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PROCESS FOR ELECTRODEPOSITION OF ZINC AND ANODE THEREFOR

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This invention relates to anodes for use in the electrodeposition of zinc, and is particularly directed to zinc anodes which contain small amounts of magnesium.

In processes for the electrodeposition of zinc it is customary to maintain the zinc content of the zinc plating baths by the use of zinc anodes, but considerable difficulty is experienced by reason of the fact that the anode efficiency is greater than the cathode efficiency. In other words, the zinc metal of the anode is dissolved in the bath more rapidly than zinc metal is deposited from the bath onto objects being plated. As a result of the rapid solution of the anode the bath soon contains excessive amounts of zinc compounds.

For the best results it is desirable that a zinc plating bath remain as near as possible to a definite formula, and changes in bath composition resulting from the rapid solution of zinc anodes causes considerable difficulty. In the recently developed processes for the electrodeposition of bright zinc deposits it is particularly important that the bath composition be held rigidly within limits if the best possible results are consistently to be obtained.

In addition to the difficulties arising from the rapid solution of zinc anodes in zinc plating baths, further difficulties result from the fact that the anodes do not dissolve evenly and from the fact that a black sludge is formed which floats in the bath and on the surface of the bath. The presence of black sludge is particularly disadvantageous in processes for the deposition of bright zinc from cyanide baths since this black sludge interferes with the production of a smooth and bright plate.

When a zinc plating bath has such an amount of zinc dissolved therein that it becomes necessary to correct the bath composition, this can be done by removing some of the zinc. Or, as is more customarily the practice, the excess of zinc compounds may be diminished by discarding a portion of the solution and correcting the composition of the remaining solution by the addition of bath constituents other than zinc compounds. It will of course be apparent that such procedures are uneconomical and time-consuming.

It has been proposed to compensate for the high anode efficiency of zinc anodes in cyanide baths by replacing some of them with insoluble iron or steel anodes. This expedient results in a diminution of the amount of zinc dissolved per unit of electrical current passed into the bath, and in effect reduces the anode efficiency.

Unfortunately this type of procedure is not entirely satisfactory because when the bath is standing idle the iron or steel anodes accelerate the rate of corrosion of the zinc anodes, thus causing the zinc to dissolve rapidly and unevenly during periods when the bath is not in operation. It is, moreover, generally accepted that insoluble anodes cause destructive oxidation of cyanide during electrolysis. Such oxidation is considered to destroy the valuable cyanides and to produce deleterious carbonates.

It has also been proposed to use zinc-aluminum alloy anodes. By such use of aluminum in a zinc anode the anode efficiency is slightly decreased since zinc-aluminum alloys are slightly less soluble than pure zinc metal. This proposed use of zinc-aluminum alloy anodes was primarily suggested for acid-zinc plating baths and has been found most useful in this relation.

Unfortunately the use of aluminum in zinc anodes does not solve the problem of maintaining zinc plating baths at a constant composition. The effect of adding aluminum is too small to secure a balance of anode and cathode efficiencies. This is particularly true when the anodes are used in cyanide baths, perhaps because the aluminum is alkali soluble.

I have found that the difficulties heretofore experienced in the art may largely be overcome by the addition of small amounts of magnesium to zinc anodes. By selecting a proper amount of magnesium, anodes having an efficiency corresponding closely to the cathode efficiency of the baths in which they are to be used may readily be produced. By the use of such anodes it is possible to maintain the balance of bath constituents for a much longer period than has heretofore been practicable, particularly with cyanide baths.

The use of the zinc-magnesium anodes of my invention is particularly advantageous in conjunction with cyanide-zinc plating baths for the deposition of bright zinc deposits since by the use of the anodes of my invention it is possible

to hold the bath composition within rigid limits with a minimum of effort and cost.

The zinc-magnesium alloy anodes of my invention are further characterized by the fact that they dissolve uniformly in zinc plating baths and produce a minimum amount of black sludge. Particularly when relatively large amounts of magnesium, say in the range around 0.1%, is used, the amount of black sludge is markedly decreased. In any event the presence of magnesium in the anode causes any black sludge which does form to settle directly to the bottom of the bath and the disadvantage heretofore encountered of the black sludge floating in the bath and on the surface of the bath is obviated. The action of magnesium in promoting even corrosion and in preventing deleterious black sludge formations makes the zinc-magnesium alloy anodes of my invention particularly valuable for use in cyanide-zinc plating baths for the production of bright smooth deposits.

