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CHROMIUM PLATING

Jesse E. Stareck, Royal Oak, and Edgar J. Seyb, Jr., Oak Park, Mich., assignors, by mesne assignments, to Metal & Thermit Corporation, New York, N. Y., a corporation of New Jersey

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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. This unfavorable effect of conventional chromium plating has naturally limited the usefulness of these plated steels.

A principal object of the invention is to provide a method for chromium plating hard, high strength steel without substantial loss of fatigue strength. The method is particularly directed to the plating of steel articles for use at ordinary temperatures under conditions of repeated stress and strain that approach the fatigue limit of the steel. It has been found that a high fatigue strength may be obtained in the plated article if the chromium deposited on it contains a large number of fine cracks such that it exhibits a low residual stress. The resultant chromium plated 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 involving repeated loading. Thus the field of application of the plated steel is enlarged.

The method, in brief, comprises electrodepositing chromium on the article by passing a current of 1/4 to 6 a. s. i. (amperes per sq. inch) to the article as cathode in an aqueous chromium plating bath at a temperature of 90 to 130° F. The bath comprises essentially 100 to 400 g./l. of CrO₃, 0.5 to 4.0 g./l. of dissolved sulfate, SO₄⁼, and 1.0 to 10.0 g./l. of dissolved silicofluoride, SiF₆⁼. The catalyst radicals are supplied by suitable sulfate-containing and silicofluoride-containing compounds as hereinafter described. The sum of dissolved sulfate and dissolved silicofluoride varies with the CrO₃ concentration as follows: as the CrO₃ increases from a lower limit of 100 g./l. to an upper limit of 400 g./l., the lower limit of said sum increases linearly from 1.5 to 5.0 g./l. while the upper limit of the sum increases linearly from 2.0 to 14.0 g./l. Stated another way, at a concentration of 100 g./l. of CrO₃, the said sum may vary from 1.5 to 2.0 g./l., and at a concentration of 400 g./l. of CrO₃, the sum may vary from 5.0 to 14.0 g./l. Also, as the sum of the catalysts increases within the above ranges, the plating bath temperature should increase within said range. The following table illustrates the relation between CrO₃ and catalyst concentrations.

TABLE 1

CrO ₃	Sum of SO ₄ +SiF ₆
100	1.5 to 2.0
150	2.0 to 4.0
200	2.6 to 6.0
250	3.2 to 8.0
300	3.8 to 10.0
350	4.4 to 12.0
400	5.0 to 14.0

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The preferred concentration of the sum of the catalysts, as the CrO₃ varies from 100 to 400 g./l., is 1.6 to 6.0 g./l. at the lower limit and 2.3 to 10.7 g./l. at the upper limit; these relationships being linear. The preferred CrO₃ concentration is 150 to 250 g./l., for which range the preferred sulfate concentration is 0.8 to 2.5 g./l., the silicofluoride concentration is 1.2 to 5.0 g./l., the sum of the catalysts is 2.3 to 3.8 g./l. at the lower limit and 3.7 to 6.5 g./l. at the upper limit, and the temperature is 130 to 150° F.

The bath solution may be made up in several ways. In one way, which is preferred, the solution is made up from chromic acid, two catalyst-supplying compounds, namely, strontium sulfate and an alkali metal silicofluoride, and two soluble non-catalytic compounds one of which is a strontium compound and the other of which is an alkali metal compound. The alkali metal of the catalytic and non-catalytic compounds is the same and is selected from the class consisting of sodium and potassium. The non-catalytic compounds have the effect of controlling the concentrations of the dissolved sulfate and silicofluoride radicals in the bath by influencing the solubility of the salts used to introduce the radicals into the bath. Specific non-catalytic compounds are strontium carbonate, strontium oxide, strontium chromate, strontium hydroxide, potassium hydroxide, potassium bichromate, potassium carbonate, potassium chromate, sodium bichromate, sodium carbonate, sodium hydroxide, sodium chromate. The amount of the strontium sulfate and of the alkali metal silicofluoride, is, in each case, sufficient to saturate the bath with dissolved sulfate and silicofluoride and to provide an insoluble residue of each salt in the bath. The soluble non-catalytic strontium and alkali metal compounds are each present in an amount sufficient to adjust or suppress the concentrations of the strontium sulfate and alkali metal silicofluoride, respectively, in solution in the bath from the unsuppressed saturation concentrations of the latter two compounds to lower concentrations corresponding to the sums of sulfate and silicofluoride noted in Table 1 above.

