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UNITED STATES PATENT OFFICE.

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PROCESS OF ELECTRODEPOSITING CHROMIUM AND OF PREPARING BATHS THEREFOR.

No Drawing. Application filed December 19, 1925. Serial No. 76,529.

To all whom it may concern:

Be it known that I, COLIN G. FINK, a citizen of the United States of America, residing at New York, county of New York, and State of New York, have invented certain new and useful Improvements in Processes of Electrodepositing Chromium and of Preparing Baths Therefor, of which the following is a specification.

This invention relates to the electrodeposition of chromium, and to the preparation of electrolytic solutions for use therein, and aims to provide improvements therein.

For nearly a century there has appeared in the literature considerable matter in respect to chromium plating, and in that literature the use of chromic acid as an electrolyte, as well as the use of various so-called addition agents has been proposed. Notwithstanding these disclosures, a practical and commercially available process of electroplating chromium has not heretofore been known, nor have any of the attempts to establish the commercial art of electrodepositing chromium ever satisfied the test of actual commercial requirements. What attempts have been made have always given uncertain and unreliable results and have resulted in ultimate failure as a reliable or satisfactory commercial process.

According to my invention, I pass an electric current (from an anode to a cathode, the latter serving as the object on which the metal is to be deposited) through a suitable chromium-carrying electrolytic solution, in the presence of a catalyst. The catalyst is, as usual, a bystander which does not enter into the electro-chemical decomposition. The chromium-carrying electrolyte which I have found suitable for my process, is a solution of chromic acid, its degree of concentration as regards baths of commercial interest ranging from about 150 grams per litre to saturation.

The catalytic agent which I use is one having an acid radical which is stable in the bath and which remains stable under the actions which occur in the process when the current is passed through the bath. This catalytic agent is one which performs its action at the cathode. Substances which I find available as catalytic agents and which remain stable, are acids and bases having a sulphate radical; acids and bases having a fluoride radical; acids and bases which have a phosphate radical; and acids and bases which have a borate radical.

The amount of the catalytic agent or agents (stable radicals) means the total of such agents whether of one kind or another that are actually in the bath, that is, all of the stable radicals must be computed, whether of one kind or another, and whether originally in the chromic acid, in the catalytic agent, or otherwise entering the bath, and this is best ascertained by analysis of the final solution and not computed from analyses of the several materials entering into it such as chromic acid, catalytic agent, etc., as these are difficult to make and the analyses such as are now supplied with these materials cannot be relied upon. The quantities of catalytic agent (stable radicals) which is necessary in the bath for reliable results should be total within the limits given, and the bath made up by adding to or subtracting from the quantity of catalytic agent (stable radicals) already present in the chromic acid solution the necessary amount to bring the total amount up to or down to the given limits, and regulated within said given limits for continuous operation.

When unstable radicals are present in the solution, account must be taken thereof and of their evanescent character. Therefore, when unstable radicals (as acids and bases having a nitrate or organic radical) are present, they must be initially included in the totality of catalytic agent, and replaced as they are lost, the replacement rationally being with stable radicals. Alternatively, the unstable radicals may be initially eliminated. The bath reaches a permanent efficacy when the total catalytic agent or agents are stable radicals (and the concentration of chromic acid is maintained).

I maintain on the cathode a definite film of hydrogen, which must not be too thin or too thick. I have discovered that the chromium ion needs to be protected as it gives up its charge on reaching the cathode. This protection I provide by means of the hydro-

gen film. I maintain this film by the electric current, and I make the amount or value of the total current greatly in excess of that carried as a charge by the chromium ions which are deposited. This excess of current energy I employ in releasing hydrogen at the cathode to maintain said film. My observation is that, activated by the catalytic agent, chromic acid, or it may be another compound of chromium formed in the bath) undergoes reduction when the current is passed, releasing a chromium ion in the field of attraction of the cathode. It moves with a certain velocity toward the cathode. The hydrogen film should not be so thick as to prevent the discharge of this chromium ion at the cathode. Yet it should be thick enough to protect the chromium ion from oxidation during nascence and until the cathode is reached and the ion discharges. The chromium ion, I find, needs this protection of the hydrogen film, since the chromic acid is an active oxidizing agent and the chromium ion is extremely sensitive to oxidation. The density and thickness of this hydrogen film is definable in terms of current density and temperature, and the current densities and temperatures which correspond to efficacious hydrogen film thickness are best found empirically. To do this, I immerse a copper or brass sheet of metal as a cathode in a bath of known composition and temperature and regulate the current (by the rheostat for example) up to or down from a strength where no deposit occurs, until a spectre-like mist or cloud appears against the background of the copper or brass cathode, which is a visual indication of the initiation of the deposition of chromium. Noting the current density at which the mists appear when increasing and decreasing the current strength from above and from below those densities at which no deposit occurs, the current density limits for the given temperature of the bath, are ascertained. The current density limits for ranges of temperature are likewise ascertained.

