

1

2,905,603

ZINC PLATING

William H. Safranek and Hugh R. Miller, Columbus, Ohio, assignors, by mesne assignments, to American Zinc Institute, New York, N.Y., a corporation of New York

No Drawing. Application September 4, 1957
Serial No. 681,906

5 Claims. (Cl. 204—55)

This invention relates to zinc electroplating, and particularly to a method and compositions for electroplating bright, leveling zinc.

One object of the invention is to provide a method for eliminating or reducing the costs of polishing and buffing of die castings prior to electroplating with copper, nickel, and chromium. Heretofore, zinc die castings had to be polished and buffed by costly mechanical procedures to eliminate scratches, pits, cold shut, and other surface irregularities to make their surfaces sufficiently smooth for producing a mirrorlike finish by plating with copper, nickel, and chromium. Although several leveling-type copper and nickel plating processes are employed commercially, they do not result in a satisfactory mirrorlike appearance unless the die cast surfaces are first smoothened mechanically. However, by zinc plating with the process of this invention, a smooth bright finish can be obtained on zinc die castings without the need for polishing or buffing them. When the zinc-plated die castings are subsequently electroplated with leveling copper and nickel, and finally with chromium, an excellent mirrorlike appearance is obtained.

Another object is to provide a method for improving the corrosion resistance of electroplated zinc die castings. It has been established that surface pores in die cast surfaces seldom are removed completely by mechanical polishing or buffing, and it has been established further that such pores, which usually are neither filled nor bridged by copper, nickel, and chromium plating, are the focal points for corrosion when electroplated die castings are exposed outdoors. However, by zinc plating according to this invention, surface pores are filled or bridged with zinc plate. Copper, nickel, and chromium then can be electroplated with no discontinuities or pits, thereby improving the corrosion resistance of the electroplated die castings.

A further object of this invention is to provide a method for improving the appearance of zinc-plated steel parts. Although several processes are employed commercially for electroplating bright zinc, they have little or no leveling power and, as a result, steel parts stamped from hot rolled steel and other parts fabricated from commercial cold rolled steel with a No. 1 or No. 2 finish have an inferior, frosty or hazy appearance after zinc plating by prior art processes. The appearance of such parts, however, is improved greatly by zinc plating according to the present invention. Surfaces are more nearly mirrorlike and irregularities such as scratches and pits are covered or hidden, because of the exceptional leveling power of the zinc plate deposited by the present process.

Other objects and advantages of the present invention are apparent from the disclosure herein.

It has been found in the present invention that certain critical ranges of composition and operating conditions are necessary to provide optimum polishing of scratches and leveling, especially pore filling.

Table I below lists preferred and useful ranges of bath compositions and operating conditions according to the present invention.

2

TABLE I
Bath composition

	Preferred concentration range	Useful concentration range
Zinc sulfate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$g./l.	230 to 250	150-400.
Ammonium chloride.....g./l.	10 to 20	Optional up to 50.
Aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$g./l.	25 to 35	Do.
Glycyrrhizin, ammoniated.....g./l.	1.0 to 3.0	0.5 to 7.0.
Glycerin.....g./l.	5 to 7	Optional up to 7.
Tergitol OS, ¹ wetting agent percent by volume.....	1.0 to 1.5	Optional up to 1.5.
pH.....	3.1 to 3.7	2.0 to 4.0.
Boric Acid.....		Optional up to 45 g./l.

Operating conditions

	Preferred range	Useful range	Range of ratios
Periodic current reversal cycle:			
Forward.....seconds.....	14-18	4-60	For.....1.3 to 15.
Reverse.....do.....	4-6	1-45	
Cathode current density:			
Forward.....amp./sq. ft.....	150-250	50-500	For.....0.3 to 3.0.
Reverse.....amp./sq. ft.....	200-400	30-800	
Temperature.....° F.....	130-155	90-180	

¹ Tergitol OS is a 38 percent solution of sodium sulfate derivative of 2-ethyl hexanol-1 $\text{C}_4\text{H}_9\text{CH}-\text{CH}_2\text{SO}_3\text{Na}$.



Other typical conditions

Agitation:
Work bar—30-60 c.p.m., 1 to 4 inch stroke.
Air—sufficient to raise the solution level about one inch.
Anode current density—30 to 60 amp./sq. ft.
Voltage (between cathode and anode):

Direct, 5 v.....Range 4-10
Reverse, 10 v.....5-15
Plating rate—0.002 to 0.004 inch/hour.
Time—15-60 minutes.
Thickness of deposit—0.0005 to 0.004.

