United States Patent Office

2,800,437

Patented July 23, 1957

2,800,437

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

No Drawing. Application July 26, 1955, Serial No. 524,579

14 Claims. (Cl. 204—37)

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 mixed catalyst plating bath of the kind, and under the conditions, described hereinafter and then baking the plated steel at 200 to 800° F. 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 method, in brief, 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 also be plated. A current of 1 to 6 a. s. i. (amperes per sq. inch) is passed to the article as cathode in an aqueous chromium plating bath at a temperature of 120 to 170° F. The bath comprises essentially 400 to 800 g./l. of CrO_3, 0.5 to 6.0 g./l. of dissolved sulfate, $SO_4^=$, and from a tenth or more, say 0.1 to 0.5, up to 16.0 g./l. of dissolved silicofluoride, $SiF_6^=$. 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 CrO_3 concentration as follows: as the CrO_3 increases from a lower limit of 400 g./l. to an upper limit of 800 g./l., the lower limit of said sum increases linearly from 2.7 to 4.4 g./l. while the upper limit of the sum increases linearly from 9.0 to 17.0 g./l. Stated another way, at a concentration of 400 g./l. of CrO_3, the said sum may vary from 2.7 to 9.0 g./l., and at a concentration of 800 g./l. of CrO_3, the sum may vary from 4.4 to 17.0 g./l. The following table illustrates the relation between CrO_3 and catalyst concentrations.

TABLE 1

CrO_3	Sum of SO_4+SiF_6
400	2.7 to 9.0
450	2.9 to 10.0
500	3.1 to 11.0
550	3.3 to 12.0
600	3.6 to 13.0
650	3.8 to 14.0
700	4.0 to 15.0
750	4.2 to 16.0
800	4.4 to 17.0

The preferred CrO_3 concentration is 500 to 700 g./l., for which range the preferred sulfate concentration varies from 0.6 to 5.3 g./l., the silicofluoride concentration varies from 1.0 or 1.5 to 12.0 g./l., the sum of the catalysts is 3.1 to 4.0 g./l. at the lower limit and 9.0 to 12.5 g./l. at the upper limit, and the temperature is 120 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 the 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 strontium 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 preceding types of bath solution 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 either of the two just described 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 know 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 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 in the range of 28C to 47C, particularly 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 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 may be at least 85% of the strength of the original unplated steel. Strengths of at least 70% of the unplated steel are readily obtainable, while strengths of at least 60% are satisfactory for many purposes. The chromium plate after baking has a whitish, satiny appearance.

Several illustrative baths are described in the following examples, including plating conditions.

Examples 1 to 8

A number of plating baths were made up, the CrO_3 and catalyst content of which are set forth below in Table 2. The baths of Examples 1–7 are mixed catalyst baths, while that of Example 8 is a standard or conventional sulfate bath included for comparison. For the bath of Example 2 there was dissolved in water a dry mixture comprising chromic acid, sodium bichromate, sodium silicofluoride, and strontium sulfate, so that the resulting solution had the composition set forth in Table 2. The standard sulfate bath of Example 8 was prepared by dissolving chromic and sulfuric acids in water. The baths of the other examples were prepared by dissolving in water a mixture comprising chromic acid, sodium silicofluoride or magnesium silicofluoride hexahydrate, and sodium sulfate; in some instances hydrofluosilicic acid was used in place of magnesium silicofluoride hexahydrate and sulfuric acid in place of sodium sulfate. Steel test specimens were plated in the various baths under the conditions noted in the table. These fatigue test specimens were the same, prepared from 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, had a hardness of Rockwell C43, a fatigue strength of 109,000 p. s. i., and a tensile strength of 222,500 p. s. i.

TABLE 2

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.	C. E., percent
1	41	400	1.8	2.7	4.5	150	3	12.6
2	35	600	2.2	1.6	3.8	150	3	10
3	50	600	4.3	2.6	6.9	130	3	17.5
4	65	600	3.3	9.0	12.3	130	3	11
5	71	600	5.3	3.5	8.8	150	3	13
6	78	700	4.7	7.0	11.7	130	3	11
7	80	700	3.2	4.7	7.9	150	3	9
8	C	250	2.5	0	2.5	130	2	------

Fatigue strength data of several of the chromium plated specimens are given in Table 3 together with the plate thickness. The fatigue tests were performed with a rotating beam fatigue machine of the R. R. Moore type.