The amount of stable radicals (catalytic agent) in the bath should approximate 2.5 grams, be not less than 1 gram, and not exceed 5 grams of sulphate radical, or an equivalent amount of the other radicals herein mentioned, per litre of a solution containing 250 grams per litre of chromic acid.

The amount of catalytic agent (stable radicals—or stable and unstable) will be proportional to the concentration of chromic acid in the solution. That is, for a solution containing 500 grams per litre of chromic acid, the amount of sulphate radicals will be twice the amount given for a solution containing 250 grams per litre of chromic acid.

Knowing the amount of sulphate radicals to use per litre of solution, it is a simple matter to ascertain the amount of any radical which is equivalent to a given quantity of sulphate radicals.

If there are mixed stable radicals in the bath, the amount of each of the several radicals should equal an eqivalent amount of sulphate radicals. If there are unstable radicals in the bath, these should be initially included with the other radicals in the total given above, the unstable radicals being calculated as an equivalent amount of sulphate radicals. As the unstable radicals disappear, their deficiency should be made up with an equivalent amount of stable radicals (sulphate for example).

According to my invention, the bath may advantageously be made from commercial grades of chromic acid. This commercial acid contains a number of radicals (stable and unstable) which act as catalytic agents. The amount of these radicals is determined, and there is then added to the bath (or eliminated therefrom) enough of the catalytic agent to make the total radicals in the bath equal or equivalent to 2.5 grams of sulphate radicals. The unstable radicals are replaced in course of time with stable radicals.

The hydrogen film of proper thickness may be obtained over quite a range of temperatures, by suitably adjusting the current-density at the cathode. For temperatures of 15° C. to 40° C., the proper film is obtained with current densities from ¼ to 1 ampere per square inch.

The present invention accordingly provides a practical, reliable and commercially available process for electro-depositing chromium from chromic acid solutions and a reliable and commercially adaptable method of preparing the chromic acid bath or electrolyte.

What is claimed is:—

1. A method of electrodepositing chromium from solutions of chromic acid, comprising reducing chromic acid at the cathode in the presence of a catalyst and of a protecting hydrogen film.

2. A method of electrodepositing chromium from solutions of chromic acids, comprising reducing chromic acid at the cathode in the presence of a catalyst and of a protecting hydrogen film, said film being of a thickness sufficient to prevent oxidation of the chromium ion released at the cathode and admitting of the ion passing therethrough to the cathode.

3. A method of electrodepositing chromium from solutions of chromic acid, comprising reducing chromic acid at the cathode in the presence of a catalyst and of a protecting hydrogen film, said film being of a thickness maintained by an excess of current determined as described.

4. In a method of electrodepositing chro-

mium from solutions of chromic acid, reducing the chromic acid at the cathode by a catalyst, said catalyst being a radical which normally is an anion.

5. In a method of electrodepositing chromium from solutions of chromic acid, reducing the chromic acid at the cathode by a catalyst, said catalyst being a sulphate radical not exceeding the proportion of 5 grams per litre of solution having a concentration of 250 grams chromic acid, or an equivalent amount of an equivalent radical or radicals.

6. In a method of electrodepositing chromium from solutions of chromic acid, reducing the chromic acid at the cathode by a catalyst, said catalyst being a sulphate radical not exceeding the proportion of 5 grams per litre of solution having a concentration of 250 grams chromic acid, or an equivalent amount of an equivalent radical or radicals, the total of said radicals being stable radicals.

7. In a method of electrodepositing chromium from solutions of chromic acid, reducing the chromic acid at the cathode by a catalyst, the total of said catalyst being stable and unstable radicals, not exceeding an amount equivalent to the proportion of 5 grams of sulphate radicals per litre of solution containing 250 grams of chromic acid.

8. In a method of electrodepositing chromium from solutions of chromic acid, reducing the chromic acid at the cathode by a catalyst, the total of said catalyst being stable and unstable radicals not exceeding an amount equivalent to the proportion of 5 grams of sulphate radicals per litre of solution containing 250 grams of chromic acid and replacing the unstable radicals during the progress of the deposition to maintain the aforesaid total amount of cataylst.

