

[54] **CHROMIUM PLATING METHOD**

[75] Inventors: **Edgar J. Seyb, Jr.**, Oak Park;
Richard E. Woehrle, Berkley, both
of Mich.

[73] Assignee: **M & F Chemicals Inc.**, Greenwich,
Conn.

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Related U.S. Application Data

[60] Continuation-in-part of Ser. No. 202,648, Nov. 26,
1971, abandoned, which is a division of Ser. No.
869,343, Oct. 24, 1969, abandoned.

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204/206, 204/207

[51] Int. Cl. **C23b 5/58**, B60l 9/00, C23b 5/06

[58] Field of Search 204/27, 28, 206, 279, 51,
204/207-211; 191/1 A

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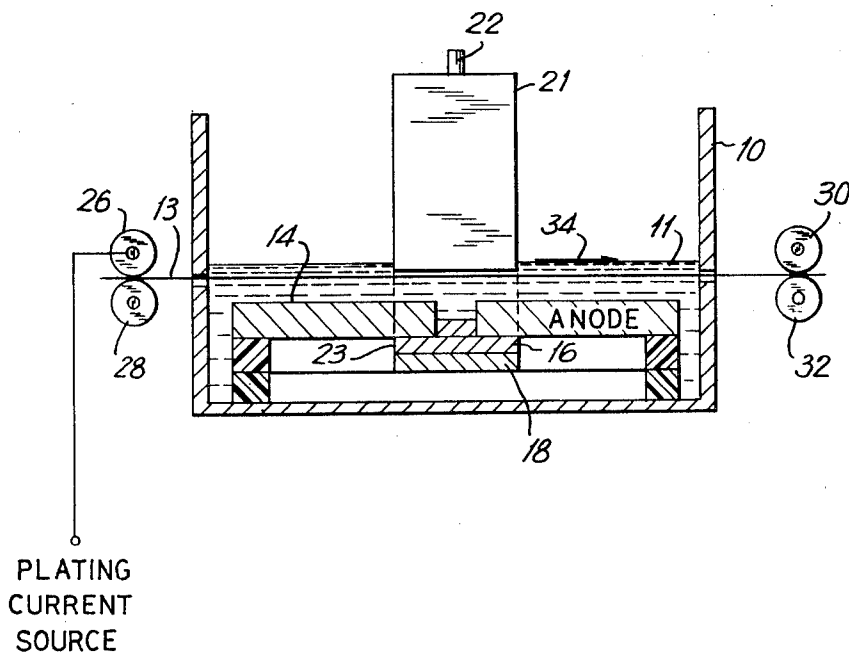
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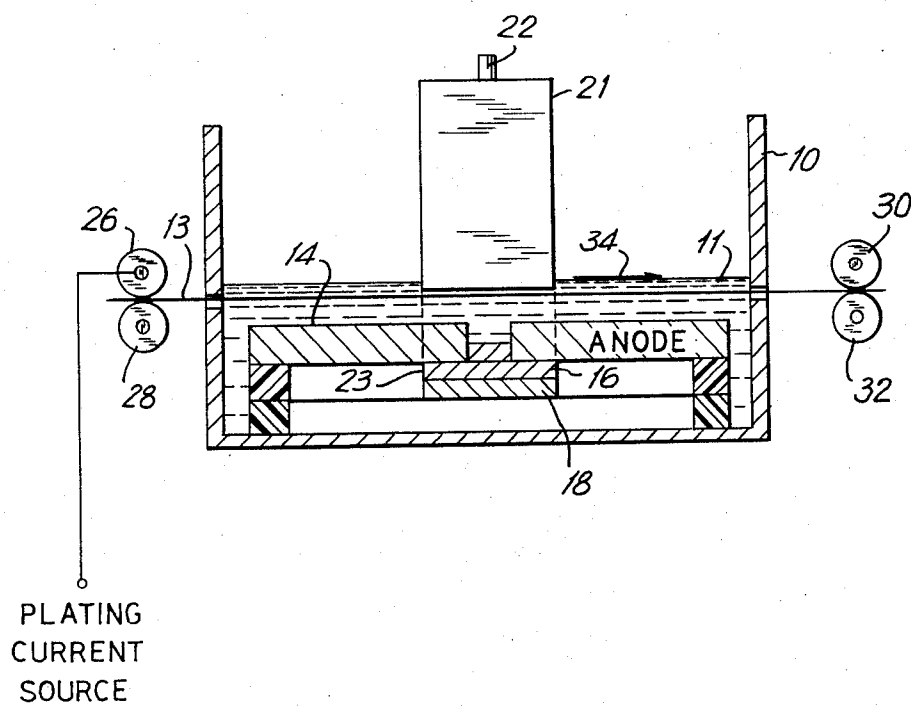
Primary Examiner—John H. Mack
Assistant Examiner—Aaron Weisstuch
Attorney, Agent, or Firm—Kenneth G. Wheelless;
Robert P. Auber