TABLE 3

Deposit No.	Plate thickness, mils	Fatigue Strength, p. s. i.			
		Unbaked	After baking for 2 hrs. at—		
			350° F.	550° F.	750° F.
35	11.9	22,500			
	11.8		67,500		
	11.7			75,000	
50	8.6			67,500	
	8.7				82,500
80	4.5			67,500	
	4.7				77,500
C	10	57,400			
	10		38,700		
	10				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 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 chromium plating bath at a temperature of 120 to 170° F., said bath comprising essentially 400 to 800 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 6.0 g./l. of dissolved sulfate, $SO_4^=$, and 0.1 to 16.0 g./l. of dissolved silicofluoride, $SiF_6^=$, respectively, the sum of dissolved sulfate and dissolved silicofluoride varying with the CrO_3 concentration as follows: as the CrO_3 increases from 400 to 800 g./l., the lower limit of said sum increases linearly from 2.7 to 4.4 g./l. and the upper limit of said sum increases linearly from 9.0 to 17.0 g/l., 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 said hard steel having a fatigue strength of at least 60% of that of the original unplated steel.

2. 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 chromium plating bath at a temperature of 120 to 170° F., said bath comprising essentially 400 to 800 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 6.0 g./l. of dissolved sulfate, $SO_4^=$, and 0.1 to 16.0 g./l. of dissolved silicofluoride, $SiF_6^=$, respectively, the sum of dissolved sulfate and dissolved silicofluoride varying with the CrO_3 concentration as follows: as the CrO_3 increases from 400 to 800 g./l., the lower limit of said sum increases linearly from 2.7 to 4.4 g./l. and the upper limit of said sum increases linearly from 9.0 to 17.0 g./l., 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 about 1 to 4 hours, and thereby producing a chromium plated article of said hard steel having a fatigue strength of at least 60% of that of the original unplated steel.

3. 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 to 6 a. s. i. to said article as cathode in an aqueous chromium plating bath at a temperature of 120 to 150° F., said bath comprising essentially 500 to 700 g./l. of CrO_3, a sulfate containing compound and a silicofluoride-containing compound each in an amount to provide, as catalysts, 0.6 to 5.3 g./l. of dissolved sulfate, $SO_4^=$, and 1.0 to 12.0 g./l. of dissolved silicofluoride, $SiF_6^=$, respectively, the sum of dissolved sulfate and dissolved silicofluoride varying with the CrO_3 concentration as follows: as the CrO_3 increases from 500 to 700 g./l., the lower limit of said sum increases linearly from 3.1 to 4.0 g./l. and the upper limit of said sum increases linearly from 9.0 to 12.5 g./l., 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 750° F. for about 2 hours, and thereby producing a chromium plated article of said hard steel having a fatigue strength of at least 85% of that of the original unplated steel.

4. A method according to claim 1 in which said bath is free of compounds acting to suppress the concentrations of dissolved sulfate and dissolved silicofluoride.

5. A method according to claim 1 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 1, and the alkali metal of said alkali metal compound being the same as that of said alkali metal silicofluoride.

6. A method according to claim 1 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 1, and the alkali metal of said alkali metal compound being the same as that of said alakil metal silicofluoride.

7. A method according to claim 1 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 1.

8. A method according to claim 1 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 1, 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.

9. The method of claim 1 wherein the steel of the unplated article has a hardness of at least 28C Rockwell.

10. The method of claim 1 wherein the steel of the unplated article has a hardness of 33C to 47C Rockwell,

11. The method of claim 1 wherein the fatigue strength of the steel of said unplated article is at least 60,000 p. s. i.

12. The method of claim 1 wherein chromium is plated on the article to form a coating 5 to 15 mils thick.

13. The method of claim 1 wherein said plated article is heated at a temperature of 350 to 800° F. for about 2 hours.

14. The method of claim 1 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.

References Cited in the file of this patent

UNITED STATES PATENTS

2,450,296	Passalacqua	Sept. 28, 1948
2,640,021	Passal	May 26, 1953
2,640,022	Stareck	May 26, 1953
2,686,756	Stareck et al.	Aug. 17, 1954