating a metal alkoxide such as nickel alkoxide of ethylene glycol at a relatively low temperature, say, of at least about 200° C. to deposit the nickel therefrom.

These and other objects will be apparent from the specification that follows and the appended claims.

The present invention provides a convenient inexpensive method of depositing a metal such as nickel on a substrate such as glass, metal, or a ceramic base by heating a metal alkoxide such as nickel alkoxide of ethylene glycol at a relatively low temperature, say preferably about 200° C., to break the nickel-oxide bond homolytically and deposit the nickel in a powdery film or mirror-like film on the substrate.

The metals that can be deposited as above described from their respective alkoxides are nickel, cobalt, cadmium, tin and lead. These metals are all listed in the electromotive series above hydrogen and below iron. See Lange's Handbook of Chemistry, Ninth Edition, pages 1212-1218.

Metal alkoxides of more electropositive metals such as iron, zinc, manganese and chromium are not suitable in accordance with the present invention to obtain a deposit of powder or a metallic film.

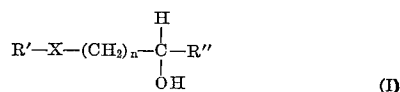
Although it is not completely understood and applicant does not wish to be strictly held to his theory, it is believed that ordinarily difficult to break metal-oxygen bond can be broken in the particular alkoxides herein-after described because the organic portion of the alkoxide molecule, by virtue of chelation or intramolecular coordinate bonding of the metal atom to a sulfur, nitrogen, or oxygen atom other than that of the alkoxide linkage, reduces the energy required to sever homolytically the bond between the metal and the alkoxide oxygen. This

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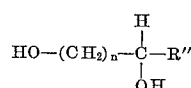
reduction in energy is sufficient to make possible the thermal deposition of metals less electropositive than iron. When metals more electropositive than iron are used, their bond energies are presumably similarly affected, but the energy requirements remain too high for such reduction. For metals below hydrogen in the electromotive series, the energy requirements for formation of the metal are sufficiently low that they may in some cases form metal on heating even if the modification of the energy requirement by chelation or coordinate bonding is non-existent. Thus, this invention is most clearly demonstrable in a range of compositions where no other known mechanism suffices to explain the reactions.

Suitable alkoxides of cadmium, cobalt, nickel, tin and lead can be prepared as described in copending application Serial No. 64,705, filed October 25, 1960, now abandoned, of Charles H. Fuchsman and assigned to the same assignee as the present application. As therein disclosed, the preferred alcohols for preparing the alkoxides are polyfunctional alcohols having a functional group such as an oxygen atom or a sulfur atom at a position alpha or beta to the carbon atom carrying the hydroxyl group that enters into the hydrocarbon reaction. Alcohols having the above structure and exemplified by glycols such as ethylene glycol, thiodiethanol and 1,3-propylene glycol.

In accordance with the above description of the preferred polyfunctional alcohol, suitable alcohols are those having the general formula:



or



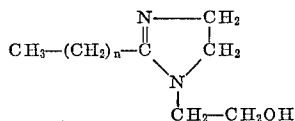
wherein R' is alkyl, aryl, alkaryl, aralkyl, cycloalkyl, alkoxyalkyl, alkoxyaryl, aroxyalkyl, aroxyaryl, alkoxy-cycloalkyl, cycloalkoxyalkyl, hydroxyalkyl, hydroxycycloalkyl, and hydroxyalkoxyalkyl; X is oxygen or sulfur, R'' is hydrogen or one of the radicals listed for R', and n is 1 or 2.

While primary alcohols are preferred, secondary alcohols may also be used as indicated below in the specific examples. Thus, R'' in Formula I may be hydrogen, or an alkyl group, such as methyl, ethyl, propyl, isopropyl, butyl, t-butyl, amyl, t-amyl, hexyl, cyclohexyl, 2-ethyl hexyl, nonyl, decyl, dodecyl, lauryl, cetyl, and octadecyl; or, these alkyl groups may contain oxygen attached to two carbon atoms or to a single carbon atom. In the latter case, the oxygen may be singly bonded to such carbon atom as hydroxyl. The radical R' includes the same radicals as mentioned above as useful for R'' with the exception of hydrogen, and additionally aryl radicals such as phenyl and naphthyl; alkaryl radicals such as cresyl, xylyl, mesityl, p-ethylphenyl, p-t-butylphenyl, p-2-ethylhexylphenyl, p-1,1,3,3-tetramethylbutylphenyl, p-dodecylphenyl; aralkyl radicals such as benzyl, phenylethyl, phenylcyclohexyl; cycloalkyl radicals such as cyclohexyl, cyclopentyl, methylcyclohexyl; alkoxyalkyl radicals, such as methoxy ethyl, ethoxymethyl, ethoxy-

