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METHOD OF CHROMIUM PLATING

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This invention relates to an improved method for chromium plating hard, high strength steels.

Conventional chromium plating of such steels is accompanied by such a high loss of fatigue strength that failure of the steel usually occurs under repeated loading; moreover, the loss in fatigue strength increases with increasing strength of the steel. Baking of the plated steel, such as is customary to help counteract the effect of hydrogen embrittlement, further reduces the fatigue strength, the reduction being more marked as the thickness of the plate increases.

This unfavorable effect of chromium plating has naturally limited the usefulness of these plated steels, and although attempts have been made to lessen the effect, for one reason or another no practical method has evolved for producing a satisfactory result. It is a principal object of the invention to provide a method for chromium plating hard, high strength steel without substantial loss of fatigue strength comprising plating the steel in a chromic acid-sulfate bath of the kind, and under the conditions, described hereinafter and then baking the plated steel at 200 to 800° F. Unlike conventional sulfate baths, the present bath produces a deposit on the steel which, on subsequent baking, enables the fatigue strength to be restored to values approaching that of the original unplated steel, with the amount of strength restoration increasing with the baking temperature. The resultant chromium plated, heat treated steel enjoys the protection against corrosion and wear, and the hardness and low resistance to friction, that the chromium deposit affords, and, by virtue of the present improvement, is suitable for use under service conditions of stress and strain that approach the fatigue limit, particularly where elevated temperatures are encountered. Thus the field of application of the plated steel is enlarged.

The invention comprises electrodepositing chromium on an article of steel having a fatigue strength of at least 50,000 p. s. i. (pounds per square inch), particularly 60,000 or 70,000 to 110,000 p. s. i., although steels of higher strength may be also plated. A current of 1 to 6 a. s. i. (amperes per square inch) is passed to the article as cathode in an aqueous bath having a chromic acid, CrO_3, content of 400 to 800 g./l., preferably 500 to 700 g./l., and containing dissolved sulfate, $SO_4^=$, as catalyst. The ratio of CrO_3 to dissolved SO_4 is 75:1 to 150:1. Chromium is plated on the article at a temperature of 120 to 170° F., preferably 120 to 150° F., to form a coating at least 2 mils thick, and preferably 5 to 10 or 15 mils, after which the plated article is heated to a temperature of 200 to 800° F.

The chromic acid may be supplied to the bath as such and the sulfate in the form of any suitable compound, such as sulfuric acid.

Preferably a partially neutralized bath is used, as by insuring that it contains a quantity of dissolved M, where M is a metal having a basic reaction and is selected from the group consisting of sodium, potassium, ammonium, and calcium. M may also be written as M^{-e}, where $-e$ represents a deficiency of 1 to 2 electrons, to emphasize the fact that the metal is in the dissolved state. The quantity of M or M^{-e} should be sufficient to neutralize about 10 to 75% of the bath, and may conveniently be supplied to the bath in the form of the chromates or dichromates of sodium, potassium, ammonium, or calcium. One of the foregoing compounds, or a mixture of two or more, may be used. For example, to obtain a bath 45% neutralized, there would be dissolved in it a mixture of 100 parts of CrO_3 as such and about 82 parts of CrO_3 in the form of sodium dichromate. The 82 parts of CrO_3 neutralized to sodium dichromate would thus constitute 45% of the total of 182 parts. The amount of sodium dichromate (dihydrate) required would be approximately 122 parts. As is apparent, the extent of neutralization is based on the amount of neutralized chromic acid present. In addition to the above noted chromate and dichromate compounds, mixtures of chromic acid and a basic compound may be employed to provide partial neutralization. For example, a mixture of chromic acid and sodium hydroxide is suitable, a sufficient amount of the hydroxide being used to neutralize the desired amount of chromic acid in the form of sodium dichromate. Other basic compounds are calcium oxide, calcium hydroxide, sodium carbonate, potassium hydroxide, potassium carbonate, ammonium hydroxide, and ammonium carbonate. It is preferred to effect partial neutralization by means of a chromate or dichromate compound, preferably sodium dichromate. A partially neutralized bath gives less spray loss during operation, and, in the case of sodium dichromate and the other chromate and dichromate compounds, is more economical to operate.

Examples 1 to 10 in the following table may illustrate the preparation of several partially neutralized baths.

Referring to Example 1, a mixture of ingredients was prepared as listed, which when dissolved in water to give 1 liter of solution, provided a bath having the CrO_3 content and CrO_3/SO_4 ratio shown. The bath was 45% neutralized to the dichromate endpoint, as were the baths of Examples 2–5 and 7–10. The bath of Example 6 was made up only from chromic acid and sulfuric acid and was not a neutralized bath.

