

[54] **ELECTRODEPOSITION OF WEAR RESISTANT AND OIL RETENTIVE NICKEL COATINGS AND ARTICLE HAVING SUCH A COATING**

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[73] Assignee: **Toyo Kogyo Co., Ltd.**, Japan

[22] Filed: **Sept. 6, 1973**

[21] Appl. No.: **394,855**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 294,298, Oct. 2, 1972, abandoned.

[52] **U.S. Cl.**..... 204/49; 29/195

[51] **Int. Cl.²**..... **C25D 15/00**; C25D 15/02

[58] **Field of Search** 204/49, 16, 41; 29/195 R, 29/195 A, 195 M

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Primary Examiner—G. L. Kaplan
Attorney, Agent, or Firm—Wenderoth, Lind & Ponack

[57] **ABSTRACT**

A method for providing wear resistance and an oil retention in the surface of a workpiece by means of electroplating the workpiece in a nickel plating bath to form a layer of porous nickel on the surface of the workpiece. To this end, the nickel plating bath contains one or a mixture of powdered ceramic materials in an amount within the range of from 50 to 500 grams per liter of the plating bath and a surface active agent selected from non-ionic ethers of polyethylene glycol such as polypropylene glycol polyethylene glycol ether and secondary alcoholic ethoxylate, in an amount within the range of from 0.5 to 5.0 percent by weight based on the total amount of the plating bath.

