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CHROMIUM PLATING

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1 Claim. (Cl. 204—1)

This invention relates to chromium plating.

An object of the invention is to provide a relatively cheap, simple, commercially practicable and dependable process for coating articles with chromium.

Another object is to provide a chromic acid electroplating bath having improved operating characteristics.

Another object is to provide a process of the above type in which the necessity for close control and regulation is eliminated.

Various other objects and advantages will be apparent as the nature of the invention is more fully disclosed.

Although the various novel features which are believed to be characteristic of this invention will be pointed out with particularity in the claim appended hereto, the invention itself, as to its objects and advantages and the manner of its operation, may be better understood by referring to the following description in which a specific embodiment thereof is set forth for purposes of illustration.

In the following description and in the claim certain specific terms are used for convenience to designate various details of the invention. These terms, however, are to be given as broad an interpretation as the state of the art will permit.

In commercial chromium plating using a chromic acid bath, it has been recognized that chromium deposition will not take place in the absence of a catalyzer and that best results have been attained by closely regulating the amount of catalyzer in the bath. It has been proposed to utilize a sulphate radical as a catalyzer for a chromic acid bath and in such processes it has been found that the amount of sulphate must be regulated between close limits in order to produce satisfactory plating. This close regulation of the catalyzer complicates the commercial application of the chromium plating process and results in a non-uniform product unless extreme care is taken.

In accordance with the present invention, I overcome the above mentioned difficulties by including in the bath a substance which counteracts the critical effect of the catalyzer and permits the quantity of catalyzer to be varied over wide limits. I have found that this material also produces more desirable operating conditions and permits the use of current densities and temperatures below the limits heretofore considered practical for commercial plating.

More specifically, I employ a bath consisting of chromic acid, a soluble polychromate and a catalyzer. The polychromate may, for example, consist of a dichromate, trichromate, or tetrachromate, preferably sodium salts of these compounds because of their commercial availability although other soluble salts such as ammonium and potassium polychromates may be used.

The catalyzer may comprise a substance having a sulphate radical, such, for example, as sodium sulphate, which is usually present as an impurity in commercial grades of the chromium compounds above mentioned.

I have found that the polychromates permit a much wider variation in catalyzer content of the bath than would otherwise be possible. This may be because an excess of the catalyzer tends to retard the migration of ions, whereas the polychromate counteracts the same and tends to accelerate the migration of ions. It appears that during the electrolysis the sulphate radical of the catalyzer forms green hydroxy compounds of chromium from which, under certain conditions, the chromium is deposited at the cathode. An excess of the hydroxy compounds, however, changes the equilibrium of the bath in regard to pH concentration and retards the migration of the chromium ion to the cathode. It is my belief that the polychromate counteracts the effect of an excess of the sulphate radical and prevents the formation of such excess of chromium hydroxy compounds. In any event, in the presence of the polychromate, the range of catalyzer is such that the bath may be used until the natural fouling renders it unsuitable for further plating.

As a specific example, using from 60 to 300 g/l. of chromic acid, from 100 to 350 g/l. of sodium dichromate, and from .5 to 12 g/l. of sodium sulphate, I have found that bright cromium plate is obtained at temperatures of 20° C. to 45° C. and at current densities of from 15 to 140 amperes per square foot.

In general, the higher concentrations of sodium dichromate and sodium sulphate are used with the more concentrated chromic acid baths. Various combinations of the above substances which are suitable for the purpose are set forth in the following table:

Cr_2O_3 (g/l.)	$Na_2Cr_2O_7$ (g/l.)	Na_2SO_4 (g/l.)
60	100	.5
100	150	1
140	210	2
200	270	5
250	350	8
300	350	12+

The best results were obtained using 150 g/l. chromic acid, 240 g/l. sodium dichromate and 1 to 10 g/l. sodium sulphate at current densities of 20 to 60 amperes per square foot and at temperatures of 20° C. to 35° C. When the sulphate approaches the upper limits, the current density may be increased somewhat. With 10 g/l. or

more of sodium sulphate, current densities of 36 to 140 amperes per square foot may be employed at temperatures up to about 45° C.

When commercial chromic acid and sodium dichromate are used there is a certain amount of sodium sulphate present as an impurity. Usually there is a sufficient amount to provide enough catalyzer to carry on the chromium plating process. If the amount is deficient, however, more sodium sulphate may be added to initiate the plating operation. When the plating operation has been carried on for a length of time, the sodium sulphate gradually builds up and will maintain itself within the desired range so that no further consideration need be given thereto. It has been found that the bath becomes fouled due to dissolved base metals, dust, grease, etc., which constitutes a "drag in" long before the sodium sulphate has built up to a quantity above the chromium plating range.

In carrying out this process continuously, the chromic acid is depleted mostly by deposition and partly by "drag out" with the plated articles. The sodium dichromate is depleted largely by "drag out". This depletion of chromic acid and sodium dichromate changes the specific gravity of the bath. Hence, the specific gravity may be used as an indication of the condition of the bath and in commercial practice is the only indication used in maintaining the bath. The bath may be replenished as required using a mixture of salts containing, for example, 95 per cent chromic acid and 5 per cent sodium dichromate, a sufficient amount being added to return the bath to its original specific gravity. In this way plating may be carried on until the bath has become fouled and must be discarded, a condition which usually would not occur for many months.

A sodium sulphate catalyzer has been referred to above because this substance is present as an impurity in commercial grades of chromic acid and sodium dichromate. Other catalysts such as fluorides or fluosilicates may be used, however, in place of the sodium sulphate if desired. The dilute solutions are characterized by an unusually good throwing power which makes the process especially suitable for decorative light weight chromium coating and also for heavy chromium coatings when adequate plating time is allowed, as, for example, 3 to 10 minutes. The concentrated bath is especially suitable for the rapid production of heavy plate. Deposits having a thickness of over .00002 inch have been produced from such a bath in three to five minutes with 180 amperes per square foot current density.

A further advantage of the above process lies in the fact that substantially less lead chromate is formed at the anode than is the case with the usual chromic acid, sulphuric acid bath. Hence, the quantity of sludge deposited in the bottom of the tank is materially reduced.

A bath of this type is simple to operate inasmuch as room temperatures may be employed and no delicate adjustments are required to maintain proper plating conditions.

It is obvious that the invention is not to be limited to the exact compositions above mentioned and that various changes and substitutions may be made by persons skilled in the art. Certain specific embodiments have been given for purposes of illustration only. The invention is to be limited only in accordance with the following claim when interpreted in view of the prior art.

What I claim is:

The method of chromium plating articles which comprises connecting the articles to be plated as a cathode in an electrolyte consisting of a water solution containing from 60 to 300 grams per liter chromic acid, from 100 to 350 grams per liter sodium dichromate and the quantity of sulphate present in said chromic acid and sodium dichromate as an impurity, but within the range of .5 to 12 grams per liter, operating the bath at current densities of from 15 to 140 amperes per square foot and at a temperature of from 20° to 45° C., periodically adding chromic acid and sodium dichromate to compensate for the depletion thereof caused by the plating operation and to restore the bath to substantially its original content thereof and continuing the plating while allowing the sulphate content derived from said impurities to build up to not over about 12 grams per liter.

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