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CHROMIUM PLATING

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This invention relates to the electrodeposition of chromium from aqueous acidic hexavalent chromium solutions, and especially to the use of thorium fluorides in aqueous acidic hexavalent chromium solutions to make possible improved chromium plate from operationally simplified baths. More particularly, it relates to the use of saturation concentrations of strontium sulfate with saturation concentrations of a thorium fluoride in chromic acid solutions to make possible operationally simplified baths which give improved covering power in recessed areas (low current density areas). Not only is the chromium covering power improved, but no strong discoloration or iridescent films are formed where the chromium plate leaves off in the very low current density areas. Other advantages made possible by the use of saturation concentrations of thorium fluorides in the chromic acid baths will be detailed hereinafter.

In order to electrodeposit chromium from acidic hexavalent chromium solutions, that is, chromic acid solutions, it was early established that it was necessary to have small amounts of certain anions such as sulfate or fluoride ions present and these ions were named "catalyst" ions. In the progress of the art of chromium plating from acidic hexavalent chromium baths, the use of mixed catalyst anions, such as combinations of sulfate ions with fluoride ions, sulfate with fluosilicate ions, sulfate with fluoborate ions, sulfate with fluoaluminate ions, sulfate with fluotitanate ions, sulfate with fluozirconate ions and sulfate with boric acid were employed to make possible chromium plating baths of improved covering power, and of simpler control. In this connection, reference is made to the following U.S. Patents 1,844,751, 2,063,197, 2,042,611, 2,640,021, 2,640,022, and 2,952,590. In particular, reference is made to Lukens U.S. 2,042,611, Passal U.S. 2,640,021, and Stareck U.S. 2,640,022 and 2,952,590, for the development of the self-regulation feature of the catalyst acid anion radical content of the chromium plating baths. Lukens used saturation concentrations of the slightly soluble strontium sulfate with or without added strontium chromate, to maintain the sulfate ion concentration in chromic acid baths containing about 200 grams per liter of CrO_3 or less, Passal improved on this by also using with saturation concentrations of strontium sulfate, sparingly soluble potassium silicofluoride fluosilicate), and Stareck made further improvements by using with the saturation concentrations of strontium sulfate and potassium silicofluoride, mixed suppressing agents such as strontium chromate and potassium dichromate to better control the concentrations of sulfate and silicofluoride ions by common ion effects. Stareck also employed fluoaluminate, fluotitanate and fluozirconate ions instead of fluosilicate to use with controlled sulfate ion concentrations.

The standard or conventional chromium bath employing only the sulfate anion as catalyst and used for plating on nickel, iron, yellow brass or copper has been the 100 to 1 ratio of chromic acid anhydride (CrO_3) to sulfate ion. Thus, in a 200 gram per liter CrO_3 bath, 2 grams per liter of sulfate ion would be used, and in a 400 gram/liter CrO_3 bath, 4 grams/liter of sulfate ion would be used. If one uses instead a ratio of 200 to 1 of CrO_3 to SO_4 and plates on top of nickel, copper, yellow brass or steel, only an iridescent non-metallic chromium chromate

(rainbow) film instead of chromium plate is obtained. In particular, if chromium plating is attempted on top of a freshly plated bright nickel surface, from an aqueous solution containing, for example, 340 grams/liter (45 oz./gal.) of chromic acid and saturated with strontium sulfate at, for example, about 50–52° C. (125° F.), and using "dead" entry into this chromic acid bath (that is, the direct plating current is turned on only after the nickel plated panel is immersed in the bath), no chromium plate is obtained on the nickel sulface, only a non-metallic iridescent film of a basic chromic chromate results.

It has now been found that a fluorine-containing thorium compound such as thorium tetrafluoride, thorium fluoborate, thorium fluosilicate, or mixtures, etc., which are practically insoluble in water and only slightly soluble in chromic acid solutions containing about 100 to 500 grams/liter of chromic acid are unusual in cooperating with saturated strontium sulfate in the chromic acid baths to produce bright chromium plate of exceptional covering power on nickel, brass, copper and steel. The presence of the thorium tetrafluoride and/or the thorium fluoborate or thorium fluosilicate in the bath saturated with the strontium sulfate makes possible the deposition of bright chromium plate over a very wide cathode current density range even with dead entry of the nickel plate into the chromium plating bath. The thorium fluorides can be used in concentrations of about 0.2 gram/liter to saturation concentrations. Saturation concentrations of the thorium fluorides in the chromic acid baths do not cause any harmful effects in conjunction with saturation concentrations of strontium sulfate, such as greatly diminishing the covering and throwing power of the chromium deposit and producing dull white areas in the high current density chromium plate. In this very important respect, the saturation concentrations of thorium fluorides act quite differently than saturation concentrations of other inorganic fluorides which were tested, such as calcium fluoride, strontium fluoride, potassium or sodium fluosilicate (silocofluoride). These latter fluorides and silicofluorides when used in saturation concentrations in the chromic acid solutions diminish the covering and throwing power of the chromium plate. It is for this reason that suppressing agents (for common ion effects) must be used in conjunction with saturation concentrations of these latter fluorides.

