(12) UK Patent (19) GB (11) 2 153 387 (13) B

(54) Title of invention

Deposition of hard chromium on steel or aluminium alloy

(51) INT CL⁴; **C25D 3/10**

(21) Application No
8432194

(22) Date of filing
20 Dec 1984

(30) Priority data

(31) **3402554**

(32) **26 Jan 1984**

(33) **Fed. Rep. of Germany (DE)**

(43) Application published
21 Aug 1985

(45) Patent published
20 Jan 1988

(52) Domestic classification (Edition J)
C7B 120 458 464 717 DGF

(56) Documents cited
EP 0100133
US 3745097

(58) Field of search
C7B
Selected US specifications from IPC sub-class C25D

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GB 2 153 387 B

DEPOSITION OF HARD CHROMIUM ON STEEL OR ALUMINIUM ALLOY

This invention relates to a process for the deposition of hard chromium on workpieces of steel or aluminium alloy from an aqueous electrolyte containing chromic acid and sulphuric acid, namely from the classical chromium bath with CrO_3 content of 150 to 400 g/l, preferably of about 200 g/l, and an SO_4 content of e.g. 2 to 15 g/l, preferably about 1.2% H_2SO_4 in relation to the CrO_3 content.

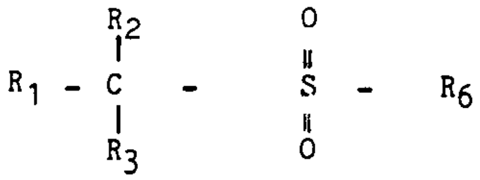
Electrolytes of the composition described are simple to manage and do not etch the workpiece to be chromium plated, or do not do so to a troublesome extent. The important disadvantage of the classical sulphuric acid chromium baths is the bad cathodic current efficiency which in practice does not exceed 15% even with the best adjustments. Deposit hardnesses that are strongly dependent upon the choice of deposition conditions, particularly on the relation between current density and temperature, and also the formation of large cracks in the deposit, must be looked upon as further disadvantages. It is an advantage that iron alloys (steel) and aluminium alloys, which as a rule are etch-sensitive in hard chromium plating, are not etched to a troublesome extent. In order to obtain bright chromium deposits even in thick layers it is known (see German Patent Specification 10 34 945) to add a brightener to the electrolyte, this being in the form of a surface-active alkyl sulphonate compound. The surface-active effect requires that the alkyl is long-chained, e.g. possesses three or more carbon atoms. The current efficiency and the exposure period are not markedly improved by the addition.

More advantageous in respect of cathode current efficiency and working range are the so-called mixed-acid chromium baths. By these are understood electrolytes which in addition to chromic acid and sulphuric acid contain fluorides and in particular complex fluorides, preferably as silicofluoric acid or its alkali or alkaline-earth salts. These electrolytes, in addition to a number of favourable properties, also exhibit troublesome defects. Amongst these are considerable attack upon the steel and aluminium alloys already emphasized above, by which etching takes place that can lead to the formation of holes and under-cutting. The conditions with other metal alloys are similar. The application of mixed-acid chromium baths is thereby limited to a large extent. In addition to this the fluorides and complex fluorides are volatile, even when working with a low-temperature bath. The composition of the bath is altered by the volatility of the fluorides and complex fluorides so that regular analyses and re-adjustments of the bath compositon are necessary.

Compared with this it is the object of the invention to provide a process for depositing with high cathodic current efficiency on steel and on aluminium alloys, from an aqueous bath that contains chromic and sulphuric acids, a hard chromium layer, this being without the danger of troublesome etching of the existing surface and without the bath composition changing by volatility of important bath components. Preferably the aim should be to achieve a working cathodic current efficiency of over 20%.

According to the present invention, there is provided a process for the electrolytic deposition, with cathodic current efficiency of more than 20%, of a non-iridescent engineering-functional hard chromium layer on a workpiece of steel or of an aluminium alloy, from an aqueous non-etching electrolyte bath containing chromic acid and sulphuric acid, with CrO_3 content of 150 to 400 g/l, and in which a saturated aliphatic sulphonic acid with a maximum of two carbon atoms and a maximum of six sulphonic acid groups or their salts or halogen derivatives is added, this being with a concentration of more than 0.5 g/l, and in which operation is with a bath temperature of 20° to 70°C and a current density of 15 to 100 A/dm^2.