TABLE 1

Exam. No.	Ingredients of Mixture			Bath Composition	
	Chromic Acid, g./l.	Sodium Dichromate Dihydrate, g./l.	Sodium Sulfate, g./l.	Total CrO_3 Content, g./l.	CrO_3 to SO_4 ratio
1	220	268	7.9	400	75:1
2	220	268	4.0	400	150:1
3	275	334	5.9	500	125:1
4	330	400	7.1	600	125:1
5	330	400	7.1	600	125:1
6	600	0	4.8 (sulfuric acid)	600	125:1
7	385	468	10.4	700	100:1
8	385	468	8.3	700	125:1
9	440	535	15.8	800	75:1
10	440	535	9.5	800	125:1

Another desirable procedure is to employ a bath that is self-regulating with respect to the sulfate concentration.

Such a bath comprises CrO_3 and, as the source of the sulfate, calcium sulfate in an amount sufficient to saturate the bath and to provide an undissolved excess of calcium sulfate. As this saturation concentration of dissolved sulfate is higher than required, a soluble calcium compound is added in an amount sufficient to suppress the concentration of dissolved sulfate from its unsuppressed saturation concentration to a lower value corresponding to said CrO_3/SO_4 ratio of 75:1 to 150:1. Thus, as dissolved sulfate is removed from the bath, as by drag out losses, sufficient excess calcium sulfate goes into solution to replace the lost sulfate. Suitable soluble calcium suppressor compounds for providing dissolved calcium are calcium oxide, calcium hydroxide, calcium carbonate, calcium dichromate, and calcium chromate. For baths containing 400 g./l. of CrO_3 there is added sufficient calcium sulfate to the solution to saturate it and then 23 g./l. of dissolved suppressor calcium is added to give a ratio of CrO_3 to SO_4 of 75 to 1; or 30 g./l. of dissolved suppressor calcium is added to give a ratio of 100 to 1; or 45 g./l. of dissolved suppressor calcium is added for a ratio of 150 to 1. For baths containing 600 g./l. of CrO_3 a 75 to 1 ratio can be obtained with 10 g./l. of dissolved suppressor calcium, a 100 to 1 ratio with 17 g./l. of dissolved suppressor calcium, and a 150 to 1 ratio with 25 g./l. of dissolved suppressor calcium. For baths containing 800 g./l. of CrO_3, a 75 to 1 ratio can be obtained from the solubility of calcium sulfate without added suppressor calcium, a 100 to 1 ratio can be obtained with 3 g./l. of suppressor calcium, and a 150 to 1 ratio can be obtained with 9 g./l. of suppressor calcium.

Specific examples of baths self-regulating with respect to sulfate are set forth in Table 2. Thus, in Example 11 a mixture comprising 87.0% by weight of chromic acid, 3.9% by weight of calcium sulfate dihydrate, and 9.1% by weight of a suppressor compound, when dissolved in water to give a solution containing 460 g./l. of mixture, will provide a plating solution containing 400 g./l. of CrO_3 and a CrO_3/SO_4 ratio of 100 to 1. The suppressor compound was calcium oxide, which was also used in Examples Nos. 12, 13, 15, 16, 20, 21, and 23. In Examples Nos. 14 and 19 the suppressor was calcium carbonate; in Example No. 17 it was calcium chromate dihydrate; and in Example No. 18 it was calcium dichromate trihydrate. No suppressor was required for Example No. 22.

TABLE 2

Exam. No.	Ingredients of Mixture, Percent			Ingredients of Bath, g./l.		
	CrO_3	Calcium Sulfate Dihydrate	Suppressor	Mixture	CrO_3	Ratio: CrO_3 to SO_4
11	87.0	3.9	9.1	460	400	100:1
12	83.2	3.7	13.1	480	400	150:1
13	92.6	3.8	3.6	540	500	75:1
14	87.2	3.6	9.2	574	500	100:1
15	87.0	3.9	9.1	575	500	150:1
16	92.6	3.8	3.6	648	600	100:1
17	84.4	3.7	11.9	663	600	100:1
18	73.5	3.7	22.8	679	600	125:1
19	87.2	3.6	9.2	688	600	150:1
20	94.6	3.9	1.5	740	700	100:1
21	92.6	3.8	3.6	756	700	150:1
22	96.4	3.6	0	830	800	75:1
23	94.6	3.9	1.5	845	800	150:1