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ethyl, propoxyethyl; alkoxyaryl radicals such as methoxyphenyl, ethoxyphenyl; aroxyalkyl radicals such as phenoxymethyl, phenoxyethyl, phenoxypropyl; aroxyaryl radicals such as phenoxyphenyl; alkoxyalkyl radicals, such as methoxycyclohexyl, ethoxycyclohexyl; cycloalkoxyalkyl radicals, such as cyclohexoxymethyl, cyclohexoxyethyl; hydroxyalkyl radicals such as hydroxymethyl, hydroxyethyl, hydroxypropyl, hydroxybutyl, hydroxyoctyl; hydroxycycloalkyls, such as p-hydroxycyclohexyl; and hydroxyalkoxy alkyl radicals such as hydroxyethoxyethyl, hydroxypolyethoxyethyl.

Also suitable as the alcohol component of the metal alkoxides or alcoholates is an alcohol having 8 to 28 carbon atoms and having a fatty acid residue of at least 8 carbon atoms in its molecular chain such as the fatty acid-imidazoline condensation product having the general formula:



where n is 6 to 12.

Also suitable is the imidazoline reaction product of oleic acid—such a material being sold commercially as Amide O by Geigy Industrial Chemicals, a Division of Geigy Chemical Corporation, Yonkers, New York.

One of the preferred alkoxides of the present invention is one formed from a cyclic ether-alcohol material having a cyclic configuration in which the hydroxyl group is attached to a carbon atom beta to the ether oxygen atom of the cyclic structure. Suitable cyclic ether-alcohol materials, preferably having about 5 to 7 carbon atoms, are tetrahydrofurfuryl alcohol and tetrahydropyrane-2-methanol.

Also suitable as the alcohol component of the alkoxides are amino alcohols preferably having about 4 to 8 carbon atoms and having a hydroxyl group in a position beta to the amino nitrogen atom. Suitable amino alcohols are diethyl aminoethanol and dimethylaminoethanol.

In general, the metal alkoxide starting materials of the present invention are produced by reacting (1) a divalent salt of a carboxylic acid (preferably acetic acid) and a suitable metal such as nickel and (2) an alcohol as previously described and thereafter removing the monocarboxylic acid formed such as acetic acid by distillation or another suitable means. Inasmuch as the boiling point of acetic acid at atmospheric pressure is relatively low, being about 118° C. and inasmuch as the acid is generally diluted, generally the reaction temperature employed in preparing the alkoxides is about 130° C. up to as high as about 158 to 168° C.

The reactions may be conducted in a solvent; or where the alcohol is liquid at the reaction temperature, an excess of alcohol may be used as the solvent. The reaction may be conducted at atmospheric pressure or under vacuum and the temperature may range from room temperature to the temperature at which the carboxylic acid produced in the course of the reaction volatilizes under the conditions of pressure employed.

In general, suitable carboxylic acids that can be used to prepare the metal alkoxide starting material are: propionic, butyric, isooctic, 2-ethylbutanoic, cyclohexane carboxylic, acrylic, 3-(2-ethylbutoxy) propionic acid in which the acid preferably has about 2 to 8 carbon atoms. but less volatile acids containing greater numbers of carbon atoms (e.g., naphthenic acids of acid value of about 300) can be used, but more extreme conditions, particularly of vacuum, may be required to conduct the necessary reaction.

The following examples are intended to illustrate the present invention and not to limit the same in any way:

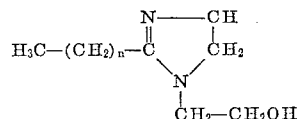
Example 1

This example illustrates the deposition of nickel from

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an alkoxide of nickel and a beta-hydroxy ethyl derivative of a coconut fatty acid-imidazoline condensation product.

The nickel alkoxide starting material was previously prepared by reacting nickel acetate with the above described alcohol, which alcohol had the following general formula prior to reaction with the nickel acetate to form the resultant nickel alkoxide:



where n is an integer from 6 to 12.

The above nickel alkoxide material was placed in a 25 x 150 mm. test tube equipped with a glass stirrer and heated with stirring by mechanical means at a temperature of about 250° C., in 50 minutes a powdery film of nickel appeared. After about 5 hours of heating, the powdery film became a continuous metal mirror deposited on the inner glass surface of the test tube. The identity of the mirror material as nickel was confirmed by X-ray analysis and by qualitative chemical analysis.

