30 up

**Kansas City
Division**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

THIS DOCUMENT CONFIRMED AS
UNCLASSIFIED
DIVISION OF CLASSIFICATION
BY J H Kachin / amh
DATE 3/9/77

5 SOLDERABILITY
PROBLEMS
CAUSED BY
GOLD ELECTROPLATE.

4 BDX-613-324

12 April 1969
MASTER

6 Prepared by
M. V. Davis
Materials Testing
Department 421

Contract # on next page

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

24 Dep. NTIS.

Technical Communications

**Kansas City
Division**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

P8645

flg

THE BENDIX CORPORATION
KANSAS CITY DIVISION
KANSAS CITY, MISSOURI

A prime contractor for the Atomic Energy Commission

Contract ~~Number~~ AT(29-1)-613. ~~USAEC~~

14

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

ABSTRACT

One of the problems encountered in soldering electroplated gold parts has been the co-deposition of a polymer-like substance with the gold. Bell Telephone Laboratories has done extensive research in this field, and their findings are outlined in this report. Additional findings of the Test Laboratory are also presented.

CONTENTS

Section	Page
INTRODUCTION	1
REVIEW OF BELL TELEPHONE LABORATORIES PAPER	2
Polymer in Gold Plate	2
Non-Proprietary Solutions	2
Proprietary Solutions	2
General Comments	2
Effect of Cathode Efficiency	3
Where the Polymer is Deposited	3
Bell Laboratories' Conclusions	4
TEST LABORATORY INVESTIGATIONS	5
Observations	5
Possible Effect of Barrel Plating Small Parts and Components	5
SUMMARY	6

INTRODUCTION

During the past 8-10 years the Test Laboratory has been asked from time to time to investigate the inability of gold electroplate to solder, or "wet" the solder material. This has been an electronic industry problem, not specifically a Bendix one, and has been widely debated and discussed in trade journals.

An early investigation (June, 1962) involving flat cable fabrication showed that some of the gold plated parts obtained from suppliers left a transparent film when the gold was dissolved in aqua regia. At the time, it was believed that the film was probably a surface film rather than a co-deposition. Parts which exhibited this condition did not wet with solder sufficiently to produce a bond between the gold plate and the part to which it was to be soldered. Parts or components made from purer gold solutions (solutions not containing metal brighteners or hardeners) appeared to wet and solder without difficulty. Parts gold plated from the proprietary "Temperex" bath soldered without difficulty, and no residual film was observed when the plate was dissolved in aqua regia. Recently, a paper¹ was submitted for publication to the magazine Plating by the Bell Telephone Laboratories, which has comprehensively investigated the presence of a film associated with gold electroplating. Bell Laboratories found that a polymer-like film is co-deposited with gold from acid cyanide type gold electroplating solutions. The essential findings of this paper are summarized in this report.

The most difficult problems associated with inability to solder gold plated parts at Bendix appeared in retrospect to start with the introduction of various acid cyanide type plating baths. The alkaline cyanide solutions, without hardeners, produced gold plate without any film formation.

This report also includes a summary of current investigations by the Bendix Test Laboratory concerning this problem. Presence of a transparent film in gold electroplated at Bendix has been confirmed, but no definite conclusions have yet been reached. Complete findings will be incorporated into future reports on this subject.

¹ Munier, G. B. "A Study of Polymer Co-Deposition with Gold During Electroplating", presented at American Electroplater's Society meeting, Boston, Massachusetts, February, 1969.

REVIEW OF BELL TELEPHONE LABORATORIES PAPER

The nature of deposits from various gold electroplating solutions was comprehensively investigated. Both proprietary and non-proprietary gold plating solutions were studied. The following is a summary of their findings.

POLYMER IN GOLD PLATE

Non-Proprietary Solutions

A series of gold solutions were prepared and test strips were electroplated from these solutions. Each of the test strips gold plated was analyzed for carbon content in the gold plate.

The carbon content was determined by a microanalytical method. The method is able to determine carbon in quantities greater than 1 microgram. The carbon content of the electroplate is a measure of the quantity of polymer formed.

