⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: 0 087 288
A1

⑫

EUROPEAN PATENT APPLICATION

㉑ Application number: 83300852.7

㉒ Date of filing: 18.02.83

(51) Int. Cl.^{3}: C 23 F 7/26
C 23 F 7/02

㉚ Priority: 19.02.82 FR 8202816

㊸ Date of publication of application:
31.08.83 Bulletin 83/35

(84) Designated Contracting States:
AT BE CH DE GB IT LI NL SE

(71) Applicant: M & T CHEMICALS, INC.
One Woodbridge Center
Woodbridge, New Jersey 07095(US)

(72) Inventor: Jeannier, Eliane
6 Rue Albert Thomas
F-91300 Pontoise(FR)

(74) Representative: Ellis, John Clifford Holgate et al,
MEWBURN ELLIS & CO. 2/3 Cursitor Street
London EC4A 1BQ(GB)

(54) **Bath and method for black chromate plating of zinc and cadmium surfaces.**

(57) An aqueous bath for black chromate plating of a surface of zinc, zinc alloy or cadmium alloy containing sulphate ions, 5 to 40 g/l of hexavalent chromium, 0.25 to 30 g/l of copper ions, 0.1 to 5 g/l of silver ions and/or molybdic ions, 30 to 120 g/l of acetic acid and 0 to 6 g/l of formic acid. Such surfaces plated by the method using the said bath produces a shiny black adherent coating giving good protection against corrosion of the substrate.

Croydon Printing Company Ltd.

"BATH AND METHOD FOR BLACK CHROMATE PLATING OF ZINC AND CADMIUM SURFACES".

The present invention relates to new bath permitting, by chromium plating, to obtain a shiny black coating on surfaces of zinc, or zinc-or cadmium-containing alloys.

The protection of surfaces of zinc, or of zinc-or cadmium-containing surfaces by chromium-plating said surfaces, has already been described.

The solutions used to this effect contain essentially chromium (for example in sodium or potassium dichromate and or chromic acid form), sulphate ions and, in some cases a metallic compound giving rise to the formation of a suitably coloured chromate deposit.

Amongst the metallic compounds that can be used, there are the silver salts (for example silver nitrate) which lead to the formation of a shiny black chromium plating film, which looks good but of which the resistance to corrosion is affected by metallic pollutions (zinc, iron, etc.).

However, the baths usable for obtaining these silver-containing coatings are rather expensive to prepare and to maintain. For this reason, attempts have been made to find compounds of metals other than silver which, when used in chromium-plating baths, could give black, shiny and corrosion-resistant coatings.

A chromium-plating bath has recently been described which contains besides chromium (6) and sulphate ions, a copper salt and a mixture of acetic acid and formic acid. Unfortunately, when using this kind of bath, the deposit obtained is dull, this making it less interesting at the industrial level.

It is the object of the present invention to overcome this drawback by proposing a method for chromium-plating surfaces of zinc, or of zinc or cadmium alloys, the said method producing a shiny black coating with good adherence to the support and ensuring a good protection against corrosion of the support, which method consists in placing the support to be chromium-plated in contact with a bath containing:

5 – 40 g/1 , expressed in Cr, of hexavalent chromium,

sulphate ions,

0.025 – 40 g/l of cupric ions,

0.1 – 5 g/l of ions selected from silver and the molybdic ion,

30 – 120 g/l of acetic acid,

and 0 – 6 g/l of formic acid.

The invention further relates to the baths used in carrying out the said method.

It will be noted:

- that the quantities of chromium ions to be used are substantially the same as those currently used in the chromium-plating baths,

that sulphate ions are used, as known, the effect of these ions being, all other things being equal, to improve the plating speed and also the adherence of the deposits to the support, especially when said sulphate ions are added in the form of sodium sulphate and sulphuric acid;

said sulphate ions can also be added in the form of a copper sulphate for example,

- and that cupric ions will be used in any case, these ions producing a chromium-plating of a very pleasant colour,

- that the shiny finish of the deposits is obtained due to the presence, with the cupric ions, of another ion selected from silver or the molybdic ion.

It is known that the use of silver has already been recommended, but the simultaneous use of copper ions and silver ions has never been described. When simultaneously using these two ions, the operation will take place, according to the invention, in the presence of preferably 0.025 — 0.2 g/l of copper ions and preferably 0.1 — 0.2 g/l of silver ions. It is inside these ranges of concentration that the best results are obtained.

The use of molybdic (MoO_4^{--}) ions with the copper ions, also produces according to the invention, a shiny black deposit with excellent anti-corrosion properties. The simultaneous use of copper ions and molybdic ions implies that fairly large quantities of these ions are used;

the best results are obtained when operating with concentrations of between 15 and 30 g/l of copper ions and between 0.15 and 5 g/l of molybdic ions (MoO_4^{--});

- that in all cases (whether using the copper-silver combination, or the copper-molybdate combination or the copper-silver-molybdate combination) the baths will contain acetic acid; the concentrations of that acid are variable and can be between about 30 and about 120 g/l. Advantageously, they will be between 65 and 90 g/l,
- that, finally, in the special case of a copper-molybdate bath, it is advantageous to use, in addition to acetic acid, a certain quantity of formic acid, the preferred concentration of this acid being about 3 g/l.

The conditions of operation, to obtain the chromium-plating according to the invention can be the conditions conventionally used for chromium-plating zinc or cadmium surfaces. These conditions are for example:

- a pH obviously acid, between 0.5 and 4,
- a temperature approaching the ambient temperature, i.e. between about 15 and 40°C,

- a period of contact of the piece to be treated and the bath, which can vary, depending on the baths, between 10 seconds and 10 minutes,
- with or without stirring.

