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## ELECTROLYTIC DEPOSITION OF TUNGSTEN

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 dated August 8, 1944. Divided and this application  
 July 12, 1944, Serial No. 544,652

6 Claims. (Cl. 204—45)

This invention relates to an improved method of electrolysis, including the electrodeposition of metals, particularly tungsten, and to the composition of the electrolyte. This application is a division of the continuation-in-part application Serial No. 509,199, filed November 6, 1943, of application Serial No. 21,809, filed May 16, 1935, and a division of copending application Serial No. 151,854, filed July 3, 1937, now Patent No. 2,355,070, of August 8, 1944.

In the procedures heretofore employed in the electroplating art, it has been found advantageous for various reasons to prepare an electrolyte in which the metal to be deposited is in the form of a complex compound. As a result of extended experience and experiment, cyanides have been found especially suitable and are used in large amounts in electrolytic baths, and many technical practices of electrolysis and electroplating depend upon them. Such practices have been adopted and adhered to, in spite of the well-known intensely poisonous character of cyanides and cyanide solutions and the danger which is consequently incurred throughout the plants in which such compounds must be stored, handled, operated with and replenished from time to time.

Other procedures have been followed, it is true, but these, in general, entail the use of two or more solutions operating as a batch process. Operating in this way it is necessary to add chemicals to certain parts of the system and to withdraw and discard worthless by-products from others. In thus destroying or converting the components of the electrolyte to some other form, these processes of the prior art involve the unnecessary and hence wasteful consumption of reagents and of electric current or energy, as well.

It is accordingly an object of this invention to provide an improved method of electrodeposition in which satisfactory or improved results may be accomplished and in which compounds other than the cyanides, and which are essentially non-poisonous, may be used.

Another object is to provide a method in which the current efficiency may be improved. A further object is to obtain a brighter plate.

It is also an object to provide an electrolytic process and an electrolytic medium wherein the reaction consists in effecting electrolytic transfer of the metal (anode) to metal (cathode) without side reactions or at least without side reactions resulting in the cumulative formation of ancillary by-products, and in which the only

cumulative product is that of the electrolytically deposited metal on the cathode, and in which the only required addition is that of replenishing such metal in the system, as a metal at the anode. Economy of reagents and of electric current, accordingly are objects of the invention. Other objects will appear from the following disclosure.

A salient feature of the present invention is the discovery that tungsten is subject to a uniform electrolysis and undergoes a dependable dissolution and regular deposition of the metal under the influence of an electric current, if the electrolyte is of substantially uniform composition between the anode and the cathode and contains a hydrocarbon polyamine such as ethylene diamine. It may be further enhanced if an excess of the hydrocarbon polyamine is present. The hydrocarbon polyamine added—whether in excess or not—does not appear to be permanently affected by the electrolysis and even after prolonged use of the bath it is found upon analysis to remain undiminished in its total content.

The hydrocarbon polyamine combines with the metal or with the cation of the electrolyte and particularly with the metal component of the salt, to form therewith a complex ion which is readily susceptible to ionization, electrolytic transfer to the cathode, and discharge of the metal ion and deposition of the metal in solid form thereon. The metal content of the electrolyte is replenished by the direct corrosion and dissolution of the anode.

By the expression "electrolytic deposition" as used in the present application and in the claims, is to be understood the electrolysis of an electrolyte, containing one or more metals in solution, and forming a continuous liquid medium between the cathode and a soluble metal anode, which includes the separation and deposition of said dissolved metal or metals upon the cathode, and simultaneously dissolving of the metal anode, thereby replenishing and maintaining the metal content of the electrolyte.

The anodes, formed of tungsten, are uniformly and regularly dissolved into the electrolyte without disintegration and the resulting formation of residual granules or powder.

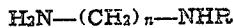
The process is characterized by being applicable to metals which are able to form complex cations containing a hydrocarbon polyamine. The proof that such complex ions are formed is that the metals in the form of the complex ion can exist in alkaline solution whereas the cor-

responding simple metal ions are precipitated when made alkaline, as by the hydroxide of an alkaline metal.

