27
2/20/80
24 to NTIS

MASTER

GEPP-TIS-470

CYANIDE EVOLUTION FROM A POTASSIUM GOLD CYANIDE PLATING BATH

R. J. Antepenko
Chemistry Laboratory

February 12, 1980

General Electric Company
Neutron Devices Department
P. O. Box 11508
St. Petersburg, Florida 33733

Prepared for the
U. S. Department of Energy
Albuquerque Operations Office
Under Contract No. DE-AC04-76DP00656

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Printed in the United
Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy $ ~~4.00~~ 5.— ;Microfiche $2.~~95~~ 3.50

ABSTRACT

When a gold plating console was installed in a production area at the General Electric Neutron Devices Department (GEND), the console was placed adjacent to a ten percent sulfuric acid activation bath. Since the bath contains cyanide as a component of the gold salts, the danger of having the gold bath adjacent to the acid bath was questioned. This paper describes an experiment used to measure the amount of hydrogen cyanide gas released as a result of the accidental addition of sulfuric acid to the gold bath.

A distillation apparatus was used to collect hydrogen cyanide gas released from a sample of the gold bath by additions of either dilute or concentrated sulfuric acid. Cyanide concentrations were determined by an ion-selective electrode method.

Similar hydrogen cyanide gas evolution data were obtained from the addition of either dilute sulfuric acid or concentrated sulfuric acid. Both studies were performed with plating bath samples at 70°C and using a constant air sampling flow rate. The results show hydrogen cyanide gas release was a function of the plating bath pH. Air samples collected over a portion of the gold bath at pH 5.6 and at either room temperature or at a 70°C operating temperature were found to contain 2 μg/l hydrogen cyanide. Air samples collected over the bath sample at pH 4.1 to 4.3 contained 40 μg/l hydrogen cyanide. A rapid increase in hydrogen cyanide was found in air samples collected over plating bath samples below pH 2.5.

A quantity of reagent grade concentrated sulfuric acid was added to the test bath, which was equivalent to the addition of a 9-pound bottle of the acid to the 30-gallon production bath. Air samples were found to contain 1400 μg/l of hydrogen cyanide.

TABLE OF CONTENTS

ILLUSTRATIONS

TABLE

INTRODUCTION

Production gold plating electronic components at GEND require a neutral gold bath containing an organophosphonic acid. The deposits are smooth and fine grained, the bath is stable and useful for plating various electronic parts. The gold bath contains 24 ± 8 g/l gold prepared from potassium gold cyanide salt and 50 g/l of an organophosphonic acid with the bath pH adjusted between pH 5 and 6 with potassium hydroxide.

The bath contains no free cyanide added to buffer the system, to provide solution conductance, or to stabilize the gold. The only cyanide present is introduced as the gold cyanide salt and in solution it is strongly complexed with the gold. Therefore, this bath is assumed to be stable and resistant to hydrogen cyanide release under normal operating conditions.

However, concern was expressed over the proximity of the gold bath to the sulfuric acid activation bath. An accident potential was recognized should sulfuric acid be inadvertently added to the plating bath during routine maintenance. Therefore, a study was made to determine the amount of hydrogen cyanide gas that would be evolved if sulfuric acid were accidentally added to the gold bath.

EXPERIMENTAL

Figure 1 illustrates the apparatus used to study the effects of adding sulfuric acid to the gold bath. The apparatus and procedure for collecting the hydrogen cyanide gas was similar to that described in Reference 1. The procedure, with modification, was as follows.

PROCEDURE

A 250-ml volume of gold plating solution was placed into the 1000-ml reaction flask. The solution surface area was approximately 120 cm^2. The solution was heated to 70°C with a Variac* controlled heating mantle. The temperature was monitored with a thermometer placed in the flask side arm, which was filled with glycerol. The air flow over the reaction flask was created by a tubing pump, which pulled air into the bottom of the reaction flask and through the gas dispersion/cyanide collection tube. An air flow of 33 ml/min was

---

*Trademark, General Radio Co.