It is possible, and desirable, to employ a single bath having the characteristics of both the partially neutralized and the self-regulating baths and thus obtain the advantages of both these baths. As an example:

Example 24

A mixture was prepared comprising, on a weight basis, 50.0% of chromic acid, 42.1% of sodium dichromate dihydrate, 4.8% of calcium hydroxide, and 3.1% of calcium sulfate dihydrate. By dissolving 766 grams of this mixture in enough water to make 1 liter of solution, a bath solution was obtained having 600 g./l. of CrO_3 and a CrO_3 to SO_4 ratio of 125:1. The bath was 45% neutralized. The dissolved calcium not only acts to suppress the concentration of dissolved sulfate but also helps to partially neutralize the bath, so that such action may be taken into account when selecting the amount of neutralization desired. It will be understood that the extent of neutralization is determinable by experiment as well as by calculation.

The unplated steel may have a hardness of at least 20C Rockwell. The upper limit of hardness may be as desired, for example up to 54C. Good results are obtainable in the range of 28C or 33C to 47C Rockwell. Alloy or high quality steels are quite suitable for plating by the present method but the invention is not limited to them. As noted, substantial thicknesses of chromium may be deposited on the steel, being at least 2 mils and usually ranging from 2 to 15 mils, but often going up to 30 mils, or to whatever greater thickness that may be desired. Plating times may vary widely, for example from 1 to 24 hours or more. Good cathode current efficiencies are obtainable.

Following plating, the steel article is baked at a temperature of 200 to 800° F. for about 1 to 4 hours, usually for 2 hours. For steels having lower draw temperatures the preferred baking temperature is 350 to 550° F. The fatigue strength of the resulting chromium plated, baked steel article is as high as 90 to 95% of the strength of the original unplated steel. Strengths of at least 70% of the unplated steel are readily obtainable and are satisfactory for many purposes. The chromium plate after baking has a whitish, satiny appearance.

The following examples, Nos. 25 to 36, may further illustrate the invention. Standard steel fatigue test specimens were plated in several of the baths described above under the conditions noted in Table 3 below. All of the baths were 45% neutralized to the dichromate endpoint except those from Examples 6 and 18. The bath from Example 6 was not neutralized while that from Example 18 was 17% neutralized. The specimens were the same, comprising one-half inch round bar stock of SAE 4140 steel. Each specimen was 3 7/16" long and had a central portion that was reduced to a diameter of ¼". The specimens had been heat-treated and had a hardness of Rockwell C43. The fatigue strength of the specimen steel was 109,000 p. s. i. and the tensile strength was 222,500 p. s. i.

TABLE 3

Exam. No.	Deposit No.	Bath from Exam. No.	CrO_3, g./l.	Ratio of CrO_3 to SO_4	Temp., °F.	C. D., a. s. i.	C. E., percent
25	2	1	400	75:1	160	5	19.5
26	7	2	400	150:1	130	3	12.0
27	10	3	500	125:1	130	3	12.1
28	16	4	600	125:1	130	2	8.5
29	17	5	600	125:1	130	3	12.0
30	18	6	600	125:1	130	3	12.0
31	A-11	18	600	125:1	130	3	12.8
32	A-12	24	600	125:1	130	3	12.1
33	29	7	700	100:1	130	3	8.5
34	30	8	700	125:1	130	3	8.0
35	32	9	800	75:1	130	3	6.0
36	34	10	800	125:1	130	3	5.5

Fatigue strength data of a number of the chromium deposits of Table 3 are given in Table 4 along with information on the plate thickness. The fatigue tests were determined with a rotating beam fatigue machine of the R. R. Moore type. For comparison, data are included on a deposit, identified as No. C, produced by a conventional sulfate bath containing 250 g./l. of chromic acid and 2.5 g./l. of sulfate and operated at 130° F. and 2 a. s. i.

TABLE 4

Deposit No.	Plate thickness, mils	Fatigue Strength, p. s. i.			
		Unbaked	After baking for 2 hrs. at—		
			350° F.	550° F.	750° F.
10	11.4		67,500		
	11.6			85,000	
	11.3				95,000
16	10.7	25,000			
	10.7		75,000		
	10.3			95,000	
17	8.4		82,500		
	8.9			92,500	
	8.5				92,500
17	1.2		85,000		
	1.2			95,000	
	1.1				92,500
17	4.7		85,000		
	4.7			97,500	
	4.7				102,500
18	8.6		82,500		
	8.7			87,500	
	8.8				97,500
A-11	6.1			87,500	
A-12	6.3			87,500	
29	10.8		77,500		
	12.0			85,000	
	12.0				87,500
30	8.1		72,500		
	7.6			75,000	
	7.7				87,500
C	10.0	57,400			
	10.0		38,700		
	10.0				53,800

Unless otherwise specified, the reference in the claims to the CrO_3 content of the baths is intended to include the amount of CrO_3 added per se and the amount added in the form of a chromate or dichromate salt.