An advantage of the foregoing bath solution is that it is self-regulating with respect to the concentrations of dissolved sulfate and dissolved silicofluoride.

Another way for making a suitable bath solution is like that just described except that the non-catalytic strontium compound is omitted. The amount of the strontium sulfate and the alkali metal silicofluoride, is, in each case, sufficient to saturate the bath with dissolved sulfate and silicofluoride and to provide an insoluble residue of each salt in the bath. The soluble non-catalytic alkali metal compound is present in an amount sufficient to adjust or suppress the concentration of the alkali metal silicofluoride in solution in the bath from the unsuppressed saturation concentration of the latter to a lower concentration such that the sum of the dissolved sulfate and silicofluoride corresponds to the ranges set forth in Table 1. The concentration of dissolved sulfate is the unsuppressed saturation concentration and that of dissolved silicofluoride is the suppressed saturation concentration. As may be evident, in this bath the concentrations of dissolved sulfate and dissolved silicofluoride are self regulated, but the sulfate concentration is not controlled by a non-catalytic compound.

A further way for making a suitable bath solution is one in which only the dissolved sulfate concentration is adjusted by means of a non-catalytic compound. Strontium sulfate and an alkali metal silicofluoride are used as catalyst-supplying compounds, each in an amount sufficient to saturate the bath with dissolved sulfate and dissolved silicofluoride and to provide an insoluble residue of each salt in the bath. A soluble non-catalytic stron-

tium compound is added in an amount sufficient to adjust or suppress the concentration of the strontium sulfate in solution in the bath from the unsuppressed saturation concentration of the latter to a lower concentration such that the sum of the dissolved sulfate and dissolved silicofluoride corresponds to the ranges set forth in Table 1. The concentration of dissolved sulfate thus becomes the suppressed saturation concentration and that of dissolved silicofluoride is the unsuppressed saturation concentration. As before, in this bath the concentrations of dissolved sulfate and dissolved silicofluoride are self regulated, but only the sulfate concentration is controlled by a non-catalytic compound.

It is apparent from the two types of bath solution just described that either the sulfate or the silicofluoride concentration may be regulated by means of a suitable non-catalytic compound of the kind above set forth.

Still another way for making a suitable bath solution is one like the next preceding one but in which no suppressor or non-catalytic compounds are used. Besides chromic acid, the solution comprises two soluble catalyst-supplying compounds, namely, a sulfate radical bearing compound and a silicofluoride radical bearing compound. Compounds of varying solubility may be used, including those readily soluble in the bath solution, those sparingly soluble therein, and those of intermediate solubility, all of which compounds are intended herein as being soluble compounds. Specific sulfate-supplying compounds include readily soluble compounds like sulfuric acid, sodium sulfate, potassium sulfate, chromium sulfate; sparingly soluble compounds like strontium sulfate; and compounds of intermediate solubility such as calcium sulfate. Specific silicofluoride-supplying compounds include readily soluble compounds like hydrofluosilicic acid and magnesium silicofluoride; sparingly soluble compounds like potassium silicofluoride; and compounds of intermediate solubility like sodium silicofluoride. After the bath solution has been initially made up to the required concentrations, as indicated in Table 1, the catalyst content is maintained by dissolving catalyst-supplying compounds in the bath as required, that is, in amounts equivalent to the amounts of catalyst radicals to be replaced. Compounds that are readily soluble may require more frequent addition than those sparingly soluble since the latter may sometimes be added in excess so as to saturate the bath and to provide an undissolved residue. The bath analysis should be available when required in order to determine when additions are necessary. When solutions of readily soluble catalyst-supplying compounds, such as sulfuric acid and hydrofluosilicic acid, are used to replenish the bath, they should, of course, be of known strength. So long as the concentration requirements of Table 1 are satisfied, sparingly soluble compounds may be employed alone or in conjunction with one or more other more soluble compounds, it being evident that the former will not always be used in saturation amounts; readily soluble compounds are useful either alone, as in the case of sulfuric and hydrofluosilicic acids, or in combination with one or more other readily or less soluble compounds; and compounds of intermediate solubility may also be used alone or in combination with other compounds. In making up or replenishing a non-suppressor type bath, the use of a catalyst-supplying compound which would act as a suppressor in regard to another catalyst-supplying compound is omitted; for example, if potassium silicofluoride is present in the bath or is used to supply silicofluoride, then potassium sulfate is not used as the source of supply of sulfate, a salt like sodium sulfate being used instead.

