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2,947,674

METHOD OF PREPARING POROUS CHROMIUM WEARING SURFACES

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This application is a continuation-in-part of our application, Serial No. 616,376, filed October 17, 1956, and now abandoned, and the invention relates to a method of producing porous wear-resistant chromium surfaces on cylinder bores, piston rings and the like.

A thin layer of chromium on at least one of the wearing surfaces subjected to sliding friction is known to greatly improve wear resistance providing the surface has certain porosity characteristics. One method of providing the porosity is to sand blast a smooth surface and to thereafter chromium-plate it. Another method, as described in the Van der Horst United States Patent No. 2,314,604, is to make the part anodic and apply a direct current of sufficient magnitude and sufficient time.

It is an object of the present invention to provide a method of inexpensively producing very uniformly pitted and porous chromium surfaces.

Another object is to provide a method of pitting chromium surfaces without using the expensive and inconvenient electrical equipment usually required to supply direct current.

It is a still further object of the present invention to provide a more uniformly pitted and porous coating of chromium for the surfaces of cylinder bores, pistons and other wearing surfaces.

We have found that alternating current can be used to induce porosity on chromium surfaces of wearing members. It is important that alternating current be applied within certain critical limits.

Broadly stated, the present invention comprises a method of producing a highly porous layer of an electro-deposited chromium, which comprises the steps of placing a wearing member having a smooth surface, such as an electrolytically deposited chromium layer, in a suitable electroplating bath, passing an alternating current between said layer as one electrode and another electrode equally spaced therefrom at a density of 5 to 120 amperes per square decimeter for a sufficient time to pass 50 to 500 ampere minutes of electricity from each square decimeter of the surface of the chromium layer to form a porous surface, and thereafter honing said surface, as desired.

The magnitude of the current and the total quantity of electricity per unit of area are important factors which must be controlled to produce the required surface characteristics. When the alternating current density is less than 5 amperes per square decimeter the time required for production of the surface becomes unduly long. The preferred current density is between 50 and 100 amperes per square decimeter; when the density is above 120 amperes per square decimeter, the amount of porosity formed tends to decrease rapidly. The quantity of electricity used can be varied dependent on the depth of porosity desired relative to the outer surface and the thickness of the originally deposited coating. Except in the pores formed, the amount of replating during one-half of the cycle is apparently equal to the amount of chromium

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removed so that the weight of the chromium layer is reduced only slightly by continued application of the alternating current. Generally, the amount of alternating electricity preferably applied is between 100 and 400 ampere minutes per square decimeter of area, although with thick coatings as much as 500 ampere minutes may be used and with thin coatings as little as 50 ampere minutes is effective. The voltage used is always just sufficient to produce the required current density.

The bath used is preferably simply a sulfur-free solution of chromic acid. The concentration is relatively unimportant and baths of from $\frac{1}{10}$ normal to about saturated appear to be equally effective. Generally a dilute bath such as N/10 chromic acid is preferably used.

Chromic acid is preferred primarily because of less tendency for contamination of a plating bath. Any electrolyte may be used, however, including all acids, bases and salts to obtain the desirable porosity in accordance with the present invention. Electrolyte on the acid side, with the exception of chromic and phosphoric acids, and some salts such as alkali metal chlorides are quite corrosive to iron and promote rusting if not completely removed. It is therefore desirable to use metal protecting acids or alkaline materials such as metal cleaning material all of which do not promote rusting. Examples of alkaline electrolytes are alkali metal hydroxides, carbonates, silicates, and phosphates including sodium carbonate, sodium hydroxide, tri-sodium phosphate, sodium orthosilicate, the corresponding potassium, lithium and even ammonium compounds (when existent) and particularly mixtures of any one or more as for example present in alkaline electro cleaners which also preferably have a wetting agent present.

Acid electrolytes which may be used include sulfuric acid, sulfamic acid and even hydrochloric acid in addition to the more desirable acid electrolytes above mentioned. Corrosive salts such as sodium, potassium, and ammonium chlorides, etc., like HCl may be used to obtain advantages of the invention but are not desirable because of the danger of not completely removing them from the surfaces after completion of the alternating current treatment. The concentration of any of the electrolytes is not critical if the power cost is not considered as voltage may be raised to obtain the necessary current concentration. In practice it is usually not desirable to use concentration of total electrolytes much less than $\frac{1}{10}$ Normal because resistance becomes greater and more power is therefore required although lower concentrations such as .05 Normal can be used with increased voltage.

