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[54] CHROMIUM ELECTROPLATING

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[30] Foreign Application Priority Data

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[58] Field of Search.....204/51, 43, 44, 105, 123

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[57] ABSTRACT

An improved electrolytically deposited chromium coating is provided having an improved mirror-like brightness using an aqueous solution in the nature of a Bornhauser solution and ions of the class consisting of hexafluoroantimonate and hexafluostannate, as stable catalysts and brightening agents and within a critical content of about 0.7 to 4 percent with relation to the chromium trioxide content.

2 Claims, No Drawings

CHROMIUM ELECTROPLATING

This application is a continuation of my copending application Ser. No. 578,965, filed Sept. 13, 1966, now abandoned, based on the priority date of corresponding German application Ser. No. R 42442 VIb/48a, filed Jan. 18, 1966.

This invention relates to an electroplating bath solution or plating procedure for providing an improved chrome plated metal surface. It particularly pertains to an improved catalytic or brightening means for such a bath.

It has been an object of my invention to provide a new and improved catalytic anion complex for a chromium plating solution and one which will also serve as a brightening agent in a special chromium plating solution such as the Bornhauser solution that has a sodium tetrachromate electrolyte containing tetrachromate ions as the predominant chromium-containing constituent;

Another object has been to provide a catalytic complex agent or ingredient that will have improved stability in a chromium plating solution, that will have a decreased consumption in use, and that will enable the obtaining of an improved chromium plating or coating;

A further object of the invention has been to provide catalytic means having a better dissociating action in a chromium plating solution;

A further object has been to provide an improved chromium plating process;

A still further object has been to devise a process and utilize catalytic means that will enable better control of the type of chromium deposit accomplished and particularly, to provide a single layer coating which has a cracked structure, a crack free or a micro cracked structure;

These and other objects of my invention will appear to those skilled in the art from the description and claims.

It is recognized by those skilled in the art that suitable catalyst ions are needed for the electrodeposition of a chromium coating from an aqueous chromium acid solution. Heretofore such catalyst ions have included sulfate ions (SO_4^{--}), fluoride ions (F^-) and fluosilicate ions (SiF_6^{--}). The use of fluoaluminate ions (AlF_6^{--}), fluoborate ions (BF_4^-), fluotitanate ions (TiF_6^{--}), and fluozirconate ions (ZrF_6^{--}) has also been proposed. Such catalyst ions may be added to the solution either singly or in certain combinations with other effective catalysts, preferably with sulfate ions, either as free acid (e.g. sulphuric acid) or in the form of soluble salts, preferably salts of alkali metals or alkaline earth metals with hydrofluoric or fluosilicic acid. However, barium salts may not be employed when sulfate ions are present, since an insoluble barium sulfate will be precipitated.

I have discovered that complex hexafluoroantimonate or stannate ions (SbF_6^- and SnF_6^{--}) or both are highly advantageous within a critical range as catalyst ions (dissolved in the aqueous solution) for the electrodeposition of chromium in an electroplating bath solution of the class containing chromic acid and also containing sodium tetrachromate ions as the predominant chromium-containing constituent in solution. Further, as to the latter type of solution, such catalysts serve as brighteners to thus eliminate the normal dull matte finish. The complex chemical compositions of these two types as employed, either singly or in combination in a chromium plating solution have been found to produce a greatly improved stability in the electrolyte as, for example, compared with an electrolyte catalyzed with fluoaluminate, fluoborate, fluosilicate, fluotitanate, or fluozirconate ions. Further, the consumption of the new catalysts is materially decreased to provide a process that is much more economical. The color brightness approaches a mirror brightness, in that it is more lightened and particularly so when antimony and tin hexafluoride are included. Also, the corrosion resistance of crack free deposits or coatings that have been obtained is much better than deposits resulting from the use of fluoaluminate, fluotitanate or fluozirconate.

It is well known that there are four types of plating surfaces that may be obtained in a chromium plating operation, e.g., a so-called conventional cracked surface, a so-called crack-free

surface, a so-called micro-cracked surface and a so-called double chromium surface. A solution utilizing the catalysts of the present invention may be controlled, particularly from the standpoint of bath composition, temperature and current density, to desirably provide any one of these four types of surfaces, and to do so while assuring an excellent density of the coatings. I have also found that covering power and current efficiency of the bath are improved, and that properties of the coatings and particularly, brightness, ductility, hardness, abrasion and corrosion resistance and crack formation are improved.

The complex catalyst ions of the invention have been found suitable for use in all chromic acid electrolytes employed for depositing bright chromium coatings, as well as in solutions that contain mono-, di-, tri- and tetrachromates. As intimated above, additional improved results are obtained in chromium plating solutions utilizing sodium tetrachromate as the predominant chromium-containing constituent, in that a brightening action is obtained and the efficient temperature range of operation is such that it may be kept below a point where the sodium tetrachromate would normally tend to break down (below about 100°F), without adversely effecting the operation. However, I have also found that my complexes permit the use of higher temperatures, in that they tend to limit such a breakdown.