13 Claims, 6 Drawing Figures

FIG. 1

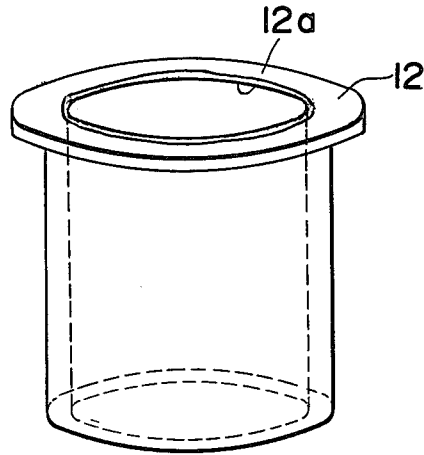


FIG. 2

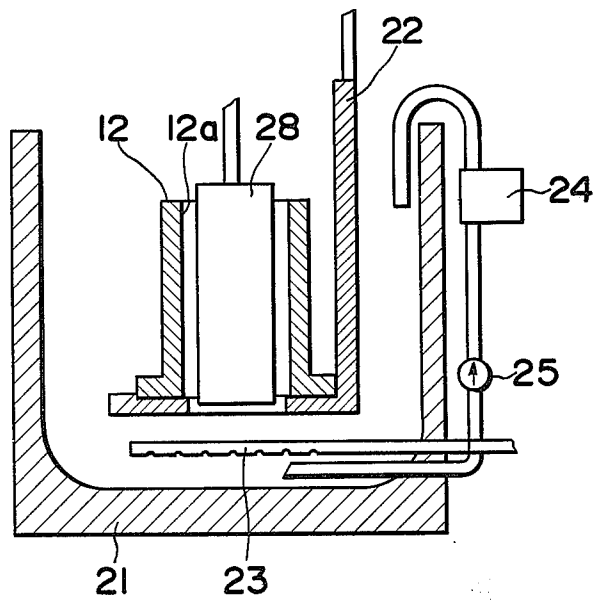


FIG. 3

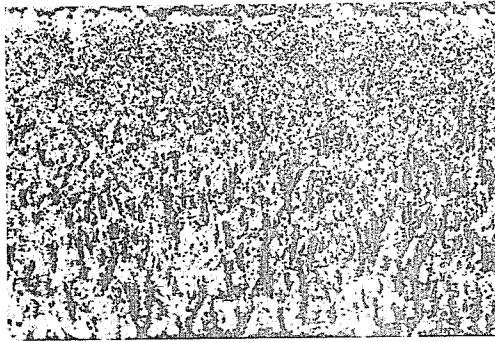


FIG. 4

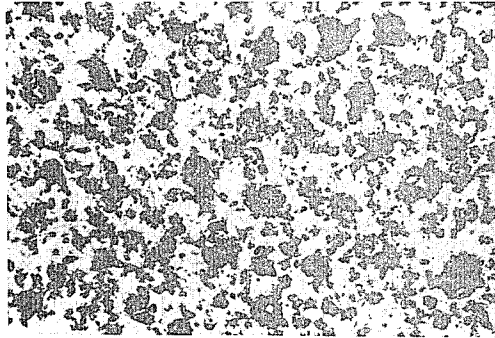


FIG. 5

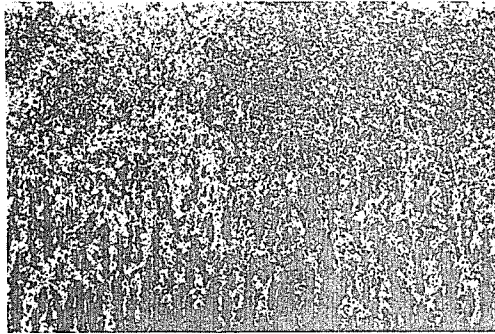
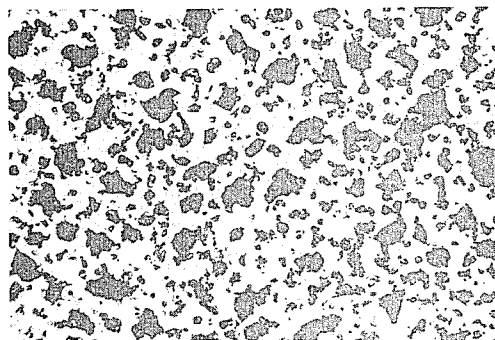


FIG. 6



ELECTRODEPOSITION OF WEAR RESISTANT AND OIL RETENTIVE NICKEL COATINGS AND ARTICLE HAVING SUCH A COATING

This is a continuation-in-part application of application Ser. No. 294,298, filed Oct. 2, 1972, now abandoned.

The present invention relates to a method for electroplating the surface of a workpiece and, more particularly, to an electroplating method for producing the workpiece surface having a sufficiently high resistance to abrasion or wear resistance and capable of providing sufficient lubrication for a coating member with which the workpiece having the electroplated surface cooperates in sliding engagement.

The present invention also pertains to the electroplating method for providing a wear resistance and oil retention to the workpiece surface where undesired or unfavorable friction will be exerted by its coating member during sliding engagement therebetween unless otherwise such workpiece surface is suitably surface-treated or oiled, and to the provision of the workpiece of which such surface to be slidably engaged with the coating member is electroplated in accordance with the method herein disclosed.

It is to be noted that examples of the surface to be slidably engaged with the coating member (which surface is hereinafter referred to as 'sliding surface') can be found in various mechanical and/or structural elements such as bearings, valve seats, piston rings, cylinders, shafts and cylinder sleeves.

A conventional method of similar character to that disclosed herein is disclosed in the Japanese Pat. Publication No. 3806/1961, published on Apr. 24, 1961, or the U.S. Pat. No. 3,514,389 patented on May 26, 1970. According to the method of these patents, electroplating of the sliding surface of the workpiece is performed by the addition of powdered ceramic material such as silicon carbide in an electroplating bath for the purpose of imparting a high wear resistance to the sliding surface thereof.

The method and apparatus disclosed in the above numbered patents function satisfactorily. However, there can be found a problem left still unsolved in connection with the oil retention the sliding surface of the workpiece must have for smooth sliding engagement with its coating member which slides in contact with said sliding surface.

Accordingly, an essential object of the present invention is to provide an improved electroplating method with which the surface having a sufficiently high wear resistance and a sufficiently high oil retention can be produced on a workpiece.

