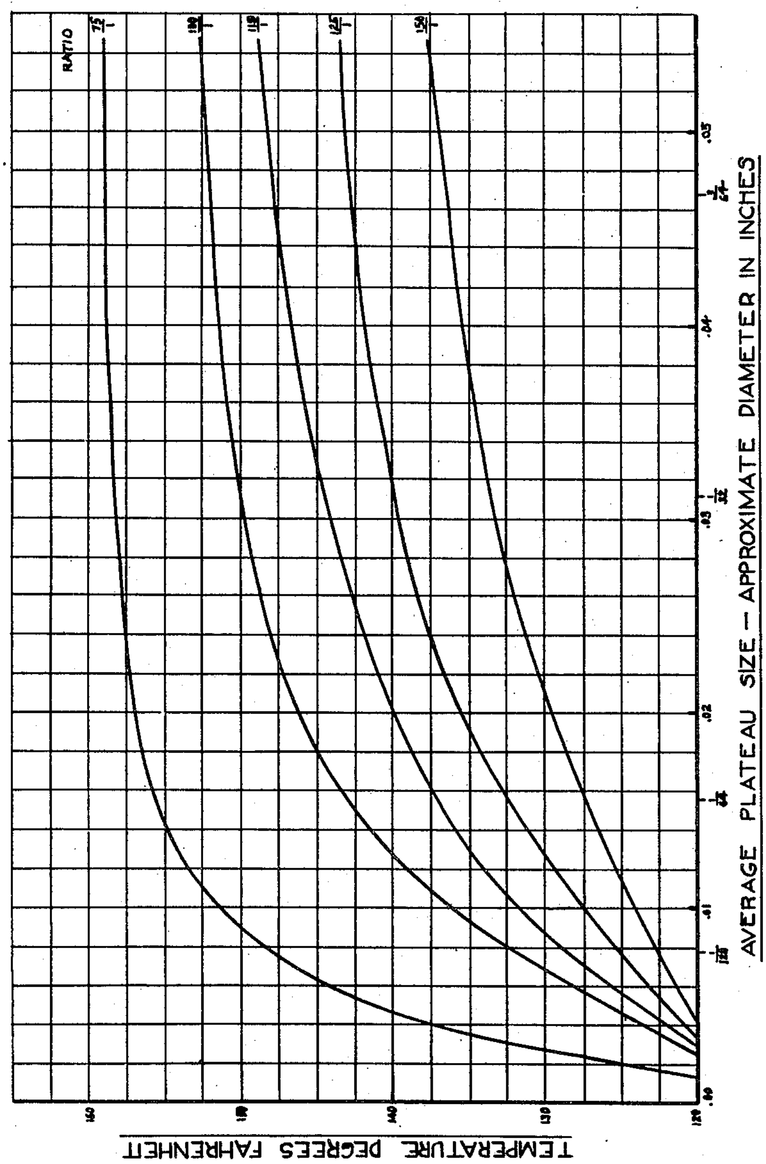
Nov. 11, 1947. T. H. WEBERSINN ET AL 2,430,750

METHOD OF ELECTROPLATING TO PRODUCE FISSURE NET-WORK CHROMIUM PLATING

Filed July 18, 1944



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Patented Nov. 11, 1947

2,430,750

UNITED STATES PATENT OFFICE

2,430,750

METHOD OF ELECTROPLATING TO PRODUCE FISSURE NETWORK CHROMIUM PLATING

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Application July 18, 1944, Serial No. 545,506

4 Claims. (Cl. 204—35)

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This invention relates to methods of electrodepositing chromium in which the conditions of deposition are so correlated and controlled as to give a chromium plate which is predisposed to the formation of fissure net-works and which upon etching give mud-crack type surfaces having plateau areas which do not exceed a desired size; said surfaces being particularly suited after mechanical finishing to frictional contact with other surfaces.

It is desirable in some applications of chromium to parts subject to frictional wearing-effects to avoid any tendency of the contacting parts to seize, scuff, or score, especially in apparatus working under heavy loads at high speeds, such as rotary seals, compressors, internal combustion engines, etc. It has heretofore been proposed to pit or indent the surface of chromium electrodeposits to avoid such tendency to seize, scuff or score.

We have discovered that by using the usual commercial current densities and any suitable chemical or electrochemical method of etching, mud-crack producing types of chromium plate are obtained by correlating composition of the chromium plating bath with temperature of the bath and maintaining these correlated conditions during the plating operations.

