

Aug. 8, 1944.

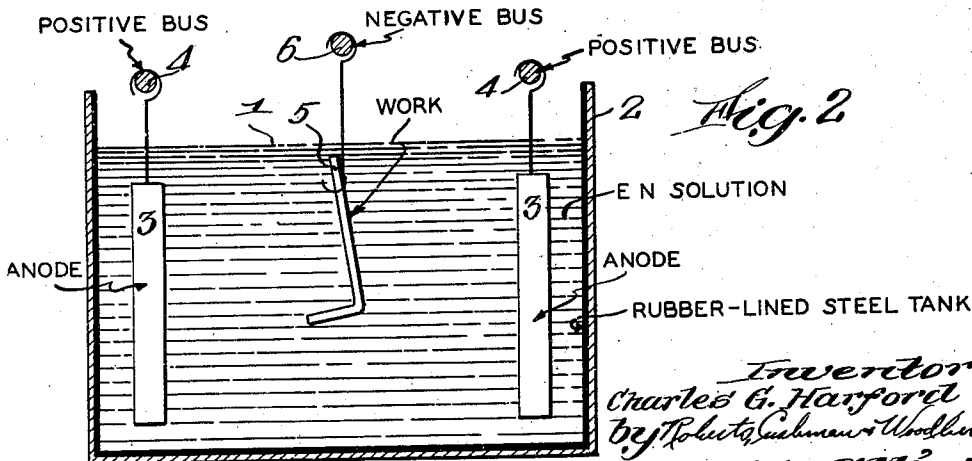
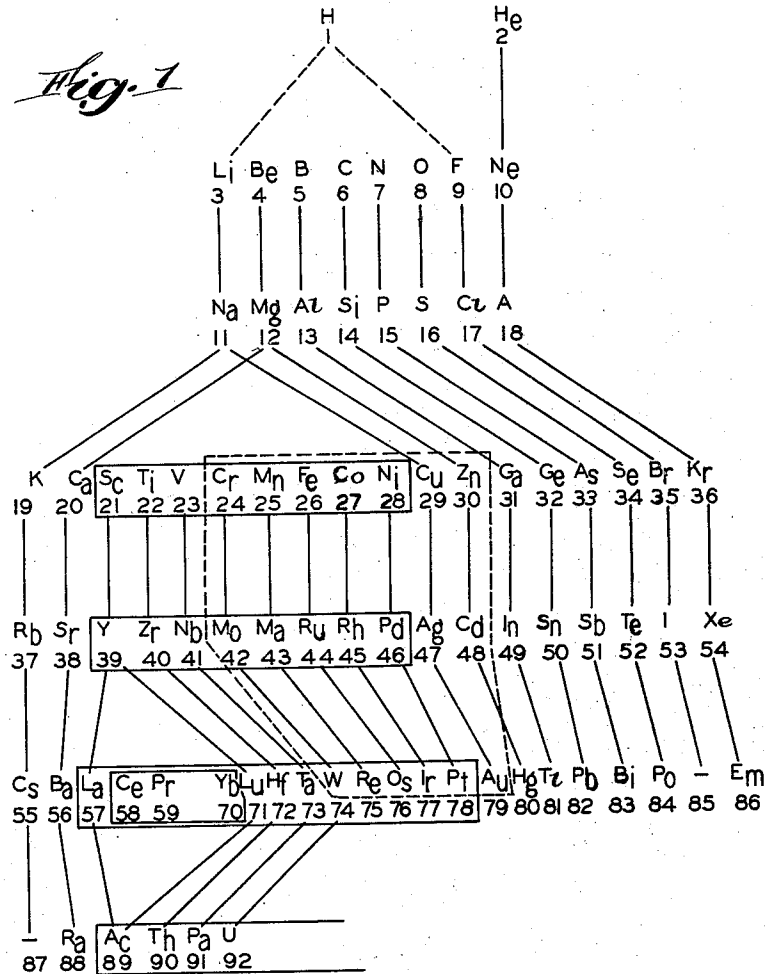
C. G. HARFORD

2,355,070

ELECTROLYTIC DEPOSITION OF METAL

Filed July 3, 1937

Fig. 1



Inventor:
Charles G. Harford
by Robert G. Schuman & Woodbury
His attys.

