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DETERMINATION OF SULFURIC ACID IN CHROMIUM PLATING SOLUTIONS USING GRAVIMETRIC ANALYSIS

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ABSTRACT

The determination of sulfuric acid in chromium plating solutions is studied in the presence of chromic acid, Cr(III) ions, and Fe(III) ions. The control of the concentration of these four chemical components is necessary to optimize the chromium plating process. In the absence of expensive chemical instrumentation, a gravimetric method suitable for this industrial application is developed in this report. This method uses chromic acid reduction and sulfate precipitation and is a modified version of the standard sulfate precipitation analysis since it allows the presence of chromic acid. The optimum operating range of sulfuric acid is 2.40 to 3.10 g/l, and the resulting precisions are in the range of 0.24 to 0.31 g/l, providing marginal control of these plating solutions supported by seven years of testing.

KEYWORDS

Chemical Analysis

Sulfuric Acid

Chromium Plating Solutions

Gravimetric Analysis

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INTRODUCTION

The determination of sulfuric acid in chromium plating solutions is studied in the presence of chromic acid, Cr(III) ions, and Fe(III) ions. The control of the concentration of these four chemical components is necessary to optimize the chromium plating process.

In general, sulfuric acid concentrations are commonly determined using gravimetric, turbidimetric, or titrimetric methods (refs 1-5). Large concentrations of chromic acid in chromium plating solutions severely interfere with the determination of small sulfate concentrations. For gravimetric and turbidimetric methods, barium or lead ions are commonly used as precipitating agents for sulfate ions, but these ions also precipitate chromate ions. For titrimetric methods, hydroxide ion is commonly used as a titrant for sulfate ions, but chromate ion is also titrated and masks the sulfate.

In the absense of expensive chemical instrumentation, a gravimetric method suitable for this industrial application is developed in this report. This method uses chromic acid reduction and sulfate precipitation and is a modified version of the standard sulfate precipitation analysis since it allows the presence of chromic acid. The general background for chromate ion reduction to Cr(III) ions is extensive (refs 1-5).

EXPERIMENTAL PROCEDURE

Strict analytical chemistry methods and procedures are followed throughout this experimental section. An excellent source of reference for these methods and procedures is by Fritz and Schenk (ref 1).

One analytical reagent grade standard solution is required. This solution is a 5.0 ± to 0.1-percent filtered barium chloride solution.

Preparation of a chromium plating solution sample for gravimetric analysis requires that 10 ml of the sample solution be pipetted into a 250-ml beaker. In addition, 40 ml of acetic acid, 10 ml of hydrochloric acid, and 25 ml of ethyl alcohol should be added. The solution should be slowly boiled and stirred down to a total volume of 25 ml. Then 150 ml of hot deionized water should be added to this beaker, stirred, and the solution placed in a convection oven for 18 hours at 75 to 80°C. Again, 150 ml of hot deionized water should be added to this beaker and stirred, and the solution brought to a boil. Then 25 ml of the standard barium chloride solution should be added to the beaker and stirred, and again the solution should be placed in a convection oven for four hours at 75 to 80°C. This solution should be carefully filtered through #42 Whatman paper minimizing sample precipitate "creep." The sample precipitate and paper should be carefully washed with hot deionized water to remove all visible traces of chromium. The filter paper and sample precipitate should be carefully placed in a properly prepared porcelain crucible that was previously weighed to 0.0001 gram. The crucible should then be placed in a muffle oven for one hour at a charring temperature of 400°C. Next, the crucible should be heated for another hour at 800°C, and then it should be immediately placed in a desiccator for one hour. Following that, the crucible and sample precipitate should be immediately reweighed to 0.0001 gram. The weight of the barium sulfate precipitate is the difference between the two crucible weighings. All sample solutions should be analyzed in triplicate.

RESULTS AND DISCUSSION

Experimental sulfate gravimetric data are presented in Table I for chromium plating sample solutions one and two. The gravimetric precipitation consists of the following equation for sulfate:

$$H_2SO_4 + BaCl_2 \leftrightarrow BaSO_4 + 2HCl \quad (1)$$

The solubility product constant (Ksp) for barium sulfate is 1.1×10^{-10} from Reference 1. An excess of barium ion is required in Eq. (1).

The calculation to determine the sulfuric acid concentration in the original chromium plating sample solutions is:

$$\text{g/l } H_2SO_4 = (42.02)\ (\text{grams of } BaSO_4 \text{ precipitate}) \quad (2)$$

From Eq. (2), the values of 2.22 and 2.71 g/l sulfuric acid are respectively calculated for sample solutions one and two for the data given in Table I.

It is useful to evaluate the variations in precision for the materials and methods used. Tables II and III present these data for the 10-ml class-A pipet and 20-gram porcelain crucible, respectively.

Without chemical instrumentation, the data by this method are marginally sufficient to adequately control the sulfuric acid in these chromium plating processes. The optimum operating range of sulfuric acid is 2.40 to 3.10 g/l, and the resulting precisions are in the range of 0.24 to 0.31 g/l, providing marginal control of these plating solutions supported by seven years of testing. The gravimetric analyses chapters of References 1 and 2 explain in great detail the reasons for poor sulfate precision by this method.

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TABLE I. EXPERIMENTAL GRAVIMETRIC DATA FOR CHROMIUM PLATING SAMPLE SOLUTIONS

Replicate	Sample One Barium Sulfate (grams)	Sample Two Barium Sulfate (grams)
1	0.0532	0.0650
2	0.0531	0.0648
3	0.0524	0.0640
X(avg)	0.0529	0.0646

TABLE II. PRECISION OF A 10-ml CLASS-A PIPET

Replicate	Volume (ml)*
1	10.03
2	10.00
3	9.98
4	9.99
5	9.98
6	10.04
X(avg)	10.00
Sn	0.02

*Volumes are calculated from the weight-volume relationship of a pipetted deionized water solution corrected for temperature.

TABLE III. PRECISION OF WEIGHING A 20-g PORCELAIN CRUCIBLE

Replicate	Crucible Weight (grams)
1	20.0873
2	20.0872
3	20.0872
4	20.0875
5	20.0874
6	20.0874
X(avg)	20.0873
Sn	0.0001

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