

1

3,337,430 ULTRAHIGH-SPEED CHROMIUM ELECTRODEPOSITION

Andy Albert Johnson, Oak Park, Mich., assignor to M & T Chemicals Inc., New York, N.Y., a corporation of Delaware

No Drawing. Filed Aug. 5, 1963, Ser. No. 300,107
7 Claims. (Cl. 204—51)

This invention relates to a novel method for electroplating bright, decorative chromium plate at very high plating speeds. It also relates to novel chromium plating baths.

Chromium plating has found wide use as a means for producing a bright, durable, decorative coating on various articles. The high luster which is produced thereon greatly enhances the attractiveness, serviceability, and aesthetic appeal of the plated article.

It has been found through long experience with chromium electroplating that bright chromium plate could not be achieved at high plating speeds. The high cathode current densities required to produce rapid plating could not be satisfactorily employed with known chromium plating baths since the chromium plate obtained would be dull, highly porous, and usually "burned." Consequently, cathode current densities have, in practice, been limited to about 3–75 amperes per square decimeter (a.s.d.) at which level only about .02–.5 micron of bright chromium is deposited per minute.

It will be apparent that these necessarily slow plating speeds have been a serious inconvenience to commercial platers, since the speed of production lines is often limited by the chromium plating operation. In spite of the seriousness of this long-standing problem, no practical solution to it may be found in the prior art.

A satisfactory bath for plating bright chromium at very high speeds should be capable of producing a thickness of about 5 microns of bright chromium plate at a rate of at least about 1.25, and preferably at least about 2.5 microns per minute. Thus, not only must the plating speed be high, but the plate must remain bright until a desirable commercial thickness is obtained. These highly desirable results, which may be attained by practice of this invention, have not heretofore been achieved in actual practice.

The term "bright" in describing bright chromium electrodeposits, as used herein, is limited to surfaces which have sufficient reflectivity to render a well defined and recognizable image. The bright range of deposits is also divided into two subdivisions—deposits referred to as "mirror-bright" and deposits referred to as "bright." The mirror-bright deposits are those which have the reflectivity ordinarily associated with a good mirror. The bright deposits have a lesser degree of reflectivity than a good mirror, but sufficient reflectivity to render a well defined and recognizable image. These bright deposits are sufficiently bright as plated to be acceptable decorative finishes. Their degree of brightness may be improved by a buffing operation to achieve mirror brightness. The term "bright chromium" encompasses those deposits which are mirror-bright and bright, as defined herein.

It is an object of this invention to provide a novel process for electroplating bright, decorative chromium plate at very high plating speeds. It is a further object to provide novel chromium electroplating baths. Other objects will be apparent to those skilled in the art upon reading the following disclosure.

2

In accordance with certain of its aspects, this invention relates to the novel process for electroplating bright chromium plate at high plating speeds which comprises maintaining a chromium plating bath containing chromic acid and sulfate wherein the variables (a) chromic acid concentration, CrO_3 , (b) ratio of CrO_3 to SO_4^{2-} plus SiF_6^{2-} , (c) proportion $\text{SiF}_6^{2-}/\text{SO}_4^{2-}$, and (d) temperature are within the limits

CrO ₃ -----	g./l.	100–400
Ratio -----		25–100
Proportion -----		0–4
Temperature -----	° C.	27–94

and wherein at least two of said variables are within the limits

CrO ₃ -----	g./l.	150–250
Ratio -----		25–70
Proportion -----		0–2
Temperature -----	° C.	60–82

maintaining in said bath an anode and a cathode; and passing an electric current through said anode, said bath, and said cathode at a cathode current density of at least about 150 a.s.d., thereby electroplating bright chromium on said cathode at a rate of at least about 1.25 microns per minute.

In accordance with certain of its aspects, this invention relates to novel chromium electroplating baths containing chromic acid and sulfate characterized by their ability to produce bright chromium plate at very high plating speeds, wherein the variables chromic acid concentration, ratio, proportion, and temperature are within the limits

CrO ₃ -----	g./l.	100–400
Ratio -----		25–100
Proportion -----		0–4
Temperature -----	° C.	27–94

and wherein at least two of said variables are within the limits

CrO ₃ -----	g./l.	150–250
Ratio -----		25–70
Proportion -----		0–2
Temperature -----	° C.	60–82

The process of this invention is particularly suitable for plating bright chromium at very high plating speeds, i.e., at deposition rates of at least about 1.25 microns per minute. In certain of its preferred embodiments, this invention permits attainment of plating speeds of greater than 2.5 microns per minute and even as high as about 10 microns per minute. Thus, practice of this invention gives results which are 2.5 to 20 times faster than those commonly obtained from prior art processes. It is a particular advantage of this invention that the chromium plate obtained at these very high plating speeds may be bright and lustrous, a result which has not heretofore been attainable.