In the light of the foregoing description, the following is claimed:

1. A method for reducing the loss of fatigue strength following chromium plating of an article of steel having a fatigue strength of 60,000 to 110,000 p. s. i., comprising electrodepositing chromium on the article by passing a current of 1 to 6 a. s. i. to said article as cathode in an aqueous bath having a CrO_3 content of 500 to 700 g./l. and containing dissolved sulfate, $SO_4^=$, as catalyst at a temperature of 120 to 150° F., said bath containing calcium sulfate as the source of said dissolved sulfate, the amount of calcium sulfate being sufficient to saturate the bath and to provide an undissolved excess of calcium sulfate, said bath also containing a soluble calcium compound in an amount sufficient to suppress the concentration of dissolved sulfate from the unsuppressed saturation concentration of the latter to a lower value corresponding to a CrO_3/SO_4 ratio of 75:1 to 150:1, said bath containing, and being partially neutralized by, a quantity of dissolved M, where M is a metal having a basic reaction and is selected from the group consisting of sodium, potassium, ammonium, and calcium, said quantity of dissolved M being sufficient to neutralize about 10 to 75% of said bath, plating chromium on the article to form a coating about 2 to 15 mils thick, heating the plated article to a temperature of 350 to 550° F. for about 2 hours, and thereby producing a chromium plated article of said steel having a fatigue strength of at least 90% of that of the unplated original steel.

2. A method for reducing the loss of fatigue strength following chromium plating of an article of steel having a fatigue strength of 60,000 to 110,000 p. s. i., comprising electrodepositing chromium on the article by passing a current of 1 to 6 a. s. i. to said article as cathode in an aqueous bath having a CrO_3 content of 500 to 700 g./l. and containing dissolved sulfate, $SO_4^=$, as catalyst at a temperature of 120 to 150° F., the ratio of CrO_3 to said dissolved sulfate being 75:1 to150:1, said bath containing, and being partially neutralized by, a quantity of dissolved M, where M is a metal having a basic reaction and is selected from the group consisting of sodium, potassium, ammonium, and calcium, said quantity of dissolved M being sufficient to neutralize about 10 to 75% of said bath, plating chromium on the article to form a coating about 2 to 15 mils thick, heating the plated article to a temperature of 350 to 550° F. for about 2 hours, and thereby producing a chromium plated article of steel having a fatigue strength of at least 90% of that of the unplated original steel.

3. A method for reducing the loss of fatigue strength following chromium plating of an article of steel having a fatigue strength of 60,000 to 110,000 p. s. i., comprising electrodepositing chromium on the article by passing a current of 1 to 6 a. s. i. to said article as cathode in an aqueous bath having a CrO_3 content of 400 to 800 g./l. and containing dissolved sulfate, $SO_4^=$, as catalyst at a temperature of 120 to 150° F., the ratio of CrO_3 to said dissolved sulfate being 75:1 to 150:1, plating chromium on the article to form a coating about 2 to 15 mils thick, heating the plated article to a temperature of 350 to 800° F. for about 1 to 4 hours, and thereby producing a chromium plated article of said steel having a fatigue strength of at least 70% of that of the unplated original steel.

4. A method for reducing the loss of fatigue strength following chromium plating of an article of steel having a fatigue strength of at least 50,000 p. s. i., comprising electrodepositing chromium on the article by passing a current of 1 to 6 a. s. i. to said article as cathode in an aqueous bath having a CrO_3 content of 400 to 800 g./l. and containing dissolved sulfate, $SO_4^=$, as catalyst at a temperature of 120 to 170° F., said bath containing calcium sulfate as the source of said dissolved sulfate, the amount of calcium sulfate being sufficient to saturate the bath and to provide an undissolved excess of calcium sulfate, said bath also containing a soluble calcium compound in an amount sufficient to suppress the concentration of dissolved sulfate from the unsuppressed saturation concentration of the latter to a lower value corresponding to a CrO_3/SO_4 ratio of 75:1 to 150:1, said bath containing, and being partially neutralized by, a quantity of dissolved M, where M is a metal having a basic reaction and is selected from the group consisting of sodium, potassium, ammonium, and calcium, plating chromium on the article to form a coating at least 2 mils thick, heating the plated article to a temperature of 200 to 800° F., for a sufficient duration to produce a chromium plated article of steel having a fatigue strength of at least 70% of that of the unplated original steel.