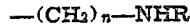
Hydrocarbon polyamines contain carbon, nitrogen, and hydrogen and no other elements. They are thus distinguished from ammonia, and also from the alkylamines which contain oxygen, both of which are unsuitable for use in the present process. Hydrocarbon polyamines suitable for use in the present invention contain at least two atoms of nitrogen, each of which is joined to a carbon atom but not to a nitrogen atom; they are water-soluble and definitely basic. Examples of suitable hydrocarbon polyamines are ethylene diamine, propylene diamine, and the polyethylenes amines. The latter are considered to be condensation products of ethylene diamine with itself or with other aliphatic amines; one of the simplest of such products would be:



The general formula of hydrocarbon polyamines suitable for use in connection with this process is therefore:



where  $n$  is 2 or more and R is hydrogen or the radical



R being the same as just explained.

The process of the invention, as described in the above mentioned applications, may be carried out, for example, with salts of certain monovalent metals, such as silver, with salts of bivalent metals, such as copper, cadmium, zinc, and nickel, with salts of trivalent metals, such as iron and chromium, and salts of tetravalent or hexavalent metals, such as platinum and tungsten, in the presence of the polyamine. In these metallic polyamine complexes, the polyamine and the metal are attached to each other by the secondary valances of the nitrogen and of the metallic atoms. Since only secondary valences are involved, the entrance of the polyamine into the cation does not alter the charge or valence of the cation.

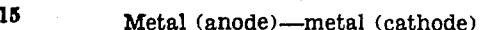
In practice, it is now found that when tungsten is made the anode, with respect to an electrically conductive cathode, and an aqueous fluid electrolyte is provided, extending from the surface of one to the surface of the other without interruption, containing a soluble hydrocarbon diamine as above defined—the application of an electrical potential or current between the electrodes will result in the dissolution of the anode and the electrolytic deposition of the metal upon the cathode, without side reactions and without change of regulation other than the addition of metal as metal to the anode and removal of the deposited metal on the cathode.

It is found that a water solution of the amine alone is sufficient for such operation—the metal from the anode dissolving and forming complex cations in the electrolyte and undergoing electrolytic deposition without the addition of any salt of the metal and without any indication that salt formation of the metal occurs. On the other hand, a salt of the metal or metals involved may be present to advantage, especially where it is economical to employ.

In either case, however, it is essential that the fluid medium of the electrolyte between the anode and cathode be unobstructed, continuous, and preferably uniform, as by agitation.

It will be observed that the electrolytic solu-

tion is contained in a single vessel, which is preferably lined with rubber, and forms a continuous medium between the anode or anodes (which are connected to the positive bus bars, 5 and are composed of the metal or metals to be deposited) and the cathode or cathodes, which are connected to the negative bus bar, and upon which the metal is to be deposited. The uniformity of the electrolytic solution during operation may be promoted by agitating the electrolyte with any suitable means (not shown) but is substantially automatically preserved throughout the reaction which is accurately represented, in its net effective result, by the equation



for there is no cumulative consumption or conversion of the other constituents of the electrolyte into by-products and hence no necessity for replacement or reconversion, even upon long and continuous operation.

It is found that hydrocarbon polyamines react with ionized salts of tungsten in aqueous solution, to form various orders of compounds.

25 The number of compounds so formed varies, in accordance with the number of secondary valences (as set forth in theories of Werner complexes), but need not be gone into here in any great detail as the invention will be clear from the disclosure herein.

30 It is generally preferable to use at least 2 mols of hydrocarbon polyamine to one mol of the salt of tungsten, and best results range between about 2½ and 6 mols of the polyamine to one of the salt.

35 More polyamine may be used, but there is no particular advantage in so doing.

Typical and representative examples of the practical application of this invention will now be described in its relation to electroplating, with 40 respect to tungsten and to various salts of the metal.

In the example, the ethylene diamine is given on the anhydrous basis, although it is customarily available in the form of a 40% or 60% solution in 45 water.

In carrying out the process of this invention, the temperature of the bath is preferably at, or somewhat above, room temperature—generally between 25° C. and 40° C.

