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PROCESS FOR THE ELECTROLYTIC
DEPOSITION OF CHROMIUM

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The process which has hitherto been used on the technical scale for the electrolytic production of chromium deposits consists essentially in using chromic acid as the electrolyte. Deposition of chromium, however, only takes place from these solutions when using relatively high current densities, which must be at least above 2 amps per square decimeter. It is objectionable to work with chromic acid baths in view of the devices necessary for removing the unhealthy chromic acid mist and not without danger to the operator.

It has already been proposed to use chromium sulphate, chrome alum, chromium chloride, chromium acetate, chromium boro-fluoride or mixtures of these or other chromium salts, but these cannot be used on the large scale in a practical sense. Chromium deposited from trivalent chromium compounds, or chromium compounds of still lower valency usually strips off very easily. A deposit of chromium can also only be obtained from these solutions by using very high current densities. Data as to the use of current densities of 10 amps, 40 amps and even 67 amps per square decimeter have been given in the literature. The deposits are very brittle owing to the high degree of occlusion of hydrogen, and usually contain small quantities of chromium oxide.

The invention relates to a process which allows of producing a ductile bright chromium deposit which does not strip off even when the layer is thick, and without using chromic acid. The new process is characterized by the feature that the electrolytic deposition of the chromium is effected from chromium solutions which are kept as neutral as possible, to which are added substances which retain the oxide of the chromium or other metals or corresponding basic salts in solution, even in a neutral bath. According to the present invention trivalent chromium compounds such as chromium acetate, sulphate, chloride and the like can be used as the initial substances in composing the bath. The simple form of the chromium salts or other chromium compounds which is usually violet in colour or a complex form usually green can be used for this purpose. Sodium citrate, Rochelle-salt or other salts of an acid having a similar action such as oxalic acid, phenol-sulphonic acid, etc., are used as the substances added to the bath. Alcohol, glycerine, sugar and similar compounds may also be used as the addition substances as they are also suitable for retaining chromium oxide in solution even when the bath has a neutral reaction. Small quantities of the substances mentioned have a favour-

able effect upon the deposition of the chromium, but the full effect only comes into play when these addition substances are present in such quantities as to prevent any deposition of oxide while the bath is in use.

The bath composed in this manner is made as neutral as possible, the hydrogen number pH in the electrolyte being kept more or less within the limits of 4 to 6. It is preferable to approach more nearly to the upper limit of the hydrogen number since it has been found that the current yield is more favourable thereby. The presence of divalent chromium compounds in the electrolyte does not in general have an adverse effect as long as the neutral reaction is not adversely influenced thereby. The electrolyte must consist essentially of tri-valent chromium compounds particularly as it is reasonable to suppose that the deposition of the metal is to take place from the trivalent condition. There is no object in adding hexavalent compounds which are capable of adversely affecting the neutral reaction of the bath. The higher degree of acidification should not, however, be made under any circumstances. It is advantageous to add merely weak boric acid or similar acids or salts in order to buffer the hydrogen ion concentration.

Separation of oxide impurities from the electrolyte during electrolysis is completely avoided in a neutral chromium plating bath containing suitable amounts of addition substances such as Rochelle salts, sodium citrate and the like or deposition of firmly adherent ductile and bright chromium deposit is effected even at room temperature. The bath may, however, also be warmed during use. Temperatures between 20 and 60 degrees Celsius are principally used in practice.

The deposition of metal from the new chromium plating bath is carried out according to the invention using low densities upwards of about 0.25 amp per square decimeter; the production of technically useful chromium deposits has not hitherto been carried out with current densities even approaching such low values. Whilst in practice current densities of 0.5 to 1 amp per square decimeter are generally used in carrying out this new process there is on the other hand nothing to prevent the use of higher current densities such as two or three amps per square decimeter, but the use of such high current densities in the new process is solely for the purpose of accelerating the deposition of the metal and does not as in the other processes render possible primarily deposition of metal.