Another important object of the present invention is to provide the improved electroplating method of the above mentioned character which can be practiced without increasing the number of steps of manufacture and, hence, without increasing the cost of manufacture of the workpiece of which the surface is electroplated in accordance with the present invention.

A further object of the present invention is to provide the improved electroplating method of the above mentioned character wherein a workpiece is electroplated in a nickel plating bath containing therein a surface active agent in addition to the powdered ceramic material to permit the resultant electroplated layer on the surface of the workpiece to represent a rigid and po-

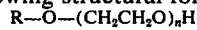
rous structure to provide sufficiently high wear resistance and sufficiently high oil retention.

It is to be noted that the present invention has been developed with the aim of providing not only wear resistance, but also oil retention, in the sliding surface of any one of the workpieces which may be used in any apparatus or machine where oiling is impossible or, if not impossible, hard to be performed by any reason well understood by the manufacturer of such apparatus or machine, for example, by the reason of the design.

In any event, according to the present invention, one of the most important features resides in the fact that the nickel plating bath contains therein 0.5 to 5.0 wt % a surface active agent selected from non-ionic ethers of polyethylene glycol, such as secondary alcoholic ethoxylate and polypropylene glycol. polyethylene glycol ether in addition to the powdered ceramic material contained in an amount within the range of from 50 to 500, preferably from 50 to 300 grams per liter.

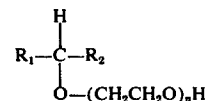
Suitable non-ionic ethers of polyethylene glycol include those sold under the trademarks Peregol, Igepal and Pluronic, which denote a substance of polyethylene glycol type, i.e., polyoxyethylene being in a form of ether. It may be more adequately called "Nonionic polyoxyethylene ether".

The secondary alcoholic ethoxylates are secondary alcohols having an oxyethylene radical which have the following structural formula:



In other words, they are polyoxyethylene alkyl ethers.

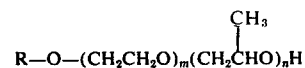
Of the surfactants discussed above, the substance most practicably applicable within the scope of the present application is the one having the following structural formula:



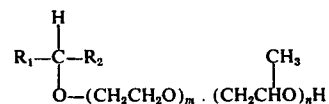
wherein R_1 and R_2 are alkyl radicals with the number of R_1 and R_2 carbon atoms being from 1 to 10 and R_1 carbons + R_2 carbons being from 10-20 and $n = 5-20$.

When $n < 5$, aqueous solvency is aggravated, whereby practice of the invention is impossible, and when $n > 20$, aqueous solvency is improved but porous results are not present. Accordingly, polyoxyethylene alkyl ethers having the molecular weight of approximately 390 - 1200 are suitable.

The polypropylene glycol polyethylene glycol ethers are polyoxyethylene polyoxypropylene ethers, for example:



The ones which are most practicably applicable in the present invention have the following structural formula:



wherein R_1 and R_2 are alkyl radicals with the number of carbon atoms in R_1 and R_2 being 1-10 and R and the sum of R_1 carbons + R_2 carbons being 10-20 and $m + n = 5 - 20$ wherein m and $n \geq 0$. Accordingly, polyoxyethylene polyoxypropylene alkyl ethers having a molecular weight of approximately 400 - 1500 are suitable.

By the electroplating method of the present invention, an electroplated surface having a rigid and porous structure can be advantageously obtained on a workpiece, which is very hard to wear and capable of providing sufficient lubrication for a coating member with which the workpiece having the electroplated surface cooperates in sliding engagement. Particular attention is called to the fact that the nickel-electroplated layer has a plurality of porosities extending substantially transversely of the surface of a workpiece to be electroplated. These porosities are effective to provide oil retention in the electroplated surface. In view of this fact, once the porosities in the electroplated surface have been impregnated with oil, oiling the electroplated surface, which acts as the sliding surface, is substantially no longer necessary.

