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ELECTROPLATING WITH ZINC.

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To all whom it may concern:

Be it known that I, JOSEPH HAAS, Jr., citizen of the United States, and resident of Muncie, in the county of Delaware and State of Indiana, have invented certain new and useful Improvements in Electroplating with Zinc, of which the following is a specification.

My invention relates in general to the electroplating of zinc or its alloys upon iron or steel in cyanide baths. Such cyanide plating baths are widely used because of their greater throwing power as compared with other baths which have been proposed for zinc plating.

Hitherto the commercial zinc plating of ferrous articles in cyanide baths has been subject to certain limitations. For example, it has been considered impracticable in cyanide baths to zinc plate iron or steel castings at all. Morover, the plating of articles of wrought iron or wrought steel has been attended with some difficulty in respect to articles of irregular surface, the difficulty being that those portions of the article which are more remote from the anode receive too thin a coating. In the plating of small ferrous articles this difficulty becomes so pronounced that hitherto it has been deemed impracticable to zinc plate such articles by the basket method in cyanide baths.

In investigations to determine the cause of these difficulties, I have found that it is due to the relatively low discharge potential of hydrogen upon cast iron, which causes hydrogen to be deposited rather than zinc. Researches also show that the single potential of an alloy is lower than that of its controlling constituent in the electrochemical series, and with certain exceptions, that the lower the electrode potential of a metal or alloy, the more easily is hydrogen deposited upon it. It has also been observed in plating cast iron and steel in the same bath, that more hydrogen is evolved upon the cast iron than on the steel, evidencing that the discharge potential of hydrogen on cast iron is much lower than that of hydrogen on steel. This is further evidenced by the common practice in plating copper on cast iron to use less free cyanid than plating on steel, too much cyanid in either case causing only evolution of hydrogen.

In order to successfully deposit zinc on cast iron in a cyanid bath, the factors to be considered are the discharge potential of hydrogen; the electrode potential of the cathode metal; and the electrode potential of the metal to be deposited, all three being affected by the crystalline structure of the cast iron cathode. The general rule may be said to be that if the discharge potential of hydrogen on the cathode metal is low, or below the electrode potential of the deposited metal, and the difference between the electrode potential of the deposited metal and the discharge potential of hydrogen is great, hydrogen only is deposited. If the difference is not great, both hydrogen and metal are deposited while if the discharge potential of hydrogen considerably exceeds the electrode potential of the deposited metal, the metal alone is deposited.

Where cast iron is first plated with copper or nickel, zinc can readily be deposited from a cyanid bath, due to the discharge potential of hydrogen being raised, but this is an added expense and coatings of copper or nickel on cast iron are likely to be porous, and when porous are not corrosion-preventative but stimulate corrosion.

The problem is solved according to this invention by bringing the discharge potential of hydrogen closer to the potential of zinc in a cyanid bath without an extra electroplating bath, by depositing the zinc in the presence of a metal electrochemically active to prevent corrosion, such a metal is mercury which has the effect in a cyanid electroplating bath of bringing the discharge potential of hydrogen so near the potential of zinc that zinc will be deposited together with a small percentage of mercury. In other words, the presence of mercury has the effect of making the difference between the discharge potential of hydrogen and the potential of zinc so much less than the difference between the discharge potential of hydrogen on cast iron and the potential of zinc, as to secure a good deposit of zinc on cast articles not heretofore satisfactorily coated with zinc by electroplating.

Other improvements result from my invention among which are the following:

1. The color, smoothness, fineness of grain structure, resistance to corrosion, and hardness of the zinc mercury deposit are superior

to those formerly obtained of zinc alone from cyanid baths.

2. The current efficiency at the cathode is markedly increased.

3. The anode wastage due to chemical corrosion is decreased.

4. The zinc coatings do not readily stain in the solution or when dried out, or when subsequently handled during assembling.

As illustrations of my invention, I will now describe the same as applied to the zinc plating of various types of iron and steel articles.

Example I: to plate gray or white iron castings such as pipe fittings, for example, I proceed as follows:

The fitting is first cleaned, preferably by sand blasting, until all of the scale and loose dirt are removed, and a clean iron surface is exposed. Should the surface of the fitting again become rusted, or otherwise fouled and dirty before going to the plating tank, it should then be again cleaned preferably by dipping in muriatic acid solution of about 1.09 specific gravity after which it is rinsed in clean water and allowed to remain in a hot caustic solution containing one to five per cent NaOH until ready for the plating operation.

The fitting so cleaned may then be dipped in a mercury solution containing for example:

Mercuric chloride	4 oz.
Nitric acid sp. g. 1.4	$\frac{1}{16}$ oz.
Water to make	1 gallon.

The fitting is then immediately suspended in a zinc cyanide plating solution to which has been added a small amount of a soluble mercury compound. Excellent results are obtained from a bath of the following composition:

Water	1 gal.
Zinc cyanide	4 ozs.
Sodium cyanide	4 ozs.
Sodium hydroxid	2 ozs.
Mercuric oxid	$\frac{1}{10}$ oz.

This may be accomplished by immersing the cleaned zinc anode in a saturated solution of mercuric chloride for a suitable period, forty-eight hours, for example. During the immersion the surface is scoured from time to time with a wire brush or other suitable means.

