Patented Jan. 22, 1946 2,393,517

UNITED STATES PATENT OFFICE

2,393,517

PROCESS FOR ELECTROPLATING ZINC

Richard H. Burns, Muncie, Ind., assignor to Indiana Steel & Wire Company, Muncie, Ind., a corporation of Indiana

No Drawing. Application August 19, 1943, Serial No. 499,254

4 Claims. (Cl. 204—55)

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

More particularly, my invention relates to the use in such an ammoniacal electrolyte for zinc plating, of a special anode which can be used in any ammoniacal zinc-bearing 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 zinc-bearing electrolytes in which such decomposition of ammonia occurs with some types of anode.

The electroplating of zinc, which constitutes the subject-matter of the present application, is a species under certain generic claims in my co-pending application Serial No. 499,253, filed concurrently herewith on August 19, 1943.

Ammoniacal electroplating solutions have many advantages in the plating of zinc; which forms with the ammonia a zinc-ammonia complex salt. The acid which co-operates with the zinc 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 zinc-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, with acetic acid and phosphoric acid also highly desirable.

When aqueous solutions of these zinc-ammonia complex salts, generally and preferably with excess ammonia present, are used as electrolytes in the electroplating of zinc on some cathode—which, for instance, may be a stationary object, or may be a ferrous wire moving through the electrolyte—the zinc-ammonia salt complex is ionized to deposit the zinc 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 zinc 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 zinc deposit. The decomposition of the ammonia thus involves either considerable trouble and expense to introduce new ammonia, or loss of the ammoniacal properties of the electrolyte, especially of the benefits of the ammonia in regenerating the electrolyte and in providing smoothness of zinc 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, magentite 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 zinc-ammonia salt. 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 zinc-ammonia salt, in which the zinc of the salt is 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 zinc 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.

The zinc-ammonia salt is most conveniently zinc-ammonia chloride; but may be zinc-ammonia acetate, phosphate, sulfate, etc., as noted above, although my invention is probably of greatest benefit when the salt is zinc-ammonia chloride, acetate, or phosphate. As already noted, these are included in the generic claims of my co-pending application Serial No. 499,253, filed August 19, 1943; although specifically they are the subject-matter of this present application.

In the operation of my apparatus, the zinc of the electrolyte salt is deposited on the cathode by the action of the electric current; and the aqueous solution constituting the electrolyte is regenerated by adding zinc thereto by whatever regenerating system is used. If the electrolyte salt is zinc-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 the 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 zinc-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 zinc, consisting in passing an electric current from a magnetite-surface anode to a cathode, through an aqueous ammoniacal solution of a zinc-ammonia salt, to deposit the zinc of said salt on the cathode.

2. The process of electroplating zinc as set forth in claim 1, in which the salt is zinc-ammonia chloride.

3. The process of electroplating zinc as set forth in claim 1, in which the salt is zinc-ammonia acetate.

4. The process of electroplating zinc as set forth in claim 1, in which the salt is zinc-ammonia phosphate.

RICHARD H. BURNS