The baths proposed according to the invention have a remarkable penetrating effect and spreading power and the chromium plating can be extended for a considerable period without stripping being evident. Bright deposits are easily obtained which remain brilliant even when deposition in thick layers takes place, and a matte surface is only produced with great thicknesses similarly as already known in the production of thick nickel deposits. The plating is extraordinarily easy to polish and only slightly brittle as apparently less hydrogen is occluded than in the chromium plating processes hitherto known. In order to obtain particularly bright chromium deposits compounds of other metals, colloids or substances having capillary action such as, for example, hydroxyl derivatives of aromatic hydrocarbons or derivatives thereof which prevent the growth of crystals are added to the electrolyte according to the present invention.

When the bath is in use care must be taken that no oxidation of the electrolyte to chromium compounds of high valency takes place at the anode. Anodic oxidation may be prevented for example, by using soluble chromium anodes, and without using a diaphragm, adding if necessary, reducing agents such as bi-sulphite, chromous salts or the like. Insoluble anodes may also be used if the anode chamber is cut off by a diaphragm and an anolyte is used which has no adverse effect on the catholyte, for example, graphite or carbon may be used for the anode and a solution of Rochelle salt as the anolyte. The anolyte has preferably a lower concentration than the catholyte in order to prevent the anolyte from penetrating through the diaphragm into the cathode chamber. It has been found preferable to stir the electrolyte. It is also advantageous to filter the bath continually and this is an advance in chromium plating baths as the use of circulating baths for chromium plating has not been hitherto proposed, and it has also been found that the presence of dissolved carbon dioxide in the catholyte has an advantageous effect. Saturation with carbon dioxide can be obtained for example, by suspending chromium carbonate in linen bags in the cathode chamber. The catholyte is thus continually maintained saturated with carbon dioxide so as to provide for the neutral reaction of the bath. Articles of very complicated shapes, and of any metal can be plated with chromium by means of electrolytes of this type directly and more particularly without using special auxiliary anodes. Small articles can also be chromium plated in mass in this way in the usual mass galvanizing apparatus.

In order to explain the invention by way of example the preparation of several chromium plating baths suitable for carrying out the new process in practice is given in the following:—

(1) 150 grammes of chromic acetate are dissolved in a litre of water and the solution is boiled in order to drive off excess acetic acid. 50 grammes of Rochelle salt and 20 grammes of boric acid a litre are then added, the whole solution is again boiled if necessary and carefully filtered, the electrolyte being then ready for use.

(2) 200 grammes of chromium carbonate are mixed in a litre of water with sufficient quantity of tartaric acid and boiled until the solution contains neutral chromium tartrate. 50 grammes of sodium acetate are then added and also 25 grammes of boric acid, the whole liquor is then well boiled and filtered.

(3) 250 grammes of chromium sulphate, 50

grammes of Rochelle salt, 50 grammes of sodium acetate and 10 grammes of boric acid are boiled in a solution of water and then the whole is filtered.

The aggregate adjustment of hydrogen ion concentration to the desired value can be effected by neutralization of the bath or by evaporation of the excess acid. It is advantageous for this purpose to use substances for the composition of the bath which contain acids, which are easily volatile on heating, particularly in the presence of water, e. g. acetic acid hydrochloric acid, carbonic acid or the like. Lower or higher concentrations can, of course, be used instead of those given in the examples as long as the constituents of the bath do not crystallize out to any great extent.

I claim:

1. A process for the electrolytic deposition of chromium in ductile firmly adherent deposits, comprising passing an electric current through a bath containing a solution of a trivalent chromium compound maintained as nearly neutral as possible and to which are also added substances which retain the basic compounds of the metal in solution.

2. A process for the electrolytic deposition of chromium comprising passing an electric current through a bath containing a solution of a trivalent chromium compound and a soluble organic hydroxy compound capable of retaining the basic compounds of the metal in solution, said bath being kept as nearly neutral as possible.

3. A process for the electrolytic deposition of chromium comprising passing an electric current through a bath containing a solution of a trivalent chromium compound, and Rochelle salt, said bath being kept as neutral as possible.

4. A process for the electrolytic deposition of chromium comprising passing an electric current through a bath, containing a solution of a trivalent chromium compound, maintained as nearly neutral as possible, to which are also added substances capable of retaining the basic compounds of the metal in solution in neutral solution and adding to the anolyte a reducing agent.