[57] **ABSTRACT**

This invention relates to a method of electroplating a bright protective chromium plate which comprises maintaining a chromium plating bath containing chromic acid and sulfate; maintaining an anode in said bath; passing through said bath a continuously moving continuous strip of thin-gauge metal; passing an electric current through said anode, said bath, and said cathode thereby electroplating a bright protective plate on said moving strip of thin-gauge metal whereby said strip of metal is maintained as cathode, the improvement comprising preventing "arc burns" by passing immediately and without rinsing said moving strip of metal, bearing at least some portion of the contents of said plating bath, from said bath, into contact with a cathodic contact roll outside of said bath, said contact roll, having a contact surface of a metal selected from the group consisting of cast iron, high carbon steel, and carbides each member of said group having a carbon content of at least about 0.7 percent by weight.

2 Claims, 1 Drawing Figure





CHROMIUM PLATING METHOD

This application is a continuation-in-part of U.S. Patent application Ser. No. 202,648, filed Nov. 26, 1971, now abandoned which is a divisional application of U.S. Pat. application Ser. No. 869,343, filed Oct. 24, 1969, now abandoned.

This invention relates to a novel process for electroplating bright, protective deposits of chromium plate on strip metal. More particularly this invention is directed to the electrodeposition of bright, protective chromium plate onto a continuous metal strip moving at high velocity.

Chromium plating of strip metal such as so-called "can stock" may be carried out continuously by passing a continuously moving strip of metal through a plurality of baths wherein the metal may be cleaned, pretreated, washed, and chromium plated. In these steps (particularly the latter), the metal strip may be rendered cathodic by contact with an appropriate source of current.

Typically this may be effected by passing the strip into contact with, e.g. over, a rotating contact roll which may be formed of steel, e.g. stainless steel. Attempts to carry out this operation have been unsuccessful. The moving strip carries with it liquids such as chromic acid solution between successive chromium plating steps. This solution which typically contains inter alia chromic acid, sulfates, fluorides, etc., is highly corrosive and oxidative. The solution may react with the metal, e.g. steel, contact rolls to form a chromate film on the surface thereof or to etch away portions of the roll. In some cases chromium metal deposits may appear on the contact roll itself. As the result of these and other factors, the current carrying ability of the roll may decrease to the point where arcing or sparking may occur or undesirable direct electrical connections may result in high current flow on isolated areas of the contact roll.

Although this may result in increased consumption of electric power, it is primarily disadvantageous in that it generates imperfections on the surface of the moving strip. Specifically the arcing or sparking from the roller to the strip produces on the strip a series of perforations, discontinuities, imperfections, blotches, and areas of decreased corrosion resistance. Furthermore, burned areas may appear on the contact roll. The resulting strip is thus unsatisfactory because of the poor visual appearance of the strip, as well as because of the decreased corrosion resistance of such strip. A reduction in either property may be sufficient to render the plated strip metal unsatisfactory from the commercial standpoint.

It is an object of this invention to provide a method of chromium plating a continuous strip moving at high velocity. It is a further object of this invention to permit current to be passed to a continuously moving strip from a cathodic contact roll with minimum arcing or sparking. Other objects will be apparent to those skilled in the art upon inspection of the following detailed description of the invention.

This invention relates to a method of electroplating a bright protective chromium plate which comprises maintaining a chromium plating bath containing chromic acid and sulfate; maintaining an anode in said bath; passing through said bath a continuously moving continuous strip of thin-gauge metal; passing an electric

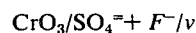
current through said anode, said bath, and said cathode thereby electroplating a bright protective plate on said moving strip of thin-gauge metal whereby said strip of metal is maintained as cathode, the improvement comprising preventing "arc burns" by passing immediately and without rinsing said moving strip of metal, bearing at least some portion of the contents of said plating bath, from said bath, into contact with a cathodic contact roll outside of said bath, said contact roll having a contact surface of a metal selected from the group consisting of cast iron, high carbon steel, and carbides each member of said group having a carbon content of at least about 0.7 percent by weight.

The metal strip employed in the practice of this invention may be, e.g. iron, including its alloys such as stainless steel, etc. In practice of the invention the metal may be a strip or coil of extreme length, typically 30,000 meters or more. The metal may commonly have a thickness of 0.10-2.5 mm., say 0.2 mm. and a width of 0.5-2.0 meters, say 1.0 meter. This metal strip may also be pre-plated with e.g. copper, nickel, etc.