The following example illustrates our invention:

Three identical steel sleeves, which were previously electroplated with approximately 0.015 inch of chromium, were selected for testing. Each of the sleeves had an inside diameter of $\frac{1}{4}$ inches and were $\frac{1}{8}$ inches in length so that their areas were each 3.559 square decimeters.

Each of the sleeves, in turn, was clamped in a jig and an identical lead electrode was inserted concentrically in each sleeve and clamped in place so that the distance from all parts of the sleeve to the surface of the electrode is the same. This assembly was then placed in an electrolytic bath of N/5 chromic acid. Electrical connections were made to a variable voltage alternating current source so that the plated chromium sleeve would be one electrode and the lead electrode would be the other electrode. Sixty cycle alternating current was passed between the electrodes in accordance with the following table. The sleeves were then honed to the same diameter as required for a cylinder liner.

The honed surfaces of Sleeves No. 1 and 2 were found to have an extremely uniform porosity and to have ex-

Table

Sleeve No.	Area, dm. ²	(Alternating Current) Treating Data		Time, Min.	Current Density, Amps./dm. ²	Total Alternating Current Per Unit Area, Amp.-min. dm. ²	Porosity After Precision Honing (Approx. Percent)
		Potential Volts	Current Amps.				
1.....	3,559	17	300	4	84.4	211.0	25-30
2.....	3,559	17	150	5	42.2	337.6	27-30
3.....	3,559	17	500	2.5	140.6	352.0	none

cellent wear resistance. Sleeve No. 3 had no appreciable porosity and did not exhibit satisfactory wear-resistant properties. The current density is, as shown above, clearly critical.

Sulfur-free chromic acid baths are preferred but any of the electrolytes previously mentioned may be substituted for the chromic acid in the above example and similar results obtained.

Generally we prefer about 1 or 2 pounds of NaOH, KOH, Na₂CO₃ or sodium orthosilicate per gallon of water when these alkaline materials are used although the concentration may be varied widely.

The products of the present invention have been found to possess greater hardness than those products prepared by treating an identical surface with reverse D.C. current as proposed in the prior art. The pores also appear sharper, and depth control has been superior. It is also found that dimension change is very minor during A.C. treatment so that time may be saved by reducing the initial plating time.

It is to be understood that, in accordance with the provisions of the patent statutes, various modifications of the procedure herein illustrated can be made without departing from our invention.

Having described our invention, what we claim is:

1. A method of producing a porous layer of an electrolytically deposited chromium, which comprises the steps of placing a wearing member having relatively non-porous layer of electrolytically deposited chromium in a bath of an acid solution of a chromium salt the chromium being present in amounts not substantially less than in a $\frac{1}{10}$ normal chromic acid solution and said bath being substantially free of sulfate, passing an alternating current between said layer and another electrode equally spaced therefrom at a density of 5 to 120 amperes per square decimeter for a sufficient time to pass 50 to 500 ampere minutes of electricity from each square decimeter of said surface of the chromium layer to provide a pitted porous surface, and thereafter honing said surface as desired.

2. The method of claim 1 wherein the bath comprises chromic acid as the principal electrolyte.

3. A method of producing a pitted porous layer of an electrodeposited chromium, which comprises the steps of placing a wearing member having a chromium plated wearing surface in a substantially sulfur-free chromic acid bath of at least $\frac{1}{10}$ Normal, passing an alternating current between said chromium plated surface as one electrode and another electrode in said bath, controlling said alternating current so that the current density is between 50 and 100 amperes per square decimeter and the current-time product is not substantially greater than 500 ampere-minutes per square decimeter of the surface area, and thereafter honing the surface.

4. A method of producing a porous layer of electrolytically deposited chromium, which comprises the steps of placing a wearing member having a relatively non-porous layer of electrolytically deposited chromium in a bath consisting essentially of water, and a material selected from the group consisting of alkali metal and ammonium hydroxides and salts thereof, chromic acid, and phosphoric, sulfuric and hydrochloric acids passing an alternating current between said layer and another electrode substantially equally spaced therefrom at a density of 5 to 120 amperes per square decimeter for a sufficient time to pass 50 to 500 ampere minutes of electricity from each square decimeter of the surface of said chromium layer to provide pores in said surface, and thereafter honing said surface, whereby a wearing surface having porosity for retaining lubricating oil while having excellent hardness and wear resistance is obtained, the total concentration of material in said bath being at least .05 normal.

5. The method of claim 4 wherein the material is alkaline.

6. The method of claim 4 wherein the material comprises an alkali metal hydroxide.

References Cited in the file of this patent

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