The accompanying drawing is a graph showing the correlations of bath composition ratios, temperatures, and average sizes of fissure network after etching under conditions hereinafter specified.

The compositions of our chromium plating baths should be maintained so that the ratios of grams per liter of chromic acid (CrO_3) to grams per liter of total catalyst acid radicals expressed as sulphate (SO_4) are from 50 over 1 to 150 over 1. Thick electrodeposits of chromium on the order of three to fifteen thousandths of an inch are ordinarily used. To produce chromium electrodeposits predisposed to the formation of fissure net-works and which upon etching give mud-crack type chromium surfaces, bath temperatures from about 120° F. (49° C.) to 160° F. (71° C.) with baths having the aforementioned ratios have been used. In practice, a bath temperature within said limits is selected and maintained.

Suitable cathode current densities for bath temperatures from 120° F. to 160° F. are in the range 1 to 12 amperes per square inch, the higher current densities being used at the higher temperatures. Lower and higher current densities may be used, but with lower current densities the current efficiences and rate of plating are

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lower, and with higher current densities there is the likelihood of treeing.

Compared with a bath maintained at a chromic acid-catalyst acid radical ratio of 100 over 1, temperature and current density being the same, a bath maintained at a higher ratio, 125 over 1 for example, will produce a chromium electrodeposit predisposed to the production, upon etching under the same conditions within limits hereinafter set forth, of mud-crack type chromium surfaces of larger plateau size than the first. Conversely baths maintained at a ratio less than 100 over 1, all other conditions remaining the same, will result in smaller plateau sizes.

For baths having low ratios, there is a minimum temperature within the range 120° F. to 160° F. below which mud-crack type chromium surfaces capable of being mechanically finished to produce average plateau sizes of the order of $^1/_{64}''$ diameter cannot be practically obtained. Thus, for a bath having a ratio of 100 over 1, for example, operated at temperatures substantially below 130° F., mud-crack type chromium surfaces capable of being mechanically finished to produce average plateau sizes of the order of $^1/_{64}''$ diameter will not be produced. Moreover, when such a bath is operated at temperatures higher than 130° F., but below 160° F., mud-crack type chromium deposits will be produced having plateau areas which increase in size as the temperature increases. For baths having ratios higher than 100 over 1 but less than 150 over 1 temperatures lower than 130° F. can be used to obtain satisfactory mud-crack type chromium surfaces. With the lower ratios, the higher temperatures are preferred, and for the lower temperatures the higher ratios are preferred; with the higher ratios, both the lower and higher temperatures may be used, but for a particular size of plateau, they must be correlated keeping all other conditions constant. For a given temperature, the plateau size increases with the increase in ratio, and for a given ratio, the plateau size increases with increase in temperature. Change in temperature has a greater relative effect on change in size of plateau than change in ratio.

The etching to develop the net-works of fissures in the predisposed chromium electrodeposit may be done in any suitable manner. It may be done electrochemically, with the article connected as the cathode, or chemically and electrochemically combined, or chemically, as discovered by Webersinn (set forth in application Sr. No. 510,210); or anodically, or otherwise.

The formation of the net-works of fissures may be carried out electrolytically by immersing the chromium deposit as a cathode in a suitable solution. Solutions of oxalic acid, sulphuric and chromic acids, sulphuric acid, phosphoric acid, hydrochloric acid, citric acid, ferric sulphate, are examples of those which have been used. Many other electrolytic solutions of acids and salts which have a low pH may be used. Warm or hot solutions are used, the activity thereof increasing with increase of temperature. Concentration of these solutions also affects their activity. With the article having the predisposed chromium electrodeposit thereon, immersed in the electrolytic solution, and connected as a cathode, a current of proper density is passed for the necessary length of time to give the desired plateau size and fissure depth. Very high current densities may prevent the formation of the net-works of fissures; current densities of ¼ to 3 amperes per square inch are generally satisfactory for cathodic etching. Short time etching results in shallow fissures; prolonged etching results in excessive removal of chromium and subdivision of plateaus which on subsequent mechanical finishing tend to crumble.

The formation of the net-works of fissures may be carried out electrolytically and chemically in combination, whereby the chromium electrodeposit is acted on while it is cathodic during the passage of an electric current of proper density for a few minutes in a suitable electrolyte, after which the treatment is continued by chemical action in the same or another bath without current. This may be carried out in a succession of cycles if desired. After the chromium has been activated by the cathodic action which takes place during the passage of the current, evolution of hydrogen continues after the current has been stopped. The electrolytic solution may be one of those described above. The degree of etching has a similar effect to that described above.