It is a particular feature of the novel process of this invention that it is possible to chromium plate metal without any pretreating or conditioning. For example, if a coil or steel strip is received free of superficial contaminants (such as oil or grease or gross rust areas) it may be subjected to electroplating in the as-received condition. If, however, the continuous metal strip bears a film of grease or oil, it may be desirable to anodically (or cathodically) pretreat the metal strip in an alkaline electro-cleaner. This alkaline electro-cleaner may contain 30-225 g/l of active ingredient. The alkaline electro-cleaner bath may contain inorganic salts, that is, hydroxides, silicates, borates, phosphates, etc., including sodium alkyl sulfates, may be present. The bath may be operated at 60°C.-100°C., say 80°C. with anodic current density of 3-10 asd., say 5 asd. This procedure may thus be used to remove oil and greases.

When the strip bears a substantial portion of gross rust areas, it may be pretreated by acid-immersion. The acid used may comprise 1 to 20 percent, say 10 percent of a suitable mineral acid, typically hydrochloric acid or sulfuric acid.

The chromium plating bath which may be employed in practice of this invention may be an aqueous solution containing 10 g/l-500 g/l, typically 150 g/l-300 g/l, say 225 g/l chromic acid CrO_3 . The bath may also contain catalysts, as herein defined, the ratio of chromic acid to catalysts typically being 10:1 to 150:1, say 80:1. The ratio, as the term is used in this application, refers to the ratio of



wherein each of the quantities is specified in g/l. The symbol F^- may refer to the fluoride-containing catalysts which may be e.g. fluoride or silicofluoride $\text{SiF}_6^{=}$, or other fluoride-containing ions as set forth infra. The symbol ν represents an integer which may be 2 for fluoride complexes, e.g. $\text{SiF}_6^{=}$ and 0.25 for fluoride ion or. Typically, the concentration of catalyst in the bath may be 0.7-50.0 g/l, preferably 1.5-6.0 g/l. The catalyst may include sulfate $\text{SO}_4^{=}$, typically provided as sulfuric acid, strontium sulfate, etc. The sulfate ion may typically comprise 5-85 percent, preferably 10-50 percent, say 30 percent of the total catalyst concentration. It is a particular feature of this invention that the chromium plating bath contains fluoride, typically supplied

as fluoride ion F⁻ or as a complex fluoride. Typically, complex fluorides may include fluoroaluminates, fluoroaluminates, fluorotitanates, fluoroborates, etc. The preferred fluoride ion may be silicofluoride SiF₄, preferably provided as potassium silicofluoride. The preferred catalyst may comprise fluoride in the amount of 15-95 percent, typically 50-90 percent, say 70 percent of the total catalyst.

In the practice of this invention, the temperature of plating may be 27°C.-90°C., typically 50°C.-70°C., say 60°C.

A typical illustrative bath which may be used in the practice of this invention may include the following wherein, unless otherwise specified, all concentrations are in grams per liter (g/l):

TABLE I

Component	Minimum	Maximum	Preferred
CrO ₃	150	300	275
SO ₄ ⁼	0.75	3.0	1.4
SiF ₆ ⁼	1.5	6.0	3.4

*Typically added as sodium sulfate

**Typically added as sodium silicofluoride

The typical illustrative bath of Table I used in the practice of this invention may be formed by dissolving the noted solid compositions in aqueous medium to form a bath containing, e.g. 150 g/l to 300 g/l of CrO₃ and corresponding quantities of the other components.

In practice of the process of this invention a continuous strip of thin-gauge metal, typically so-called "can stock," a steel strip having a thickness of 0.1 to 0.3 mm. and a width of 0.5-2.0 meters may be passed through a series of plating baths. Commonly the strip may be passed through 3-25, typically 5 baths.

As the moving strip is passed between the chromium plating baths, it may pass into contact with, preferably under, a cathodic contact roll having a contact surface which contains a metal selected from the group consisting of cast iron, high carbon steel, and carbides each member of said group having a carbon content of at least about 0.7 percent. The contact roll may be a solid roll i.e. one having a substantially uniform composition throughout its entire mass. Alternatively, it may be a roll having a main body of supporting electrically conductive material e.g. metal, copper, etc. and a surface which has a carbon content of at least about 1.0 percent. Preferably the carbon content may be less than 3.5 percent. It may typically be greater than 0.7 percent; and it may typically be less than 2.5 percent. Commonly, it may contain 2-3 percent carbon.

In a preferred embodiment of the invention, the cathodic contact roll may be fabricated completely from a composition having a carbon content of at least 0.7 percent. Preferably the roll may be formed from iron compositions having a carbon content of at least about 2 percent. The preferred compositions may include cast iron, i.e. iron having more than about 1.7 percent carbon and preferably about 2-6 percent carbon. Typical of such cast iron may be those noted in Table II infra.

