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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.

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 addition agents for use in electrogalvanizing processes, which addition agents 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 certain addition agents. In order to acquaint those skilled in the art with the nature of our addition products 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 smaller 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 agents was investigated. The addition agents tried were pyridine and triethylene tetramine.

A series of solutions was prepared in which the concentration of the addition agent varied from 0.005 M to 0.015 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."

Examples of specific embodiments of our invention, in terms of operating data obtained from our experiments, will now be given.

Table I.—Operating data and observation of samples plated at 0.006 M pyridine

Sample number	Current density, amperes per sq. ft.	Av. solution temp., °C.	Time of run, min.	Color	Luster
EE 1	600	17	5	Light grey	Matte.
EE 2	400	17	7	do	Mirror.
EE 3	200	15	10	do	Do.
EE 4	150	17	10	Dark grey	Matte.
EE 5	160	15	12	Light grey	Mirror.
EE 6	800	16	4	do	Do.
EE 7	700	17	5	do	Do.
EE 8	600	17	5	do	Do.
EE 9	500	17	6	do	Do.
EE 10	1,000	17	3	do	Matte.
EE 11	300	16	10	do	Mirror.

Table II.—Samples plated at 0.008 M pyridine

Sample number	Current density, amperes per sq. ft.	Av. solution temp., °C.	Time of run, min.	Color	Luster
EB 1	600	16	5	Light grey	Matte.
EB 2	200	16	15	do	Semi-met.
EB 3	190	16	16	do	Do.
EB 4	180	16	17	do	Mirror.
EB 5	170	16	18	do	Do.
EB 6	160	16	20	do	Do.
EB 7	150	16	21	Dark grey	Do.
EB 8	150	16	10	do	Do.
EB 9	160	16	10	do	Do.
EB 10	160	16	11	Light grey	Do.
EB 11	250	17	12	do	Do.
EB 12	230	17	13	do	Do.
EB 13	200	17	10	do	Do.
EB 14	300	17	10	do	Do.
EB 15	400	17	7	do	Do.
EB 16	500	18	6	do	Do.
EB 17	600	18	5	do	Do.
EB 18	1,000	19	3	do	Do.

Table III.—Samples plated at 0.010 M pyridine

Sample number	Current density, amperes per sq. ft.	Av. solution temp., °C.	Time of run, min.	Color	Luster
EA 3	600	16	5	Light grey	Matte.
EA 9	220	17	15	do	Semi-met.
ED 1	600	16	5	do	Do.
ED 6	150	15	21	do	Do.
ED 9	100	15	15	Dark grey	Matte.
ED 10	130	15	12	do	Do.
ED 11	140	15	11	do	Do.
ED 12	150	15	11	Light grey	Semi-met
ED 13	200	15	10	do	Do.

Table IV.—Samples plated at 0.012 M pyridine

Sample number	Current density, amperes per sq. ft.	Av. solution temp., °C.	Time of run, min.	Color	Luster
EF 1	600	17	5	Light grey	Semi-met.
EF 2	200	17	11	do	Matte.
EF 3	150	17	10	do	Do.
EF 4	100	17	15	Dark grey	Do.
EF 5	130	17	13	Light grey	Semi-met.
EF 6	115	17	12	Dark grey	Matte.
EF 7	400	18	7	Light grey	Semi-met.
EF 8	300	18	10	do	Do.
EF 9	800	18	4	do	Do.

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

Table V.—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
GA 1	600	18	5	Light grey	Matte.
GA 2	200	18	10	Dark grey	Met.
GA 3	150	17	10	do	Do.
GA 4	100	15	15	do	Do.
GA 5	300	15	10	Light grey	Do.
GA 6	400	16	8	do	Semi-met.
GA 7	250	15	12	do	Met.
GA 8	270	15	10	do	Do.
GA 9	1,000	18	3	do	Matte.
GA 10	200	20	10	Dark grey	Met.

Table VI.—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
GC 1	600	17	5	Dark grey	Semi-met.
GC 2	200	17	10	Light grey	Met.
GC 3	300	16	10	do	Semi-met.
GC 4	250	15	12	do	Do.
GC 5	100	15	15	Dark grey	Met.
GC 6	150	15	12	do	Do.
GC 7	200	15	11	Light grey	Do.
GC 8	300	15	7	do	Do.
GC 9	400	16	7	do	Semi-met.
GC 10	500	17	7	do	Do.
GC 11	1,000	20	3	do	Do.

Table VII.—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
GB 1	600	18	5	Dark grey	Matte.
GB 2	200	18	10	do	Do.
GB 3	1,000	20	3	do	Do.
GB 4	2,000	22	1½	Light grey	Met.
GB 5	100	18	15	Dark grey	Semi-met.
GB 6	50	15	15	do	Mirror.
GB 7	150	14	10	Light grey	Do.
GB 8	180	14	8	do	Do.
GB 9	200	15	15	do	Do.
GB 10	300	16	10	do	Met.
GB 11	400	16	7	do	Semi-met.
GB 12	500	17	6	do	Met.
GB 13	50	17	15	Dark grey	Semi-met.
GB 14	600	16	5	Light grey	Met.
GB 15	250	16	10	do	Mirror.
GB 16	200	16	10	do	Do.
GB 17	200	16	10	do	

The following conclusions are apparent from ths foregoing data. Bright zinc deposits may be obtained from acid zinc sulfate solutions by using pyridine as an addition agent at concentrations of 0.006 to 0.010 M and current densities between 150 and 600 amperes per square foot. 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:

The process of producing bright electrodeposited 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 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 pyridine and being present in the bath in quantity to provide a molar concentration in the range from 0.006 to 0.010.

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