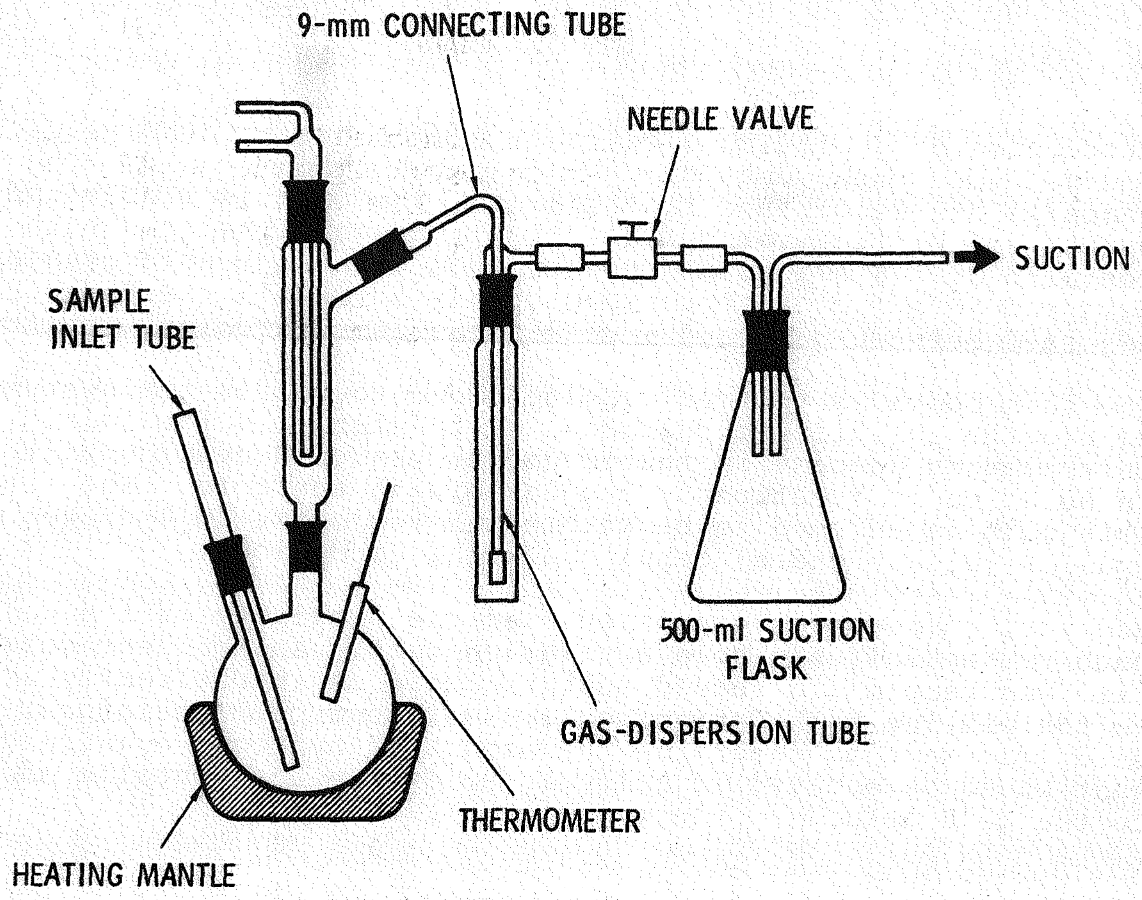

Figure 1. Cyanide Distillation Apparatus

estimated with a bubble flowmeter. Fifty ml of sodium hydroxide solution (50 g/l) was placed in the gas dispersion tube to absorb hydrogen cyanide gas. A buret was used to dispense the sulfuric acid through the sample inlet tube and into the reaction flask. A minimum 15-minute gas sampling time was used to provide sufficient time for gas evolution.

After the appropriate gas sampling time, the system was disconnected at the suction flask. The cyanide collecting tube was removed and a second tube containing 50 ml of fresh sodium hydroxide solution was immediately connected. The air/acid inlet tube was removed and the solution pH was measured using a long-shaft combination pH electrode. The apparatus was reconnected and the next volume of sulfuric acid was added to the flask.

The cyanide collected in the sodium hydroxide sampling solution was measured with a cyanide-ion selective electrode. The cyanide concentration was graphically determined from an analytical working curve as described in Reference 1.

This procedure allowed the measurement of total evolved hydrogen cyanide released during the sampling period. Also, the needle valve and pump were not altered to assure constant air flow throughout the study.

RESULTS

The analytical results from the gold plating bath studies using either dilute or concentrated sulfuric acid are presented in Table 1. The data show hydrogen cyanide gas release was a function of the plating bath pH. The relationships between the volume of sulfuric acid added to the bath versus bath pH and the hydrogen cyanide concentration in air samples collected above the bath versus bath pH are presented graphically in Figures 2 and 3.

The curves in Figure 2 show that the gold bath has very little buffering capacity with the addition of sulfuric acid. Each milliliter of dilute sulfuric acid (1:1, v/v), or 0.5 ml of concentrated sulfuric acid, added to the test bath represents the addition of $\sim$0.92 lb of concentrated sulfuric acid to the 30-gallon production bath. Thus, the accidental addition of a 9-lb bottle of concentrated sulfuric acid would decrease the plating bath to below pH 1.5.