The steels to which the invention is applicable are those having a fatigue strength of at least 50,000 p. s. i. (pounds per square inch). The upper limit of fatigue strength may be as desired, although particularly good results are obtainable with steels having a fatigue strength of 60,000 or 70,000 to 110,000 p. s. i. Steels of this

kind are quite susceptible to fatigue strength reduction on chromium plating, the reduction increasing as the strength of the unplated steel increases.

The unplated steel may have a hardness of at least 20C Rockwell, the upper limit being as desired, say 54C. Good results may be secured if the hardness is 28C or 33C to 47C Rockwell. Alloy or high quality steels are suitable for plating by the present method, but the invention is not limited to them. Substantial thicknesses of chromium are deposited on the steel, ranging from 1 to 30 or more mils, and preferably from 5 to 15 mils. Plating times may vary widely, for example from 1 to 24 or more hours.

Chromium electrodeposits exhibit the characteristic of stress, a property which changes with the thickness of the deposit and which, by means of a spiral contractometer, can be measured throughout the course of a plating operation. With this instrument the stress in a long continuous section of chromium plate is transferred to the underlying base metal comprising a long, helically wound strip of thin metal having one end free to rotate. The stress in the plate can be calculated from the amount of rotation. It has been found that initially, the stress in a deposit increases very rapidly during the first few moments of plating until it exceeds the tensile strength of the deposit, at which point crack-lines form in the chromium to relieve the high tensile stress. As the thickness of the plate increases, the stress gradually decreases, approaching zero stress, and the number of the crack-lines increases. The number of crack-lines may readily be determined by counting them as described below in Examples 1-14. The crack-lines become finer as their number increases. It has been further found in some cases that as the plate thickness increases, the stress decreases so that it becomes negative in value as distinguished from the positive values previously obtained. This behavior is illustrated in Table 2 below which sets forth stress data, as obtained by the spiral contractometer, at various plate thicknesses for three baths identified as noted. The composition of these baths, their operating temperature, and current density are given in Examples 1, 2, and 3 of Table 4. In each run in Table 2 the stress was already dropping by the time the first readings on the contractometer were taken.

TABLE 2

Chromium thickness, mils	Stress, 1,000 p. s. i.		
	Run 17-1 using bath of Ex. 2	Run 19-3 using bath of Ex. 3	Run 24-2 using bath of Ex. 1
0.02		210	
0.04	120		
0.05			200
0.06	84	150	
0.07			99
0.10	53	114	
0.14	36		38
0.20	31	71	17
0.30	23	45	6
0.40			0
0.50	17	26	
0.70	13	13	
0.75			-0
1.0	10	6	-12
1.4	8		
1.5		-0.5	-16
2.0	7	-3	-17
2.4	6		
2.5		-5	-17
3.0	5	-5	-17
3.4	5		
3.5		-6	-16
4.0	5	-6	

A correlation exists between the stress and the number of crack-lines. As an illustration, three deposits were plated on steel specimens (described below in Examples 1-14) and exhibited the properties listed in Table 3. Each deposit was 2 mils thick, a representative value since the stress tends to level off at such thickness, as indicated

in Table 2. The first two deposits (3500 and 1300 crack-lines per inch, respectively) were produced from baths described in Examples 1 and 7 of Table 4, while the third deposit (22 crack-lines per inch) was obtained from a bath having 315 g./l. CrO_3 , 1.2 g./l. sulfate, 3.0 g./l. silicofluoride, and operated at 140° F. and 3 a. s. i.