It was also found that adding boric acid up to saturation concentrations to the chromic acid baths containing the thorium tetrafluoride or the thorium fluoborate, or the thorium fluosilicate did not adversely affect the activation and "catalyst" properties of the thorium fluorides. In fact it helped the activation effect. Adding fine silica powder or silicic acid or sodium silicate to the chromium plating baths containing the thorium fluorides did not adversely affect the activation and catalyst properties of the thorium fluorides in the chromic acid baths containing saturation concentrations of strontium sulfate. In the case of boric acid additions of about 1 gram/liter to saturation appear to give small but definite cooperative effect. About 6 to 8 grams per liter of the thorium fluorides appear to be more than sufficient to saturate the chromic acid baths. The best or optimum covering power chromium plating baths were obtained by the use in chromic acid baths containing 300–350 grams/lier CrO_3, of saturation concentrations of strontium sulfate and saturation concentrations (2 to about 6 grams/liter) of thorium tetrafluoride and/or thorium fluoborate, or thorium fluosilicate, and with the use of perfluoro para ethyl cyclohexyl sulfonic acid in concentrations of about 1 to 3 grams/liter.

Whether thorium tetrafluoride (ThF_4) ionizes to $ThFl_3^+$, $ThFl_2^{++}$, etc., and these complex ions are also activators in the chromium bath is not known, but re-

gardless of its mechanism of ionization, the fact is that saturation concentrations of the thorium tetrafluoride or thorium fluoborate or thorium fluosilicate cooperate with saturation concentrations of strontium sulfate to give chromium plating baths of high covering power on nickel, steel, stainless steel, copper, brass and aluminum. As far as we have been able to ascertain this is the first time thorium fluorides have been used in acidic hexavalent chromium plating baths. The thorium cation makes possible the simplest regulation of the fluoride, silicofluoride (fluosilicate) and fluoborate ion concentrations in chromic acid solutions.

Instead of using strontium sulfate as the source of the sulfate ion, it is possible to use with the thorium fluorides any source of sulfate ion that is less than about one hundredth the concentration of chromic acid and preferably in the ratio of about 120 to 1 to about 200 to 1 of chromic acid anhydride (CrO_3) to sulfate ion.

Actually, once it was found that the concentration of fluorides or complex fluorides could be simply controlled at low concentrations with the use of the thorium cation without the need of the additional variable of soluble suppressing salts, it now became possible to use the sulfate ion concentration at maximum efficiency for maximum covering power over bright nickel surfaces of varying degrees of passivity. Bright nickel plate obtained from a nickel plating bath that has been freshly treated with activated carbon, or obtained from a freshly made up bath, is easier to chromium plate with good covering power and with the absence of whitish streaks in the chromium plate than bright nickel obtained from heavily used baths or from bright nickel baths containing high concentrations of brightener for maximum leveling and brilliance. The bright nickel plates from the latter baths are more passive, and this condition often requires a higher concentration of sulfate ion or fluoride ion in the chromium plating bath than would otherwise be necessary to obtain a bright chromium plate free of white streaks and with maximum covering power. Since it is far easier to analyze for sulfate ion in the chromium plating bath than fluoride ion, it is thus much simpler to obtain maximum chromium coverage on any of the bright nickel surfaces described above, from a chromium plating bath with low and controlled concentrations of fluoride or complex fluoride ions by merely gradually raising the sulfate ion concentration above that given by saturation concentrations of strontium sulfate. That is, by the use of saturation concentrations of both the thorium fluorides and the strontium sulfate, the acidic hexavalent chromium bath in general needs no control of the catalyst concentrations, but if the bright nickel is overly passive, a small addition of sulfuric acid or sodium sulfate can very easily control and eliminate any whitish streaks in the chromium plate. Of further help in eliminating white streaks in the chromium plate is the use of a pre-dip of the bright nickel plate in dilute chromic acid (about 5 to 15 grams/liter of chromic acid) before entry into the chromium bath.