These and other objects and features of the present invention will become apparent from the following description taken in conjunction with preferred examples with reference to the accompanying drawings, in which;

FIG. 1 is a perspective view of a cylinder sleeve for an internal combustion engine, of which the inner peripheral surface is nickel-electroplated by the method of the present invention,

FIG. 2 is a schematic side sectional view of electroplating equipment which may be used in the execution of the method of the present invention,

FIG. 3 is a photomicrograph, as magnified 115 times, showing a side sectional view of the electroplated surface obtained by the method of an Example I according to the present invention,

FIG. 4 is a photomicrograph, as magnified 460 times, showing a sectional top plan view of FIG. 3,

FIG. 5 is a photomicrograph, as magnified 115 times, showing a side sectional view of the electroplated surface obtained by the method of another Example II according to the present invention, and

FIG. 6 is a photomicrograph, as magnified 460 times, showing a sectional top plan view of FIG. 5.

Before description of the present invention proceeds, it is to be noted that, for the sake of better understanding of the present invention, the method herein described is disclosed as applied to a cylinder sleeve for an internal combustion engine.

The cylinder sleeve is shown by 12 in FIG. 1, wherein the inner peripheral surface 12a is provided with an electroplated nickel layer interlocking thereto. According to the present invention, this electroplated nickel layer contains therein particles of powdered ceramic material and represents a porous structure as will be clearly understood later.

An equipment for practicing the method of the present invention may be of any conventional type and comprises, as shown in FIG. 2, a tank 21 adapted to contain therein a suitable amount of electrolyte of the composition as will be described later, and a supporting frame 22 which is suspended in any suitable manner to permit it to be immersed in the electrolyte within the tank 21 and also to be removed away from the tank 21, said portion of said supporting frame 22 carrying

thereon the cylinder sleeve 12 in an upright position. So far as shown, the equipment further comprises a perforated tube 23 through which compressed air may be blown into the electrolyte in the tank 21 for keeping it in continuous agitation and a regenerator 24 for circulating the electrolyte from the bottom of the tank 21 to the top thereof by means of a hydraulic pump 25 for the purpose of keeping the electrolyte in motion or for regeneration if necessary. An anode 28 suitably connected with a power source (not shown) downwardly extends through a bore of the cylinder sleeve 12 carried by the supporting frame 22 with the peripheral surface of said anode 28 equally spaced from the inner surface of the cylinder sleeve 12. The cylinder sleeve 12 may be rigidly attached to the supporting frame 22 by any suitable method to ensure that the inner surface 12a thereof is equally spaced from the anode 28.

However, to achieve the various objects of the present invention, the electrolyte or plating bath is prepared by the use of one of nickel compounds such as nickel sulfate, nickel chloride and nickel sulfamate with addition of ammonium chloride for avoiding the passive state of the nickel compound used and a pH regulator such as boracic acid. The use of nickel sulfamate is particularly recommended for the nickel solution in the case where nickel is desired to be deposited in bright form so that little or no polishing is necessary.

The nickel solution thus prepared must contain one or a mixture of known powdered ceramic materials including metallic oxides such as aluminum oxide, metallic carbides such as silicon carbide and titanium carbide and metallic nitrides such as boron nitride and titanium nitride. The amount of the powdered ceramic material must be within the range of from 50 to 500 grams per liter 300, grams per liter with respect to the nickel solution: If this amount is smaller than the lowermost limit of 50 grammes, no nickel deposit having a sufficient wear resistance can be obtained and, if greater than the uppermost limit of 500 grams, the electroplating conditions will be badly affected with respect to improvement of the wear resistance in relationship to the increment. However, the uppermost limit of 300 grams per liter is recommended so that the powdered ceramic material can be uniformly dispersed in the nickel solution.

The powdered ceramic material to be used must be of a particle size of 0.5 to 9 μ preferably, 1 to 5 μ . The addition of the ceramic material of the particular size in the particular amount is necessary to obtain the high wear resistance in the resultant electroplated nickel layer containing therein the ceramic particles in an amount within the range of from 250 to 2,000 particles per 10,000 square micron (10,000 μ^2).