UNITED STATES PATENT OFFICE

2,355,070

ELECTROLYTIC DEPOSITION OF METAL

Charles G. Harford, Quincy, Mass., assignor to
Arthur D. Little, Inc., a corporation of Massachusetts

Application July 3, 1937, Serial No. 151,854

19 Claims. (Cl. 204—52)

This invention relates to an improved method of electrolysis, including the electro-deposition of metals, and to the composition of the electrolyte.

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 electro-deposition 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 certain monovalent or polyvalent metals are subject to a uniform electrolysis and undergo 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 the metal to be deposited or plated out, are uniformly and regularly dissolved into the electrolyte without disintegration and the resulting formation of residual granules or powder.

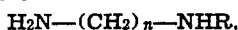
The process is characterized by being applicable to metals which are able to form complex cations containing a hydrocarbon polyamine. The proof that such complex ions are formed is that the metals in the form of the complex ion can exist in alkaline solution whereas the corresponding simple metal ions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

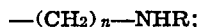
are thus distinguished from ammonia, and also from the alkylolamines which contain oxygen, both of which are unsuitable for use in the present process. Hydrocarbon polyamines suitable for use in the present invention contain at least two atoms of nitrogen, each of which is joined to a carbon atom but not to a nitrogen atom; they are water-soluble and definitely basic. Examples of suitable hydrocarbon polyamines are ethylene diamine, propylene diamine, and the polyethylene 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 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 valences 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.

It follows, therefore, generically from the inherent ionic structure of the metals, that those metals presenting the Werner type of configuration are susceptible to the application of the invention. Metals presenting this type of configuration are characterized as being those which are capable of forming complex ions with electrically neutral compounds—such as the hydrocarbon polyamines, typified by ethylene diamine, propylene diamine, and the polyethylene amines above mentioned. And this relationship (as determinative of the metals with which the process of the invention may be carried out and those with which it is not applicable), has been affirmed by experiments.

This is explained by the physical chemists as follows:—metals which exhibit the required type of ion formation or structure are those which ionize and which, in such ionization, leave a partially filled or incomplete electron shell in the residue of the ion after ionization has taken place. There are some metals, however, which leave incomplete electron shells, upon ionization, and hence fall within this definition but with which the process of the invention is not applicable because they form ions only with great difficulty—namely: Ti , V , Zr , Nb , Lu , Hf , Ta . The rare earths also present an exception and do not come within the scope of this invention because, although they leave an incomplete electron shell upon ionization, this shell presents the condition of not being the exterior shell and is consequently so protected by a complete electron shell that it does not influence the chemi-

cal properties of the whole to any extent, and does not render the ion susceptible to complex ion formation of the Werner type. Certain other metals (for example, Th and U) falling within this definition in respect of their ionic structure and which leave incomplete electron shells upon ionization nevertheless are so heavy that they have a strong tendency to form simple positive ions instead of complex ions of the Werner type or acquire a structure thereby which is so closely related to that of the inert gases (such as argon) that they do not react with the hydrocarbon polyamine to form complex ions therewith effectively.

The metals with which the invention may be carried out are indicated in the chart of Fig. 1, in which the symbols of the elements are shown in the order of their atomic numbers, arranged in accordance with the periodic table. The metals with which the present invention is applicable are enclosed by the dotted line.

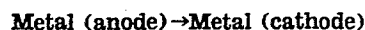
Fig. 2 is a more or less diagrammatic illustration of the type of electrolytic cell and indicative of the type of electrolysis with which the process may be practiced—namely, one in which the electrolyte is continuous from electrode to electrode.

In practice, it is now found that when one of the metals contained in the above group 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.

In Fig. 2 it will be observed that the electrolytic solution 1 is contained in a single vessel 2, which is preferably lined with rubber, and forms a continuous medium between the anode or anodes 3 (which are connected to the positive bus bars 4, and are composed of the metal or metals to be deposited) and the cathode or cathodes 5, which are connected to the negative bus bar 6, 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 con-

version 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 the metals set off in Fig. 1 with respect to which this invention is operable (i. e. those within the dotted line), in aqueous solution, to form various orders of compounds. The number of compounds so formed with respect to each metal 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.

