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ELECTRODEPOSITION OF BRIGHT ZINC

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1 Claim. (Cl. 204—55)

This invention relates generally to the electrodeposition of zinc, and particularly to a process and materials by means of which bright, continuous deposits of zinc may be obtained electrolytically from acid zinc sulfate solutions.

The present application is a division of our application Serial No. 413,502, filed October 3, 1941, for Electrodeposition of bright zinc.

In the past, most of the methods used in electrogalvanizing resulted in dark or dull plates which had neither eye-appeal nor too great utility as protective coatings because of the coarseness and non-uniformity of the deposit on the plated objects.

Heretofore the electroplating of zinc from sulfate solutions was carried on almost universally at rather low current densities, usually of the order of 20 amperes per square foot. Much higher current densities, approximating 1000 amperes per square foot, have been employed recently in the electrodeposition of zinc; however, this work has been directed exclusively to the electro-winning of zinc from its ores.

A primary object of our invention is to provide a method for galvanizing metals to a bright finish by electrolytic means, employing commercially attractive current densities.

Another object of the invention is to provide an addition agent for use in electrogalvanizing processes, which addition agent will effect a bright deposit of zinc over a wide range of current density.

Other and ancillary objects and advantages of our invention will become apparent to those skilled in the art from the following description and explanation of the invention.

We have discovered that bright zinc may be deposited electrolytically, between certain limits of current density, from acid zinc sulfate solutions which contain triethylene tetramine as an addition agent. In order to acquaint those skilled in the art with the nature of our addition product and the range of current density within which a satisfactory bright zinc deposit may be obtained, we will now set out the findings of our experiments and illustrate our process by several specific examples.

In the procedure followed in our investigations it was found desirable to maintain constant all known variables except the one under consideration. Accordingly, solutions of known concentrations in zinc sulfate, sulfuric acid, and the addition agent were subjected to electrolysis at different current densities. The cathodes employed were low-carbon, bright-annealed, steel wires, 0.106 inch in diameter and approximately seven inches long. Four inches of this length were immersed in the plating solution, giving a cathode area of 0.00925 square foot. In order to insure a uniform current density distribution

around the periphery of the cathode, provision was made for rotating it at between substantially 15 and 20 revolutions per minute. The test samples were plated until a deposit corresponding to the commercial designation of about two ounces per square foot was obtained.

The cathodes were cleaned by subjecting them to an anodic pickling treatment in a 10% sulfuric acid solution for one minute at a current density of approximately 600 amperes per square foot.

The anodes employed in our experiments were pure lead and had an area of approximately eleven times that of the cathode, thus making the anode current density correspondingly small than that of the cathode.

The variables of temperature, acidity, and concentration of zinc sulfate were kept practically constant. It was discovered that predictable results could be obtained when the temperature of the plating solution was maintained between 14° C. and 20° C., the acidity at approximately 0.5 N, and the concentration of zinc sulfate between 20% and 24%. Under these conditions the effect of current density and concentration of the addition agent was investigated.

A series of solutions were prepared in which the concentration of the addition agent varied from 0.11 M to 0.15 M. Each solution was treated electrolytically at a number of current densities and the appearance of the plated object (cathode) observed. The luster characteristic of each sample was classified according to its reflectivity: "matte," meaning a dull finish, showing no luster whatever; "semi-metallic" referring to the borderline case between matte and metallic luster; "metallic" referring to a good reflective deposit; and "mirror" denoting only the most highly reflective deposits. Whenever the term "bright" is used in this application to describe the luster characteristic of the zinc deposit, it is intended to include all the degrees of luster covered by the terms "semi-metallic," "metallic," and "mirror."

The effect of triethylene tetramine as an addition agent is shown in the following tables:

Table I.—Operating data and observation of samples plated at 0.11 M triethylene tetramine

Sample number	Current density, amperes per sq. ft.	Av. solution temp., °C.	Time of run, min.	Color luster
GA1.....	600	18	5	Lt. grey matte.
GA2.....	200	18	10	Dk. grey met.
GA3.....	150	17	10	Do.
GA4.....	100	15	15	Do.
GA5.....	300	15	10	Lt. grey met.
GA6.....	400	16	8	Lt. grey semi-met.
GA7.....	250	15	12	Lt. grey met.
GA8.....	270	15	10	Do.
GA9.....	1,000	18	3	Lt. grey matte.
GA10.....	200	20	10	Dk. grey met.

Table II.—Samples plated at 0.13 M triethylene tetramine

Sample number	Current density, amperes per sq. ft.	Av. solution temp., °C.	Time of run, min.	Color luster
GC1.....	600	17	5	Dk. grey semi-met.
GC2.....	200	17	10	Lt. grey met.
GC3.....	300	16	10	Lt. grey semi-met.
GC4.....	250	15	12	Do.
GC5.....	100	15	15	Dk. grey met.
GC6.....	150	15	12	Do.
GC7.....	200	15	11	Lt. grey met.
GC8.....	300	15	7	Do.
GC9.....	400	16	7	Lt. grey semi-met.
GC10.....	500	17	7	Do.
GC11.....	1,000	20	3	Do.

Table III.—Samples plated at 0.15 M triethylene tetramine

Sample number	Current density, amperes per sq. ft.	Av. solution temp., °C.	Time of run, min.	Color luster
GB1.....	600	18	8	Dk. grey matte.
GB2.....	200	18	10	Do.
GB3.....	1,000	20	3	Do.
GB4.....	2,000	22	13½	Lt. grey matte.
GB5.....	100	18	15	Dk. grey met.
GB6.....	50	15	15	Dk. grey semi-met.
GB7.....	150	14	10	Lt. grey mirror.
GB8.....	180	14	8	Do.
GB9.....	200	15	15	Do.
GB10.....	300	16	10	Do.
GB11.....	400	16	7	Lt. grey met.
GB12.....	500	17	6	Lt. grey semi-met.
GB13.....	50	17	15	Dk. grey met.
GB14.....	600	16	5	Lt. grey semi-met.
GB15.....	250	16	10	Lt. grey met.
GB16.....	200	16	10	Lt. grey mirror.
GB17.....	200	16	10	Do.

It will thus be observed that bright zinc deposits may be obtained from acid zinc sulfate solutions by using triethylene tetramine as an addition agent at concentrations of about 0.15 M and current densities between 150 and 600 amperes per square foot.

Having described our invention, what we claim and wish to protect by Letters Patent is:

- 10 The process of producing bright electro-deposited zinc which comprises plating zinc onto a cathode at a current density in the range from 150 to 600 amperes per square foot of cathode surface from a bath at a temperature approximately that of the range 14° to 20° C., said bath
- 15 consisting of zinc sulfate, water, sulfuric acid and an addition agent, the bath containing from 20% to 24% of zinc sulfate, and being approximately half-normal in acidity from said sulfuric acid, said addition agent being triethylene tetramine and being present in the bath in quantity to provide a molar concentration of about 0.15.

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