Table 1. The Effect of Sulfuric Acid Addition to Gold Plating Solution at 70°C

Trial No.	Total Acid Addition (ml)	Solution (pH)	PPM CN*	Weight HCN** (μg)	Air Sample*** (ml)	HCN in Air**** (μg/l)
Study A - Dilute Sulfuric Acid (1:1, v/v)						
1	0	-	0.014	0.73	495	2*****
2	0	5.61	0.022	1.1	729	2
3	1.0	4.95	0.081	4.2	528	8
4	2.0	4.13	0.38	20	495	40
5	3.0	2.72	0.96	50	495	100
6	4.0	2.20	2.2	114	528	220
7	5.0	1.90	4.7	244	561	440
8	6.0	1.75	10.8	561	726	770
9	7.0	1.57	11.5	597	495	1210
10	8.5	1.42	12.0	623	495	1260
11†	10.0	1.28	13.5	701	495	1420
12	15.0	0.93	19.5	1010	495	2050
13	15.0	0.8	35.0	1820	495	3670
Study B - Concentrated Sulfuric Acid						
1	0	5.58	0.027	1.4	495	3
2	1.0	4.30	0.33	17	495	4
4	3.0	1.84	5.2	270	495	550
5†	5.0	1.27	13	576	495	1360
6	10.0	0.59	50	2600	495	5250

*Cyanide concentration found in 50-ml sample collection solution.

**Calculated weight of HCN gas in the collecting solution.

***Total air sample volume calculated as air flow rate (33 ml/min) x sampling time.

****Micrograms per liter (μg/l) HCN calculated in air sample.

*****Bath solution at room temperature.

†This addition is similar to addition of 9 lbs of H_2SO_4 to 30 gal. gold bath.