Example 2

A bright nickel mirror was deposited on a glass substrate, which was the inner wall of a test tube, by heating in the test tube the nickel alkoxide of Example 1 in accordance with the methods described therein, except that an equal amount of nonyl phenol was used to dilute the nickel alkoxide. A powdery metal deposit of nickel appeared in 45 minutes and the formation of a nickel mirror from the powdery deposit occurred in three hours.

Example 3

The nickel alkoxide of an alcohol that is the beta hydroxy ethyl derivative of oleic acid-imidazoline condensation product was heated at 205° C. for about 30 minutes as in Example 1 to provide a powdery nickel film. Continued heating for about a total time of about 2½ hours produced a mirror-like deposit.

Example 4

An equal mixture of nonyl phenol and the nickel alkoxide of Example 3 was heated at 205° C. to deposit nickel therefrom. The time for first film formation and the time for mirror formation was about the same as reported in Example 3.

Example 5

Nickel alkoxide of nonyl phenoxy ethanol was prepared by heating about equal molar amounts of nickel acetate tetrahydrate and nonyl phenoxy ethanol in xylene under reflux for about 3 to 4 hours and the reaction mixture filtered to obtain a dark green solution as the filtrate in a manner similar to that described and claimed in the previously described copending application of Charles H. Fuchsman.

The dark green solution was stripped of solvent, and the solution heated to slowly form a nearly white solid material of paste-like consistency. On continued heating, the paste-like mass became fluid again and dark green in color. Heating was continued at 205° C. and the system held under aspirator vacuum to remove acetic acid.

Upon continued heating at 205° C., a mirror-like deposit of nickel was obtained on the inner glass wall of the reaction vessel. A portion of the nickel apparently was deposited at about 205° C. as a mirror even before all the nickel had been converted to the nickel alkoxide.

Example 6

During preparation of the Ni alcoholate of diethylene glycol mono-n-butyl ether (commercially available as Dowanol-19), the fine mist on the upper flask wall (at 245–250°) deposited a nickel mirror while only 25% of the Ni had been converted to alcoholate.

Example 7

Using the following solid derivatives of glycols, 1.0 g. of solid was suspended in 10 g. of mineral oil (Nujol) in a 20 ml. test tube and heated in an oil bath at $205 \pm 5^\circ \text{C}$. without agitation:

Metal	Alcohol	Product
Nickel-----	Ethylene glycol----	Powdery film. dull metallic gray.
Do-----	Hexylene glycol----	Do.
Lead-----	Do-----	Do.
Cobalt-----	Ethylene glycol----	Mirror-bright and reflective.
Do-----	Thiodiethanol-----	Powder only.
Cadmium-----	Ethylene glycol----	Mirror.
Do-----	Hexylene glycol----	Powder only.

Example 8

A lead mirror was deposited from a lead alkoxide dissolved in mineral oil having a boiling point over about 370°C . The alkoxide used was the lead alkoxide of the beta-hydroxy ethyl derivative of a coconut fatty acid-imidazoline condensation product, this particular alcohol being described in Example 1 and being sold commercially by Geigy Chemical as Amine C. The temperature employed in depositing the lead was 205°C . and the time was about one hour.

In the above examples, cadmium, cobalt, nickel, tin and lead may be substituted in whole or part for the metal actually used to obtain nearly equivalent results and, thus, to provide at least some of the benefits of the present invention. Of these metals, as previously indicated, nickel and cobalt are highly preferred. Also, in the above examples, as previously indicated, other alkoxides or alcohols can be used to produce the metal powder, the powdery film or the mirror-like film. For instance, alcohols that can be substituted for the alcohols actually employed to provide substantially equivalent results are the following: tetrahydrofurfuryl alcohol, ethylthioethanol, triethanolamine, trimethylolpropane, pentaerythritol dicaprate, 1,3-propane diol, ethoxytriglycol, propylene glycol, ethylene glycol mono methyl ether, ethylene glycol mono-n-hexyl ether, N,N-diethyl aminoethanol.

Also in addition to the above preferred alcohols, metal alkoxides of the polyfunctional alcohols having a functional group alpha or beta to the hydroxyl group (as previously described herein) can be substituted for the particular metal alkoxide used in the examples to provide at least some weakness of the metal-oxygen bond and the subsequent deposit of the metal.