TABLE 3

Crack-lines per inch	Stress, 1,000 p. s. i.
3,500	-17
1,300	-3
22	60

The more numerous the crack-lines, the lower is the measured stress, and conversely, the fewer the crack-lines, the higher the stress. The correlation applies over a wide stress range, varying from a positive tensile stress of about +80,000 p. s. i. to a negative compressive stress of -15,000 or -20,000 p. s. i. Between about -15,000 and -20,000 p. s. i. the stress tends to level off such that further increases in the number of crack-lines is not accompanied by more negative stress values. The correlation holds for thicker deposits, say those of at least 1 mil thickness. By counting the number of crack-lines in a deposit it is possible to obtain an indirect semi-quantitative measure of the stress in the deposit and to compare one deposit with another.

The number of crack-lines in chromium plate deposited on hardened high strength steel is also correlated with the fatigue strength of the plated steel, as shown in Table 4. In this case the more numerous the crack-lines, the higher is the fatigue strength of the plated steel. It follows that deposits exhibiting high tensile stress result in a severe lowering of the fatigue strength of the steel, whereas deposits of low stress give much less lowering of the fatigue strength. It is desirable to deposit on the steel a plate having 1000, preferably 1200, to 10,000 crack-lines per inch. In terms of stress, the plate should range from +5000 p. s. i. tensile stress, preferably 0 p. s. i., to -20,000 p. s. i. compressive stress. Steel plated with deposits of this character will exhibit at least 70%, preferably at least 85%, of the fatigue strength of the unplated steel. Strengths of at least 70% of the unplated steel are satisfactory for many purposes.

The crack pattern of a deposit is determined early in the plating operation, say after about 0.5 mil of chromium is deposited. A consequence of this fact is that an article may be plated to a point where a desirable crack pattern, i. e., numerous crack-lines, has been established and then transferred to another bath of the same type but operated at a higher speed, so that a desirable plate of required thickness may be obtained in a shorter time. Another characteristic of the method is that the crack pattern of a deposit may be changed during plating as by periodically reversing the current. By comparing Examples 3 and 7, it will be seen that periodic current reversal can lead to a plate having more numerous crack-lines.

An incident of the chromium plating of steel in chromic acid plating baths is the embrittlement of the steel by hydrogen released during the plating operation. This is illustrated in Examples 15 and 16. Where embrittlement of the chromium plated steel is a factor to be considered in connection with the end use of the steel, it can be prevented or substantially minimized by applying a barrier metal such as a copper strike between the steel and the chromium. Copper strike films may be applied by

plating the steel in a suitable copper plating bath for a short time to deposit about 0.01 to 0.1 or 0.2 mil of copper. The fatigue strength of the resulting copper plated, chromium plated steel, by comparison with a like steel similarly chromium plated but not copper plated, is not affected by the presence of the copper barrier. Suitable copper plating baths include conventional cyanide copper baths and copper sulfate-sulfuric acid baths, as described in "Principles of Electroplating and Electroforming," Blum and Hogaboom, revised 3rd edition, 1949, pages 295 and 290, respectively; and conventional pyrophosphate copper baths, as described in U. S. Patents 2,250,556, 2,437,865, and 2,493,092.

The invention may be illustrated by the following examples, the purpose of which may be noted briefly. Examples 1 to 14 show various mixed catalyst, self-regulating plating baths, some within and some outside of the invention and including a standard or conventional sulfate bath, their operation under varying conditions, crack properties of the plate produced by the baths, and fatigue strengths of the plated steel specimens. Examples 15 and 16 illustrate the effect of hydrogen embrittlement and a means of avoiding or minimizing it.