Furthermore, as one of the features of the present invention, the nickel solution must also contain a surface active agent within the range of from 0.5 to 5.0 percent by weight based on the total amount of the nickel solution. Examples of this surface active agent are nonionic ethers of polyethylene glycol such as secondary alcoholic ethoxylate and polypropylene glycol-polyethylene glycol ether. The addition of this surface active agent in the specified range of amount is essentially necessary because the porous structure in the electroplated layer having at least 15 porosities of more than 5 μ , preferably, more than 10 μ , in diameter per 10,000 μ^2 can be obtained on the surface of a workpiece only when any one of nonionic ethers of polyethylene glycol is employed. More specifically, if the

amount of the surface active agent used is smaller than 0.5 wt%, the porous structure will not be satisfactorily obtained and, if more than 5 wt%, no substantial improvement in the porous structure will be observed, but merely waste of the surface active agent will be incurred.

The surface active agent thus added to the nickel solution must be uniformly dispersed in the plating tank by a suitable stirring means, for example, by blowing compressed air into the nickel solution at a flow rate of, for example, 10 liters per minute, through the perforated tube. As is well known to those skilled in the art, the supply of compressed air through the perforated tube must be continued throughout the electroplating operation to keep the nickel solution in continuous agitation.

In order to obtain the porous structure in the nickel electroplated layer on the surface of the workpiece, in addition to the employment of the surface active agent, the current to be applied to the anode 28 may be of a current density within the range of from 5 to 30 amperes per square decimeter (dm^2) while the temperature of the plating bath is within the range of from 40° to 70°C with the pH value being within the range of from 3.5 to 5.3.

The present invention will be hereinafter described by way of example. However, it is to be noted that the present invention is not to be limited thereby.

EXAMPLE I

The surface of a workpiece made of aluminum alloy, which is usually employed as a material for the rotary engine housing, was electroplated in the plating bath of the following composition by the application of electric current of 20 A/ dm^2 in current density for two hours at the bath temperature of 60°C. while the compressed air was supplied at 10 l/min. with respect to two liters of the plating bath. The pH value was adjusted to 5.0.

Composition	gram/l
Ni(SO ₃ NH ₂) ₄ H ₂ O	444
NiCl ₂ ·6H ₂ O	10
H ₃ BO ₃	35
Saccharin	1
SiC	100

The surface active agent was secondary alcoholic ethoxylate employed in an amount of 1.0 wt%.

The result of this Example I is shown in FIGS. 3 and 4 which are photomicrographs of side sectional and sectional top plan view of the resultant nickel deposit of approximately 0.44 millimeter in thickness, respectively. From these photomicrographs of FIGS. 3 and 4, it is clear that the nickel deposit is formed with a plurality of porosities which are represented by elongated dark portions extending transversely of the surface of the workpiece. Among these porosities, there can be found the ceramic particles which are represented by the scattered dark portion.

The rotary piston engine wherein the inner surface of the peripheral wall was electroplated by the method of this Example I was tested. Prior to this test and during assembly of the rotary piston engine tested, the inner surface of the peripheral wall was treated such as to permit the porosities in the nickel plated layer to be pregnated with lubricating oil. The result of this test showed that no abnormal abasion was observed on the

inner surface of the peripheral wall when the engine was disassembled after an automotive vehicle mounted therewith had run approximately 100,000 kilometers. On the other hand, a similar test with the rotary piston engine wherein the inner surface is conventionally electroplated without the addition of the surface active agent showed that 10,000 to 20,000 kilometer run of the vehicle resulted in considerable formation of traces of abnormal abrasion over the inner surface of the peripheral wall of the engine housing.

EXAMPLE II

Electroplating was carried out under the same conditions as in the preceding Example I except for the type of surface active agent, which was employed in the form of polypropylene glycol polyethylene glycol ether in an amount of 2.5 wt%.

