

UNITED STATES PATENT OFFICE

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CHROMIUM PLATING

No Drawing.

Application filed November 25, 1927. Serial No. 235,757.

This invention relates to chromium plating; and it comprises a method of maintaining a chromium plating bath containing CrO_3 at its maximum efficiency wherein said bath is treated from time to time with barium chromate to remove excess amounts of SO_4^{--} ion therein; all as more fully hereinafter set forth and as claimed.

Chromium plating is always accomplished with the aid of a bath containing CrO_3 as its main constituent. As the CrO_3 disappears by the plating action of the current, replenishment of the chromium content of the bath is necessary and this is ordinarily accomplished by the addition of solid commercial "chromic acid". A good bath of this type is that known as "Sargent's solution" (Trans. Am. Elec. Soc. 1920, vol. 37, page 479). All these baths contain in addition to the CrO_3 certain small proportions of Cr_2O_3 and of a negative mineral ion; usually SO_4^{--} . The presence of these accessory bodies is necessary and a certain rather nice proportioning between these three bodies is also necessary for efficient work. In particular, the amount of sulfate ion present must be kept within rather a narrow range. In my own work I desire that the bath shall contain very nearly 0.25 per cent SO_4^{--} . I do not desire, for my own purposes, that it shall contain substantially more or substantially less than this amount.

In the use of any bath however, using commercial chromic acid for replenishing the chromium content, the amount of sulfate builds up. This is for the reason that commercial CrO_3 always contains some SO_3 , it being ordinarily made by adding strong sulfuric acid to bichromate solution. This gives a bright red precipitate of CrO_3 which is freed as much as possible of mother liquor on a suction filter and is afterwards dried and packaged. Instead of using a suction filter a centrifugal is often employed. Sometimes the CrO_3 is washed with a little sulfuric acid to free it of sodium sulphate. Concentrated nitric acid is sometimes used but no other washing liquid is practicable. Commercial CrO_3 therefore inevitably contains some sulfuric acid as an impurity. The amount of the impurity may range from several per cents

with bad material down to 0.1 per cent or lower. Standard specifications require an amount of sulfuric acid not exceeding 0.2 per cent. Whatever the amount of sulfuric acid, or of sodium bisulfate, in the chromic acid used for replenishment, the sulfuric acid ion content of the bath builds up in time, while, as stated, it is not desirable to have this content exceed a certain limit.

I have found that I can continue the use of baths beyond the time when they would be customarily discarded because of the accumulation of sulfuric acid by the expedient of stirring into the bath from time to time a small amount of barium chromate; the amount being that equivalent to the excess of sulfuric acid present over and above the necessary amount. Any excess of added barium chromate over this amount will reduce the SO_4^{--} ion below the optimum content. Elimination of SO_4^{--} down to perhaps 0.05 per cent is possible but not desirable. While in each case baths differ somewhat, each operator with a given bath has a certain optimum content, neither more nor less, which he regards as desirable. In my own case, as stated, I want 0.25 per cent. In my own practice, when the sulfuric acid accumulates above my desired 0.25 per cent, say up to 0.30 or above, I add the amount of finely powdered chromate which will react with the excess and bring back the SO_4^{--} content to 0.25 per cent.

Barium chromate is insoluble in CrO_3 solutions and by reaction with sulfates, it forms barium sulfate which precipitates as a harmless mud, setting free CrO_3 which joins the electrolyte. Neither the chromate nor the barium sulfate has any injurious effect on the efficiency of the bath.

I find it desirable to use a freshly precipitated and washed barium chromate made by precipitating barium chloride or barium nitrate by sodium chromate and washing, as it is more readily reactive than dried and aged material. The wet, pasty precipitate of barium chromate can be added directly to the bath. After addition it is desirable that the chromate be kept in suspension by some form of stirring for rather a prolonged pe-

riod; an hour or so. This is for the reason that the quantities of sulfuric acid to be removed are quite minute and reaction is rather slow.

- 5 Instead of adding the calculated amount of barium chromate to the solution, an excess can be added. This removes all the SO_4^{--} down to perhaps 0.05 per cent. The excess of barium chromate settles out and can
10 be removed. Afterwards, the SO_4^{--} content can be brought back to my desired optimum of 0.25 by an addition of chromium sulfate or in other ways. But it is simpler to add the calculated amount of barium chromate.
15 In lieu of using barium chromate I may employ commercial barium hydroxide either in suspension or in solution; using, as before, the calculated amount. Barium carbonate is another compound which may be used.
20 Freshly precipitated carbonate is best. Such compounds I consider equivalents of barium chromate. However, I regard barium chromate as the best form in which to utilize barium compounds for my purposes.

25 What I claim is:—

1. In plating chromium from CrO_3 plating baths containing small amounts of Cr_2O_3 and SO_3 in which it is desirable to maintain the SO_3 content between a fixed minimum and a
30 fixed maximum, the process of replenishing and maintaining the bath which comprises adding thereto from time to time commercial chromic acid containing variable amounts of SO_3 as an impurity and also adding solid
35 barium chromate to the bath from time to time in amounts sufficient to maintain the SO_3 between the desired minimum and maximum content in solution in the bath.

2. In the lengthening of the life of chromium plating baths containing CrO_3 and replenished by addition of commercial CrO_3 the process which comprises standardizing such a bath from time to time by addition of
40 barium chromate or equivalent.

- 45 In testimony whereof, I have hereunto affixed my signature.

CHAD H. HUMPHRIES.

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