The action of magnesium in the zinc-magnesium alloys of my invention is entirely different from the action of metals such as aluminum. Aluminum, for instance, is itself soluble in both acid and cyanide zinc-plating baths and zinc alloys containing it are likewise soluble, tho they dissolve slightly less rapidly than pure zinc.

Magnesium on the contrary is not soluble in cyanide zinc plating baths, and its effect in reducing the solubility of zinc anodes is entirely disproportionate to the amounts used if judged by the action of metals heretofore added to zinc.

The magnesium in the zinc-magnesium anodes of my invention apparently causes the formation of a film of alkali insoluble magnesium compound on the surface of anodes which are in use. This film polarizes the anodes, in a measure resisting the passage of current between the anode and the bath. The effect of the magnesium is directly proportional to the amount present, and by the use of a suitable amount of magnesium, zinc-magnesium alloys of almost any desired efficiency can be made.

Electrolytic zinc anodes for use in cyanide-zinc plating baths normally have an anode efficiency of 100 to 105%, while the normal cathode effiiciency in similar baths is around 80 to 95%. The anode efficiency of such electrolytic zinc anodes may be reduced to fall within the range of cathode efficiencies by the addition of magnesium to the zinc metal, for instance, 0.18% of magnesium being sufficient under one set of conditions to give an electrolytic zinc-magnesium alloy anode having an anode efficiency of 85%. It is of course particularly desirable to be able to reduce the anode efficiency of electrolytic zinc anodes because the high purity of this type of anode renders it desirable for bright zinc processes.

Many zinc anodes however are not made from electrolytic zinc but are made of somewhat less pure zinc obtained by distillation methods. These anodes are much used for zinc plating, and they have found considerable application in the plating of bright zinc from cyanide-zinc plating baths. These less pure anodes dissolve somewhat more slowly than do the electrolytic anodes, the usual anode efficiency being around 100% for commercial grade zinc anodes.

Considerably smaller amounts of magnesium are sufficient to reduce the anode efficiency of zinc anodes to the required amount when commercial zinc from distillation processes is used. For instance 0.11% of magnesium was sufficient to give a zinc-magnesium anode having an efficiency of 85% when the zinc was of a commercial grade obtained by distillation.

The use of magnesium is particularly advantageous with the use of anodes which are less pure than the electrolytic zinc because the magnesium tends to reduce the amount of black sludge formed and further causes this sludge to drop to the bottom of the tank where it cannot interfere with the bright plates. As a result, it is entirely feasible to produce brilliant zinc plates from cyanide-zinc plating baths using commercial grades of zinc obtained by distillation if magnesium is incorporated in the metal according to the teachings of my invention.

It will readily be understood that various other metals may be included in the zinc anodes in conjunction with magnesium in accordance with the practices already known in the art. I may for instance use magnesium jointly with aluminum or mercury, or I may use all three to obtain their joint effects.

It will further be apparent that since the impurities present in commercial grades of zinc cooperate with magnesium to produce anodes of low efficiency it may conceivably be advantageous in some circumstances to add such impurities jointly with magnesium to zinc metal which, by reason of its higher purity, dissolves too rapidly and would require an excessive amount of magnesium to obtain the desired anode efficiency.

In order that my invention may be better understood, the following examples are given:

Example I

Molten zinc obtained in a zinc distillation process was transferred in the molten state to a gas-fired graphite crucible and the temperature raised from about 450° C. up to a temperature of about 600° C. Eight hundredths per cent of magnesium was then added to the zinc by introducing finely divided magnesium into the molten zinc and maintaining it below the surface until it was dissolved in the zinc. After the magnesium was alloyed with the zinc, the mixture was further heated and the alloy was then cast into a form suitable for use as anodes.

The zinc used was of commercial grade frequently employed for the manufacture of zinc anodes. The zinc contained about 0.07% of cadmium and 0.005% of iron. It also contained 0.10% of lead and the cast anodes, accordingly, contained these impurities in addition to the added magnesium. For testing the anodes, a cyanide-zinc plating bath of the type recently developed for the deposition of brilliant zinc was made up as follows:

	Grams per liter
Zinc cyanide ($Zn(CN)_2$)	60.
Sodium cyanide (NaCN)	52.5
Sodium hydroxide (NaOH)	78.
Molybdic acid (MoO_3)	7.5

Using the above bath and the zinc magnesium alloy anodes above produced, excellent deposits were obtained. The anodes dissolved evenly and without the formation of deleterious black sludge. The small amount of sludge which formed sank to the bottom of the bath and did not interfere with the plating operation.