The pieces to be treated according to the invention have of course a coating of black and shiny chromate which is very adherent and constitutes a good protection against corrosion.

It is however possible to further improve the properties of these coatings, and in particular in certain cases, the shiny finish of the deposit, and its efficiency as a protector against corrosion, by submitting the piece thus coated to a post-rinse with a phosphating bath. The usable phosphating baths are known per se and have already been recommended for certain applications, such as for example for polishing certain deposits. It is considered that in the case of the deposits according to the invention (copper-silver or copper-molybdates) such rinsing baths are specifically efficient and especially advantageous in that they improve the protective effect of the coatings. Amongst the baths usable, the following are given by way of example and non-restrictively:

- baths containing up to 5% by weight of phosphoric acid,
- baths containing between 5 and 20 g/l of sodium hexametaphosphate,
- baths containing between 0.5 and 15 g/l of monosodium phosphate and between 0.5 and 15 g/l of monopotassium phosphate.

As indicated hereinabove, the exact composition of phosphating baths can vary to large extents, but very good results have always been obtained with the special baths indicated hereinabove.

The conditions required for this phosphating treatment are usually as follows:

- ambient temperature, i.e. between 15 and 40°C,
- duration between 10 seconds and 5 minutes, in general about one minute.
- with or without stirring.

The following examples are given by way of information and non-restrictively.

Example 1

To protect a steel coated with a layer of zinc.

A bath was prepared for this purpose containing:

- chromium (6) ions		
. sodium dichromate	30	g/l
- sulphate ions		
. sodium sulphate	4	g/l
. sulphuric acid	8	g/l
- copper ions		
. copper sulphate ($CuSO_4.5H_2O$)	0.4	g/l
- silver ions		
. silver nitrate	0.3	g/l
. acetic acid	80	g/l

The piece to be protected was dipped into this bath, at ambient temperature (20-27°C) with air-stirring of the bath, and for a duration of 2 minutes.

The resulting shiny black piece was then rinsed and dipped into a phosphating bath containing 12 g/l of sodium hexametaphosphate, for one minute at 20°C, without stirring.

The piece removed from the bath was then dried.

Example 2

A bath was prepared containing:

- chromium (6) ions		
. sodium dichromate	30	g/l
. chromic acid	35	g/l
- sulphate ions		
. brought in copper sulphate($CuSO_4.5H_2O$) form		
- copper ions		
. copper sulphate	85	g/l
- molybdic ions		
. ammonium molybdate	2	g/l
- acetic acid	85	g/l
- formic acid (25%)	10	cc/l

The piece to be treated was dipped in this bath (at 20°C) for about 2 minutes. The resulting piece, once removed from the bath and after rinsing, can be given the phosphating treatment to improve the polished finish and resistance to corrosion of the protective coating.

CLAIMS:-

1. An aqueous bath for producing a black chromate plating of a zinc surface or of a surface of a zinc alloy or a cadmium alloy characterized by a content of:

- (i) sulphate ions;
- (ii) 5 to 40 g/l of hexavalent chromium;
- (iii) 0.025 to 30 g/l of copper ions;
- (iv) 0.1 to 5 g/l of silver ions and/or molybdic (MoO_4^{--}) ions;
- (v) 30 to 120 g/l of acetic acid;
- (vi) 0 to 6 g/l of formic acid.

2. An aqueous bath according to Claim 1, wherein the amount of copper ions is 0.025 to 0.2 g/l and the amount of silver ions is 0.1 to 0.2 g/l.

3. An aqueous bath according to Claim 1, wherein the content of copper ions is 15 to 30 g/l and the content of molybdic ions is 0.15 to 5 g/l.

4. An aqueous bath according to Claim 3, containing formic acid in a quantity of about 3 g/l.

5. A method for producing a black chromate plating of a zinc surface or of a surface of a zinc alloy or a cadmium alloy characterized in that an article with a surface of zinc, zinc alloy or cadmium alloy to be chromium plated is dipped in an aqueous bath as defined in any one of Claims 1 to 4 for sufficient time to produce a black chromate layer of the required thickness.

6. A method according to Claim 5, wherein the bath is at a temperature of 15° to 40°C.

7. A method according to Claim 5 or Claim 6 wherein the time of immersion is 10 seconds to 10 minutes.

8. A method according to any one of Claims 5 to 7, wherein the bath is at a pH of between 0.5 and 4.

9. A method according to any one of Claims 5 to 8, wherein the thus plated article is rinsed and then dipped into a phosphating bath.

European Patent
Office

EUROPEAN SEARCH REPORT

0087288
Application number

EP 83 30 0852

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	CHEMICAL ABSTRACTS, vol. 90, no. 18, April, 1979, page 190, no. 140877z, Columbus, Ohio, US & PL - A - 83 483 (INSTYTUT MECHANIKI PRECYZYJNEJ) 30.04.1977 * Abstract; example in last paragraph of page 1 of the patent *	1,5-7	C 23 F 7/26 C 23 F 7/02

Y	PLATING AND SURFACE FINISHING, vol. 68, no. 10, October, 1981, pages 54-56 V.G. ROZOVSKY et al.: "Corrosion resistance of black chromate conversion films on zinc" * Page 54 *	1-8	

Y	DD-A- 136 979 (A. STRAUCH) * Claim 1; page 3 *	1,2,5-8	TECHNICAL FIELDS SEARCHED (Int. Cl. 3)

Y	GB-A- 618 667 (J.E. STARECK) * Claims; page 3 *	1-8	C 23 F 7/26 C 23 F 7/02

Y	US-A-3 097 978 (I.L. NEWELL) * Claim 1; column 5, table II, ex. K *	1,9	

A	US-A-2 524 577 (J.E. STARECK)		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19-05-1983	TORFS F.M.G.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document
T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

EPO Form 1503. 03.82