Methanesulphonic acid, ethanesulphonic acid, methanedisulphonic acid, 1,2-ethanedisulphonic acid, salts of the above-mentioned acids, and methanesulphochloride are particularly suitable. Expressed as a structural formula, the subject of the invention is the use of an organic compound of structure.................................



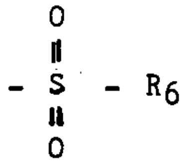
$$R_1 - \overset{R_2}{\underset{R_3}{C}} - \overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}} - R_6$$

in which R_1 can be

- H

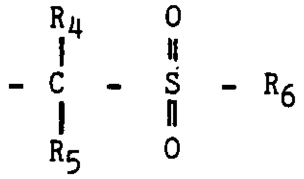
or - CH_3

or



$$- \overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}} - R_6$$

or

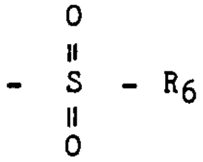


$$- \overset{R_4}{\underset{R_5}{C}} - \overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}} - R_6$$

in which R_2 - R_5 can be

- H

or



$$- \overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}} - R_6$$

and in which R_6 can be

- OH

or - OMe (an oxygen compound with a metal)

or - Halogen

for the purpose stated.

According to a preferred manner of performing the invention the saturated aliphatic sulphonic acid ~~organic compound~~ is formed in the electrolyte by chemical or electrochemical reactions.

Variations of the manner of performance are as follows:-

Salts of elements of Group VI of the Periodic Table may be added, such as selenium salts and/or tellurium salts in a concentration of 1 to 20 mg/l, and/or Cr_2O_3 in a concentration of up to 15 g/l may be added. It is obvious that $SrSO_4$ and other strontium salts can also be added.

The organic compound disclosed functions according to the invention with surprising effects. Although the bath possesses the advantages of a classical chromium bath the cathodic current efficiency is noticeably improved. Troublesome etching of the surface is not observed. This applies particularly to surfaces of steel and aluminium alloys. Even at high bath temperatures the bath does not change in compositon due to the volatility of essential components. It is within the scope of the invention to add boric acid to the bath, up to saturation point, for the improvement of throwing power.

In the following the invention is explained by means of examples.

1. A classical sulphuric acid chromium electrolyte with 250 g/l CrO_3 and 1.1% H_2SO_4, in relation to the CrO_3 content was prepared. A testpiece was chromium plated at 55°C with a cathodic current density of 50 A/dm^2. The cathodic current efficiency - related to the reduction of the Cr^{+6} to Cr - amounted to 15.0%. The deposits were macro-cracked. 1g of methanesulphochloride was added to this electrolyte. A testpiece was chromium plated under the above conditions. The current efficiency now amounted to 23.9%. The deposits were fine-cracked.

2. 3 g/l of methanesulphonate was dissolved in an electrolyte of 180 g/l CrO_3, saturated with $SrSO_4$, and a testpiece was chromium plated under the conditions of Example 1. The current efficiency amounted to 24.8%, with fine-cracked deposits.

3. An electrolyte of 200 g/l CrO_3, 6 g/l H_2SO_4 and 5 g/l ethanesulphonate produced under the conditions of Example 1 resulted in

a cathodic current efficiency of 24.7% with a fine-cracked structure.

4. An electrolyte of 300 g/l CrO_3, 3.3 g/l H_2SO_4, 4 g/l methanesulphonate acid and 3.5 mg/l SeO_2 produced a cathodic current efficiency of 26% with a cathodic current density of 55 A/dm^2 and a working temperature of about 55°C.

5. A current efficiency of 25.7% was obtained when, under the conditions of Example 1. an electrolyte of 300 g/l CrO_3, 4 g/l H_2SO_4 and 3 g/l methanedisulphonic acid was used. The deposits were fine-cracked.

6. Steel testpieces were tested for attack under classical polarization conditions at 0.2 - 0.8 A/dm^2, i.e. below the cathodic current density necessary for chromium deposition. at 55°C.