9. In a method of electrodepositing chromium from solutions of chromic acid, reducing the chromic acid at the cathode by a catalyst, the total of said catalyst being stable and unstable radicals not exceeding an amount equivalent to the proportion of 5 grams of sulphate radicals per litre of solution containing 250 grams of chromic acid and replacing the unstable radicals with stable radicals during the progress of the deposition to maintain the aforesaid total amount of catalyst.

10. In a method of electrodepositing chromium from solutions of chromic acid, reducing the chromic acid at the cathode by a catalyst, the total of said catalyst being stable radicals not exceeding an amount equivalent to the proportion of 5 grams of sulphate radicals per litre of solution containing 250 grams of chromic acid.

11. In a method of electrodepositing chromium from solutions containing compounds thereof, maintaining at the cathode a hydrogen film sufficient to protect the chromium ion from oxidation while depositing on the cathode.

12. In a method of electrodepositing chromium from solutions containing compounds thereof, maintaining at the cathode a hydrogen film sufficient to protect the chromium ion from oxidation while depositing on the cathode, said hydrogen film being maintained by current of densities for different degrees of temperature ascertained as herein described.

13. A method of electrodepositing chromium from solutions of chromic acid, comprising reducing chromic acid at the cathode in the presence of a catalyst and of a protecting hydrogen film, the total of said catalyst being stable radicals not exceeding an amount equivalent to the proportion of 5 grams of sulphate radicals per litre of solution containing 250 grams of chromic acid.

14. A method of electrodepositing chromium from solutions of chromic acid, comprising reducing chromic acid at the cathode in the presence of a catalyst and of a protecting hydrogen film, the total of said catalyst being stable and unstable radicals not exceeding an amount equivalent to the proportion of 5 grams of sulphate radicals per litre of solution containing 250 grams of chromic acid, and replacing the unstable radicals during the progress of the deposition to maintain the aforesaid total amount of catalyst.

15. A method of electrodepositing chromium from solutions of chromic acid, comprising reducing chromic acid at the cathode in the presence of a catalyst and of a protecting hydrogen film, said film being of a thickness sufficient to prevent oxidation of the chromium ion released at the cathode and admitting of the ion passing therethrough to the cathode, the total of said catalyst being stable radicals not exceeding an amount equivalent to the proportion of 5 grams of sulphate radicals per litre of solution containing 250 grams of chromic acid.

16. A method of preparing solutions for electrodeposition of chromium, comprising dissolving commercial grades of chromic acid ascertaining the amount of catalytic radicals therein, and adding to or removing from said solution sufficient catalytic radicals to make a total amount of catalytic radicals present in the solution equivalent to the proportion of 5 grams or less of sulphate radicals per litre of solution containing 250 grams of chromic acid.

17. A method of preparing solutions for electrodeposition of chromium, comprising dissolving commercial grades of chromic acid ascertaining the amount of catalytic stable and unstable radicals therein, removing the unstable radicals, and adding to or removing from said solution sufficient catalytic (stable) radicals to make a total amount of

catalytic radicals present in the solution equivalent to the proportion of 5 grams of sulphate radicals per litre of solution containing 250 grams of chromic acid.

18. A process for the continuous electrodeposition of chromium, comprising regulating the content of stable radicals (catalytic agent) in the bath to an amount not exceeding the proportion of 5 grams of sulphate radicals per litre of solution containing 250 grams of chromic acid.

In witness whereof, I have hereunto signed my name.

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DISCLAIMER.

1,581,188.—*Colin G. Fink*, New York, N. Y. PROCESS OF ELECTRODEPOSITING CHROMIUM AND OF PREPARING BATHS THEREFOR. Patent dated April 20, 1926. Disclaimer filed June 20, 1928, by *United Chromium, Incorporated*, assignee by mesne assignments.

Hereby disclaims:

(*a*) From claims 1, 2, 4, 11, and 12 any method of electrodepositing chromium in which regulating a radical component of the bath (other than or in addition to the chromic acid radical) is not practiced in maintaining the efficiency thereof;

(*b*) From claims 5, 6, 10, 13, and 15 any method of electrodepositing chromium in which regulating within the limits specified a radical component of the bath (other than or in addition to the chromic acid radical) is not practiced in maintaining the efficiency thereof.

[*Official Gazette July 10, 1928.*]

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