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METHOD OF MINIMIZING "PATCHINESS" IN ETCHED CHROMIUM ELECTRODEPOSITS

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1 Claim. (Cl. 204—35)

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This invention relates to methods of minimizing "patchiness" in etched chromium electrodeposits, and provides improvements therein.

Methods are known for producing so-called "porous" chromium by etching thereof; vide Van der Horst U. S. Patent 2,314,604, and the Webersinn and Hyner U. S. Patent 2,430,750. Within the knowledge of the art are the conditions for electrodepositing chromium which predispose the electrodeposit to the formation of fissure networks on etching, and various methods and means of etching the predisposed chromium electrodeposit to develop the fissure network. The chromium electrodeposit, after etching, is mechanically finished (usually by grinding, polishing or honing). The finished chromium has utility for resisting frictional wear, and is extensively used on the bores of cylinders of internal combustion engines, piston rings, thread guides, and many other uses where resistance to frictional wear is important. The so-called etched "porous chromium" is usually produced of two types, one known as the "pitted" type, and the other as the "channel" or "mud-crack" type.

In producing etched "porous chromium" a condition known as "patchiness" is encountered and until now it has not been known how to overcome such condition. "Patchiness" is the result of the uneven action of the etching. This uneven action consists of either or both a different rate of etching at different areas, or a varying time-lag in the commencement of the etching action at different areas. The result is patches of surface area etched to slightly different levels or degrees. After finishing (honing for example) the surface presents a patchy appearance which is objectionable, and which in severe cases impairs the functioning of the chromium as a wearing surface.

I have discovered a simple and effective method of minimizing "patchiness."

I have discovered that by reducing, at or during the end-part of the period in which the chromium is being electrodeposited, the cathode current density to a low value with respect to the current density at which the chromium has been electrodeposited, "patchiness" is eliminated or minimized when the chromium so electrodeposited is etched.

The amount (or density) of the current in the aforesaid terminal part of the electrodeposition need not be sufficient to actually deposit chromium, but can during the whole or a part of said end-part of the electrodeposition be below an amount at which chromium is electrodeposited.

The desired effect is obtained in the same bath

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in which the electrodeposition of the chromium is done and without interruption of the current. The predisposed chromium electrodeposit may then be transferred to the tank in which the etching is done without intermediate treatment other than the usual rinsing with water.

The chromium electrodeposit to which my invention is applied may be any one which is predisposed to the formation of either "pitted" type or "channel" type porosity, electrodeposited from a chromic acid catalyst acid radical plating bath by any known method for producing such predisposed chromium. In such known methods, the ratio of chromic acid to sulphate acid radical ranges from 25 to 1 to 150 to 1; the temperature ranges from 71° C. (160° F.) to 25° C. (77° F.); and the current densities are of the ranges usually employed in commercial industrial or so-called "hard" plating, as described in my article on "Chromium Plating" in Modern Electroplating published by The Electrochemical Society, in 1942, Tables II and III, pages 122 and 123, a preferred range of current densities being from ¼ to 16 amperes per square inch.

In the practical art of electrodepositing chromium predisposed to the formation of so-called "porous" chromium, CrO_3 to SO_4 ratios from 25 to 1 to 125 to 1, temperatures 50° C. to 65° C. and current densities from 2 to 5 amperes per square inch, are those usually employed.

For so-called "pitted" type porosity a specific mode of procedure for plating chromium is as follows:

CrO_3, 250 g./l.
SO_4, 6.25 g./l.
Ratio, 40 to 1
Temperature, 55° C.
Current density, 3 amps./sq. in.
Time, 55 min./thousandth inch

For so-called "channel" type porosity a specific mode of procedure for plating the chromium is as follows:

CrO_3, 250 g./l.
SO_4, 2.17 g./l.
Ratio, 115 to 1
Temperature, 60° C.
Current density, 3.5 amps./sq. in.
Time, 40 min./thousandth inch

Chromium electrodeposits for treatment to form so-called "porous" chromium are usually one or more thousandths of an inch thick, and in practice the plating is continued the requisite amount of time (obtained from tables or experience) for

the plating conditions, principally current density and temperature, employed for obtaining the desired thickness of electrodeposit, all of which is well within the knowledge of the art.

According to the present invention, an electrodeposit of chromium, plated under conditions which predispose it to the formation of either "pitted" type or "channel" type porosity, while in the tank in which the plating is done, without interruption of the current flow, has the current flowing thereto reduced to such an amount that the cathodic current density corresponds to a plating current efficiency of 6% to 0% and the current flow continued at the reduced current density for about one to ten minutes, after which the chromium electrodeposit is removed from the plating solution, and etched and otherwise treated, as may be required to produce the so-called etched "porous chromium." The reduced current density at the aforesaid end-period in the plating tank need not be sufficient to actually electrodeposit chromium. Five minutes, as a general rule, is a good length of time for continuing the current flow at the reduced current density, for practical use.

Example

Chromium had been electrodeposited for 9 hours on steel from a 250 g./l. chromic acid plating bath having a CrO_3 to SO_4 ratio of 115 to 1, temperature 50° C. (122° F.) and a mean normal cathode current density of 3 amperes per square inch.

Without interrupting the flow of current, the cathode current density was reduced to 0.4 ampere per square inch (current efficiency 3.1%) and the current flow continued at said reduced current density for 5 minutes. Current densities of 0.1 to 1 ampere per square inch have also been used. The chromium plated article was then removed from the plating bath and rinsed.

Formation of fissure networks was carried out on these chromium electrodeposits following known procedures. Specifically, some were made cathode in a hot solution (70° C.) of oxalic acid (100 g./l.) at one-quarter ampere per square inch, for 30 minutes; others were immersed in a cold

1:1 hydrochloric acid solution (12° Beaumé) for 10 minutes; and others were treated anodically in a chromic acid solution for 25 ampere-minutes per square inch.

Chromium electrodeposits, after treatment in accordance with the foregoing at reduced current density in the end-part of the plating period, on and after etching and honing, have all shown an absence of "patchiness." Commonly, etched porous chromium produced under the same conditions, but without the aforesaid end-period treatment exhibited "patchiness."

What is claimed is:

A method of minimizing patchiness in porous chromium consisting essentially of electroplating chromium predisposed to the formation of porous chromium in a plating bath having CrO_3/SO_4 ratios from about 25 to 1 to 150 to 1, at temperatures of about 77° F. to 160° F., and current densities from about ¼ to 16 amperes per square inch appropriate to the temperature of the bath, and etching the said chromium electrodeposits to form porous chromium, characterized by continuing the passage of current in the plating bath, in the end part of the plating period, to the chromium already deposited, at a reduced cathodic current density corresponding to a plating current efficiency of 6% to 0% for 1 to 10 minutes.

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