All of the data obtained seems to indicate that the thorium fluorides are operating more as activators of passive surfaces of nickel, brass or copper, that is, of the surface being plated upon, than as catalyst, in the sense that sodium or potassium silicofluoride or fluosilicic acid or calcium fluoride act as catalysts in promoting chromium plating from pure chromic acid solutions, such as 100–500 grams/liter concentrations of chromic acid. For example, about 1 gram/liter of sodium or potassium silicofluoride or calcium fluoride added to the pure chromic acid solutions will act as catalyst and make possible the electrodeposition of chromium metal, whereas 1 gram/liter and higher additions up to saturation of the thorium fluorides do not make possible significant electrodeposition of chromium from pure chromic acid solutions containing, for example, about 300–400 grams/liter CrO_3.

The acidic hexavalent chromium plating baths may be made up from straight chromic acid anhydride or chromic acid, or from mixtures with dichromates, chromates, and polychromates. It is generally preferred to use straight chromic acid or chromic acid anhydride. The presence of cations such as Na, K, Li, Mg and Ca are not detrimental, but they are best kept in low concentration values. The important metallic cations are the metallic cations of this invention, the thorium and thorium fluoride complexes to control the fluoride concentration which is normally difficult to control, unlike the sulfate concentration which is easy to control. Strontium ions may be present from strontium chromate or dichromate, but it is generally preferred that the strontium ions should be mainly from the saturation concentrations of strontium sulfate.

Thus, with the use of the saturation concentrations of the thorium fluorides with saturation concentrations of strontium sulfate there is no need to use common ion effects to control the catalyst concentrations, that is, there is no need, for example, to use potassium dichromate in high concentrations to obtain a significant common ion effect with potassium silicofluoride when the latter is used as a co-catalyst with sulfate. The presence of high concentrations of potassium ions tends to cause the salting out of the important and valuable stable antimisting agent perfluoro n-octyl sulfonic acid, and this is a drawback in this respect, besides the fact that it is an added variable.

The thorium tetrafluoride, thorium fluoborate, thorium silicofluoride (fluosilicate), can be replaced partially or entirely by other thorium fluorides such as thorium fluoaluminate, thorium fluotitanate, thorium fluozirconate, thorium oxyfluoride and mixtures thereof and any of these single or mixed salts can be used with saturation concentrations of strontium sulfate.

Below are listed several examples of baths of this invention.

Example I

340 grams/liter (45 oz./gal.) of chromic acid anhydride (CrO_3)
Saturation concentrations of $SrSO_4$ (excess present)
Saturation concentrations of thorium tetrafluoride (1–4 grams/liter)
0 to saturation concentrations of boric acid
0 to 3 grams/liter of perfluoro para ethyl cyclohexyl sulfonic acid (1 to 3 grams/liter preferred)
Temperature 115–130° F. (46–55° C.)

Example II

200–400 grams/liter of CrO_3
Saturation concentrations of $SrSO_4$ (excess present)
Saturation concentrations of thorium fluoborate (2–6 grams/liter, excess present)
1–3 grams/liter of perfluoro para ethyl cyclohexyl sulfonic acid
Temperature 105–140° F.

Example III

150–400 grams/liter CrO_3
Saturation concentrations of $SrSO_4$ or 140 to 1 ratio of CrO_3/SO_4
0.4 to 3 grams/liter of thorium tetrafluoride, thorium fluoborate, thorium fluosilicate, thorium fluoaluminate, thorium fluotitanate, thorium fluozirconate, or mixtures
0 to saturation concentrations of boric acid
5 grams/liter of perfluoro para ethyl (or methyl) cyclohexyl sulfonic acid (or the Na, K, Ca, etc., salt)
Temperature 105–140° F.

Example IV

200–400 grams/liter CrO_3
Saturation concentrations of thorium fluosilicate (2–6 grams/liter)
Saturation concentrations of strontium sulfate
1–3 grams/liter of perfluoro para ethyl cyclohexyl sulfonic acid
Temperature 105–140° F.