The formation of the net-work of fissures may be carried out chemically by immersing the chromium electrodeposit in a solution which attacks chromium. Examples of such solutions are hydrochloric acid or warm sulphuric acid. In many cases the chromium electrodeposit must be activated before the attack begins; this activation may be conveniently accomplished by electrolyzing the chromium cathodically. With activation, solutions such as described above for electrolytic etching can be used for chemical etching, and the degree of etching has a similar effect to that described above.

The progress of the formation of the fissure net-work in the course of etching can be observed visually, by removing the article from time to time and examining it.

It is a characteristic of the predisposed chromium electrodeposits produced in accordance with this invention that, when subjected to etching of the character described herein, the attack thereon occurs at lines in the electrodeposit, and is largely confined to lines provided the etching is not too prolonged, thus developing fissure net-works of a nature which give mud-crack type chromium surfaces which retain their mud-crack type characteristics after mechanical finishing.

Fissure net-works having deep and narrow fissures with relatively large size plateaus are advantageous since there is less crumbling of the chromium in subsequent mechanical finishing operations, less of the chromium need be removed in these mechanical finishing operations to obtain the desired smoothness on the surface of the plateaus, and from this it follows that to obtain the same thickness of chromium with a mud-crack type surface on a finished article less chromium need be deposited than where the nature of the fissure net-works is such as to require considerable removal of chromium in the mechanical finishing operation to obtain the desired smoothness of the surface.

On cylinder bores of high output internal combustion engines, it has been found that a mud-crack type chromium surface having plateaus one-sixty-fourth to one-thirty-second of an inch in diameter are especially advantageous. The present invention enables mud-crack type chromium surfaces with plateaus of such size, and of other sizes, to be readily and reproducibly obtained, in conjunction with suitable etching treatments, such for example as those described in the aforesaid Webersinn application.

Specific examples of practices in which the present invention is utilized follow:

EXAMPLE I

Chromium electrodeposition

Bath:

Chromic acid (CrO_3)	g./l.	250
Sulphate (SO_4)	g./l.	2.50
(No other catalyst radicals present.)		
Ratio		100/1
Temperature	°F.	140
Current Density	amps. per sq. in.	4

Etching

Bath:

Phosphoric acid	g./l.	290
Potassium dichromate	g./l.	10
Trivalent chromium (added as pot. chrome alum)	g./l.	2
Temperature	°F.	160
Cathodic treatment (for 15 min.)	amps. per. sq. in.	.5

Result

Mud-crack type surface with average plateau size approximately 1/80″ diameter.

EXAMPLE II

Chromium electrodeposition

Bath and plating conditions same as Example I, except ratio 115/1.

Etching

Same as Example I.

Result

Mud-crack type surface with average plateau size approximately 1/50″ diameter.

EXAMPLE III

Chromium electrodeposition

Bath and plating same as Example I, except ratio 125/1.

Etching

Same as Example I.

Result

Mud-crack type surface with average plateau size approximately 1/32″ diameter.

EXAMPLE IV

Chromium electrodeposition

Bath: Same as Example I (ratio 100/1).

Temperature °F	150
Current density amps. per. sq. in	4.5

Etching

Same as Example I.

Result

Mud-crack surface with average plateau size approximately 1/32".

EXAMPLE V

Chromium electrodeposition

Bath: Same as Example I, except ratio 75/1.

Temperature °F	155
Current density amps. per. sq. in	4.5

Etching

Same as Example I.

Result

Mud-crack type surface with average plateau size approximately 1/70" diameter.

The chromium electrodeposits were in each example from five to six thousandths of an inch thick.

The correlation between chromic acid-catalyst acid radical ratio, temperature of the plating bath and average plateau size to be produced in the chromium electrodeposit for the degree of etching given above, is shown by the accompanying graph. For example, if it be desired to obtain a one-sixty-fourth of an inch average diameter of plateau, the ordinate extending from the one-sixty-fourth mark on the horizontal line of the graph (axis of abscissas) intersects all five ratio curves, and the temperature for each ratio is found by the abscissa which extends to the vertical line on the graph (axis of ordinates) from the points of intersection of the ordinate at the one-sixty-fourth mark with each of the ratio curves. The abscissas from each of these points of intersection give the temperatures as follows: ratio 75 over 1, approximately 156° F.; ratio 100 over 1 approximately 143° F.; ratio 115 over 1, approximately 137° F.; ratio 125 over 1, approximately 132° F.; and ratio 150 over 1, approximately 127° F. With this knowledge as a guide the plater is enabled to base his choice of a correlated ratio and temperature of plating bath and a degree of etching equivalent to that given above for a given average plateau size.