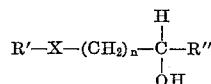
Although the exact temperature employed to break the metal-oxygen bond of the metal alkoxide may vary somewhat depending upon the alcohol and, in some cases, the metal salt originally used to produce the alkoxide as for instance when the nickel alkoxide is produced by the reaction of nickel acetate and ethylene glycol and the reaction product heated without removing the same from the reaction vessel or further purifying or treating the same, generally a temperature of at least about 180°C . should be employed to break the above described metal-oxygen—particularly in the case of metals such as nickel and cobalt that are higher in the electromotive series than a metal such as lead. Preferably, the decomposition temperature used should be at least about 200°C . and generally the best results are obtained at about 200 to 220°C ., although occasionally such as described in Example 6, a temperature of $245\text{--}250^\circ \text{C}$. or higher say, about 270°C ., may be required to obtain a metallic mirror or even an elemental metal powder.

It is also apparent that modifications of the invention may be made without changing the spirit thereof, and it is intended that the invention be limited only by the appended claims.

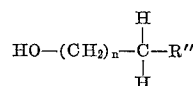
What is claimed is:

1. A method comprising the steps of heating a metal

alkoxide of (A) a metal that is in the electromotive series between iron and hydrogen, and (B) an alcohol to a temperature of at least about 180°C . and sufficient to deposit said metal from said alkoxide on a substrate, the alcohol being selected from a member of the group consisting of (1) an alcohol having about 8 to 28 carbon atoms and having a residue of a fatty acid in its molecular chain of at least 8 carbon atoms, (2) a polyfunctional alcohol having the general formula:

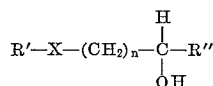


15 wherein R' is a radical selected from the group consisting of alkyl, aryl, alkaryl, aralkyl, cycloalkyl, alkoxyalkyl, alkoxyaryl, aroxyalkyl, alkoxy-cycloalkyl, cycloalkoxy-alkyl, hydroxyalkyl, hydroxycycloalkyl and hydroxy-alkoxyalkyl; X is selected from the group consisting of oxygen and sulfur, R'' is selected from the group consist-
20 ing of hydrogen and R' radicals; and n is an integer from 1 to 2, (3) a polyfunctional alcohol having the general formula:

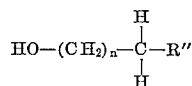


25 wherein R'' is selected from a member of the group consisting of hydrogen and R' radicals and n is an integer from 1 to 2, (4) a cyclic ether-alcohol compound having a cyclic structure including an ether oxygen atom and a hydroxyl group attached to a carbon atom in a position beta to said ether oxygen atom, and (5) an organic amino alcohol having a hydroxyl group attached to a carbon atom in a position beta to the amino nitrogen atom.

2. A method of obtaining an elemental nickel from a nickel alkoxide comprising the step of heating to a temperature of about 180° to 270°C . to deposit nickel on a substrate, a nickel alkoxide of an alcohol of the group consisting of (1) an alcohol having about 8 to 28 carbon atoms and including a fatty acid residue of at least 8 carbon atoms in its molecular chain (2) a polyfunctional alcohol having the general formula:



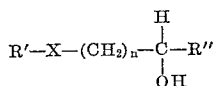
30 wherein R' is a radical selected from the group consisting of alkyl, aryl, alkaryl, aralkyl, cycloalkyl, alkoxyalkyl, alkoxyaryl, aroxyalkyl, alkoxy-cycloalkyl, cycloalkoxy-alkyl, hydroxyalkyl, hydroxycycloalkyl and hydroxyalkoxyalkyl; X is selected from the group consisting of oxygen and sulfur, R'' is selected from the group consisting of hydrogen and R' radicals; and n is an integer from 1 to 2, (3) a polyfunctional alcohol having the general formula:



35 wherein R'' is selected from a member of the group consisting of hydrogen and R' radicals and n is an integer from 1 to 2, (4) a cyclic ether-alcohol compound having a cyclic structure including an ether oxygen atom and a hydroxyl group attached to a carbon atom in a position beta to said ether oxygen atom, and (5) an organic amino alcohol having a hydroxyl group attached to a carbon atom in a position beta to the amino nitrogen atom.

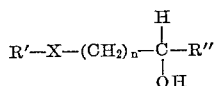
3. A method of depositing metal from an alkoxide on a substrate, the method comprising heating a metal alkoxide of a metal that is one of the electromotive series above hydrogen and below iron and a polyfunctional alcohol to a temperature of at least about 200°C . and suffi-

cient to deposit said metal on a substrate, said alcohol having the general formula:



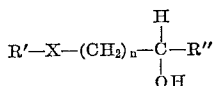
wherein R' is a radical selected from the group consisting of alkyl, aryl, alkaryl, aralkyl, cycloalkyl, alkoxyalkyl, alkoxyaryl, aroxyalkyl, alkoxy-cycloalkyl, cycloalkoxyalkyl, hydroxyalkyl, hydroxycycloalkyl and hydroxyalkoxyalkyl; X is selected from the group consisting of oxygen and sulfur, R'' is selected from the group consisting of hydrogen and R' radicals; and n is an integer from 1 to 2.