Examples 1 to 14

A number of plating baths were made up, the CrO_3 and catalyst content of which are set forth below in Table 4. The baths of Examples 1-8 and 10-14 are mixed catalyst baths, while that of Example 9 is a standard or conventional sulfate bath included for comparison. For the baths of Examples 1-3, 5, 7, 8, and 12-14 there was dissolved in water a dry mixture comprising chromic acid, potassium bichromate, strontium chromate, potassium silicofluoride, and strontium sulfate, so that the resulting solution had the composition set forth in Table 4. For Examples 4 and 11 a similar dry mixture was used, but sodium salts rather than potassium salts were employed. The standard sulfate bath of Example 9 was prepared by dissolving chromic and sulfuric acids in water, and the bath of Example 6 was made by dissolving chromic, sulfuric, and silicofluoric acids in water. Example 10 was prepared from a dry mixture containing chromic acid, strontium sulfate and potassium silicofluoride. Due to the presence of the salts, the baths of Examples 1-5, 7, 8 and 11-14 were partially neutralized, that of Example 4, for example, being about 40% neutralized. Steel test specimens were plated in the various baths under the conditions noted. These fatigue test specimens were the same, prepared from one-half inch round bar stock of SAE 4140 steel. Each specimen was $3\frac{7}{16}$ " long and had a central portion that was reduced to a diameter of $\frac{1}{4}$ ". The specimens had been heat-treated, had a hardness of Rockwell C43, and a fatigue strength of 109,000 p. s. i. Fatigue strength, stress, and crack data on the chromium plated specimens appear in the table. The fatigue tests were performed with a rotating beam fatigue machine of the R. R. Moore type. Stress in the chromium deposits was measured by means of the spiral contractometer noted above, an instrument manufactured by Champion Manufacturing, Co., New York, N. Y. Crack-lines were determined by microscopically examining the surface of a specimen at 600 X: an arbitrary straight line one inch long was selected in the microscopic field and the average number of crack-lines, including filled-in lines, which crossed such arbitrary line was counted.

TABLE 4

Example No.	Deposit No.	CrO ₃ , g./l.	SO ₄ , g./l.	SiF ₆ , g./l.	SO ₄ +SiF ₆ , g./l.	Temp., °F.	C. D., a. s. i.	Thick-ness, mils	No. of Crack-lines per in.	Fat. Str., 1,000 p. s. i.
1	R-89	180	1.0	2.0	3.0	110	1	10	3,500	97.5
2	6	225	1.5	4.2	5.7	150	2	10	2,900	90.5
3	2a	225	1.3	2.9	4.2	130	2	10	2,000	83.5
4	4	225	1.3	2.9	4.2	130	2	10	2,000	78.4
5	5	175	1.2	2.7	3.9	120	2	10	1,700	76.0
6	6c	225	1.5	4.2	5.7	150	2	10	1,700	73.5
7	2	225	1.3	2.9	4.2	130	2	10	1,300	72.5
8	6b	225	1.5	4.2	5.7	150	6	10	1,000	57.4
9	1	250	2.5	0	2.5	130	2	10	400	16.7
10	9	300	1.7	4.0	5.7	85	3	10	44	13.4
11	10	320	0.9	2.0	2.9	140	3	10	17	87.5
12	16	225	1.5	4.2	5.7	150	2	1	-----	77.5
13	17	225	1.5	4.2	5.7	150	2	2	-----	82.5
14	18	225	1.5	4.2	5.7	150	2	5	-----	-----

The deposit of Example 2 was tested for adherence by striking the specimen near its edge with a hammer; excellent adherence was indicated by the absence of chipping. In Example 3 the current was reversed for 10 seconds during each 10 minutes of plating time; as this example is otherwise the same as Example 7, it is apparent that the current reversal produced more numerous crack-lines and improved the fatigue strength of the specimen. In Example 6 the current was reversed for 20 seconds per each minute of plating time. Example 4 demonstrates that good results are obtainable with a bath neutralized to a substantial extent. In Examples 12, 13, and 14 are illustrated lower thicknesses of plate. The bath, operation, and plated product of Examples 9, 10, and 11 are not within the invention, being included for illustrative purposes, that is, to show that baths not within the invention do not give satisfactory results; thus, Example 9 serves to show that the results obtainable by the baths and operating conditions of the invention are not obtainable by the standard sulfate bath; in Example 10 the results were affected by the fact that the plating temperature was too low for the level of catalyst concentration; and too low a catalyst concentration was responsible for the poor results of Example 11. Bright plate was deposited in Examples 1-9 and 12-14; in Example 10 it was gray matte; and in Example 11 it was satiny matte.

Example 15

A strip of SAE 4130 steel, measuring 1" x 0.032" x 5" and having a hardness of Rockwell 45C, was given a 2-minute copper strike in a cyanide copper plating bath at 3.5 volts and then placed with an identical control strip (having no copper strike) in a chromium plating bath identical to that of Example 7. The bath was operated under the conditions described in Example 7 to plate on each strip a chromium deposit of 1 mil thickness. Both strips were then tested in an Amsler multiple bend tester under comparable conditions to determine the number of bends required for fracture. The copper strike, chromium plated strip fractured after 22 bends, whereas the control strip fractured after 14 bends.