5. A process for the electrolytic deposition of chromium comprising passing an electric current through a bath, containing a solution of a trivalent chromium compound maintained as nearly neutral as possible, to which are also added substances capable of retaining the basic compounds of the metal in solution in neutral solution and adding to the anolyte sodium-bisulphite as a reducing agent.

6. A process for the electrolytic deposition of chromium which comprises passing an electric current through a bath consisting of a catholyte containing a dissolved trivalent chromium compound and substances capable of keeping the basic compounds of the metal in solution in neutral solution, and an anolyte containing a salt of a hydroxy acid, said anolyte being of lower concentration than said catholyte and separated therefrom by a diaphragm.

7. The process of electrodepositing chromium which comprises establishing a bath containing a solution of a trivalent chromium compound and maintaining said solution in practically a neutral condition, and passing an electric current through said chromium electroplating bath in a neutral condition to cause the electrodeposition of chromium therefrom.

8. The process of electrodepositing chromium which comprises establishing a bath containing a

solution of a trivalent chromium compound and maintaining said solution in practically a neutral condition, adding substances to said bath to retain basic compounds in a solution, and passing an electric current through said chromium electroplating bath in a neutral condition to cause the electrodeposition of chromium therefrom.

9. The process of electrodepositing chromium which comprises establishing a chromium plating bath, a trivalent chromium compound and a soluble organic hydroxy compound capable of retaining basic compounds in a solution, maintaining said bath in a practically neutral condition, and passing an electric current through said chromium plating bath to cause the electrodeposition of chromium.

10. The process of electrodepositing chromium which comprises establishing a chromium plating bath, containing a trivalent chromium compound and a soluble organic hydroxy compound capable of retaining basic compounds in a solution, maintaining said bath in such a condition that its pH value lies in a range between about 4 and about 6, and passing an electric current through said chromium plating bath to cause the electrodeposition of chromium.

11. The process of electrodepositing chromium which comprises establishing a chromium plating bath, containing a trivalent chromium compound and a soluble organic hydroxy compound capable of retaining basic compounds in a solution, maintaining said bath in such a condition that its pH value is about 6, and passing an electric current through said chromium plating bath to cause the electrodeposition of chromium.

12. The process of electrodepositing chromium which comprises establishing a chromium plating bath, containing a trivalent chromium compound and a soluble organic hydroxy compound capable of retaining basic compounds in a solution, maintaining said bath in such a condition that its pH value is about 4, and passing an electric current through said chromium plating bath at a low current density of about 0.25 to about 1.0 ampere per square decimeter to cause the electrodeposition of chromium.

13. The process of electrodepositing chromium which comprises establishing a bath containing a solution of a trivalent chromium compound and maintaining said solution in practically a neutral condition, inserting an object to be plated in said bath for use as a cathode, inserting a soluble anode containing chromium, and passing an electric current through said bath by means of said soluble anode and said cathode.

14. The process of electrodepositing chromium which comprises establishing a bath containing a solution of a trivalent chromium compound and maintaining said solution in practically a neutral condition, and reducing the chromium in said bath at the cathode while said bath is in a neutral condition.

15. A practically neutral chromium plating bath comprising a solution of a trivalent compound of chromium, and an agent to maintain said bath in practically neutral condition.

16. A practically neutral chromium plating bath comprising a solution of a trivalent compound of chromium, a soluble organic hydroxy compound capable of retaining basic compounds in a solution, and an agent to maintain said bath in practically neutral condition.

17. A practically neutral chromium plating bath comprising a solution of a trivalent compound of chromium, Rochelle-salt, and an agent to maintain said bath in practically neutral condition.

18. A practically neutral chromium plating bath comprising a solution of a trivalent compound of chromium, and an agent to maintain said bath in practically neutral condition with a pH value lying within the range of about 4 to 6.

19. A practically neutral chromium plating bath comprising a solution of a trivalent compound of chromium, and an agent to maintain said bath in practically neutral condition with a pH value of about 6.

20. A practically neutral chromium plating bath comprising a trivalent compound of chromium, boric acid, Rochelle-salt and an organic addition substance.

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