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PROCESS FOR ELECTROPLATING

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My invention relates to a new process of electroplating, with an ammoniacal electrolyte.

More particularly, my invention relates to the use in such an ammoniacal electrolyte of a special anode which can be used in any ammoniacal electrolyte with no substantial danger of the decomposition of the ammonia in that electrolyte; and more especially to the use of such an anode in those ammoniacal electrolytes in which decomposition of ammonia occurs with some types of anode.

Ammoniacal electroplating solutions have many advantages, in the plating of various metals. Among such metals are zinc, cadmium, nickel, cobalt, copper, silver, platinum, rhodium, and palladium; all of which will act with the ammonia to form metal-ammonia complex salts. The acid which co-operates with the metal and the ammonia to form these salts may be any one of a number of acids, such as hydrochloric acid, acetic acid, phosphoric acid, carbonic acid, sulfuric acid, nitric acid, tartaric acid, and citric acid, to make metal-ammonia chlorides, acetates, phosphates, carbonates, sulfates, nitrates, tartrates, and citrates, respectively; and of these various acids the most desirable, from some standpoints, such for instance as recovery of metal, is probably hydrochloric acid.

When aqueous solutions of these metal-ammonia complex salts, generally and preferably with excess ammonia present, are used as electrolytes in the electroplating of the metal on some cathode—which, for instance, may be a stationary object, or may be a ferrous wire moving through the electrolyte—the metal-ammonia salt complex is ionized to deposit the metal on the cathode, and initially to liberate the acid ion at the anode. Ammonia is also liberated. It would be expected that oxygen would also be liberated; but unexpectedly the oxygen content of the gas which actually is evolved is often very low, while the nitrogen content of that gas is very high. The liberated ammonia and the liberated acid ion, and perhaps oxygen if it is in fact liberated, apparently are initial reactants in a complex set of reactions, not fully understood but probably occurring at the anode, which to a greater or less extent frequently result eventually in the decomposition of ammonia, both to set nitrogen free and to form some nitrogen-containing intermediate-oxidation products. That decomposition of ammonia reduces the ammonia content of the ammoniacal electrolyte. That decomposition of ammonia is especially marked with certain acid ions, notably those of hydrochloric acid, acetic acid, and phosphoric acid.

This decomposition of ammonia is especially objectionable when the electrolytic plating solution is used in a system involving the regeneration of the electrolyte, by the introduction of more metal to take the place of that which has been deposited on the cathode. The presence of free ammonia is essential for this regeneration; and is also essential to get a smooth metal deposit. The decomposition of the ammonia thus involves either considerable trouble and expense to introduce new ammonia, or loss of the amomniacal properties of the electrolyte, especially of the benefits of the ammonia in regenerating the electrolyte and in providing smoothness of metal deposit; or both.

I have found that both the nature of the acid ion and the nature of the anode play a vital part in the cycle of chemical operations that results in this decomposition of ammonia. The decomposition of ammonia is especially marked when the acid ion is of hydrochloric acid, acetic acid, and phosphoric acid; and is less marked with some other acids. Thus when the acid ion is of those acids where such decomposition of ammonia is most marked, as when hydrochloric acid or acetic acid or phosphoric acid is used, it is most important to provide, if possible, an anode of a nature which will prevent or minimize that decomposition.

I have found that if an anode is used which has its exposed surface of ferroferric oxide, Fe_3O_4, this decomposition of ammonia is greatly reduced, and for practical purposes is substantially avoided, regardless of the character of the acid ion of the ammoniacal electrolyte; so that such an anode can be used universally for any ammoniacal electrolyte. Such an anode is most valuable, of course, in those electrolytes in which the nature of the acid ion tends most greatly to produce decomposition of the ammonia.

Since ferroferric oxide as it occurs in nature is called magnetite, I shall refer to the surface of my anode as made of magnetite; although it may be either naturally occurring ferroferric oxide or synthetic ferroferric oxide. If synthetic ferroferric oxide, or synthetic magnetite, is used, it may be produced by heating iron or various iron compounds in known manner.

My magnetite anode may be made wholly of magnetite, if desired. However, magnetite is a rather poor electrical conductor, so that it is desirable to make the path for the current through the magnetite as short as possible. To that end, I prefer to make the magnetite anode with a core of some good conductor, such as iron or zinc or copper or silver, and to provide the magnetite as a fairly thin covering over the entire surface of that core where it would otherwise be exposed to the electrolyte, so that the electrolyte at the anode comes in contact with the magnetite only.

If desired, the magnetite may be wholly magnetite, with no admixture. However, the magnetite may be mixed with lesser amounts of oxides of other metals, such for instance as copper

oxide; and that has some advantage both in reducing the electrical resistance of the anode and in making the anode less brittle. If copper oxide is used, I prefer that its amount should not be more than 20%.