Example 16

In another series of tests, seven steel bar specimens, Nos. 1 to 7, identical to those used in Examples 1-14, were taken. Nos. 1 and 2, unplated, were used as controls. Nos. 3 and 4 were given a copper strike as described in Example 15. Nos. 3 and 4, along with Nos. 5 and 6, were then plated with a 10-mil deposit of chromium in a bath identical to, and under the same conditions as Example 7. Specimen No. 7 was given a copper strike separately and chromium plated separately in the same way as described for Nos. 3 and 4. Specimen Nos. 1 to 6 were then tested for embrittlement by a reduction in area method wherein the lower the percent reduction in area, the greater is the embrittlement. The results are as follows:

TABLE 5

Specimen No.	Treatment	Reduction of Area, Percent
1	Control, unplated	47.0
2	do.	43.0
3	Copper strike, chromium plated	30.0
4	do.	32.0
5	Chromium plated	4.8
6	do.	4.7

The reduction in area values are based on the unplated diameter. As is evident, the use of a copper strike substantially helps to prevent embrittlement. Specimen No. 7 was subjected to a fatigue test, as described in Examples 1-14, and found to have a fatigue strength of 78,800 p. s. i., which is of the same order as that for deposit 2 of Example 7.

Unless otherwise specified, the reference in the claims to the CrO₃ content of the baths is intended to include the amount of CrO₃ 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 hardness of 33C to 47C Rockwell and a fatigue strength of 70,000 to 110,000 p. s. i., comprising electrodepositing chromium on the article by passing a current of 1/4 to 6 a. s. i. to said article as cathode in an aqueous chromium plating bath at a temperature of 130 to 150° F., said bath comprising essentially 150 to 250 g./l. of CrO₃, a sulfate-containing compound and a silicofluoride-containing compound each in an amount to provide, as catalysts, 0.8 to 2.5 g./l. of dissolved sulfate, SO₄=, and 1.2 to 5.0 g./l. of dissolved silicofluoride, SiF₆=, respectively, the sum of dissolved sulfate and dissolved silicofluoride varying with the CrO₃ concentration as follows: as the CrO₃ increases from 150 to 250 g./l., the lower limit of said sum increases linearly from 2.3 to 3.8 g./l. while the upper limit of said sum increases linearly from 3.7 to 6.5 g./l., said plating temperature increasing within said range as said sum of dissolved catalysts increases, plating chromium on the article to form a deposit about 5 to 15 mils thick, said deposit being characterized by having 1200 to 10,000 crack-lines per inch and a compressive stress of 0 to -20,000 p. s. i., and thereby producing a chromium plated article of hard steel having a fatigue strength of at least 85% of that of the original unplated steel.

2. The method of claim 1 wherein, prior to chromium plating, a copper strike is deposited on said steel article to minimize any embrittlement of the steel article in said chromium plating bath.

3. 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 $\frac{1}{4}$ to 6 a. s. i. to said article as cathode in an aqueous chromium plating bath at a temperature of 90 to 180° F., said bath comprising essentially 100 to 400 g./l. of CrO_3 , a sulfate-containing compound and a silicofluoride-containing compound each in an amount to provide, as catalysts, 0.5 to 4.0 g./l. of dissolved sulfate, $\text{SO}_4^{=}$, and 1.0 to 10.0 g./l. of dissolved silicofluoride, $\text{SiF}_6^{=}$, respectively, the sum of dissolved sulfate and dissolved silicofluoride varying with the CrO_3 concentration as follows: as the CrO_3 increases from 100 to 400 g./l., the lower limit of said sum increases linearly from 1.5 to 5.0 g./l. while the upper limit of said sum increases linearly from 2.0 to 14.0 g./l., said plating temperature increasing within said range as said sum of dissolved catalysts increases, plating chromium on the article to form a deposit about 1 to 30 mils thick, said deposit being characterized by having 1000 to 10,000 crack-lines per inch and a stress of +5000 to -20,000 p. s. i., and thereby producing a chromium plated article of hard steel having a fatigue strength of at least 70% of that of the original unplated steel.

