

- [54] **METHOD OF MAKING MICROCRACK CHROMIUM COATINGS**
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- [58] **Field of Search**..... 204/41, 43 T, 48, 49

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FOREIGN PATENTS OR APPLICATIONS

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[57] **ABSTRACT**

A method of forming microcrack chromium coatings in which an intervening or intermediate coating of nickel, cobalt, nickel-iron, nickel-cobalt or iron-cobalt is applied to a substrate and the chromium coating is electrodeposited thereon. The intermediate coating is applied from a bath containing the metal or metals and a pyridine derivative, especially a nicotinic or isonicotinic compound.

5 Claims, No Drawings

METHOD OF MAKING MICROCRACK CHROMIUM COATINGS

CROSS-REFERENCE TO RELATED APPLICATION

The present application is related to the commonly assigned copending application Ser. No. 216,724 filed Jan. 10, 1972 by myself and another and entitled "METHOD OF AND BATH FOR PRODUCING MICROCRACK CHROMIUM COATINGS," now U.S. Pat. No. 3,753,872.

FIELD OF THE INVENTION

The invention relates to the formation of microcrack chromium coatings on a substrate and, more particularly, to a method of producing such coatings whereby an intermediate coating is first applied to the substrate.

BACKGROUND OF THE INVENTION

In the aforementioned earlier application, there is described a method of applying a microcrack chromium coating, by electroplating, on a substrate which has been previously received an intervening or intermediate coating of high inner stress and low yield point consisting of nickel, cobalt, nickel-iron, nickel-cobalt or iron-cobalt.

The chromium coating is then deposited upon this intervening coating by electroplating from a conventional chromium-plating bath.

The intervening coating was applied from an electrolyte containing the metal ions and, in addition to ammonium ion and chloride ion, at least one aromatic, aliphatic or aromatic-aliphatic carboxylic acid, salt or acid anhydride.

In the aforementioned system, the intervening layer was preferably nickel applied from a bath to which the carboxylic acid was added in the form of its anhydride. In general the carboxylic acid, acid anhydride or salt was provided in a concentration of 5 to 70 grams per liter (g/l), in amounts corresponding to the limit of solubility of the carboxylic acid in the bath.

Preferably the carboxylic acid was the aromatic acid phthalic acid and was present in an amount of 20 to 60 g/l. The crack count was between 300 and 850 cracks/cm and the ultimate deposited chromium coating fulfilled all of the requirements set forth in the aforementioned application.

OBJECTS OF THE INVENTION

It is the principal object of the present invention to provide an improved method of coating a substrate with microcrack chromium.

It is another object to extend the principles originally set forth in the above-identified copending application.

SUMMARY OF THE INVENTION

I have found that relatively small concentrations of pyridine derivatives, especially nicotinic or isonicotinic compounds, added to the electrolyte for the deposition of the intervening or intermediate coating, can markedly increase the number of cracks/cm well beyond the upper limit stated above.

Since it has previously been proposed to add nicotinic acid to a bath for the galvanic application of a bright nickel coating to a substrate, it is altogether surprising that pyridine derivatives including nicotinic acid, can be used for the formation of microcrack chro-

mium deposits by incorporating them in baths from which the intervening layer is deposited.

The pyridine derivatives are added individually or in combination and in amounts between 0.01 and 8 g/l. The most reproducible and satisfactory results are obtained when the additive is nicotinic acid or isonicotinic acid and when the additive is present in an amount of 0.01 to 5 g/l preferably about 0.4 g/l. Otherwise the practice set forth in the aforementioned copending application is used.

Thus, the microcrack chromium layer may be applied as described in French Pat. No. 1,447,970 or Dettner Elze, Band II pages 184-188, *Hanser Verlag*, Munich, 1966. Preferably the intervening coating is a nickel layer deposited from a nickel electroplating bath of conventional composition but including at least 5 g/l of the aromatic carboxylic acid with the range of the carboxylic acid being between 5 and 70 g/l but preferably 20 to 60 g/l.

As noted, the nickel-plating bath (or the cobalt-containing plating bath as the case may be) will contain the usual substances employed in the deposition of the respective coatings. Reference is made in this respect to the *ENCYCLOPEDIA OF ELECTROCHEMISTRY*, Reinhold Publishing Corp., New York 1964. The metal ions may be present in an amount ranging from 30 to 100 g/l and will be nickel, cobalt and combinations thereof with one another or with iron, the metal ions being introduced into an aqueous bath in the form of the sulfate, sulfamate, chloride, fluoroborate, fluoride and/or acetate. Best results are obtained when the bath contains 10 to 150 g/l of chloride ion, the chloride being introduced as the nickel, cobalt, iron ammonium, magnesium or alkali metal (lithium, sodium, potassium) chloride. 10 to 100 g/l of ammonium, ion may also be present and, where desired, boric acid is employed in conventional quantities.

More specifically, the bath according to the present invention is an aqueous solution containing 100 to 400 g/l (preferably 220 g/l) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (or a corresponding cobalt or iron salt in electrochemically equivalent quantity or a mixture of cobalt, nickel and iron salts in electrochemically equivalent quantity) and 10 to 200 g/l (preferably 80 g/l) of ammonium acetate. The bath for application of the intervening coating may include the carboxylic acids mentioned earlier and, if desired, one or more brighteners and/or one or more antifoaming surfactants or wetting agents in accordance with conventional principles.