It is generally preferable to use at least 2 mols of hydrocarbon polyamine to one mol of the salt of the metal to be plated, and best results range between about $2\frac{1}{2}$ and 6 mols of the polyamine to one of the salt. More polyamine may be used, but there is no particular advantage in so doing. In a few cases, notably silver (see Examples 4 and 5), the ratio of polyamine to salt may be reduced as low as 1 to 1, although results are better if the ratio is at least 2 to 1. The following discussion with respect to copper and ethylene diamine is illustrative.

Copper sulfate in solution, with proper amounts of a hydrocarbon polyamine—for example, ethylene diamine—will form the following complex compounds (in which the cations contain both ethylene diamine and copper). The symbol En represents ethylene diamine



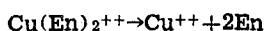
- (1) Cupric triethylene diamine sulfate $\text{CuEn}_3\text{—SO}_4$
- (2) Cupric di-ethylene diamine sulfate $\text{CuEn}_2\text{—SO}_4$
- (3) Cupric ethylene diamine sulfate CuEn—SO_4

Of these complex compounds of copper, the cupric triethylene diamine sulfate in aqueous solution is relatively unstable and may decompose spontaneously to form the cupric diethylene diamine sulfate, liberating ethylene diamine:



On the other hand, in adding ethylene diamine to copper sulfate solution, it is observed that when something over one molal equivalent of the ethylene diamine has been added there is a tendency for a precipitate to separate from the solution. Upon continued addition of the ethylene diamine, to the amount of two molal equivalents, this precipitate dissolves. It is believed that this precipitate is the copper ethylene diamine sulfate (or a basic salt of the same) which is somewhat less soluble than the other two compounds, into which, however, in the presence of additional ethylene diamine, it is successively converted.

Excess of En over the minimum amount required to form the complex ion (in this case CuEn_2) is advisable; its function being to repress the concentration of free metal ion. In the case of copper the reaction is:



and according to the theory of ionic equilibria the relation:

$$\frac{(\text{Cu}^{++}) \times (\text{En})^2}{(\text{Cu(En)}_2^{2+})}$$

equals a constant where the concentrations in brackets are expressed in mols per liter. From

this expression it is seen that when excess En is added to a solution the concentration of Cu^{++} must decrease if the left-hand side of the expression remains constant. It is desirable to depress the total concentration of Cu^{++} , first, because, as is well known in the plater's art, better deposits are obtained when the concentration of free metal ion is low; and second, because when the free metal ion concentration is low, insoluble compounds are less likely to crystallize out.

The cupric di-ethylene diamine sulfate, made as above and recrystallized from dilute alcohol solution, and that prepared by treating a solution of $\text{Cu(NH}_3)_4\text{SO}_4$ with ethylene diamine and removing the liberated ammonia by heating under reduced pressure, and recrystallizing from alcohol solution, are identical both by analysis and crystalline formation.

It was found that electrolytic baths prepared by dissolving these purified crystals, and an electrolytic bath prepared as above described by adding appropriate proportions of copper sulfate and ethylene diamine, were equally susceptible and satisfactory for use in electroplating or electrodeposition operations.

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

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

Example 1

For plating copper, using copper anodes and a bath containing copper sulfate, an electrolytic bath may be prepared by dissolving copper sulfate in water and then adding ethylene diamine, in the following proportions:

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	196 grams
Ethylene diamine	94 grams
Water	810 cc.
	1 liter

A still more effective composition may be prepared in the following proportions:

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	139 grams
Ethylene diamine	135 grams
H_2SO_4 (98% conc.)	8 cc.
Water	q. s.
	1000 cc.

With an electrolyte solution of this composition, the molal ratio of ethylene diamine; copper salt is 4:1 in comparison with a ratio of 2:1 in the preceding formula, and a decided improvement in operation is observed. The pH value of this latter solution is 8.8.

Preferably the sulfuric acid is diluted with some of the water before adding to the other components.