The most economical form to obtain the thorium cation is as the hydrated thorium oxide, that is, as thorium hydroxide. This hydrated thorium compound can be added directly to acidic hexavalent chromium plating baths containing for example, potassium or sodium fluosilicate (silicofluoride) or fluosilicic acid, and by formation of thorium fluosilicate immediately put the fluoride concentration in optimum concentration. This likewise would also be true if the chromic acid bath had calcium fluoride or hydrofluoric acid present, or strontium fluoborate or fluoboric acid present, or the ferric, aluminum, zirconium or titanium complex fluoride anions present, that is the particular thorium fluoride would form preferentially and put the fluoride ion under control of the thorium cation. In making up new chromium plating baths, the thorium fluosilicate, fluoborate or fluoride could be formed directly in the chromic acid bath by adding the thorium hydroxide to the proper molar quantity of the particular fluoro acid, or the thorium fluosilicate, fluoborate, or tetrafluoride could be added as such to the bath. The same procedure can be followed for thorium fluoaluminate, thorium fluotitanate and thorium fluozirconate. Concentrations of the thorium fluorides greater than about 8 grams/liter are usually not necessary as this concentration leaves a sufficient excess of undissolved thorium fluoride compound at the bottom of the plating solution to allow for maintenance and easy control.

Instead of using thorium hydroxide, thorium chromate, bichromate, thorium carbonate, thorium oxalate, or thorium sulfate could be added to the baths containing the fluo-acids or their salts. If excess sulfate ions are present they can be eliminated by adding barium carbonate or hydroxide or strontium carbonate.

With plating of thick chromium of 1 to 10 miles thickness or higher, the plate obtained is very bright with the saturation concentrations of a thorium fluoride and saturation concentrations of strontium sulfate in chronic acid concentrations of 300–350 grams/liter, at bath temperatures of 115–125° F., also the plate is much less prone to stress-cracking. Thus, for crack-free bright chromium plate up to about 0.1 mil, it is less critical to use than many previous crack-free formulations. Also, it is suitable to use these chromium baths to obtain single or dual layers of micro-cracked chromium by using the more dilute concentrations of chromic acid such as 180–200 grams/liter.

What is claimed is:

1. A bath for the electrodeposition of chromium plate comprising an aqueous acidic hexavalent chromium solution containing a ratio of concentrations of CrO_3 to sulfate ion greater than about 100 to 1, and less than about 200 to 1, and containing at least one fluorine-containing thorium compound in a concentration of about 0.2 gram/liter to saturation concentrations.

2. A bath in accordance with claim **1** wherein said hexavalent chromium solution is chromic acid in a concentration of about 100 to about 500 grams/liter.

3. A bath in accordance with claim **1** wherein said bath contains thorium tetrafluoride.

4. A bath in accordance with claim **1** wherein said bath contains thorium fluoborate.

5. A bath in accordance with claim **1** wherein said bath contains thorium fluosilicate (silicofluoride).

6. A bath in accordance with claim **1** wherein said bath contains thorium fluoaluminate.

7. A bath in accordance with claim **1** wherein said bath contains thorium fluotitanate.

8. A bath in accordance with claim **1** wherein said bath contains thorium fluozirconate.

9. A bath in accordance with claim **1** wherein said sulfate ion is derived from saturation concentrations of strontium sulfate in said acidic hexavalent chromium plating solution.

10. A method of electrodepositing chromium which comprises passing current from an anode to a cathode to be coated in an aqueous acidic hexavalent chromium solution containing a ratio of concentrations of CrO_3 to sulfate ion greater than about 100 to 1 and less than about 200 to 1, and containing at least one fluorine-containing thorium compound in a concentration of about 0.2 gram/liter to saturation concentrations.

11. A method in accordance with claim **10** wherein said hexavalent chromium solution is chromic acid in a concentration of about 100 to about 500 grams/liter.

12. A method in accordance with claim **10** wherein said bath contains thorium tetrafluoride.

13. A method in accordance with claim **10** wherein said bath contains thorium fluoborate.

14. A method in accordance with claim **10** wherein said bath contains thorium fluosilicate (silicofluoride).

15. A method in accordance with claim **10** wherein said bath contains thorium fluoaluminate.

16. A method in accordance with claim **10** wherein said bath contains thorium fluotitanate.

17. A method in accordance with claim **10** wherein said bath contains thorium fluozirconate.

18. A method in accordance with claim **10** wherein said sulfate ion is derived from saturation concentrations of strontium sulfate in said acidic hexavalent chromium plating solution.

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