The bath according to the present invention should be at a pH between 1 and 6 (preferably between 3 and 4) as adjusted with hydrochloric acid or aqueous ammonia, the electrodeposition of the intervening coating should be carried out with a current density up to thirty amperes per square decimeter (A/dm^2) and preferably between 5 and 15 A/dm^2 , at a temperature of 20° to 70°C (preferably 40° to 45°C) and for a period of 10 seconds to 10 minutes (preferably 1 to 3 minutes).

When the intervening coating is then electroplated with chromium from a sulfuric acid or mixed-acid electrolyte as described in the aforementioned copending application, depending upon the thickness of the chromium coating and the parameters of the chromium plating bath, the ultimate coating has a crack count of 1200 cracks/cm² or more.

Basically, therefore, the bath for deposition of the intervening layer includes, in addition to the metal ion,

ammonium ion and chloride ion of the prior application and the usual additives previously mentioned, a pyridine derivative as described. The following pyridine derivatives have been found to be especially effective.

Isonicotinic acid hydrazide in an amount up to 5 g/l (preferably 0.1 to 0.3 g/l), pyridine-3-carbinol in amounts up to 5 g/l (preferably 0.4 g/l), pyridine-4-aldehyde in amounts up to 5 g/l (preferably 0.2 to 3.4 g/l), L-nicotine in amounts up to 5 g/l (preferably 0.2 to 0.4 g/l), 1-(3-pyridyl)-2-(4-pyridyl)-ethylene in an amount up to 2 g/l (preferably 0.1 g/l), 4-pyridylacrylic acid in an amount up to 8 g/l (0.4 g/l preferred), and pyridine-3-aldoxime in an amount up to 5 g/l (preferably 0.2 to 0.4 g/l).

SPECIFIC EXAMPLES

Example I

220 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
60 g/l $\text{NH}_4\text{OOCCH}_3$
pH 3.5 (established with HCl)
0.4 g/l 3-pyridinecarbinol
with or without
1 ml/l Butene-2-diol-1,4
with or without
1 ml/l commercial wetting agent
Temperature: 35°-45°C
Current density: 5-15 A/dm²
Deposition Time: 30 sec.-10 min.
Crack count: up to 1500 cracks/cm

Example II

200 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
80 g/l NaOOCCH_3
pH 3-4 (established with HCl)
0.2 g/l isonicotinic acid hydrazide
with or without
1 ml/l Butene-2-diol-1,4
with or without
1 ml/l wetting agent
Temperature: 40°C
Current density: 5-15 A/dm²
Deposition time: 30 sec.-10 min.
Crack count: up to 1500 cracks/cm

Example III

220 g/l NiCl_2
50 g/l Citric acid
45 ml/l concentrated ammonium hydroxide solution
pH 3.0-4.0 (established with HCl or ammonia)
0.1 g/l isonicotinic acid hydrazide
with or without
1.0 ml/l Butene-2-diol-1,4
with or without
2.0 ml/l wetting agent
Temperature: 35-45°C
Current density: 5-15 A/dm²
Deposition Time: 30 sec.-10 min.

Crack Count: up to 1500 cracks/cm

Example IV

180 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
100 g/l $\text{NH}_4\text{OOCCH}_3$
pH 3.5 (established with HCl)
0.4 g/l 4-Pyridylacrylic acid
with or without
1.5 ml/l Butene-2-diol-1,4
with or without
1.5 ml wetting agent
Temperature: 35°-50°C
Current density: 5-15 A/dm²
Deposition time: 30 sec.-10 min.
Crack count: up to 1500 cracks/cm.

Instead of the preferred nickel chloride in each of the foregoing examples, the corresponding cobalt or iron salt in combination with the cobalt and nickel salt were used in chemically equivalent quantities and in each case the chloride was replaced by the sulfamate, sulfate fluoroboride, fluoride, citrate and acetate with similar results. When 20 to 60 g/l of phthalic acid was added in each instance, the crack count was increased still further.

I claim:

1. A method of coating a metal substrate with microcrack chromium, comprising applying a first metallic layer to said substrate by electroplating nickel, cobalt or a combination of either with the other or with iron onto said substrate from an aqueous acidic electroplating bath containing the respective metal ions, ammonium ion and chloride ion together with a microcrack-increasing quantity of at least one pyridine derivative and thereafter electrodepositing a chromium layer upon said first layer to produce a microcrack coating, said pyridine derivative being selected from the group which consists of nicotinic acid and isonicotinic acid, isonicotinic acid hydrazide, pyridine-3-carbinol, pyridine-4-aldehyde, L-nicotine, 1-(3-pyridyl)-2-(4-pyridyl)-ethylene, 4-pyridylacrylic acid and pyridine-3-aldoxime and being present in said bath in a concentration between 0.1 and 5 g/l, said bath further containing 20 to 60 g/liter of phthalic acid.

2. The method defined in claim 1 wherein said first layer is electroplated onto said substrate at a current density of up to 30 A/dm² for a period of 10 seconds to 10 minutes and said bath has a temperature between 20° and 70°C and a pH of 1 to 6.

3. The method defined in claim 2 wherein said pH is substantially 3 to 4, said current density is substantially 5 to 15 A/dm², said temperature is 40° to 45°C and said period is 1 to 3 minutes.

4. The method defined in claim 3 wherein said bath contains 100 to 400 g/l of nickel chloride.

5. The method defined in claim 4 wherein said bath contains 10 to 200 g/l of ammonium chloride.

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