The chromium plating baths which may find use in the practice of this invention may typically comprise water, chromic acid (CrO_3), and sulfate ion (which may have been added as sulfuric acid or salts thereof). Optionally, the baths may contain active fluoride, or complex fluorides such as silicofluorides, fluoaluminates, fluozirconates, fluotitanates, etc., and fume-suppressants, etc. The plating apparatus which is employed in conjunction with these baths may include a regulatable source of electric current, an anode which may typically be a lead anode, and a

cathode on which chromium metal is electrodeposited.

In the chromium plating art, a chromium plating bath may be described by reference to various parameters including:

(a) Chromic acid concentration,

(b) Ratio (which is here taken as the numerical value obtained by dividing the chromic acid concentration by the sum of the concentrations of the catalyst anions, such as sulfate ion and silicofluoride ion, all of which are expressed in grams per liter),

(c) Proportion (which is the numerical value obtained by dividing the silicofluoride or other complex fluoride ion concentration by the sulfate ion concentration, both of which are expressed in grams per liter),

(d) Bath temperature.

It has been found that the desirably high, bright plating speeds may be realized if four of the bath variables, viz. chromic acid concentration, ratio, proportion, and temperature are maintained within certain narrow limits and at least two of said variables are maintained within certain specific limits. Although any two of these variables may be within the specific limits, preferably the chromic acid concentration and/or temperature will be. Preferably at least 3 of said variables may be maintained within the specific limits.

In accordance with this invention, the chromic acid concentration in the novel baths may fall within the narrow limits of 100-400 grams per liter (g./l.) and specific limits of 150-250 g./l. Preferably, the narrow limits may be about 100-300 g./l.

The ratio of the novel baths of this invention may fall within the narrow limits 25-100 and the specific limits 25-70. Preferably, the narrow limits may be about 25-90 and the specific limits may be about 40-60, say 50.

The proportion of the novel baths may typically be maintained within the narrow limits 0-4 and the specific limits 0-2. Preferably, the narrow limits may be 0-3 and the specific limits may be 0-1, say 0.

Bath temperature may typically be maintained within narrow limits 27-94° C. and specific limits 60-82° C. Preferably, the narrow limit may be 49-88° C. and the specific limits may be 60-77° C. say 65° C.

The novel chromium electroplating baths of this invention may be capable of producing bright chromium plate at high plating speeds when electrolyzed at high cathode current densities. High cathode current densities may be those greater than about 150 a.s.d. Typically, the novel baths may be electrolyzed at about 150-600, say 300 a.s.d., the particular current density being chosen in accordance with the high plating speed desired. It is an outstanding feature of this invention that the high current densities which may be employed may permit attainment of bright chromium plate at very high rates of deposition.

The very high rates of deposition obtained by practice of this invention may be advantageous in the plating of bright, decorative chromium plate of varying thicknesses. Preferred embodiments of the invention may produce as much as about 10 microns per minute of bright chromium plate.

Practice of this novel invention wherein two of the noted variables are maintained within the noted specific limits and the remaining variables are maintained within the noted narrow limits is illustrated by the following examples.

For Examples 1-4, a bath having the composition

CrO₃ ----- g./l. 275
Ratio ----- 40
Proportion ----- 3

was made up and maintained at an operating temperature of 71° C. Thus, the temperature and ratio variables were within their respective specific limits and the chromic acid concentration and proportion were outside their specific limits but within their narrow limits. Nickel-plated brass panels were employed as cathodes and a lead anode

was used. The systems were electrolyzed at a cathode current density of 150, 300, 450 and 600 a.s.d. for a total of one minute and the thickness of bright chromium plate deposited was measured. The results are shown in Table I wherein thickness is given in microns.

TABLE I

Example	Current Density (a.s.d.)	Thickness Plated, microns
1-----	150	2.42
2-----	300	5.0
3-----	450	8.3
4-----	600	9.85

It should be noted that even the lowest of these thickness values represents an improvement in plating speed of about 500% over results obtained in present commercial practice.

