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## 3,291,707

BRIGHT ZINC ELECTROPLATING TECHNIQUE Harold G. Abbey, Jamaica, and George B. Schore, Great Neck, N.Y., assignors to Abbey Automation Systems, Inc., New York, N.Y., a corporation of Delaware No Drawing. Filed Feb. 19, 1963, Ser. No. 259,730 2 Claims. (Cl. 204-55)

This invention relates generally to zinc electroplating, and more particularly to an improved technique for eco- 10 nomically, rapidly and safely applying a lustrous, finegrained protective zinc coating.

Zinc is extensively used as a corrosion-resistant coating on steel rods and pipes, cast iron parts, and numerous other products or basis metals requiring protection. For 15 applying fine-grained, lustrous deposits of zinc, the electroplating solution is generally of the cyanide type containing various organic and inorganic brightening agents. The common bath for this purpose consists of solutions of zinc cyanide with certain amounts of sodium cyanide 20 and caustic soda. A zinc coating upon an article plated from a cyanide bath is ordinarily gray in color and stains readily. A distinct improvement in appearance and in other physical characteristics is obtained by incorporating brightening agents in the cyanide bath.

A major objection to the application of zinc by way of cyanide solutions is that it creates serious problems of waste disposal. Cyanide wastes are the most toxic produced in metal finishing, and in many instances the legal limit set for free cyanide is zero. While industrial waste 30 fluoborate per gallon of water, the ratio of zinc to treatment systems are available to dispose of cyanide, they add materially to the overall cost and space requirements of zinc plating operations. Another drawback to zinc cyanide plating lies in the fact that it gives poor results on castings of malleable iron. Moreover, the efficiency of cyanide zinc is poor, for large amounts of hydrogen gas are evolved, which causes embrittlement of the basis metal.

Attempts have been made in recent years to carry out zinc plating by means of acid fluoborate baths. Such 40 baths generally include ammonium chloride as well as zinc fluoborate. While acid fluoborate processes have the advantage of avoiding poisonous cyanide fumes, they nevertheless have had limited commercial success.

Heretofore, the acid fluoborate process has given poor 45 results, for in operation the ammonium chloride tends to break down, whereby chloride ions are released which adversely affect the deposit. Moreover, it has been the practice to operate at relatively high temperatures (over 80° F.) and this has given rise to a coarse-grained coating 50 of poor appearance. Also the low plating voltages heretofore indicated in fluoborate plating have resulted in a slow rate of deposition, a poor throw into the recesses of the article being plated, and a deposit deficient in brightness.

Accordingly, it is the primary object of the invention to provide a zinc electroplating technique which is free of noxious waste, and which is economical, efficient and rapid in operation. A salient feature of the invention is that it is easy to maintain balance within the operating 60 range.

More specifically, it is an object of this invention to provide a zinc fluoborate plating technique which does not require ammonium constituents, and which produces fine-grained and lustrous platings of high quality without 65 hydrogen embrittlement or other deleterious effects on the basis metal.

Also an object of the invention is to provide a fluoborate plating technique operating at relatively high voltages to produce a very heavy zinc coating in a short 70 period. A significant advantage of the process in accordance with the invention is that it is markedly superior

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to zinc cyanide baths for the plating of iron castings and the like.

A further object of the invention is to provide a zinc plating technique of the above-described type, which is effective both in barrel and in still plating operations.

Briefly stated, these objects are accomplished by plating at relatively low temperatures (room temperature or less) in a bath consisting of zinc fluoborate in a water solution to which is added a small quantity of licorice dissolved in alcohol, the plating being carried on at high voltages in excess of 10 volts. A more detailed description of the invention will now be given.

The zinc plating operation in accordance with the invention is preferably carried out in tanks constructed of rubber or plastisol-lined steel, although ceramic or molded synthetic resin tanks may also be used. The tank is provided with cooling coils, preferably constructed of carbon, or impervious graphite material used in heat exchangers. Pure zinc cast anodes are employed, with an anode-to-cathode ratio of at least 1 to 1, preferably 2 to 1.

When barrel plating, the equipment used is preferably of the type described in the patents to H. G. Abbey, No. 2,979,181, issued April 11, 1961, and No. 3,171,005, 25 issued February 23, 1965, whereby a positive, arc-free contact is made when the barrel is brought down into the tank to rotate therein and thereby tumble the parts being plated.

The plating bath content is 20 to 50 ounces of zinc fluoborate acid being such as to give a pH factor of 3.0 to 4.0. The pH factor, if below these limits, may be increased by adding zinc powder to the acid. The pH factor is determined colorimetrically. Fluoboric acid is a complex acid formed by the combination of hydrogen fluoride and boron trifluoride, the zinc salt being called zinc fluorobate.

The only other constituent in the bath is an organic brightening agent, preferably in the form of licorice. In order efficiently to introduce the licorice in the bath, it is essential first to dissolve the leguminous herb in a small quantity of alcohol, which is preferably methyl alcohol, but ethyl alcohol may also be used. The amount of such brightening agent added to the bath is 0.1 to 0.4 ounce per gallon of water. It has been found that licorice produces a fine-grained structure.

Contrary to the usual practice, the operating voltage for barrel plating is relatively high, in the order of 20 to 50 volts, with a high operating current density of 100 to 800 amperes per square foot. In the case of still plating, the voltage range may be lower, in the order of 10 to 20 volts.

To avoid hydrogen evolvement and the consequent embrittlement of the metal, it is important that the bath 55 be maintained cool, in the temperature range of 60° F. to 80° F. Chilling of the bath may be effected by cooling coils, or by circulating the plating solution.

In a zinc plating process as described above, heavy zinc coatings of bright lustrous appearance are formed rapidly, even on iron castings, and the hazards and embrittlement encountered in cyanide plating are avoided. While we have described a preferred technique in accordance with the invention, it will be obvious that many changes may be made therein without departing from the essential spirit of the invention as defined in the annexed claims.

What is claimed is:

1. The process of barrel plating zinc on a base, comprising the steps of

(a) immersing a zinc anode and said base in an aqueous zinc fluoborate electroylte consisting essentially of 20 to 50 ounces of zinc fluoborate per gallon of water, the ratio of zinc to fluoboric acid being such as to afford a pH of 3.0 to 4.0, the electrolyte containing 0.1 to 0.4 ounce of brightening agent per gallon of water, said agent having been introduced in said electrolyte as a concentrated solution of 5 licorice dissolved in a small quantity of block of 5

(b) applying a voltage between said base and said anode having a value in the range of 20 to 50 volts to produce an operating current density in the range of 100 to 800 amperes per square foot to deposit 10 pure zinc on said base, and

(c) cooling said electrolyte in the course of zinc electroplating to maintain a temperature range of 60° F.
to 80° F.

2. The process as set forth in claim 1, wherein said alcohol is methyl alcohol.

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