The ammonium chloride increases the conductivity of the bath, but can be omitted or replaced with other highly conducting salts. The aluminum sulfate and boric acid are buffers. The ammoniated glycyrrhizin is a brightening agent. The glycerin increases the solubility of the glycyrrhizin. The wetting agent prevents pitting.

Any other ammonium halide may be used in place of the ammonium chloride listed in Table I. When the halide is omitted a slightly higher voltage may be required. Other buffers may be substituted for the aluminum sulfate or boric acid, or both, if desired. When buffers are not used, the pH should be checked and adjusted regularly. Other wetting agents can also be substituted. The wetting agent can be omitted if the bath is maintained in a substantially pure condition, free from oil, grease, and metallic impurities such as copper, lead, and cadmium. The glycerin increases the solubility of the glycyrrhizin in the bath. Other solubility improvers such as high boiling alcohols can be substituted if desired. The glycerin or substitute can be omitted, with a resulting slight reduction of glycyrrhizin solubility.

The essentials of the bath composition are (a) zinc sulfate in the range of about 150 to 400 grams per liter, preferably about 230 to 250 grams per liter; (b) ammoniated glycyrrhizin in the range of about 0.5 to 7.0 grams per liter, preferably about 1.0 to 3.0 grams per liter; and acid concentration such as to provide a pH in the range of about 2.0 to 4.0, preferably about 3.1 to 3.7.

Table II below lists seven examples of plating baths and conditions in accordance with the present invention.

TABLE II

Examples of conditions used for plating leveling bright zinc

Example No.	I	II	III	IV	V	VI*	VII*
Supplemental constituent, * g./l.	17	17	17	13	13	17	17
Concentration of ammoniated glycyrrhizin, g./l.	6	1	1	3	3	1	1
Periodic current reversal cycle:							
Forward, seconds	16	16	15	40	60	16	15
Reverse, seconds	5	5	9	15	45	5	9
Current density:							
Forward, amp./sq. ft.	200	200	200	140	100	200	250
Reverse, amp./sq. ft.	400	400	250	280	60	400	300
Temperature, ° F	160	150	160	90	90	150	150
Plating time, minutes	30	30	40	60	50	30	30
Thickness of plate, inch	0.002	0.002	0.002	0.0018	0.00375	0.002	0.0015
Plating rate, inches/hour	0.005	0.004	0.003	0.0018	0.0045	0.004	0.003
Appearance of plate	(3)	(1 b)	(3)	(3)	(2)	(3)	(3)

* Glycerin.

* Glycerin plus 45 g./l. boric acid.

* Smooth¹ bright.

* Each bath contained:

240 g./l. zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$)30 g./l. aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$)

15 g./l. ammonium chloride

0.5 to 1.5 percent, by volume Tergitol 08 (Tergitol 08 is the sodium sulfate derivative of 2-ethylhexanol)

pH usually 3.4 to 3.8, but sometimes 2.5 to 3.1

The plating bath was continuously filtered to remove insoluble particles.

Bath voltages generally were:

5 to 7 volts for the forward part of the cycle

7 to 14 volts for the reverse part of the cycle

All baths were agitated with air, and the cathode bar was moved back and forth from 30 to 60 c.p.m. with a 1-, 2-, or 4-inch stroke.

Cathode efficiency (direct Between 95 and 100 percent.

plating period).

Anodes High-purity zinc in cotton or nylon bags (to keep anode particles away from cathode).

Racks Copper, covered with masking tape and four coats of stop-off lacquer to prevent tree formation.

* Surfaces were smoothened as follows:

Before plating, R.M.S., microinches	After plating, R.M.S., microinches	Percent leveling
40	10	75
24	9	63
7.5	4	47

* Zinc sulfate concentration was increased to 360 g./l.

Smooth, bright plates were obtained in all of the above examples. In Example II profilometer measurements were made to measure the leveling obtained with three different surfaces as indicated in footnote (b) above. The profilometer measures the root mean square (R.M.S.) of the maximum deviations on the surface from a perfectly smooth plane. The leveling obtained is the reduction in percent of the profilometer reading after the surface has been plated. The plates obtained with the present invention are noticeably smoother and brighter than those obtained by prior methods, and the leveling obtained on a given surface is substantially increased by the present invention.