The catalysts of my invention provide particularly good results in special chromium plating solutions that are mainly based on sodium tetrachromate, as well as containing free chromic acid and sulfate ions and which may also contain fluoride and other complex fluoride ions, where the molecular proportion of Na_2O to CrO_3 is within a range of about 1 to 3.5 up to 1 to 8 and, as an optimum, within a range of from 1 to 4 up to 1 to 7, and that operate within a temperature range of about 18° to 40°C or 64.4° to 104°F . In such solutions, the proportion of total chromic acid to free chromic acid (both calculated as CrO_3) should be between about 1 to 2.5 up to 1 to 5.

The complex ions of the invention may be added to the electrolyte in the form of their alkali double salts of the type $\text{M}'\text{SbF}_6$ or $\text{M}''\text{SnF}_6 \cdot \text{H}_2\text{O}$. They may also be obtained by chemical reaction in the aqueous chromium bath by adding separately suitable antimony and/or tin compounds with alkali metal fluorides. As an example, potassium fluostannate (K_2SnF_6) may be formed in this way by the addition of corresponding equivalent amounts of tin-IV-fluoride and potassium fluoride.

As customary in chromium plating solutions, the concentrations of the complex catalyst ions of the invention or, in other words, the sum of the fluoantimonate, fluostannate ions and other catalysts which may be present in the solution such, for example, sulfate or fluosilicate ions, are expressed in relation to the concentration of the chromic trioxide (CrO_3) content. In carrying out the invention, the proportion of the total amount of chromic trioxide and of any mono-, di-, tri-, or tetrachromate, expressed as total CrO_3 , e. g., 150 to 600 g/l, to all the catalysts present in the solution, must be within the range of between 0.7 and 4 percent of the total chromium trioxide content. However, as will be noted, the range of the concentration of the ions of the invention, together with other catalyst ions that may be present, is broader than previously possible utilizing known catalyst ions such as, for example, sulfate ions.

I have discovered that when the complex ions of my invention are used in conjunction with sulfate ions in a mixed catalytic plating bath, the proportion of sulfate ions can be reduced, as compared to known sulfate catalyzed or mixed electrolytes (such as containing sulfate ions and fluosilicate ions). Such reduction in quantity may be accomplished to attain the amount used in tetrachromate baths, that is, about 0.15 to 0.5 percent, as calculated in relation to the total chromium trioxide concentration. Incidentally, the proportion of the total chromium trioxide concentration to the concentration of my complex catalyst ions is expressed as the "Molar

ratio" and depends upon a number of factors, such as the type, composition, concentration and purpose of the chromium plating solution, on operating conditions, on the type and condition of the surfaces of the basis material, and on the properties of the coating required. Such a basis material may, for example, be steel, copper, copper alloy, zinc alloy (such as a zinc base die casting), an aluminum alloy, etc.

It has been determined that general operating conditions for utilizing an electrolyte in accordance with my invention containing my complex catalyst ions are not markedly different from those of known electrolytes. However, using my solution,

Deposit thickness = 0.6 to 2.5 μ

It will be further noted that in chromic acid solutions higher bath temperatures of 50° to 55° C and higher current densities of from about 10 to 30 A/dm² produce a crack-free surface, that lower temperatures of 35° to 49° C and lower densities of about 10 to 15 A/dm² produce a cracked surface, and that the use of selenium with higher bath temperatures of 37° to 55° C and the lower current density range of 10 to 20 A/dm² produces a micro-cracked surface. Example No. 13 is illustrative of the upper range of content of total catalyst of about 4 percent (10×100/250).

TABLE I.—EXAMPLES

Number	Grams/liter		Molar ratio CrO ₃ : Na ₂ O	Grams/liter					Total catalyst	Se	Bath temperature, ° C.	Current density, A./dm. ²	Deposit thickness, μ	Crack structure
	Total CrO ₃	Free CrO ₃		SO ₄	SiF ₆	SbF ₆	SnF ₆							
1.....	200	—	—	0.4	—	3.8	—	4.2	—	—	45	15	1	Cracked.
2.....	300	105	6.3:1	1.05	—	2.5	—	3.55	—	—	30	12	0.8	Do.
3.....	450	—	—	1	—	4	—	5	—	—	38	20	1.5	Do.
4.....	250	—	—	0.8	—	3.4	—	4.2	—	—	50	20	1.5	Crack-free.
5.....	400	100	4.8:1	0.9	—	3.2	—	4.1	—	—	35	16	0.6	Do.
6.....	320	120	7:1	1.5	—	0.55	—	2.05	—	0.005 to 0.02	40	10	1.2	Micro-cracked, 1,000 cracks per inch.
7.....	150	—	—	0.3	—	—	1.3	1.6	—	—	48	10	1.1	Cracked.
8.....	300	105	6.3:1	0.7	—	—	2.7	3.4	—	—	25	10	1.3	Do.
9.....	450	—	—	1	—	—	3.2	4.2	—	—	35	12	2	Do.
10.....	300	—	—	0.4	—	—	1.7	2.1	—	—	55	25	1.8	Crack-free.
11.....	400	100	4.8:1	1	—	—	2.9	3.9	—	—	50	20	1.6	Do.
12.....	320	120	7:1	1.5	—	—	0.55	2.05	—	0.005 to 0.02	38	15	2	Micro-cracked, 1,000 cracks per inch.
13.....	250	—	—	1.5	2.1	—	6.4	10.0	—	—	54	30	2.5	Crack-free.
14.....	320	120	7:1	1.5	—	0.4	0.3	2.2	—	0.005 to 0.02	39	12	1.65	Micro-cracked, 1,000 cracks per inch.