4. The method of claim 3 wherein, prior to chromium plating, a copper strike is deposited on said steel article to minimize any embrittlement of the steel article in said chromium plating bath.

5. 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 $\frac{1}{4}$ to 6 a. s. i. to said article as cathode in an aqueous chromium plating bath at a temperature in the range of 90 to 180° F., said bath comprising essentially 100 to 400 g./l. of CrO_3 , a sulfate-containing compound and a silicofluoride-containing compound each in an amount to provide, as catalysts, 0.5 to 4.0 g./l. of dissolved sulfate, $\text{SO}_4^{=}$, and 1.0 to 10.0 g./l. of dissolved silicofluoride, $\text{SiF}_6^{=}$, respectively, the sum of dissolved sulfate and dissolved silicofluoride varying with the CrO_3 concentration as follows: as the CrO_3 increases from a lower limit of 100 g./l. to an upper limit of 400 g./l. the lower limit of said sum increases linearly from 1.5 to 5.0 g./l. while the upper limit of said sum increases linearly from 2.0 to 14.0 g./l., said plating temperature increasing within said range as said sum of dissolved catalysts increases, plating chromium on the article to form a deposit at least 1 mil thick, said deposit being characterized by having at least 1000 crack-lines per inch and a stress below +5000 p. s. i., and thereby producing a chromium plated article of hard steel having a fatigue strength of at least 70% of that of the original unplated steel.

6. A method according to claim 5 in which said bath is free of compounds acting to suppress the concentrations of dissolved sulfate and dissolved silicofluoride.

7. A method according to claim 5 in which said sulfate- and silicofluoride-containing compounds are strontium sulfate and an alkali metal silicofluoride, respectively, each present in an amount sufficient to provide an undissolved excess thereof in said bath, and in which said bath contains a soluble non-catalytic strontium compound and a soluble non-catalytic alkali metal compound acting to suppress the concentrations of dissolved sulfate and dissolved silicofluoride so that the sum of dissolved sulfate and dissolved silicofluoride is within said upper and lower limits recited in claim 5, and the alkali metal of said

alkali metal compound being the same as that of said alkali metal silicofluoride.

8. A method according to claim 5 in which said sulfate- and silicofluoride-containing compounds are strontium sulfate and an alkali metal silicofluoride, respectively, each present in an amount sufficient to provide an undissolved excess thereof in said bath, and in which said bath contains a soluble non-catalytic alkali metal compound acting to suppress the concentration of dissolved silicofluoride so that the sum of dissolved sulfate and dissolved silicofluoride is within said upper and lower limits recited in claim 5, and the alkali metal of said alkali metal compound being the same as that of said alkali metal silicofluoride.

9. A method according to claim 5 in which said sulfate- and silicofluoride-containing compounds are strontium sulfate and an alkali metal silicofluoride, respectively, each present in an amount sufficient to provide an undissolved excess thereof in said bath, and in which said bath contains a soluble non-catalytic strontium compound acting to suppress the concentration of dissolved sulfate so that the sum of dissolved sulfate and dissolved silicofluoride is within said upper and lower limits recited in claim 5.

10. A method according to claim 5 in which said sulfate- and silicofluoride-containing compounds are strontium sulfate and an alkali metal silicofluoride, respectively, each present in an amount sufficient to provide an undissolved excess thereof in said bath, and in which said bath contains a soluble non-catalytic compound acting to suppress the concentration of one of said dissolved catalyst-providing compounds so that the sum of dissolved sulfate and dissolved silicofluoride is within said upper and lower limits recited in claim 5, said non-catalytic compound being selected from the class consisting of a strontium compound and an alkali metal compound, and the alkali metal of said alkali metal compound being the same as that of said alkali metal silicofluoride.

11. The method of claim 5 wherein the steel of the unplated article has a hardness of at least 28C Rockwell.

12. The method of claim 5 wherein the steel of the unplated article has a fatigue strength of at least 60,000 p. s. i.

13. The method of claim 5 wherein as the CrO_3 increases from 100 to 400 g./l., the lower limit of said sum of catalysts increases linearly from 1.6 to 6.0 g./l. while the upper limit of said sum increases linearly from 2.3 to 10.7 g./l.

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

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