

UNITED STATES PATENT OFFICE

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ELECTRODEPOSITION OF CHROMIUM

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This invention relates to the art of chromium plating and specifically to a new electrolytic solution from which metallic chromium can be electro-deposited.

It further relates to an improved electrolytic solution from which can be electroplated a hard chromium deposit which possesses superior qualities and better adhesion to the underlying metal.

It is known in the art that metallic chromium deposits from conventional electrolytes on ferrous and nonferrous products, both for decorative as well as wear purposes, have a disadvantage of being brittle and lacking ductility. This disadvantage is shown by low resistance to impacts and stresses, because of the relatively poor bond between the chromium and the underlying metal. For this reason, chromium deposits produced with the conventional electrolytes have a tendency to spall or chip when subjected to external loads or stresses.

Another disadvantage inherent in the conventional electrolytic solutions is their inability to cover evenly, recessed areas of the part being chromium plated. This well known lack of "throwing power" has, up to the present time, necessitated very careful designing of anodes in order to produce smooth and uniform deposits.

An additional inherent disadvantage of conventional electrolytes for chromium deposition is their poor current efficiency which, under commercial plating conditions, as stated in the literature, ranges from 9-12% of the theoretical yield.

A further and serious disadvantage of conventional electrolytes resides in the tendency for the bath to deteriorate after a comparatively short period of use and before a substantial portion of the active ingredients have been used up. When an electrolytic bath starts to "go bad," the fact is evidenced by decrease in throwing power, pimpling of the plate, non-uniform plating, discoloration of the plate and roughness. Various means have been resorted to in an effort to reactivate the bath when this condition appears, such as addition of fresh ingredients, but these have been generally unsuccessful and the universal practice is to throw the electrolyte away and make a new bath. Obviously, this is uneconomical and wasteful of chromium and acid.

The reason for such deterioration of the electrolyte is not fully understood, but it has been observed that, in conventional baths, the presence of trivalent chromium (Cr_3) is noted immediately after plating begins in a new bath, and the percentage of Cr_3 tends to continually increase as the bath is used. When the percentage of Cr_3

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risers to about 8% a noticeable decrease in plating efficiency and quality of the plate is evidenced and when the Cr_3 content reaches about 15% in most baths, the resistance of the bath becomes so high that plating ceases entirely.

In my improved electrolyte, the presence of Cr_3 is found, but it never exceeds 1% and tends to remain constant at less than 1% indefinitely. Plating baths made up in accordance with the disclosure herein have been operated for months without noticeable decrease in efficiency or throwing power.

It is therefore the primary object of my invention to provide an improved electrolyte for chromium plating which is characterized by high throwing power, high plating efficiency, and inherent stability when compared to conventional electrolytes.

Another object is to provide an improved process of chromium plating by means of which a plate of greater ductility and superior resistance to shock, spalling and wear is produced.

A still further object is to provide an improved process for electrodepositing chromium whereby a markedly stronger bond between the chromium layer and the underlying metal is achieved.

Other objects and advantages will be apparent from the following disclosure.

My new electrolyte is composed of an aqueous solution of chromium trioxide (CrO_3) to which is added an effective amount of complex compounds of chromium and organic acids containing hydroxy groups such as: tartaric and/or malic together with hydrofluoric acid. This complex is the active agent which permits the better deposition of chromium when electric current is passed through the electrolyte in accordance with my invention.

For the purpose of this invention it is not necessary to add the complex to the aqueous solution of chromium trioxide. Equally good results can be produced and maintained by adding the chemical reagents involved directly to an aqueous solution of chromium trioxide.

The exact structure of the chromium complex is assumed to comprise a central chromium atom with which are coordinated fluorine radicals as well as radicals derived from the tartaric and/or malic acid, possibly by oxidation, said complex possessing the ability to carry electrical charges during the process of electrodeposition, and being able at the cathode to maintain a condition necessary to deposit chromium in this improved manner.

In the formation of the complex, the chromium,

hydrofluoric acid and the tartaric and/or malic acid are believed to combine in one or more of the following ratios:

- 1 to 4 to 1
- 1 to 3 to 1½
- 1 to 2 to 2
- 1 to 1 to 2½
- 1 to 5 to ½

It is further believed that a reversible reaction is established by which, while the complex is broken down at the cathode, more of it is formed in other parts of the cell, and thus the quantities of the active agent involved in the process are relatively small.

For commercial use, I have found that to an aqueous solution of chromium trioxide (CrO₃) containing from 8-70 oz. per gallon of solution, must be added from .001-1 oz. per gallon of tartaric or malic acid, and from .1 to 3 oz. per gallon of hydrofluoric acid.

