

UNITED STATES PATENT OFFICE

2,095,995

CHROMIUM PLATING

John R. Mardick, New York, N. Y.

No Drawing. Application March 13, 1935,
Serial No. 10,796

8 Claims. (Cl. 204-1)

This invention relates to the electro-deposition of chromium from an electrolyte and has for its object the provision of an improved process and means for accomplishing the above purpose.

More specifically the invention relates to an improved electrolyte or bath for use in chromium plating and to a method of operation for chromium plating various metal objects.

Although the novel features which are believed to be characteristic of this invention will be more particularly pointed out in the claims appended hereto, the nature of the invention and its objects and advantages may be better understood by referring to the embodiment thereof which is more fully disclosed in the following description.

Successful chromium plating from an electrolyte containing chromium is dependent upon various factors, such as the nature of the chromium compound, the nature and the amount of catalyst, the temperature of the bath and the current density. The sensitivity of the plating process to all of these factors has rendered it difficult to obtain uniform results on a commercial scale and many times the particular factor at fault could not be readily located or corrected. I propose to overcome these difficulties by utilizing for the electrolyte, a chromium compound from which the chromium may be released and deposited under a comparatively wide range of conditions.

I have found that electrolytes containing certain soluble higher polychromates such as trichromates or tetrachromates have such characteristics. The presence of a small amount of suitable catalyst is required for depositing chromium from such solutions but the nature and proportions of catalyst may be varied widely without interfering with the efficient operation of the process. The catalyst may contain various radicals which have the property of promoting the deposition of chromium without combining with other substances which may be present in the bath to form compounds which would interfere with the plating operation.

As a specific example I prefer sodium trichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) or sodium tetrachromate ($\text{Na}_2\text{Cr}_4\text{O}_{13}$) because these compounds are readily available and may be prepared by well known methods. They may be prepared, for example, from sodium bichromate and nitric acid, in which case the polychromate may be crystallized out and separated from other ingredients that may be present in the solution. The polychromate may then be dissolved in water in the proportions required for plating.

I have found that solutions containing about 300 g. of soluble polychromate per liter possess the most desirable plating properties under the conditions to be specified. The range may however be extended from 60 g. to 550 g. per liter. Outside of about this range it is difficult to obtain a bright plate.

As specific examples of suitable catalysts that may be used with the above solution the following may be noted: sulphates, fluorides and fluosilicates.

Any one of the above catalysts may be used either by itself or in combination with any other catalyst. The quantity required depends somewhat upon the concentration of the polychromate solution although it may be varied over a comparatively wide range. In the case given above, viz: with 300 g. sodium polychromate per liter, about 4 g. of catalyst has been found to produce good results. In general the quantity of catalyst may vary from .5 g. to 15 g. or over per liter depending upon the polychromate concentration, more catalyst being required as the concentration of polychromate is increased.

The following table indicates the range of concentration of catalyst that may be used with various quantities of polychromate per liter. It is to be understood however that the upper and lower limits may be varied somewhat. The quantities specified have been found to be suitable for a bright plate and are given merely as illustrations:

Polychromate g. for liter	Catalyst g. for liter
60	About 0.5
100	0.75 to 2
200	1.5 to 3.5
300	2 to 6
400	3.5 to 7
500	4.5 to 10
550	6 to 12

The above electrolyte may be used at room temperatures, i. e. at temperatures from about 68 degrees F. to 90 degrees F. and comparatively low current densities are required, i. e. from 25 to 40 amperes per square foot. The temperature and current density are not critical but the best results have been obtained within about the limits given.

In the operation of this process the article to be plated is first carefully buffed, polished and cleaned by well known cleansing operations. If the surface is properly prepared it is usually un-

necessary to use a preliminary coating of a second metal such as copper or nickel. In some cases however it may be more economical to apply a preliminary coating of nickel and/or copper than to clean the surface sufficiently to receive a plate of chromium directly. When properly cleaned base metals such as copper, brass, zinc, aluminum and steel may be plated directly from the above bath.

The article, prepared as above, is placed in the bath as a cathode and an insoluble anode, preferably formed of a lead and antimony mixture, is placed in operative relation thereto and properly connected for the passage of electric current through the bath. About 3 or 4 volts are usually required under the conditions above given. The articles remain in the bath sufficient length of time to receive the proper deposit, usually from 2 to 10 minutes according to the desired thickness of the plate and may then be replaced by other articles.

After continued use the concentration of polychromate will be found to decrease due to the chromium removed and deposited at the cathode. This may be periodically replaced as required. The time for replacement may be determined analytically. The quantity of catalyzer remains about constant within the range suitable for bright plating and requires no adjustment except for unusual conditions. The catalyzer may be gradually removed, however, as a "drag out" with the plated articles and the bath may become contaminated by "drag in" of impurities with the articles to be plated. When the composition has been changed in this manner to such an extent that a bright plate can no longer be obtained it is usually desirable to replace the same with a fresh solution. If the quantity of catalyzer has been reduced below the bright plate range before the solution is to be discarded it may obviously be replaced or strengthened to the required concentration.