The electrolyte 1 may be contained in any suitable resistant vessel 2 which is preferably a non-conductor of the electric current, such as earthenware or rubber. The anode 3 (or anodes) may conveniently consist of copper strips which are connected to a source of electric current and are suspended in the solution, preferably so as to be

completely submerged, as by bus bars 4, having a chemically resistant or protected conductor. In one case, for example, using an electrolyte having the composition indicated in the formula above, sheet copper anodes were used which presented an effective area of 2.25 square feet. The cathodes consisted of brass cylinders having a total area of 0.5 square foot. These 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 were found to give satisfactory electrolytic depositions under continuous operation for two to eight hours, in daily operations, without deterioration of the electrolyte or deterioration in the rate and quality of metal deposition. Moreover at the end of a prolonged period of such daily operation (which was merely discontinued, and not on account of any failure or decline in operation) the amount of ethylene diamine remaining in the electrolyte was substantially undiminished.

While ethylene diamine is set forth in this and the following examples as the hydrocarbon polyamine used, it may be replaced by other hydrocarbon polyamines and the examples in other respects may be carried on in the same manner.

Example 2

Other soluble salts of copper than copper sulfate may be used. For example, copper chloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ may be substituted in place of the copper sulfate, and the bath prepared with ingredients as follows:

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	43 gm.
Ethylene diamine.....	44 gm.
H_2SO_4	To bring pH to about 3.8
Water.....	To make about 1000 cc.

The plating operation is carried on as described in Example 1.

Example 3

As another example of plating copper, using still another salt of copper (copper acetate) the following may be used, with ingredients of the bath in these proportions:

$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$	50 gm.
Ethylene diamine.....	44 gm.
H_2SO_4	To bring pH to about 3.8
Water.....	To make about 1000 cc.

The plating operation is carried on as described in Example 1. With a bath containing copper acetate, as in this example, particularly good results in plating directly on steel are obtained. The resulting plates have excellent adhesion and brightness, and are somewhat superior to those obtained in plating copper on steel using the baths shown in Examples 1 and 2.

The pH value of the baths for plating copper, such as those described above, is preferably between 8 and 9.5. Outside of this range, troubles with sponginess, pitting, discoloration, etc. appear. The desired pH value may be obtained in any suitable way, as by adding sulfuric acid, as shown in the above examples, or other suitable acid or acidic material.

In baths for plating copper, the ratio of hydrocarbon polyamine to copper salt is preferably about 3 or 4 to 1, as indicated by the examples. No general advantage is gained by going much higher, although the ratio may be raised as high as 10 to 1, or higher, for special purposes. When less than a 2 to 1 ratio is used, however, results are unsatisfactory, for reasons already indicated

in the discussion of the formation of insoluble precipitates.

Example 4

The plating of silver, using silver anodes and a bath containing a soluble silver salt, will be described in this example and in Example 5.

The molar ratio of hydrocarbon polyamine to salt may be somewhat less when using silver salts, than when using copper salts. A good working ratio is $2\frac{1}{2}$ mols hydrocarbon polyamine to 1 mol silver salt. The ratio may go to as low as equal molar amounts, or as high as about 10 mols polyamine to 1 of salt, but ratios much in excess of about 3:1 secure no advantages and are hence uneconomical in their tying up too much of the polyamine.

The preferred pH range of the bath for plating silver is between 9.5 and 11.5. Around pH=10 seems to be the best operating point in this range. With lower pH values the plates become pitted; with higher values (too much alkalinity) the plates are dark and discolored. As in the case of copper, the desired pH may be obtained by adding a suitable acid. Acetic or nitric acid, for example, is suitable.

The following will serve as an example of a bath using silver nitrate:

AgNO_3	43 gms.
Ethylene diamine.....	38 gms.
Acetic acid.....	To give pH of 10
Water.....	To make 1000 cc.

The plating is carried out as described in Example 1, using the apparatus shown in Fig. 2, with an anode of metallic silver. In operation, a current density of 10 to 15 amperes per square foot of the cathode was maintained. The cathode may be of any suitable metal such as brass. Temperature of the bath is advantageously about 35-40° C.

Example 5

Using the procedure under Example 4, a bath of a different silver salt (silver acetate) was made up as follows:

$\text{AgC}_2\text{H}_3\text{O}_2$	42 gm.
Ethylene diamine.....	38 gm.
Acetic acid.....	To give pH of 9.8
Water.....	To make 1000 cc.

Example 6

The plating of zinc, using zinc anodes and a bath containing a zinc salt, may be carried on with a bath having the following composition:

$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	150 gm.
Ethylene diamine.....	180 gm.
Sulfuric acid.....	To give pH of 10
Water.....	To make 1000 cc.