TABLE II

Example	Cast Iron	Carbon Content
1	Regular	3.2%

TABLE II-Continued

Example	Cast Iron	Carbon Content
2	Alloy	3.1%
3	Ductile	2.5%
4	Malleable	4.00%
5	Low Phosphate	4.40%
6	Type 1 Ni-Resist	3.0%
7	Type 2 Ni-Resist	3.0%
8	Type D-2	3.00%
9	Type D-3	2.60%

The preferred cast iron is ductile cast iron which may typically have the following composition (in per cent by weight):

C	2.5
Si	2.00
Mn	0.34
S	0.002
P	0.002

The roll may be fabricated from high carbon steel, typically at least 0.7 percent carbon, such steels may have less than 1.5 percent carbon. A typical high carbon steel may be SAE 1090 steel having 0.85 percent carbon. Another typical high carbon steel alloy may be cast steel having 1.10-1.25 percent carbon. The roll may be formed of carbides including tungsten, carbide, refractory metal carbides, etc.

In a preferred aspect of the invention, this roller may be fabricated from a plurality of small (typically 1-6 microns diameter) particles of the carbide combined within a conductive cobalt matrix. A typical composition may be formed by mixing together 75 to 95 percent of tungsten carbide having a particle size of 1-6 microns. These particles may be mixed with a conductive matrix formed of 5-25 percent cobalt. The so-formed mass, in the form of a roller, may be found to be conductive and to otherwise satisfy the objects of this invention.

In another embodiment of this invention the cathodic contact may be fabricated from a conductive metal roll by forming on the surface thereof a contact area having a carbon content of at least about 1.5 percent. Such an embodiment may include a steel support roller having a cylindrical outer surface of e.g. cast iron or tungsten carbide applied to the steel support roller.

Alternately, the roller may include e.g. a metal support assembly having a conductive bar which bears a layer of tungsten carbide which has been flame-sprayed thereon by a plasma jet. A preferred embodiment may be a solid cast iron contact roller having 3.2 percent carbon. As the high velocity moving strip passes over this roller, it is found that it is readily possible to maintain an initial current without any significant increase in contact resistance over a long period of time (i.e. about 8 hours).

Actual experimental runs, using contact rolls prepared in accordance with the invention, resulted in the preparation of improved can stock material over extended periods of time without significant arcing and/or sparking problems during operation.

Referring to the drawing, strip 13 passes between contact roll 26 and backup roll 28. A continuous electroplating line includes a plurality of substantially identical plating cells such as that shown schematically in the drawing. Strip 13 is the cathode in each cell and electrical contact is completed through the novel high

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carbon contact roll 26. Contact roll 30 is the subsequent novel contact roll and the subsequent backup roll is 32. Strip 13 moves continuously above the anodes 14, which anodes are supported by anode support means 16 and 18. Upright 21 is in contact with anode supports 16 and 18 and has thereon the positive terminal 22 for connecting the apparatus to a source of current. The entire anode assembly may be designated 23 since particular anodes and their support is conventional. The plating current source is joined to positive terminal 22 and to cathode contact roll 26 by means not shown. The plating tank 10 contains the chromium plating solution 11.

Although this invention has been illustrated by reference to specific embodiments, modifications thereof which are clearly within the scope of the invention will be apparent to those skilled in the art.

We claim:

1. In a method of electroplating a bright protective chromium plate which comprises maintaining a chro-

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mium plating bath containing chromic acid and sulfate; maintaining an anode in said bath; passing through said bath continuously moving continuous strip of thin-gauge metal; passing an electric current through said anode, said bath, and said cathode thereby electroplating a bright protective plate on said moving strip of thin-gauge metal whereby said strip of metal is maintained as cathode, the improvement comprising preventing "arc burns" by passing immediately and without rinsing said moving strip of metal, bearing at least some portion of the contents of said plating bath from said bath into contact with a cathodic contact roll outside of said bath which has a contact surface of solid cast iron having a carbon content of about 2 to 6 percent by weight.

2. A method of electroplating a bright protective chromium plate as claimed in claim 1 wherein the cathodic contact roll is composed of solid cast iron having about 3.2 percent by weight of carbon.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,870,618 Dated March 11, 1975

Inventor(s) Edgar J. Seyb, Jr. and Richard E. Woehrle

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

The Assignee is incorrectly listed as: M & F Chemicals Inc.,
Greenwich, Conn.

The Assignee should be listed as: M&T Chemicals Inc.,
Greenwich, Conn.

Signed and sealed this 15th day of July 1975.

(SEAL)

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
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