Without intending to limit myself to this explanation, I believe that the catalyzer promotes the formation of trivalent chromium during the plating process. For example, in the presence of catalyzers green chromium oxysalts, such as chromium oxysulphate when a sulphate catalyzer is used, and some chromium chromate are formed.

These salts have a decided colloidal appearance and are readily permeable to the hydrogen which is generated in all electroplating or electrolytic operations. The hydrogen, if moderate in volume, helps to reduce the chromium to the metal from the trivalent form in the above compounds. Excess concentration of hydrogen ions would repel the trivalent chromium compounds from the cathode and interfere with the deposition of metal. Such excess is avoided however in this process by reason of the low current densities and low temperatures employed.

Some of the trivalent chromium is thus reduced to the metallic form and is deposited at the cathode, and some may be reoxidized at the anode to the hexavalent form. Hence the quantity of these salts remains substantially constant or stabilizes after the bath has been in use for a short time. The required quantity thereof may be added to the bath at the beginning of the process if desired, in which case the catalyzer may be reduced in proportion, as it will not be necessary to form the salts by the action of the bath. It is preferred, however, to form the salts in the bath by use of a catalyzer as above explained because a smoother and more easily controlled

operation is thereby obtained. In any event a sufficient quantity of catalyzer and/or of the above salts is used to obtain the desired bright plate.

Among the advantages of this process it may be noted that: the plating can be carried on at room temperatures and at low current densities; the polychromate reduces the harmful effect of impurities such as an excess of sulphates which may accumulate in the bath; the plate is dense and hard; the bath does not require frequent or careful regulation; fuming and spray is reduced to a minimum; and superior throwing power is obtained.

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 a person skilled in the art. A specific embodiment has been given for purposes of illustration only. The invention is accordingly to be limited only in accordance with the following claims when interpreted in view of the prior art.

What is claimed is:

1. An electrolyte for use in chromium plating consisting of a water solution of a soluble polychromate of higher order than a bichromate and a catalyzer of the class consisting of sulphates, fluorides and fluosilicates in proportions suitable for the electrodeposition of chromium therefrom.

2. An electrolyte for use in chromium plating consisting of a water solution of a soluble polychromate of higher order than a bichromate and a catalyzer of the class consisting of sulphates, fluorides and fluosilicates in proportions such that a bright plate is obtained at current densities of 25 to 40 amperes per square foot and at temperatures of about 68 degrees F. to 90 degrees F.

3. An electrolyte for the electrodeposition of chromium consisting of a water solution containing about 60 g. to 550 g. per liter of sodium trichromate and/or of sodium tetrachromate and a catalyzer of the class consisting of sulphates, fluorides and fluosilicates.

4. An electrolyte for the electrodeposition of chromium consisting of a water solution containing about 60 g. to 550 g. per liter of a soluble polychromate of higher order than a bichromate and about .5 g. to 15 g. per liter of a catalyzer of the class consisting of sulphates, fluorides and fluosilicates.

5. An electrolyte for the electrodeposition of chromium consisting of a water solution containing about 60 g. to 550 g. per liter of a soluble polychromate of higher order than a bichromate and catalyzer of the class consisting of sulphates, fluorides and fluosilicates.

6. The method of chromium plating articles which comprises connecting the articles as a cathode in an electrolyte consisting of a water solution containing from about 60 g. to 550 g. per liter of a soluble polychromate of a higher order than a bichromate and a catalyzer of the class consisting of sulphates, fluorides and fluosilicates and passing current therethrough while maintaining the electrolyte at about 68 degrees F. to 90 degrees F.

7. The method of chromium plating articles which comprises connecting the articles as a cathode in an electrolyte consisting of a water solution containing from about 60 g. to 550 g. per liter of a soluble polychromate of a higher order than a bichromate and a catalyzer of the class consisting of sulphates, fluorides and fluo-

silicates and passing current therethrough under conditions of current density and temperature adapted to produce a bright plate.

5 8. The method of chromium plating articles which comprises connecting the articles as a cathode in an electrolyte consisting of a water solution containing a soluble polychromate of an order higher than a bichromate and a catalyzer of the class consisting of sulphates, fluor-

ides and fluosilicates in proportions such that, at the current density and temperature employed, a bright plate is produced, passing current through said electrolyte from insoluble anodes and maintaining a current density of less than about 40 5 amperes per square foot of cathode surface to be plated and a temperature of about 68 degrees F. to 90 degrees F.

JOHN R. MARDICK.