The plating is carried out by the procedure already described, using a temperature of about 25° C., a metallic zinc anode, and a current density of 10 to 20 amperes per square foot of cathode surface. The resulting plate of zinc is light, frosty, and metallic in appearance, and has excellent adhesion. Steel, copper or other suitable metal is used as the cathode.

The ratio of En to salt in this example is about 6 to 1. The working range of this ratio is the same as that for copper, i. e. between 2 and about 10.

The pH value, for best results, should be between 8 and 12. Outside this range a spongy, unsatisfactory deposit is obtained.

Example 7

For plating chromium, using a bath containing a chromium salt and anodes of metallic chromium, proceed as follows:

A solution of chromic chloride (CrCl_3), ethylene diamine, and water is prepared in the proportions shown below. The violet form of chromic chloride should be used, as the green form is insoluble in the bath. The green form is that ordinarily available commercially, but it may be converted to the violet form by heating with ammonium chloride (for example in the ratio of 2 to 1, respectively) to about 600° F. until no more vapors of ammonium chloride come off. The bath is prepared as follows:

Chromium chloride as prepared above.....	100 gm.
Ethylene diamine.....	500 gm.
Acetic acid.....	To make acid to litmus
Water.....	1000 cc.

Using metallic chromium for the anode material, electrolysis is carried out in the manner already described, and a bright coat of chromium is obtained on the cathode—which may be any suitable metal such as copper or brass. Temperature of the bath is advantageously around 40° C. As indicated, the bath should be somewhat on the acid side of neutrality.

Example 8

The following bath may be used when it is desired to plate cadmium using a bath of a cadmium salt:

$3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$	190 gm.
Ethylene diamine.....	100 gm.
Sulfuric acid.....	To give pH of 10
Water.....	To make 1000 cc.

The plating is carried out by the procedure already described, using about room temperature or slightly above—say 25 to 40° C. A metallic cadmium anode is used, and good results are obtained with current density of about 20 amperes per square foot of the cathode. Brass, steel or other suitable metal is used as the cathode.

As to the ratio of En to salt, the comments under Example 6, re zinc, apply.

The pH value, for best results should be between 9 and 10.3. Lower values give a spongy plate; with higher values there is poor adherence and little plating.

Example 9

It is possible to use more than one salt of the same metal in the plating bath, if desired. The present example illustrates this, as applied for instance in the plating of nickel. A bath is prepared having the following proportions:

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	200 gm.
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	45 gm.
Ethylene diamine.....	85 gm.
H_2SO_4	5 gm.
Water.....	To make 1000 cc.

This bath was used, with a nickel anode, to plate nickel on brass and also on steel. A smooth, dense plate resulted. Various current densities were used, ranging from 8 to 30 amperes per square foot. The pH value of the above solution is about 6; it should range neutral or slightly acidic for nickel baths.

Cobalt may be plated in the same manner, using either cobalt sulfate or cobalt chloride, or both.

Example 10

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 copper and zinc salts. The following will serve as an example of a bath for the plating of brass:

$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	54 gm.
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	71 gm.
Ethylene diamine.....	47 gm.
Water.....	To make 1000 cc.

This bath was used to plate on copper, and also on iron. A temperature of 30° C. was employed, with a current density of 18 amperes per square foot of the cathode. Brass anodes were used.

Example 11

It is possible to carry out the process of this invention without first dissolving a salt of the metal to be plated in the bath. In such 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.

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 foregoing examples serve to show the applicability of the present process specifically to most of the metals indicated in Fig 1 as being operable. The other and less common metals not so far mentioned in detail can be similarly plated, as I have demonstrated by experiments thereon. Since the same procedure is followed as those already described, I need not describe these in detail. The baths are made up as already described, and when a salt is employed, using a soluble salt of the metal, in an amount of about $\frac{1}{4}$ mol per liter of solution, and a ratio of hydrocarbon polyamine to salt of about 5 or 6 to 1. Thus, in plating iron, say onto copper, I have used ferric chloride as the soluble salt; for manganese, manganous sulfate; for gold, auric chloride.

The cathode, in operating with all of 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.

This application is a continuation in part of co-pending application Serial No. 21,809, filed May 16, 1935.