I have also found that the current densities that can be used may vary from 50 to 4,000 amps. per sq. ft. of plated area, and that the temperature may vary between 60° F. and 170° F.

For the best results I have found that the electrolyte should be made up to contain the following quantities: (CrO₃) chromium trioxide, 36-60 oz. per gal.; tartaric or malic acid .001-.25 oz. per gal.; hydrofluoric acid .5-2.0 oz. per gallon.

The best operating conditions will be temperature 110°-140° F., with current densities from 200-1000 amps. per sq. ft. of plated area.

A bath made up and used as described above will operate indefinitely. The trivalent chromium content remains constant at a value of less than 1% and the current and plating efficiency remains uniformly high. Deterioration of the bath may be quickly detected by slight "treeing" of the plate and when this occurs, the addition of a small amount of the complex will instantly restore the bath. In most instances, hydrofluoric acid alone is added, the tartaric or malic acid apparently remaining in the bath as an active ingredient without deterioration.

By the use of this electrolyte, I have found that the throwing power is greatly increased, and uneven surfaces can be plated with simple anodes and with greater uniformity in the thickness of the deposit, and primarily smoother coating in the places of high current densities, such as: corners or protruding areas.

I have also found that, when above optimum conditions are maintained, the rate at which chromium can be deposited is considerably greater than that which has been reported for the conventional electrolytes.

The great advantage possessed by chromium deposits from the new electrolyte is the unusually strong bond existing between the chromium layer and the underlying metal as is shown in the conventional bend test. This test reveals that, in conventional chromium plated deposits the cracks produced by the bending stresses are very numerous and distributed at random indicating a brittle deposit, while the deposits from my new electrolyte, the cracks are considerably fewer and distributed in the direction of the maximum stresses.

It is for this reason that chromium plating deposits from the new electrolyte are considerably more resistant to shocks and wear, and do not chip under load.

The new electrolyte has been successfully used in plating of dies, reamers, drills, gages, and a

great variety of tools in which uniform thickness of plating as well as evenly covered recessed areas are of primary importance.

For the purpose of this patent, I do not wish to limit the scope of my invention to the above named objects, because the electrolyte can be used to plate any form or type of tools and any other object which may require chromium plating for wear, abrasion, and corrosion resistance.

I claim:

1. A plating bath for electrolytically depositing chromium, being characterized by superior throwing power, high current efficiency and substantially constant low concentration of trivalent chromium, consisting essentially of an aqueous solution containing per gallon of solution from about 8 to 70 oz. chromic oxide, from about 0.1 to 3 oz. hydrofluoric acid and from about 0.001 to 1 oz. of an organic acid selected from a class consisting of malic and tartaric acids.

2. A plating bath for electrolytically depositing chromium, being characterized by superior throwing power, high current efficiency and substantially constant low concentration of trivalent chromium, consisting essentially of an aqueous solution containing per gallon of solution from about 36 to 60 oz. chromic oxide, from about 0.5 to 2 oz. hydrofluoric acid and from about 0.001 to 0.25 oz. of an organic acid selected from a class consisting of malic and tartaric acid.

3. An electroplating process which comprises electrodepositing chromium from a plating bath consisting essentially of an aqueous solution containing per gallon of solution from about 8 to 70 oz. chromic oxide, from about 0.1 to 3 oz. hydrofluoric acid and from about 0.001 to 1 oz. of an organic acid selected from a class consisting of malic and tartaric acids.

4. An electroplating process which comprises electrodepositing chromium from a plating bath consisting essentially of an aqueous solution containing per gallon of solution from about 36 to 60 oz. chromic oxide, from about 0.5 to 2 oz. hydrofluoric acid and from about 0.001 to 0.25 oz. of an organic acid selected from a class consisting of malic and tartaric acids.

5. In the electrolytic plating of chromium with a plating bath consisting essentially of an aqueous solution containing from about 8 to 70 oz. chromic oxide per gallon, hydrofluoric acid and an organic acid selected from a class consisting of malic and tartaric acids, the process of preventing the accumulation of trivalent chromium in the bath which consists in maintaining a sufficient quantity of hydrofluoric acid and organic acid in the bath to prevent the concentration of trivalent chromium in the bath from rising substantially above 1 per cent by weight, whereby the life of the plating bath can be extended substantially indefinitely.

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Certificate of Correction

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August 1, 1950

RUSSELL RAAB

It is hereby certified that error appears in the above numbered patent requiring correction as follows:

In the grant, lines 2 and 3, and in the heading to the printed specification, lines 4 and 5, for "a corporation of Michigan" read *a company of Michigan*;
and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 7th day of November, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.