4. A method of depositing a metal that is one of the electromotive series above hydrogen and below iron from an alkoxide on a substrate comprising heating to a temperature of about 180° to 270° C., the metal alkoxide of said metal and a polyfunctional alcohol having the general formula:



wherein R' is a radical selected from the group consisting of alkyl, aryl, alkaryl, aralkyl, cycloalkyl, alkoxyalkyl, alkoxyaryl, aroxyalkyl, alkoxy-cycloalkyl, cycloalkoxyalkyl, hydroxyalkyl, hydroxycycloalkyl and hydroxyalkoxyalkyl; X is selected from the group consisting of oxygen and sulfur; R'' is selected from the group consisting of hydrogen and R' radicals; and n is an integer from 1 to 2.

5. A method of depositing nickel from a nickel alkoxide comprising heating to a temperature of at least about 200° C. and sufficient to deposit nickel on a substrate, a nickel alkoxide of an alcohol having the general formula:



wherein R' is a radical selected from the group consisting of alkyl, aryl, alkaryl, aralkyl, cycloalkyl, alkoxyalkyl, alkoxyaryl, aroxyalkyl, alkoxy-cycloalkyl, cycloalkoxyalkyl, hydroxyalkyl, hydroxycycloalkyl and hydroxyalkoxyalkyl; X is selected from the group consisting of oxygen and sulfur, R'' is selected from the group consisting of hydrogen and R' radicals; and n is an integer from 1 to 2.

6. A method of depositing metal as defined in claim 1 in which said metal is cobalt.

7. A method of depositing metal as defined in claim 1 in which said metal is cadmium.

8. A method of depositing metal as defined in claim 1, in which said metal is tin.

9. A method of depositing nickel on a glass substrate comprising the steps of heating to a temperature of about 200° to 220° C. a nickel alkoxide of ethylene glycol suspended in a diluent comprising mineral oil.

10. A method of depositing cobalt on a substrate comprising the step of heating to about 200° to 220° C. a cobalt alkoxide of ethylene glycol to provide on the substrate a continuous metal mirror of cobalt.

11. A method of obtaining metallic cobalt from a cobalt alkoxide comprising the step of heating cobalt alkoxide of thiodiethanol suspended in mineral oil to a temperature of about 200° to 220° C. to deposit cobalt on a substrate.

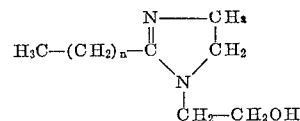
12. A method of obtaining a deposit of metallic cadmium from a cadmium alkoxide comprising heating cadmium alkoxide of ethylene glycol suspended in mineral oil to a temperature of about 200° to 220° C. to thereby deposit metallic cadmium on a substrate.

13. A method comprising the step of heating a metal alkoxide of (A) a metal that is one of the elements in the electromotive series between hydrogen and iron and (B) tetrahydrofurfuryl alcohol to a temperature of at least about 180° C. and sufficient to deposit said metal on a substrate.

14. A method comprising the step of heating a metal alkoxide of (A) a metal that is one of the elements in the electromotive series between hydrogen and iron and (B) tetrahydropyran-2-methanol to a temperature of at least about 180° C. and sufficient to deposit said metal on a substrate.

15. A method comprising the step of heating a metal alkoxide of (A) a metal that is one of the elements in the electromotive series between hydrogen and iron and (B) an organic amino alcohol containing from 4 to 8 carbon atoms and having a hydroxyl group attached to a carbon atom that is in a position beta with respect to the amino nitrogen atom to a temperature of at least about 180° C. and sufficient to deposit said metal on a substrate.

16. A method of depositing nickel on a substrate comprising heating at about 200 to 220° C. a nickel alkoxide of an alcohol having the general formula:



where n is 6 to 17, to produce a powdery film of nickel, and thereafter heating the powdery film to provide a continuous metal mirror of nickel.

17. A method of depositing nickel on a substrate in a continuous metal mirror comprising heating at about 200° to 220° C. a nickel alkoxide of an alcohol of a beta-ethanol derivative of an oleic acid-imidazoline condensation product.

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