I claim:

1. An aqueous electrolyte for the electrolytic deposition of metals, characterized by consisting essentially of a metal having an atomic structure presenting an incomplete outer electron shell, upon ionization, and a hydrocarbon alkyl diamine.
2. An aqueous electrolyte for the electrolytic deposition of metals, characterized by consisting essentially of a soluble salt of a metal having an atomic structure presenting an incomplete outer electron shell, upon ionization, and a hydrocarbon alkyl diamine.
3. An aqueous electrolyte for the electrolytic deposition of metals characterized by consisting essentially of a metal characterized by the ability to form complex cations and a hydrocarbon alkyl diamine.
4. An aqueous electrolyte for the electrolytic deposition of metals characterized by consisting essentially of a soluble salt of a metal characterized by the ability to form complex cations and a hydrocarbon alkyl diamine.
5. A process of electroplating that comprises electrodepositing copper as a bright, smooth, firmly adherent deposit from an undivided cell containing an aqueous electrolyte consisting essentially of a soluble copper salt and a sufficient quantity of an alkyl polyamine to form a complex with said salt.
6. An aqueous electrolyte for use in the electrodeposition of copper as a bright, smooth, firmly adherent deposit that consists essentially of a soluble copper salt and a sufficient quantity of an alkyl polyamine to form a complex with said salt.
7. An aqueous electrolyte for the electrolytic deposition of metals, characterized by consisting essentially of a metal, characterized by the ability to form a complex cation with a hydrocarbon alkyl polyamine, and a hydrocarbon alkyl polyamine.
8. An aqueous electrolyte for the electrolytic deposition of metals, characterized by consisting essentially of a soluble salt of a metal, characterized by the ability to form a complex cation with a hydrocarbon alkyl polyamine, and a hydrocarbon alkyl polyamine.
9. An aqueous electrolyte, for use in the electrodeposition of a metal characterized by the ability to form complex cations with a hydrocarbon alkyl polyamine, that consists essentially of a soluble salt of said metal and a sufficient quantity of a hydrocarbon alkyl polyamine to form a complex with said metal, and an acidic material.
10. A process of electroplating that comprises electrodepositing a metal, characterized by the ability to form complex cations with hydrocarbon alkyl polyamines, from an undivided cell containing an aqueous electrolyte consisting essentially of said metal and a hydrocarbon alkyl polyamine.
11. A process of electroplating that comprises electrodepositing a metal characterized by the ability to form complex cations with hydrocarbon alkyl polyamines, from an undivided cell containing an electrolyte consisting essentially of a soluble salt of said metal and a hydrocarbon alkyl polyamine.
12. A process of electroplating that comprises electrodepositing a metal characterized by the ability to form complex cations with hydrocarbon alkyl polyamines, from an undivided cell, containing an electrolyte consisting essentially of a soluble salt of said metal, a sufficient quantity of a hydrocarbon alkyl polyamine to form a complex with said salt, and an acidic material.
13. A process of electroplating that comprises electrodepositing silver from an undivided cell containing an aqueous electrolyte consisting essentially of a soluble silver salt and a sufficient quantity of an alkyl polyamine to form a complex with said salt.
14. An aqueous electrolyte for use in the electrodeposition of silver that consists essentially of a soluble silver salt and a sufficient quantity of an alkyl polyamine to form a complex with said salt.
15. A process of electroplating that comprises electrodepositing nickel from an undivided cell containing an aqueous electrolyte consisting essentially of a soluble nickel salt and a sufficient quantity of an alkyl polyamine to form a complex with said salt.
16. An aqueous electrolyte for use in the electrodeposition of nickel that consists essentially of a soluble nickel salt and a sufficient quantity of an alkyl polyamine to form a complex with said salt.
17. An aqueous electrolyte for the electrolytic deposition of metals, characterized by consisting essentially of a metal characterized by the ability to form complex cations with ethylene diamine, and ethylene diamine.
18. An aqueous electrolyte for the electrolytic deposition of metals, characterized by consisting essentially of a soluble salt of a metal characterized by the ability to form complex cations with ethylene diamine, and ethylene diamine.
19. An aqueous electrolyte for the electrolytic deposition of metals characterized by consisting essentially of a metal, characterized by the ability to form complex cations with ethylene diamine, ethylene diamine, and an acidic material.

CHARLES G. HAFORD.