The result of this Example is shown in FIGS. 5 and 6 which are photomicrographs of side sectional and sectional top plan views of the resultant nickel deposit of approximately 0.47 millimeter in thickness, respectively.

The result of a similar test with the rotary piston engine wherein the inner surface of the peripheral wall was processed by the method of this Example was similar to that obtained in the preceding Example.

In either of the foregoing illustrative examples, it is clear that the porous structure contains more than 15 porosities of 5 or more micron in diameter per ten thousand square microns, which is sufficient to provide the oil retention on the surface of a workpiece in addition to the wear resistance resulting from the provision of the electroplated nickel-layer containing powdered ceramic material of 0.5 to 9.0 μ , preferably 1 to 5 μ , in particle size within the range of from 250 to 2,000 per 10,000 square micron. Furthermore, since these porosities each substantially extend transversely of the surface of said workpiece and are substantially independent from one another as seen from FIGS. 4 and 6, the porous structure exhibits a satisfactorily high characteristic of oil retention.

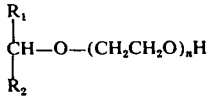
From the foregoing description of the present invention, it has now become clear that improvement of the wear resistance and provision of the porous structure can be achieved economically and advantageously by the addition of the surface active agent in the nickel solution for electrolyte.

Although the present invention has been fully disclosed by way of example, it is to be noted that various changes and modifications are apparent to those skilled in the art. For example, means for stirring the plating bath or the rate of blowing of the compressed air into the plating bath if said stirring means comprises an air blower may vary with the total amount of the plating bath and, yet, the electroplating time affects the thickness of the resultant nickel deposit. Accordingly, such changes and modifications should be construed as included within the scope of the present invention unless otherwise departing therefrom.

We claim:

1. In a method for providing wear resistance and oil retention in the surface of a workpiece by means of electroplating said workpiece in a nickel plating bath of an aqueous electrolyte to form a layer of nickel on said surface of said workpiece, the improvement which comprises said nickel plating bath containing one or a mixture of powdered ceramic material of 0.5 to 9 micron particle size in an amount within the range of from 50

to 500 grams per liter of said plating bath and a surface active agent which is a non-ionic secondary alcoholic ethoxylate having the following formula;

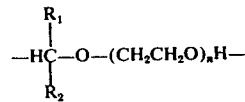


wherein R_1 and R_2 are alkyl groups of 1 to 10 carbon atoms and n is an integer from 5 to 20, said ethoxylate having a molecular weight of from about 390 to 1,200, which is in an amount within the range of 0.5 to 5.0 percent by weight based on the total amount of said plating bath whereby the resultant nickel-plated layer on the surface of said workpiece contains therein particles of said powdered ceramic material and represents a porous structure such that liquid lubricating agent can be impregnated in said porous structure to provide sufficient lubrication for a coating member with which the workpiece may cooperate in sliding engagement, the number of particles of said powdered ceramic material of 0.5 to 9.0 microns particle size in said porous structure are 250 to 2000 per 10,000 square microns and the number of porosities of 5 or more microns in diameter are more than 15 per 10,000 square microns.

2. A method as claimed in claim 1, wherein said one of said powdered ceramic materials is silicon carbide.

3. A method as claimed in claim 1, said method being carried out in such a manner that said plating bath is agitated by the blowing of compressed air supplied thereto from the bottom, said plating bath having a pH value within the range of from 3.5 to 5.3 and a temperature within the range of from 40° to 70°C, while an electric power of 5 to 30 amperes per square decimeter in current density is applied to an anode electrode immersed in said plating bath in the vicinity of the surface of said work-piece which serves as a cathode electrode.