Electrolyte 1: 300 g/l CrO_3
3.3 g/l H_2SO_4

Electrolyte 2: 300 g/l CrO_3
3.3 g/l H_2SO_4
3 g/l methanedisulphonate

Electrolyte 3: 300 g/l CrO_3
0.6 % H_2SO_4
10 g/l K_2SiF_6.

Erosion per hour measured in:

Electrolyte 1: from 0.5 - 1.0 mg/dm^2

Electrolyte 2: from 0.0 - 0.5 mg/dm^2

Electrolyte 3: from 0.8 - 1.4 g/dm^2.

The cathodic polarization was selected as experience shows that attack with small cathodic polarization is greater than when there is no external current at all, and the damage caused by etching is preferentially concentrated at the limit bordering on chromium deposition.

7. Aluminium alloy testpieces (a = $AlMg_1$, b = $AlMgSi_1$) were tested under the conditions of Example 6 (at 0.8 A/dm^2). The following results were obtained with testpieces a) of $AlMg_1$ (1 gram-molecule of magnessium to 1 gram-molecule of aluminium) and b) of $AlMgSi_1$ (1 gram-molecule of silicon to 1 gram-molecule of AlMg):-

In electrolyte 1: a) + 16.0 mg/dm^2
b) + 3.0 mg/dm^2

In electrolyte 2: a) + 8.0 mg/dm^2
b) + 8.2 mg/dm^2

In electrolyte 3: a) - 0.8 g/dm^2 erosion
b) - 1.0 g/dm^2 "

The increases in weight in electrolytes 1 and

2 may be due to formation of aluminium oxides or chromates; the large loss of weight in electrolyte 3 is undoubted.

Considerable differences also resulted when measured in the condition without any external current:

In electrolyte 2 there was erosion per hour of

20 mg/dm^2 with $AlMg_1$. and

32 mg/dm^2 with $AlMgSi_1$,

whilst with electrolyte 3:

0.75 g/dm^2 with $AlMg_1$, and

0.94 g/dm^2 with $AlMgSi_1$

went into solution.

8. The volatility of HF or SiF_4 from electrolytes that contain fluorides or complex fluorides is adequately known. An electrolyte with 300 g/l CrO_3. 1.3% H_2SO_4 in relation to the CrO_3, and 5 g/l of methanedisulphonate after standing at 50°C for three months showed no measurable loss of sulphonate and no diminution of the current efficiency.

CLAIMS

1. A process for the electrolytic deposition, with cathodic current efficiency of more than 20%, of a non-iridescent engineering-functional hard chromium layer on a workpiece of steel or of an aluminium alloy, from an aqueous non-etching electrolyte bath containing chromic acid and sulphuric acid, with CrO_3 content of 150 to 400 g/l, and in which a saturated aliphatic sulphonic acid with a maximum of two carbon atoms and a maximum of six sulphonic acid groups or their salts or halogen derivatives is added, this being with a concentration of more than 0.5 g/l, and in which operation is with a bath temperature of 20° to 70°C and a current density of 15 to 100 A/dm^2.

2. A process according to Claim 1, wherein the saturated aliphatic sulphonic acid is formed in the elctrolyte by chemical or electrochemical reactions.

3. A process according to Claim 1 or Claim 2, wherein salts of elements of Group VI of the Periodic Table are additionally added.

4. A process according to any one of Claims 1 to 3, wherein selenium salts and/or tellurium salts are added in a concentration of 1 to 20 mg/l.

5. A process according to any one of Claims 1 to 4, wherein Cr_2O_3 in a concentration of up to 15 g/l is additionally added.

6. A process as in Claim 1 and substantially as hereinbefore described with reference to any one of the examples.

Publication No.
2153387 A dated 21 August 1985

Patent Granted: WITH EFFECT FROM 20 JAN 1988
SECTION 25(1)

Application No.
8432194 filed on 20 December 1984

Priority claimed:
26 January 1984 in Germany (Federal Republic of) doc: 3402554

Title:
Deposition of hard chromium on ~~metal alloy~~ Steel or aluminium alloy
AMENDED TITLE AT GRANT

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Examination Requested: 9 January 1985

Classified to:
C7B

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Printed by the Patent Office at St. Mary Cray, 27 JUN 85