The anode efficiency was determined and it was found that the anodes made as above described and containing 0.08% of magnesium had an efficiency of about 89% in the above bath. A 200-gallon plating installation using such anodes

was operated commercially for a period of four weeks and the zinc content of the bath was substantially unchanged. In a similar period but using zinc anodes not containing magnesium, the zinc metal content of a similar bath increased by thirty grams per liter of zinc metal.

A number of zinc-magnesium alloy anodes were made up according to the procedure shown above and with the commercial zinc above described. When used with a plating bath having a composition as indicated above, the following tabulated efficiencies were obtained with anodes containing the indicated amounts of magnesium:

Percent of magnesium	Anode efficiency, percent
0.012	94.0
0.043	92.3
0.109	85.8
0.160	60.1
0.210	48.6

The anodes above shown, like the one first mentioned in this example, were uniformly dissolved in the plating bath. The amount of sludge became increasingly smaller with increasing amounts of magnesium until at 0.210% of magnesium there was substantially no black sludge formed. At 0.109% of magnesium there was very little black sludge and, of course, what black sludge did form settled to the bottom of the tank.

Example II

A zinc-magnesium alloy anode was made up according to the procedure described in the above Example I, but using 0.11% of magnesium. The zinc used was somewhat purer than that of the above example, containing only 0.05% of lead. In making the alloy 0.05% of lead was added to decrease the solubility of the anodes.

After the alloy was cast into a suitable form, the anodes were tested in a bath such as that shown in Example I and were found to have an anode efficiency of about 86%.

Since the presence of lead is so undesirable in baths for the deposition of bright zinc it does not at first appear practical to add this impurity to the zinc metal. The magnesium, however, is so efficacious in preventing the deleterious action of lead and other such impurities that it is entirely satisfactory to gain the benefits which may be had by using lead and saving on the more expensive magnesium.

As indicated above, the magnesium probably acts by forming an alkali-insoluble magnesium hydrate or cyanide film which surrounds the particles of lead and drags them to the bottom of the bath where they can do no harm. It will be observed, of course, that there must be sufficient magnesium present since otherwise the lead would be free to exercise a deleterious influence.

Example III

A zinc-magnesium alloy anode was made up using electrolytic zinc and 0.18% of magnesium. The alloy was made following the procedure used in the above Example I, the electrolytic zinc being melted directly in the graphite crucible. The zinc-magnesium alloy anodes so produced were tested in a bright zinc bath such as that shown above in Example I and it was found that the anode efficiency was about 85%.

Similar zinc-magnesium alloy anodes were found to have the following efficiencies when made up with electrolytic zinc and containing the below indicated amounts of magnesium:

Percent of magnesium	Anode efficiency, percent
0.01	102.2
0.02	103.8
0.04	103.3
0.12	96.7
0.20	83.6

While I have shown specific conditions in the foregoing for the production of zinc-magnesium alloy anodes, it will be understood that these may be made in various ways according to known metallurgical practices. It is to be observed, however, that after the magnesium is added to the zinc, the mixture should be heated to a temperature not substantially lower than about 700° C. In making up one set of electrolytic zinc anodes this precaution was not observed, the metal being poured at a temperature somewhere slightly above 600° C. and the alloy anodes so produced had an efficiency only slightly lower than that of electrolytic zinc itself. The specific temperature required to effect the required change in alloy properties can readily be determined in each specific instance by a few simple trials. The electrolytic zinc alloy anodes mentioned were re-melted and heated to a temperature of 700° C. and it was then found that the magnesium exercised its usual profound effect upon the anode efficiency.

From the foregoing it will be evident that widely varying amounts of magnesium may be used depending upon the effect desired and upon the character of the zinc which it is desired to modify. By the use of suitable amounts of magnesium it is entirely possible to adjust the anode efficiency to correspond to the cathode efficiency of substantially any commercial cyanide-zinc electroplating bath and it is principally in this connection that the invention will be found valuable. It will be understood, however, that the beneficial effects of magnesium may be obtained by the use of small amounts of magnesium which will prevent the deleterious influence of metal impurities in the anode even without obtaining a very great reduction in the anode efficiency. Very small amounts of magnesium may therefore be used to advantage.

Larger amounts of magnesium may of course be used, tho it will be understood that it will not be commercial to use excessively large amounts. In general, of course, the upper limit on the amount of magnesium used is determined by the cathode efficiency of the baths in which the anodes are to be employed.