4. An electroplating method for depositing a layer of nickel on the surface of a workpiece, which comprises placement of the workpiece in an aqueous electrolyte nickel plating bath contained in a tank, comprising means for stirring said nickel plating bath in said tank, an anode electrode and means for supporting said workpiece detachably in said plating bath such as to permit the surface of said workpiece to be relatively positioned in the vicinity of said anode while said workpiece serves as a cathode, electrolysis being performed between said anode and said surface of said workpiece upon application of an electric current to said anode, in which condition said stirring means is operated to keep said plating bath in continuous agitation, said plating bath essentially containing a nickel compound, one or more powdered ceramic materials of 0.5 to 9 microns particle size in an amount within the range of from 50 to 500 grams per liter of said plating bath and a surface active agent which is a secondary alcoholic ethoxylate having the following formula:



5 wherein R_1 and R_2 are alkyl groups of 1 to 10 carbon atoms and n is an integer from 5 to 20, said ethoxylate having a molecular weight of from about 390 to 1,200, which is in an amount within the range of 0.5 to 5.0 percent by weight, based on the total amount of said plating bath, whereby the resultant nickel plated layer on the surface of said workpiece contains therein particles of said ceramic material and has a porous structure having a substantially improved wear resistance and capable of being impregnated with liquid lubricating agent to provide sufficient lubrication for a coating member with which the workpiece may cooperate in sliding engagement.

5. A method as claimed in claim 4, wherein the number of particles of said powdered ceramic material of 0.5 to 9 microns in particle size are 250 to 2000 per 10,000 square microns and the number of porosities of 5 or more microns in diameter contained in said resultant nickel-plated layer of porous structure are more than 15 per 10,000 square micron.

6. A method as claimed in claim 4, wherein the amount of said powdered ceramic material to be added into said plating bath is within the range of from 50 to 300 grammes per liter.

7. A method as claimed in claim 4, wherein said one of said powdered ceramic material is silicon carbide.

8. A method as claimed in claim 4, wherein said porous structure is formed with a plurality of porosities each substantially extending transversely of the surface of said workpiece in a substantially isolated manner with respect to one another.

9. A method as claimed in claim 4, wherein said stirring means is compressed air supplied through a perforated tube from the bottom of the plating bath and wherein said electrolysis is carried out upon the application of the electric power of 5 to 30 amperes per square decimeter in current density while said plating bath is

10. A workpiece having formed on its surface an electroplated nickel layer, said nickel layer comprising ceramic particles contained therein, said nickel layer representing a porous structure with the number of said ceramic particles of 0.5 to 9.0 micron in particle size being within the range of from 250 to 2,000 per ten thousand square microns and the number of porosities of 5 or more microns in diameter being more than 15 per ten thousand square microns, whereby an improved wear resistance and an oil retention is imparted to the surface of said workpiece.

11. A workpiece as claimed in claim 10, wherein said porous structure is formed with a plurality of porosities, each substantially extending transversely of the surface of said workpiece in a substantially isolated manner with respect to one another.

12. The workpiece produced by the method of claim 1.

13. The workpiece produced by the method of claim 4.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

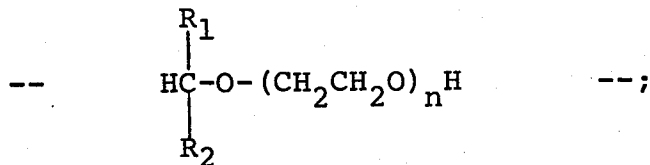
PATENT NO. : 3,929,596

DATED : December 30, 1975

INVENTOR(S) : Takao Sasame, Toshihiko Shigeta and Toshio Yamada

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8, delete the formula and insert therefore:



Column 8, claim 9, after "bath is" on the last line, add -- of a temperature within the range of from 40 to 70°C with the pH value being within the range of from 3.5 to 5.3. --.

Signed and Sealed this

fourth Day of May 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

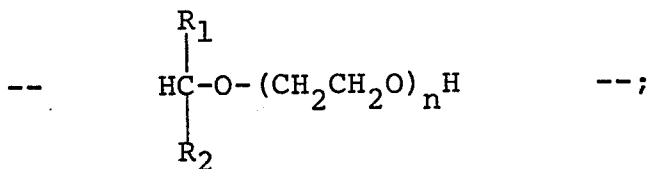
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[SEAL]

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