50 The electrolyte may be contained in any suitable resistant vessel which is preferably a non-conductor of the electric current, such as earthenware or rubber. The anode (or anodes) may conveniently consist of tungsten strips which are

55 connected to a source of electric current and are suspended in the solution, preferably so as to be completely submerged, as by bus bars, having a chemically resistant or protected conductor. In one case, for example, using an electrolyte hav-

60 ing the composition indicated in the example below, tungsten wire anodes were used. Brass cathodes were connected to a suitable source of electric current to provide a current density of 20 to 40 amperes per square foot of cathode area and 65 were found to give satisfactory electrolytic de-

positions.

While ethylene diamine is set forth in the example as the hydrocarbon polyamine used, it may be replaced by other hydrocarbon polyamines.

70 It is possible to use more than one salt of the same metal in the plating bath, if desired.

It is also possible to plate alloys by the present process. For example, brass may be successfully plated by using brass anodes and a bath of 75 copper and zinc salts.

As described in the above mentioned applications, it is possible to carry out the process of this invention by first dissolving a salt of the metal to be plated in the bath. In other cases, the metal of the anode dissolves to furnish sufficient metallic ions in the bath, and plating proceeds. Such procedure has no particular advantage when plating with most ordinary metals, but when the rarer metals are used, such as tungsten and platinum, and metals of the platinum group, it is generally inconvenient and expensive to use their salts in the bath, and adequate results can be obtained as far as such metals are concerned when an anode of the metal to be plated is placed in a bath containing a hydrocarbon polyamine and the plating carried out as described above. For instance, a tungsten anode is immersed in a bath containing 25% ethylene diamine in water. Using a brass cathode and a current density of 25 amperes per square foot a good, bright plate of tungsten was obtained. The compound of tungsten if any were formed in the bath, was not identified. The pH of the bath containing tungsten ions is about pH 7.0.

Platinum and other metals of the platinum group may be plated in the same way. Alternatively, if desired, salts of these metals may be added to the plating baths and the procedures of the preceding examples may be used.

The cathode in operating with the solutions described herein, may be substantially any clean, smooth, electrically conductive metallic surface. The operation of the reaction is smooth and continuous, forms a bright, uniform deposit of metal on the cathode, and may be prolonged for substantially any desired period of time without care or control, other than the supply of an electric current, and replenishment of the metal of the anodes,—and removal and replacement of the plated cathode, from time to time, if and when desired.

If there is any tendency for basic salts of the electrolyte to separate, as for example, at the

cathode (with solutions containing a lower ratio of hydrocarbon polyamine to metallic salt than 2:1), which might interfere with the continuity of the deposition or of the plated surface coating, this may be overcome by the addition of sulfuric acid (in case of sulfate salts or corresponding acid in case of other salts) or of the polyamine, or both. Agitation of the bath or of the cathode is likewise helpful.

10 I claim:

1. An aqueous electrolyte for the electrolytic deposition of tungsten characterized by consisting essentially of tungsten ions and an alkyl hydrocarbon polyamine and manifesting a pH value above 7.0.

2. An aqueous electrolyte for the electrolytic deposition of tungsten characterized by consisting essentially of tungsten ions and ethylene diamine and manifesting a pH value above 7.0.

20 3. A process of electrolysis that comprises electro-depositing tungsten from an undivided cell containing an aqueous electrolyte consisting essentially of tungsten ions and an alkyl hydrocarbon polyamine and manifesting a pH value above 7.0.

25 4. A process of electrolysis that comprises electro-depositing tungsten from an undivided cell containing an aqueous electrolyte consisting essentially of tungsten ions and ethylene diamine and manifesting a pH value above 7.0.

30 5. An aqueous electrolyte for the electrolytic deposition of tungsten, characterized by consisting essentially of tungsten ions and an alkyl hydrocarbon diamine and manifesting a pH value above 7.0.

35 6. A process of electrolysis that comprises electro-depositing tungsten from an undivided cell containing an aqueous electrolyte consisting essentially of tungsten ions and an alkyl hydrocarbon diamine and manifesting a pH value above 7.0.

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