For Examples 5-10, a Hull cell test was employed to determine the maximum thickness of bright chromium plate which could be obtained from various plating solutions during one minute of electrolysis. Because of the construction of the Hull cell, the current density over the length of the cathode is systematically varied. Standard nickel-plated brass Hull cell panels were masked so that only a 5 mm. strip was exposed to the bath in order to obtain the high cathode current densities required for high speed chromium plating. Chromium plating solutions which exemplify those falling within the scope of this invention were prepared by dissolving the desired amounts of chromic acid, sulfuric acid and fluosilicic acid (H₂SiF₆) in water. For example, the solution of Example 7 was prepared by dissolving 200 grams of chromic acid, 1.36 grams of sulfuric acid, and 2.74 grams of fluosilicic acid in water and further diluting with water to a volume of one liter. The noted solutions were placed in the cell and electrolyzed at a cell current of 5 amperes for one minute. The panels were then examined and the maximum thickness of bright chromium plated was determined. Results of these experiments are given in Table II wherein thickness plated is in microns. Numerical values for the noted variables were as shown and those values marked with an asterisk were maintained within their respective preferred specific limits.

TABLE II

Ex.	CrO ₃ (g./l.)	Ratio	Proportion	Temp., ° C.	Thickness Plated, microns
5-----	400	80	*0	*65	2.7
6-----	*200	80	2	*65	2.375
7-----	*200	*50	2	49	1.925
8-----	400	*50	*0	49	1.875
9-----	*200	80	*0	49	1.85
10-----	400	*50	2	65	1.675

From Table II it may readily be seen that baths of the present invention permit plating speeds of bright chromium which are as much as 5 times as high as present commercial practice.

In Examples 11-14 the same basic procedure was followed as in Examples 5-10 except that three or four of the noted variables were maintained within their respective preferred specific limits. Results of these experiments are shown in Table III.

TABLE III

Ex.	CrO ₃ (g./l.)	Ratio	Proportion	Temp., ° C.	Thickness Plated, microns
11-----	*200	*50	*0	*65	5.225
12-----	*200	*50	2	*65	6.275
13-----	*200	80	*0	*65	4.85
14-----	400	*50	*0	*65	4.05

It may be seen from Table III that when at least three of the noted variables are maintained within the specific limits, highly superior results may be obtained.

In Examples 15-29, chromium plating baths having a ratio of about 40 and a proportion of about 3 were prepared. These baths were adjusted to chromic acid concentrations of 200, 225, and 250 g./l. and were electrolyzed at cathode current densities of 150, 225, 300, 450 and 600 a.s.d. at a temperature of 71° C. Thus, three of the variables viz. temperature, ratio, and chromic acid concentration were within the specific limits and proportion was within the narrow limits. After one minute of electrolysis, the thickness of bright chromium deposited on a nickel-plated brass panel was measured and expressed in microns. Results of these experiments are presented in Table IV.

TABLE IV

Ex.	CrO ₃ (g./l.)	Cathode Current Density (a.s.d.)	Thickness Plated, microns
15.....	200	150	2.175
16.....	200	225	3.325
17.....	200	300	4.575
18.....	200	450	7.200
19.....	200	600	9.575
20.....	225	150	1.975
21.....	225	225	3.775
22.....	225	300	5.500
23.....	225	450	7.500
24.....	225	600	9.200
25.....	250	150	2.600
26.....	250	225	4.050
27.....	250	300	5.625
28.....	250	450	7.425
29.....	250	600	8.500

As may be seen from Table IV, practice of this invention, wherein at least three of the noted variables are maintained within their respective specific limits, permits attainment of outstandingly high plating speeds which may be as much as about 20 times those heretofore attainable.

The novel plated articles of this invention may comprise a basis metal with a bright chromium plate electro-deposited thereon by the process which comprises maintaining a chromium plating bath containing chromic acid and sulfate wherein the variables chromic acid concentration, ratio, proportion, and temperature are within the limits

CrO₃ -----g./l. 100-400
Ratio ----- 25-100
Proportion ----- 0-4
Temperature -----° C. 27-94

and wherein at least two of said variables are within the limits

CrO₃ -----g./l. 150-250
Ratio ----- 25-70
Proportion ----- 0-2
Temperature -----° C. 60-82

maintaining in said bath an anode and a cathode; and passing an electric current through said anode, said bath, and said cathode at a cathode current density of at least about 150 amperes per square decimeter, thereby electroplating bright chromium plate on said cathode at a rate of at least about 1.25 microns per minute.

These novel chromium plated articles which may be produced by the process of this invention may be characterized by their superior smoothness, brightness, hardness and lack of undesirable pores especially when compared to articles plated at very high plating speeds in prior art baths.

As many embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention includes all such modifications and variations as come within the scope of the appended claims.

