

NATIONAL BUREAU OF STANDARDS REPORT

9991

EVALUATION OF A PROPRIETARY IRON SULFAMATE PLATING BATH

Technical Report
To
Bureau of Engraving and Printing



U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

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Technical Report

May 1, 1968 to January 1, 1969

By

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To

Bureau of Engraving and Printing

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U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

EVALUATION OF A PROPRIETARY IRON SULFAMATE PLATING BATH

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SUMMARY

Iron deposits from the Allied Research Company's iron sulfamate plating bath were found to be extremely weak and brittle. The specimens were 1 to 40 mils thick and were deposited at a number of different operating conditions.

I. INTRODUCTION

The ideal iron plating bath would produce thick, strong, unstressed ductile and adherent deposits at rapid rates at or near room temperatures without the use of a corrosive electrolyte. Such a bath, of course, would be of great interest to the Bureau of Engraving and Printing. Practically, however, room temperature baths tend to produce brittle unusable deposits. The proprietary bath* discussed in this report was described in the supplier's literature as producing "ductile" deposits when operated at or near room temperature. As such it was of interest to the Bureau. The work reported here is an evaluation of that bath to determine its potential usefulness to the Bureau of Engraving and Printing.

* Allied Research Products, Inc.

II. MAKE-UP OF THE IRON BATH

Two baths were prepared at different times essentially in accordance with the supplier's (Allied Research Products, Inc.) instructions. The first bath was made up of:

3.6 l ferrous sulfamate concentrate
180 g sodium chloride
120 ml LP 9310 Fe (proprietary addition agent)
36 ml Snap L (proprietary wetting agent)
152 g sulfamic acid
200 ml 30% ammonium hydroxide
Distilled water to make 6 l

The bath pH measured 1.9, the specific gravity 1.240. For this bath the anode (submersed area 10 1/2 in²), tank, filter unit, etc., were rinsed with a 5% sulfamic acid solution. The filter cartridge and anode bag were seasoned in the same solution for 48 hours. Just prior to combination and dilution the ferrous sulfamate concentrate was filtered to remove accumulated oxidation products.

The bath was operated at 48°C. The temperature was maintained by an external water bath. The pH of the bath was raised to 3.0 by the addition of ammonium hydroxide to comply with the pH limits, 2.5 to 3.3, set by the supplier. The solution, which had been a clear green prior to the addition of ammonium hydroxide, developed a yellow cast and became turbid from a yellow red precipitate, presumably a ferric compound. Continuous filtration did not remove any significant quantity of the turbidity, nor did dummyping for 5 hours at 1/2 ampere.

Several sample deposits of iron were obtained from this turbid bath. These will be described later.

To clean up the bath, the pH was raised with ammonium hydroxide to 3.5. Filtration through Watman #2 filter paper removed all turbidity. The pH was then reduced to 2.5 by sulfamic acid. The addition of 3 g of iron powder seemed to reduce the remaining ferric ions inasmuch as the color became slightly bluer or less yellow.

At this stage the solution was clear. To retard oxidation, a plastic cover sheet was placed over the pyrex container and argon was bubbled through the bath so as to keep an inert layer of gas over the solution. The argon supply was maintained at all times--day and night--during the subsequent operations.

The make-up of the second bath was the same as the first, except that 180 g of ammonium sulfamate were used instead of the sulfamic acid and the ammonium hydroxide. This bath behaved in the same manner as described for the first bath. In operation this bath differed in that the anodes were not bagged and also were increased in size to 27 1/2 sq.in. of surface area. The bath was also operated through a broader temperature range. When a test specimen was not being deposited a dummy was kept plating at a low current density,

7 asf.

III. BATH OPERATING CHARACTERISTICS

The pH of the bath increases during operation and must be adjusted continually with sulfamic acid. At low current densities,

about 7 asf, the bath can be operated for days without becoming turbid though a yellow-brown precipitate, probably containing ferric ion, will gradually accumulate on the side of the container, on the anodes and anode bags and in the filter. This precipitate does not dissolve readily in sulfamic, sulfuric, nitric or hydrochloric acid, but will dissolve rapidly in phosphoric acid.

Raising the temperature or increasing the current density increases the rate of accumulation of brown precipitate. In one instance an increase in bath temperature from 55°C to 65°C produced a virtually opaque bath in a very short time. When a clear bath is in operation above 7 asf it becomes turbid quickly. The bath will also become turbid on standing if it is not closed to the atmosphere. Deposits from a turbid bath may be smooth and of good appearance. With the accumulation of precipitate, however, the tendency for nodular growth and treeing increases.

IV. SPECIMEN PREPARATION AND HANDLING

All deposits were made on coupons of either 0.010 inch or 0.040 inch thick copper. The surfaces to be plated were pumiced and bright dipped (1 part HNO_3 , 2 parts $\text{C}_2\text{H}_4\text{O}_2$, 3 parts H_3PO_4) until water-break free and rinsed with distilled water just prior to immersion in the bath. The current densities used were 7, 11, 15, 30, 60 and 70 asf (10-100 asf recommended by supplier). Deposits were made at temperatures ranging from 45° to 65°C and for times ranging from 4 to 168 hours.

V. CHARACTER OF DEPOSITS

All deposits had the same qualitative characteristics; good adhesion, high internal stress (substrates plated on one surface were always significantly warped), generally smooth with semi-bright surface, and poor ductility (the iron plate cracked when the cathode was slightly bent). The foils obtained by dissolving the copper substrate in chromic acid could not be bent double without breaking. They were obviously brittle. Heating the foils at 190°C for one hour reduced the brittleness to a significant degree, but they were still brittle. A marked improvement in ductility was observed after heating at 400°C for one hour (grain growth of pure iron begins at 200°C).

Thick deposits, deposits in excess of 10 mils, were machinable with care. These deposits could be sawed, milled and hand filed, however they exhibited a high degree of brittleness and may be compared to cast iron in this respect.

The test to determine the tensile strength of the iron deposited from this bath was in a strict sense abortive. The specimen fractured in the process of setting the holding jaws and applying the holding load which reached 25 lbs at fracture. Knowing this one could say that the tensile strength was less than 1500 psi. This was the second specimen deposited for tensile testing. The first specimen fractured during the machining operation. Deposits produced at 12 asf and 19 asf were harder (Rockwell B63 and B89, respectively) than the material now used by the Bureau of Engraving and Printing (Rockwell B57).

VI. DISCUSSION

These experiments indicate that this iron plating bath is not a promising one because of the weakness of the iron.

We encountered some difficulty in maintaining the bath in good condition. We feel that this could be a problem with continued use. The bath has a tendency, even with filtration, toward turbidity and can assume an almost opaque appearance in a relatively short time, particularly at elevated temperatures.

Additional information about sulfamate baths can be found on pages 145, 6 and 7, in the February 1968 issue of Plating in comments by Harold J. Read.

We have requested the supplier to send us some typical iron deposits which can be compared to ours. He has agreed to do so; however, in the ensuing six months they have not been forthcoming.