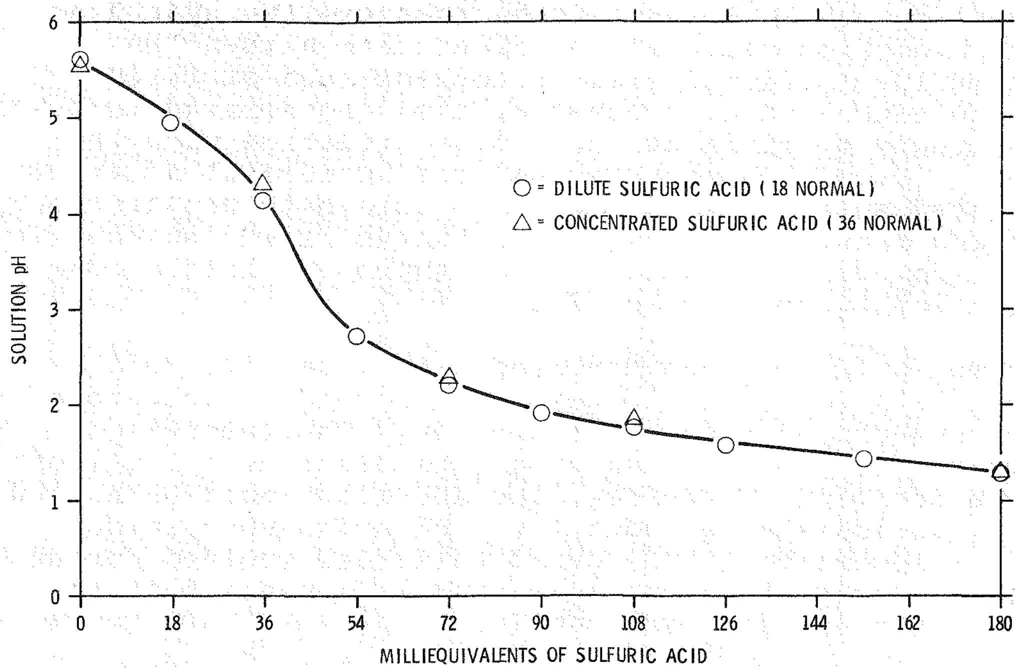

Figure 2. Gold Bath pH Versus Added Volume of Sulfuric Acid

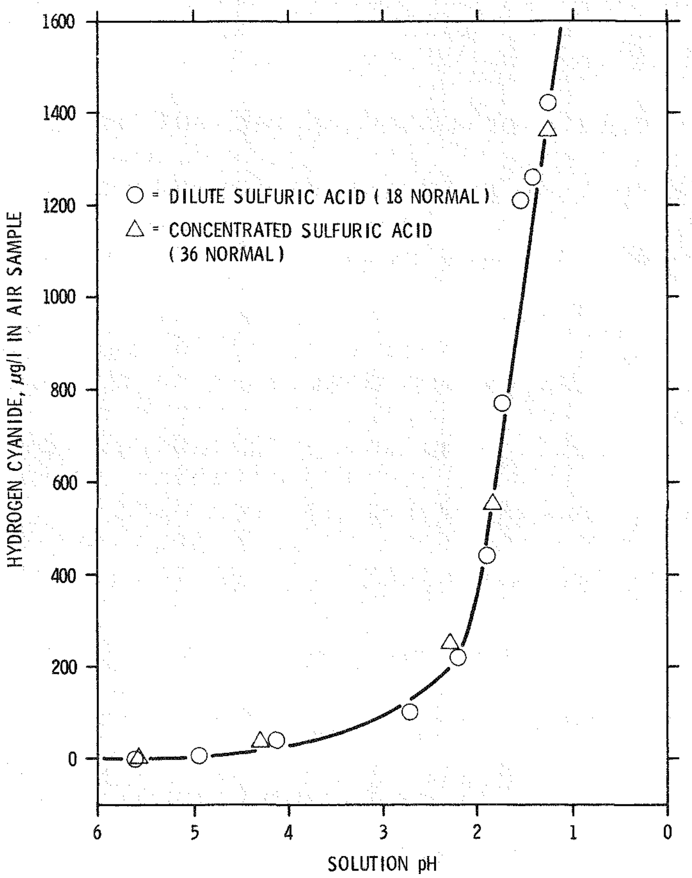

Figure 3. Hydrogen Cyanide Evolution as a Function of Gold Solution pH

The identical curves in Figure 3 show that similar hydrogen cyanide gas evolution data were obtained with either the addition of dilute sulfuric acid or concentrated sulfuric acid. In the experimental procedure, the concentrated acid was added very slowly to minimize the violent reaction with the plating bath. From this observation, the accidental addition of concentrated sulfuric acid may cause gold bath eruption out of the plating tank. The curve shows that a rapid increase in hydrogen cyanide gas was found in air samples collected over plating bath solutions below pH 2.5.

The production gold bath was prepared with potassium gold cyanide salt $[K\,Au(CN)_2]$ to contain 20 g/l gold. Laboratory analysis data verified this concentration. The theoretical cyanide content in the bath would be equivalent to 5.5 g/l of hydrogen cyanide gas. Therefore, the 250-ml of gold bath used in the study would release about 1.4 g of hydrogen cyanide gas. The total weight of hydrogen cyanide gas evolved during either sulfuric acid study was less than five percent of the theoretical amount in the bath sample.

CONCLUSIONS

The slow addition of concentrated sulfuric acid to the gold bath test sample at 70°C produced a violent reacton. From these test observations, the accidental addition of concentrated sulfuric acid may cause gold bath eruption out of the plating tank.

The slow addition of either dilute or concentrated sulfuric acid produced the immediate appearance of a light-yellow colored precipitate. The amount of precipitate formed was dependent upon the solution pH and the appearance of a precipitate would be an indication that acid was being added to the wrong bath.

The hydrogen cyanide gas release test data were collected on a 250-ml volume of gold bath using a closed distillation system. Only minimum solution agitation was possible for proper use of the gas dispersion tube for cyanide sampling. Therefore, the normal operating bath agitation as well as no agitation during plating shutdown may produce results differing from data collected in this study. The plating bath surface area and the air sampling time would also affect the rate of hydrogen cyanide gas evolution.

ACKNOWLEDGMENT

The author greatly appreciates the assistance of GEND Chemistry Laboratory Technician MaryAnn Brown in equipment set-up and data collection in this work.

REFERENCE

1. <u>Standard Methods For the Examination of Water and Wastewater,</u> American Public Health Association, American Water Works Association, Water Pollution Control Federation, 14th Ed., Washington, D.C., 20036, 1975.

DISTRIBUTION

DOE

P. M. Ramey, PAO
TIC, Oak Ridge (27)

GE

Technical Information Exchange
Schenectady (5)

GEND

R. J. Antepenko
R. W. Bonham
W. C. Brown
J. M. Carter
E. A. Duroseau
G. F. Guettler
R. Ledesma
N. H. Parsons
W. J. Powell
S. N. Suciu
R. L. Walters
W. W. Welbon

Technical Data Library
C. J. McGirr (Reproduction Masters)

Sandia Laboratories, Albuquerque

S. D. Holmes 1473

Sandia Laboratories, Livermore

H. R. Johnson 8312

University of California, Lawrence Livermore Laboratory

J. W. Dini L332