I claim:

1. The process for electroplating bright chromium plate at high plating speeds which comprises maintaining a chromium plating bath containing chromic acid and at least one catalyst anion selected from the group consisting of sulfate, fluoride, complex fluoride and mixtures thereof wherein the variables chromic acid concentration, ratio of chromic acid to the sum of the concentrations of said catalyst anions, proportion of fluoride and complex fluoride to sulfate, and temperature are within the limits

CrO₃ -----g./l. 100-400
Ratio ----- 25-100
Proportion ----- 0-4
Temperature -----° C. 27-94

and wherein at least two of said variables are within the limits

CrO₃ -----g./l. 150-250
Ratio ----- 25-70
Proportion ----- 0-2
Temperature -----° C. 60-82

- 25 maintaining in said bath an anode and a cathode; and passing an electric current through said anode, said bath, and said cathode, at a cathode current density of at least about 150 amperes per square decimeter, thereby electroplating bright chromium plate on said cathode at a rate of at least about 1.25 microns per minute.

- 30 2. The process for electroplating bright chromium plate as claimed in claim 1 wherein said chromic acid concentration is within the limits 150-250 g./l.

- 35 3. The process for electroplating bright chromium plate as claimed in claim 1 wherein said temperature is within the limits 60-82° C.

4. The process for electroplating bright chromium plate as claimed in claim 3 wherein said chromic acid concentration is within the limits 150-250 g./l.

- 40 5. The process for electroplating bright chromium plate at high plating speeds which comprises maintaining a chromium plating bath containing chromic acid and at least one catalyst anion selected from the group consisting of sulfate, fluoride, complex fluoride and mixtures thereof wherein the variables chromic acid concentration, ratio of chromic acid to the sum of the concentrations of said catalyst anions, proportion of fluoride and complex fluoride to sulfate, and temperature are within the limits

CrO₃ -----g./l. 100-300
Ratio ----- 25-90
Proportion ----- 0-3
Temperature -----° C. 49-88

- 55 and wherein at least two of said variables are within the limits

CrO₃ -----g./l. 150-250
Ratio ----- 40-60
Proportion ----- 0-1
Temperature -----° C. 60-77

- 60 maintaining in said bath an anode and a cathode; and passing an electric current through said anode, said bath, and said cathode, at a cathode current density of about 150-600 amperes per square decimeter, thereby electroplating bright chromium plate on said cathode at a rate of about 1.25-10 microns per minute.

- 65 6. The process for electroplating bright chromium plate at high plating speeds which comprises maintaining a chromium plating bath containing chromic acid and at least one catalyst anion selected from the group consisting of sulfate, fluoride, complex fluoride and mixtures thereof wherein the variables chromic acid concentration, ratio of chromic acid to the sum of the concentrations of said catalyst anions, proportion of fluoride and com-

7.

plex fluoride to sulfate, and temperature are within the limits

CrO₃ -----g./l. 100-400
 Ratio ----- 25-100
 Proportion ----- 0-4
 Temperature -----° C. 27-94

and wherein at least three of said variables are within the limits

CrO₃ -----g./l. 150-250
 Ratio ----- 25-70
 Proportion ----- 0-2
 Temperature -----° C. 60-82

maintaining in said bath an anode and a cathode; and passing an electric current through said anode, said bath, and said cathode, at a cathode current density of at least about 150 amperes per square decimeter, thereby electroplating bright chromium plate on said cathode at a rate of at least about 1.25 microns per minute.

7. The process for electroplating bright chromium plate at high plating speeds which comprises maintaining a chromium plating bath containing chromic acid and at least one catalyst anion selected from the group consisting of sulfate, fluoride, complex fluoride and mixtures thereof wherein the variables chromic acid concentration, ratio of chromic acid to the sum of the concentrations of said catalyst anions, proportion of fluoride and complex fluoride to sulfate, and temperature are within the limits

8

CrO₃ -----g./l. 100-300
 Ratio ----- 25-90
 Proportion ----- 0-3
 Temperature -----° C. 49-88

5 and wherein at least three of said variables are within the limits

CrO₃ -----g./l. 150-250
 Ratio ----- 40-60
 Proportion ----- 0-1
 Temperature -----° C. 60-77

10 maintaining in said bath an anode and a cathode; and passing an electric current through said anode, said bath, and said cathode, at a cathode current density of about 150-600 amperes per square decimeter, thereby electroplating bright chromium plate on said cathode at a rate of about 1.25-10 microns per minute.

References Cited

UNITED STATES PATENTS

1,942,469	1/1934	Barber	204-51
2,950,234	8/1960	Johnson et al.	204-51
2,952,590	8/1960	Stareck et al.	204-51
25 3,108,933	10/1963	Johnson	204-51

JOHN H. MACK, *Primary Examiner.*

G. KAPLAN, *Assistant Examiner.*