While, as above indicated, widely varying amounts of magnesium may be used, it will generally be found desirable to use from about .01% to about 1.0% of magnesium. More specifically, it will usually be found that the desired anode efficiency and character can be obtained using from about .05% to 0.3% of magnesium with electrolytic zinc or about .05% to 0.2% of magnesium with commercial zinc such as that shown in Examples I and II and obtained by distillation processes.

While the zinc-magnesium alloy anodes of my invention have been particularly discussed above in conjunction with their use in a particular cyanide-zinc plating bath, it will be understood that the type of anodes of my invention may ad-

vantageously be employed in conjunction with various other such zinc electroplating baths. They may also be used in conjunction with acid zinc plating baths, tho when used with acid baths the anodes do not exhibit the marked advantages that they do with alkaline baths.

I claim:

1. In a process for the electrodeposition of zinc from a cyanide-zinc plating bath, the step comprising employing a cast zinc anode which has an efficiency substantially corresponding to the cathode efficiency of the bath, the anode efficiency being decreased by the inclusion in the anode of about 0.01 to 1.0 per cent of alloyed magnesium and the zinc-magnesium alloy having been heated prior to casting of the anode to a temperature not substantially lower than about 700° C.

2. In a process for the electrodeposition of zinc from a cyanide-zinc plating bath, the step comprising employing a cast zinc anode which contains from about 0.01 to 1.0 per cent of alloyed magnesium, the magnesium effecting a diminution of the anode efficiency and the zinc-magnesium alloy having been heated prior to casting of the anode to a temperature not substantially lower than about 700° C.

3. In a process for the electrodeposition of zinc from a cyanide-zinc plating bath, the step comprising employing a cast zinc anode containing lead as an impurity and containing from about 0.05 to 0.2 per cent of alloyed magnesium, the magnesium effecting a diminution of the anode efficiency and the zinc-magnesium alloy having been heated prior to casting of the anode to a temperature not substantially lower than about 700° C.

4. In a process for the electrodeposition of zinc from a cyanide-zinc plating bath, the step comprising employing a cast electrolytic zinc anode containing from about 0.05 to 0.3 per cent of alloyed magnesium, the magnesium effecting a diminution of the anode efficiency and the zinc-magnesium alloy having been heated prior to casting of the anode to a temperature not substantially lower than about 700° C.

5. A cast zinc-magnesium alloy anode for cyanide-zinc plating baths, the anode being comprised of zinc and from about 0.01 to 1.0 per cent of magnesium, the magnesium regulating the anode efficiency by forming a magnesium hydrate film on the anode when it is dissolved in a cyanide-zinc bath, the zinc magnesium alloy having been heated prior to casting of the anode to a temperature not substantially lower than about 700° C.

6. A cast zinc-magnesium alloy anode for cyanide-zinc plating baths, the anode being comprised of zinc having lead as an impurity and containing from about 0.01 to 1.0 per cent of magnesium, the magnesium decreasing the anode efficiency by forming a magnesium hydrate film on the anode when it is dissolved in a cyanide bath and the magnesium acting to prevent the deleterious effects on a cathode deposit of the lead impurity, the zinc-magnesium alloy having been heated prior to the casting of the anode to a temperature not substantially lower than about 700° C.

7. A cast zinc-magnesium alloy anode for cyanide-zinc plating baths, the anode being comprised of electrolytic zinc and from about 0.01 to 1.0 per cent of magnesium, the magnesium regulating the anode efficiency by forming a magnesium hydrate film on the anode when it is dissolved in a cyanide-zinc bath, the zinc magnesium alloy having been heated prior to casting of the anode to a temperature not substantially lower than about 700° C.

8. A cast zinc-magnesium alloy anode for cyanide-zinc plating baths, the anode being comprised of zinc having lead as an impurity and containing from about 0.05 to 0.2 per cent of magnesium, the magnesium decreasing the anode efficiency by forming a magnesium hydrate film on the anode when it is dissolved in a cyanide bath and the magnesium acting to prevent the deleterious effects on a cathode deposit of the lead impurity, the zinc-magnesium alloy having been heated prior to the casting of the anode to a temperature not substantially lower than about 700° C.

9. A cast zinc-magnesium alloy anode for cyanide-zinc plating baths, the anode being comprised of electrolytic zinc and from about 0.05 to 0.3 per cent of magnesium, the magnesium regulating the anode efficiency by forming a magnesium hydrate film on the anode when it is dissolved in a cyanide-zinc bath, the zinc magnesium alloy having been heated prior to casting of the anode to a temperature not substantially lower than about 700° C.

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