Magnetite anodes as such are not new. They have been used for various purposes; but never, so far as I have been able to discover, in a system in which the electrolyte is ammoniacal in nature or is a metal-ammonia salt. The anode structure per se may be of any desired character, such for instance as that shown in any of the following patents:

No.	Name	Date
762,227	Blackman	June 7, 1904
800,181	Specketer	Sept. 26, 1905
931,513	Specketer	Aug. 17, 1909
1,302,959	Page	May 6, 1919

In operation, my electroplating system is constructed and connected in the usual manner, with the article to be plated connected as the cathode in an electroplating bath containing as the electrolyte a solution of the desired metal-ammonia salt, or salts. That article to be plated may be a moving wire, although my invention contemplates the plating of articles of any character including both stationary and moving articles. The anode of the system is my special anode, in which the surface exposed to the electrolyte is of magnetite, perhaps containing oxides of other metals. The electrolyte is of any desired metal-ammonia salt, or salts, in which the metal or metals of the salt or salts are to be plated on the cathode; and desirably contains excess ammonia. Preferably the electro-plating system is equipped with suitable apparatus for regenerating the aqueous solution constituting the electrolyte by adding metal thereto: in any suitable regenerating system, such for instance as that set forth in the Hubbell and Weisberg Patent No. 2,200,987, granted May 14, 1940.

For instance, my invention is particularly adapted for the plating of zinc, nickel, cobalt, and cadmium, in which case the electrolyte is an ammoniacal aqueous solution of a zinc-ammonia salt, or a nickel-ammonia salt, or a cobalt-ammonia salt, or a cadmium-ammonia salt; or of mixtures of two or more of these salts if a mixture of metals is to be plated.

The metal-ammonia salts are most desirably chlorides; but may be acetates, phosphates, sulfates, etc., as noted above, although my invention is probably of greatest benefit when the salts are chlorides, acetates, or phosphates. If the salt is a zinc-ammonia salt, it is most conveniently zinc-ammonia chloride. The process and apparatus using zinc-ammonia salts in the electrolyte are included in the generic claims of this application; although specifically they are the subject-matter of my co-pending application Serial No. 499,254, filed concurrently herewith on August 19, 1943.

In the operation of my apparatus, the metal of the electrolyte salt, such for instance as zinc or cobalt or nickel or cadmium if that is to be deposited as the plated metal, is deposited on the cathode by the action of the electric current; and the aqueous solution constituting the electrolyte is regenerated by adding metal thereto by whatever regenerating system is used. If the electrolyte salt is metal-ammonia chloride, chloride ions are freed at the anode. Ammonia is also freed. Subsequent reactions occur involving both the ammonia and the chloride ion, and the dissociation of oxygen from the water of the electrolyte solution; so that the gas which escapes from the solution at the anode should be mostly oxygen. With my apparatus, and with my magnetite anode, it is mostly oxygen because little or no decomposition of the ammonia occurs regardless of the character of the acid ion. With other anodes, however, the gas which escapes is often not mostly oxygen, but consists to a greater or less extent of nitrogen derived from the decomposition of the ammonia, the extent depending on the nature of the acid ion and of the anode. If the acid ion is the chloride ion, and the anode is graphite, for instance, the gas which escapes sometimes contains as much as 90% nitrogen.

An objectionable decomposition and loss of ammonia occurs, for example, in the operation of the process of the aforesaid Hubbell and Weisberg Patent No. 2,200,987, when the electrolyte solution is of zinc-ammonia chloride and the anode is of graphite, or indeed of almost anything other than the magnetite of the present invention; with the result that the gas which escapes from the solution at the anode is then not mostly oxygen, but is largely nitrogen derived from the decomposition of the ammonia.

That decomposition is avoided in large measure, if not wholly, whatever the acid ion, by the use of my magnetite anode.

I am unable at present to give a demonstrable explanation why this is so. But I have definitely established by experiment, and by contrasting the effects of the use of a magnetite anode with the effects of the use of other anodes, that it is so in fact.

Thus by the use of my magnetite anode as the anode in an electroplating system in which the electrolyte is a metal-ammonia salt, I am able to reduce if not wholly to avoid the decomposition of ammonia that otherwise may occur.

I claim as my invention:

1. The process of electroplating metal, consisting in passing an electric current from a magnetite-surface anode to a cathode, through an aqueous ammoniacal solution of a metal-ammonia salt, to deposit the metal of said salt on the cathode.

2. The process of electroplating as set forth in claim 1, in which the metal of the salt is cobalt.

3. The process of electroplating as set forth in claim 1, in which the metal of the salt is nickel.

4. The process of electroplating as set forth in claim 1, in which the metal of the salt is cadmium.

5. The process of electroplating as set forth in claim 1, in which the salt is a metal-ammonia chloride.

6. The process of plating a mixture of metals, consisting in passing an electric current from a magnetite anode to a cathode through an aqueous ammoniacal solution of a mixture of metal-ammonia salts, to deposit the metals of those salts on the cathode.

7. The process of electroplating as set forth in claim 6, in which the electrolyte contains ammonia in excess.

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