The visible results of scratch leveling obtained by the present process were demonstrated on a flat surface of a zinc die casting that had been mechanically polished with abrasive papers to provide areas of fine scratches (using metallographic paper with about 320-grit abrasive) and areas of coarse scratches (using 180-grit abrasive). The areas of fine scratches were completely leveled by plating with zinc according to the present invention and adding thin coatings of electroplated copper, nickel, and chromium in a conventional manner. The reflection of images from these areas was free from distortion. The areas of coarse scratches, which were plated along with the other areas, were substantially leveled. Only a slight distortion was apparent in the image reflection from these areas.

The pore bridging power of the zinc plate provided by the present process was compared with the pore filling power of copper plate. Photomicrographs showed that the zinc plate completely bridges pores of the same size as those which the copper plate failed to fill or bridge.

The effectiveness of the present process on steel is apparent from Table III, which includes leveling data for the zinc plate deposited on steel panels.

TABLE III

Leveling data on zinc plating steel panels

Thickness of zinc plate, millinches	Surface roughness before plating, R.M.S., microinches	Surface roughness after zinc plating, R.M.S., microinches	Percent leveling
1.0	72	29	60
2.0	72	7	91
0.5	72	19	74
1.0	72	12.5	83
1.0	60	18	70
2.0	60	8	87
1.0	60	21	65
2.0	60	10.5	82.5
1.1	53	12.5	76.5
2.2	53	6.5	88
0.6	53	27.5	48
1.2	53	16	70
1.3	50	13	74
2.6	50	5.5	89
0.7	50	22	56
1.3	50	7	86
1.3	22.5	75	66.5
2.6	22.5	5	78
0.7	22.5	9.5	57.5
1.3	22.5	5	78
1.0	21.5	7	67
2.0	21.5	5	77
1.0	21.5	10	53.5
2.0	21.5	6	72
1.0	20.5	10	51
2.0	20.5	5	75.5
0.5	20.5	10.5	49
1.0	20.5	5.5	73
1.1	20.5	9	56
2.2	20.5	5	75.5
0.6	20.5	12.5	39
1.2	20.5	6.5	68

What is claimed is:

1. A method of bright, leveling zinc electroplating comprising plating zinc upon a conductive cathode from a zinc solution consisting essentially of about 150 to 400 grams per liter of zinc sulfate, and about 0.5 to 7.0 grams per liter of ammoniated glycyrrhizin, said solution having a pH from about 2.0 to 4.0; providing the plating by a periodic current reversal cycle alternating between forward current for about 4 to 60 seconds at a cathode current density of about 50 to 500 amperes per square foot and reverse current for about 1 to 45 seconds at a cathode current density of about 30 to 800 amperes

5

per square foot, while maintaining the temperature of said solution between about 90 to 180° F.

2. The method of claim 1 in which the ratio of forward current time to reverse current time in said periodic current reversal cycle is about 1.3 to 15, and the ratio of forward cathode current density to reverse cathode current density is about 0.3 to 3.0.

3. A method of bright, leveling zinc electroplating comprising plating zinc upon a conductive cathode from a zinc solution consisting essentially of about 230 to 250 grams per liter of zinc sulfate, and about 1.0 to 3.0 grams per liter of ammoniated glycyrrhizin, said solution having a pH from about 3.1 to 3.7; providing the plating by a periodic current reversal cycle alternating between forward current for about 14 to 18 seconds at a cathode current density of about 150 to 250 amperes per square foot and reverse current for about 4 to 6 seconds at a cathode current density of about 200 to 400 amperes per square foot, while maintaining the temperature of said solution between about 130 to 155° F.

6

4. A composition of matter for bright, leveling zinc electroplating consisting of an aqueous solution consisting essentially of about 150 to 400 grams per liter of zinc sulfate, and about 0.5 to 7.0 grams per liter of ammoniated glycyrrhizin, said solution having a pH from about 2.0 to 4.0.

5. A composition of matter for bright, leveling zinc electroplating consisting of an aqueous solution consisting essentially of about 230 to 250 grams per liter of zinc sulfate, and about 1.0 to 3.0 grams per liter of ammoniated glycyrrhizin, said solution having a pH from about 3.1 to 3.7.

References Cited in the file of this patent

UNITED STATES PATENTS

2,250,842	Roberts	July 29, 1941
2,451,341	Jernstedt	Oct. 12, 1948
2,651,610	Chester	Sept. 8, 1953