5. A method for reducing the loss of fatigue strength following chromium plating of an article of steel having a fatigue strength of at least 50,000 p. s. i., comprising electrodepositing chromium on the article by passing a current of 1 to 6 a. s. i. to said article as cathode in an aqueous bath having a CrO_3 content of 400 to 800 g./l. and containing dissolved sulfate, $SO_4^=$, as catalyst at a temperature of 120 to 170° F., the ratio of CrO_3 to said dissolved sulfate being 75:1 to 150:1, said bath containing, and being partially neutralized by, a quantity of dissolved M, where M is a metal having a basic reaction and is selected from the group consisting of sodium, potassium, ammonium, and calcium, plating chromium on the article to form a coating at least 2 mils thick, heating the plated article to a temperature of 200 to 800° F. for a sufficient duration to produce a chromium plated article of steel having a fatigue strength of at least 70% of that of the unplated original steel.

6. Method of claim 5 in which said M is dissolved sodium.

7. Method of claim 5 in which said M is dissolved potassium.

8. Method of claim 5 in which said M is dissolved ammonium.

9. Method of claim 5 in which said M is dissolved calcium.

10. A method for reducing the loss of fatigue strength following chromium plating of an article of hard steel

comprising electrodepositing chromium on the article by passing a current of 1 to 6 a. s. i. to said article as cathode in an aqueous bath having a CrO_3 content of 400 to 800 g./l. and containing dissolved sulfate, $SO_4^=$, as catalyst at a temperature of 120 to 170° F., the ratio of CrO_3 to said dissolved sulfate being 75:1 to 150:1, plating chromium on the article to form a coating at least 2 mils thick, heating the plated article to a temperature of 200 to 800° F. for a sufficient duration to produce a chromium plated article of steel having a fatigue strength of at least 70% of that of the unplated original steel.

11. A method for reducing the loss of fatigue strength following chromium plating of an article of steel having a hardness of at least 20C Rockwell and a fatigue strength of at least 50,000 p. s. i., comprising electrodepositing chromium on the article by passing a current of 1 to 6 a. s. i. to said article as cathode in an aqueous bath having a CrO_3 content of 400 to 800 g./l. and containing dissolved sulfate, $SO_4^=$, as catalyst at a temperature of 120 to 170° F., the ratio of CrO_3 to said dissolved sulfate being 75:1 to 150:1, plating chromium on the article to form a coating of at least 2 mils thick, heating the plated article to a temperature of 200 to 800° F. for 1 to 4 hours, and thereby producing a chromium plated article of steel having a major proportion of the fatigue strength of the unplated original steel.

12. The method of claim 10 wherein the steel of the unplated article has a hardness of at least 33C Rockwell.

13. The method of claim 10 wherein the steel of the unplated article has a hardness of 33C to 47C Rockwell.

14. The method of claim 12 wherein chromium is plated on the article to form a coating at least 5 mils thick.

15. The method of claim 11 wherein the chromium plated article of steel that is produced has a fatigue strength of at least 70% of that of the unplated original steel.

16. The method of claim 15 wherein said sulfate, $SO_4^=$, comprises substantially the entire catalyst in the bath.

17. A method for reducing the loss of fatigue strength following chromium plating of an article of steel having a fatigue strength of at least 50,000 p. s. i., comprising electrodepositing chromium on the article by passing a current of 1 to 6 a. s. i. to said article as cathode in an aqueous bath having a CrO_3 content of 400 to 800 g./l. and containing dissolved sulfate, $SO_4^=$, as catalyst at a temperature of 120 to 170° F., said bath containing calcium sulfate as the source of said dissolved sulfate, the amount of calcium sulfate being sufficient to saturate the bath and to provide an undissolved excess of calcium sulfate, said bath also containing a soluble calcium compound in an amount sufficient to suppress the concentration of dissolved sulfate from the unsuppressed saturation concentration of the latter to a lower value corresponding to a CrO_3/SO_4 ratio of 75:1 to 150:1, plating chromium on the article to form a coating at least 2 mils thick, heating the plated article to a temperature of 200 to 800° F., for a sufficient duration to produce a chromium plated article of steel having a fatigue strength of at least 70% of that of the unplated original steel.

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