The solution is maintained at a temperature of from 40° to 50° C. The preferred voltage is from three to six volts depending upon the quantity of work being plated. When the required deposit has been secured, the fitting is removed from the solution, rinsed in cold and hot water successively, and then air dried. The bath must be replenished from time to time as the several ingredients become depleted, but the amount of mercury must not be permitted to become excessive inasmuch as in that event the permanence of the coating will be seriously impaired.

Example II: To plate large articles of wrought iron or wrought steel, such as automobile rims, the article instead of being sand blasted is cleaned by pickling alternately in alkaline and acid cleaning solutions until a chemically clean metallic surface is exposed. It may then be dipped in the mercury solution and plated as described in Example I. When plated, the rim is rinsed in cold and hot water, and air dried. The deposits thus obtained are tough and of pleasing appearance and are more resistant to corrosion and abrasion than any hitherto obtained in the art.

Example III: To plate burrs, bolts, screws, and other small articles of iron or steel, I proceed as in Example II, except that the articles are handled throughout in coarse-meshed wire baskets and are plated with a current of full six volts. The deposits obtained are of excellent color and durability; moreover, the plate is of uniform thickness throughout all parts of the basket.

As I believe I am the first to discover a means for increasing the potential of the cathode in zinc cyanide plating, and thereby reducing evolution of hydrogen and increasing the amount and quality of the coating, besides producing a novel coating I do not limit myself to any specific way of introducing the mercury except as specifically required by the appended claims.

Within the broad scope of the invention, I have obtained similar results by dipping the cathode first in a solution of a mercury salt and then plating in an ordinary cyanid bath without added mercury salt; and by plating in a cyanid bath with added mercury salt without dipping. In the former case, the mercury becomes alloyed with the first zinc deposited but upon continued plating, the percentage of mercury diminishes, and finally the coating may be practically pure zinc. With mercury in the bath, the coating is uniformly alloyed with from 1.5% to 2.0% of mercury. The most resistant and satisfactory coatings have about 2.0% of mercury. If the percentage is below about 0.2%, the advantages resulting from its use are small and its use is limited. If the percentage of mercury is above about 5.0%, the coatings are unsatisfactory in texture, are brittle and of little utility. I do not limit myself to the aforesaid mercury compounds; as I may use any mercuric compounds which is soluble in the bath. Among such compounds the oxide is preferred for the reason that it introduces into the bath no foreign anion. Mercurous compounds are not recommended as they are in

part reduced by the bath with the precipitation of metallic mercury. In the preliminary dip solution I may use mercuric nitrate, sulphate, etc.

I claim:

1. In zinc electroplating from a cyanid bath, the step which consists in depositing zinc in the presence of mercury to produce a coating of zinc alloyed with a small percentage of mercury.

2. In zinc electroplating from a cyanid bath, the step which consists in adding to a cyanid bath to be electrolyzed, a mercury salt capable of resisting reduction by the bath with consequent precipitation of metallic mercury to produce a zinc coating alloyed with a small percentage of mercury.

3. In plating ferrous articles with zinc in cyanide baths, the improvement which consists in depositing mercury in conjunction with the zinc.

4. The method of zinc plating ferrous articles which comprises applying to the surface of the article a liquid medium containing mercury and plating the article in a zinc bath containing cyanide.

5. The method of zinc plating ferrous articles which comprises coating the article with mercury and plating the article in a zinc bath containing cyanide and a soluble mercury compound.

6. The method of zinc plating ferrous articles which comprises applying to the surface of the article a liquid medium containing mercury and plating the article in a zinc bath containing cyanide and a soluble mercury compound.

7. The method of zinc plating ferrous articles which comprises dipping the article in a solution of a mercury compound and plating the article in a zinc bath containing cyanide and a soluble mercury compound.

8. The method of zinc plating ferrous articles which consists in dipping the article in an acid solution of mercuric chloride and plating the article in a zinc bath containing cyanide and a soluble mercury compound.

9. The process of zinc plating ferrous articles which comprises dipping the article in a solution containing approximately

Mercuric chloride	4 oz.
Nitric acid concentrated	$\frac{1}{16}$ oz.
Water to make	1 gallon.

and then plating the article in a bath of approximately the following composition:

Water	1 gallon.
Zinc cyanide	4 oz.
Sodium cyanide	4 oz.
Sodium hydroxide	2 oz.
Mercuric oxid	$\frac{1}{16}$ oz.

10. The method of zinc plating ferrous articles which comprises coating the article with mercury and then plating the article in a zinc cyanide bath containing mercury and with an anode amalgamated with mercury.

11. As a new composition a zinc cyanide plating bath containing mercury in solution for raising the cathode potential and alloying the coating.

12. As a new composition a zinc cyanide plating bath containing dissolved mercury equivalent to approximately $\frac{1}{16}$ oz. mercuric oxide per gallon.

13. The method of zinc plating ferrous articles which comprises plating the article in a zinc cyanide bath containing a small amount of soluble mercury compound.

14. The method of zinc electroplating ferrous articles which consists in plating the article in a zinc bath containing cyanide and approximately $\frac{1}{16}$ oz. of mercury per gallon in soluble form.

Signed at Muncie in the county of Delaware and State of Indiana this 2nd day of September A. D. 1922.

JOSEPH HAAS, JR.