there is a greater leeway as to temperature and a better control as to the type of plated surface obtained. Such chromium plating solutions, preferably as used with sulfate or fluosilicate ions, produce chromium plating baths with excellent covering and throwing powers, and higher current efficiencies (between 15 and 22 percent of the theoretical) depending on the bath temperature and current densities. They also have exceptional stability and, as previously noted, a wider current density range, and a higher economic efficiency. Within certain ranges of bath compositions and operating conditions, high corrosion resistance, single layer coatings crack and pore free or micro-crack, and double layer coatings may be produced. The double layer coatings preferably have a first crack free layer and a second micro-cracked layer. In this connection, the most suitable baths for depositing micro-cracked chromium coatings are those which contain a major amount of sodium tetrachromate, in view of the unsurpassed covering and throwing power, as obtained by the use of the complex catalysts. Using catalyst complexes of my invention, the sum of all catalysts present in the bath is critical within a range of about 0.7 to 4 percent, as expressed in relation to the total concentration of chromium trioxide or chromic acid anhydride (CrO₃) in the bath solution.

Table I is illustrative of the coatings produced in accordance with the invention. It will be noted that the examples represent ranges in the aqueous electroplating solution as follows

Total CrO₃ = 150 to 450 g/l

Free CrO₃ = up to 100 to 120 g/l

Molar ratio of CrO₃ to Na₂O when sodium oxide is added = from 4.8:1 to 7:1

SO₄ = 0.3 to 1.9 g/l

SiF₆ = up to 2.1 g/l

SbF₆ = 0.4 to 4.0 g/l

SnF₆ = 0.3 to 6.4 g/l

Total catalysts — 1.6 to 10 g/l

Se = up to 0.01 g/l; have used 0.005 up to 0.02 g/l (up to 0.015 optimum)

Bath temperature = 25° to 55° C or 77° to 131° F

Current density = 10 to 30 A/dm²

The electroplated chromium coating produced on the metal surface in accordance with the invention is characterized by its being deposited from an aqueous chromium trioxide plating solution containing hexafluoroantimonate (hexafluoroantimonate) and/or hexafluorostannate (hexafluorostannate) catalyst ions.

In preparing the bath solution, selenium may be introduced in the form of selenium dioxide (SeO₂) or selenium acid (H₂SeO₄, and fluorides in the form of alkali or alkaline earth metals. A sulfate content may be imparted by adding sulphuric acid or alkali or alkaline earth metals or aluminum or chromium-III-sulfate to a partially neutralized tetrachromate solution before introducing the soluble complexes. If desired, fluorides may be added with the complexes in the form of soluble compounds. The work piece to be chromium plated will be used as a cathode and energization will be accomplished by applying electrical energy to the cathode work piece and to an anode of a suitable material, such as tin or lead. A suitable voltage is 3 to 8 volts, preferably 4 to 6 volts.

I claim:

1. A chromium plating electrolyte for electrolytically depositing chromium plating on a metal cathode which comprises, an aqueous solution containing about 150 to 450 g/l of total chromium trioxide, free chromium trioxide of up to about 120 g/l, sodium tetrachromate ions as the principal chromium containing constituent, sulfate within a range of about 0.3 to 1.9 g/l, dissolved selenium of about 0.005 up to about 0.02 g/l, hexafluosilicate up to about 2.2 g/l, and a complex catalyst of the class consisting of hexafluostannate and hexafluoroantimonate; wherein the hexafluostannate is within a range of about 0.3 to 6.4 g/l and the hexafluoroantimonate is within a range of about 0.4 to 4 g/l, and the total catalyst content consisting of said sulfate, said selenium, said hexafluosilicate and said complex catalyst is within a range of about 1.6 to 10 g/l.

2. A chromium plating electrolyte as defined in claim 1 wherein the aqueous solution contains sodium tetrachromate with a Molar ratio of chromium trioxide to sodium oxide of about 4.8 to 1 up to about 7 to 1.

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