This application is a continuation in part of our application No. 510,970, filed November 19, 1943.

What is claimed is:

1. A method of producing articles having chromium electrodeposits thereon with a fissure net-work therein and firm plateau areas within said fissure net-work having a minimum average diameter of eight thousandths of an inch, for sustaining the frictional load of moving parts bearing on said plateaus, comprising electrodepositing the chromium from a chromic acid bath to a minimum thickness of one thousandth of an inch, at the usual commercial current densities for the bath temperature at which the plating is done, within the range 1 to 12 amperes per square inch, under correlated conditions of temperature and ratio of CrO_3 to SO_4 related to a particular average diameter plateau, within a temperature range of 120° F. and 160° F. and a CrO_3 to SO_4 ratio range of 75 to 1 and 150 to 1, etching the chromium electrodeposited as herein stated to develop a fissure net-work with plateaus therein of a particular average diameter, ranging from eight thousandths of an inch upward, to which said chromium electrodeposit is predisposed by the correlated temperature and CrO_3 to SO_4 ratio at which it is electrodeposited, and mechanically finishing the firm plateaus to produce a smooth bearing surface with said fissure net-work remaining therein, the correlated conditions of temperature and CrO_3 to SO_4 ratio for electrodepositing the chromium being further defined as follows: CrO_3 to SO_4 ratio 75 to 1 and temperature 148° F. for plateaus of eight thousandths of an inch average diameter, and progressively higher temperatures at said 75 to 1 ratio for progressively larger average diameter plateaus; CrO_3 to SO_4 ratio 100 to 1 and temperature 132° F. for plateaus of eight thousandths of an inch average diameter, and progressively higher temperatures at said 100 to 1 ratio for progressively larger average diameter plateaus; CrO_3 to SO_4 ratio 115 to 1 and temperature 129° F. for plateaus of eight thousandths of an inch average diameter, and progressively higher temperatures at said 115 to 1 ratio for progressively larger average diameter plateaus; CrO_3 to SO_4 ratio 125 to 1 and temperature 126° F. for plateaus of eight thousandths of an inch average diameter, and progressively higher temperatures at said 125 to 1 ratio for progressively larger average diameter plateaus; CrO_3 to SO_4 ratio 150 to 1 and temperature 123° F. for plateaus of eight thousandths of an inch average diameter, and progressively higher temperatures at said 150 to 1 ratio for progressively larger average diameter plateaus; and CrO_3 to SO_4 ratio values intermediate to those stated above being correlated to temperature values intermediate to those which correspond to the stated ratio values.

2. A method of producing articles according to claim 1, wherein the fissure net-work produced by the etching is of the character obtained by etching the aforesaid chromium electrodeposit in an etching solution consisting of 290 g./l. phosphoric acid, 10 g./l. potassium dichromate and 2 g./l. trivalent chromium added as potassium chrome alum at a temperature of 160° F., in which solution the chromium electrodeposit is connected as a cathode and current passed thereto for 15 minutes at a cathode current density of one-half ampere per square inch.

3. A method of producing articles having chromium electrodeposits thereon with a fissure net-work therein and firm areas within said fissure net-work having an average diameter of two hundredths of an inch for sustaining the frictional load of moving parts bearing on said plateaus, comprising electrodepositing the chromium from a chromic acid bath to a minimum thickness of one thousandth of an inch at the usual commercial current densities for the bath temperature at which the plating is done, within the range 1 to 12 amperes per square inch, under correlated conditions of temperature and ratio of CrO_3 to SO_4 related to said average plateau diameter, etching the chromium electrodeposited as herein stated to develop a fissure net-work with plateaus therein of said average diameter of two hundredths of an inch to which it is predisposed, and mechanically finishing the firm plateaus to produce a smooth bearing surface with said fissure net-work remaining therein, the correlated conditions of temperature and CrO_3 to SO_4 ratio for electrodepositing the chromium being defined in the following table, the values of temperature and ratio inter-

mediate to those tabulated being obtained by interpolation;

Ratio CrO_3 to SO_4	Temperature
	° F.
75 to 1	157
100 to 1	146
115 to 1	140
125 to 1	136
150 to 1	130

4. A method of producing articles according to claim 3 wherein said correlated CrO_3 to SO_4 ratio and temperature values are between 100 to 1 and 125 to 1 ratios and approximately 146° F. and 136° F. temperatures.

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