When no metal brighteners or hardeners were used in the make up of the gold solutions, no carbon was detected in the gold plate. When metal hardeners (or brighteners) were used, i.e., cobalt, nickel, etc., the carbon content in the deposit was as great as 1.3 weight percent.

Proprietary Solutions

Test strips were also electroplated from a series of proprietary solutions that are marketed commercially. The gold deposited from these solutions was also analyzed for carbon content.

All gold deposited from solutions using metal hardeners contained varying amounts of carbon up to 0.30 percent. Solutions where hardeners or brighteners were not employed produced a gold plate free of carbon.

General Comments

The carbon analysis was a measure of the polymer present in the gold deposit. With the exception of one proprietary solution using silver as a hardener,² all solutions above pH 7 (Alkaline) produced gold deposits having no detectable carbon content. All acid cyanide baths (below pH 7)

² One of the original bright gold solutions used at Bendix, Sel-Rex M-2 plating bath formulation, was an alkaline cyanide using silver as a brightener.

that used hardeners produced gold deposits with varying amounts of carbon content. Without hardeners these acid cyanide solutions, with one exception, deposited gold with no detectable carbon content.

This study also showed that the relationship between the weight of gold deposited and amount of carbon detected was directly proportional to the weight of gold deposited.

EFFECT OF CATHODE EFFICIENCY

The net effect of the addition of metal hardeners to the gold plating solutions is to drastically reduce the cathode efficiency. At low cathode efficiency the evolution of hydrogen is promoted. Solutions having 95% cathode efficiency with no hardener present may drop as low as 35% cathode efficiency with the addition of as little as 0.3 grams per liter of nickel or cobalt.

An ammonium citrate-acid cyanide plating bath containing no hardener, that ordinarily plates a carbon free deposit, was used to show the effect of cathode efficiency on the co-deposition of polymer. The cathode efficiency was deliberately lowered by decreasing the temperature and increasing the current density.

Deposits of gold showed increasingly higher carbon content as the cathode efficiency was dropped stepwise from 68 to 38 percent. This showed that the cathode efficiency of the plating operation was critical. Cathode efficiency should be maintained at a high level (90% or higher) when plating with acid cyanide solutions to avoid the formation of a co-deposited polymer.

WHERE THE POLYMER IS DEPOSITED

To determine if the polymer was a surface deposit, deposits known to contain detectable amounts of carbon were mechanically abraded and chemically cleaned to remove any surface films. This treatment failed to eliminate the carbon content of the gold plate.

The gold was dissolved in aqua regia fumes by a microanalytical technique and the residual film, after the dissolution of the gold, carefully washed and dried. The dried film was orange-brown in color, dispersed through with gold chloride crystals.

The undried film was of a clear transparent type. This film had not been structurally or chemically characterized as of the date of the paper.

Bell Laboratories observed that the polymer film had the identical contour as the fragment of gold plate being analyzed. The film was swollen

by the acid fuming and was 4-5 microns thick, consisting of several distinct layers 1-2 microns thick.

BELL LABORATORIES' CONCLUSIONS

A detectable quantity of organic material is co-deposited with gold plated from acid cyanide solutions. No polymer deposition was observed from non-cyanide or alkaline solutions containing no metal hardeners.

The cyanide ions are apparently polymerized by hydrogen evolution at the cathode during gold deposition, although the mechanism of this reaction is not known or postulated in the paper.

Metal hardeners, such as nickel or cobalt, in concentrations as low as 0.1% drastically lower the cathode efficiency of the acid cyanide plating bath, permitting a polymer to be co-deposited with gold.

A polymer can be co-deposited with the gold by lowering the cathode efficiency of acid cyanide baths containing no metal hardeners.

A high cathode efficiency is necessary for obtaining a gold plate free of polymer when using acid cyanide baths without metal hardeners.

In acid cyanide solutions there exists a linear relationship between total gold deposited and total carbon content in the deposit.

The polymer is not a surface phenomena. It is distributed throughout the gold plate and exists in well defined layers covering the entire cathode area.

Samples of the polymer were successfully isolated from the gold plate and microscopic examination revealed an amorphous, transparent film.

The polymer formation and co-deposition with the gold plate was not blocked by such plating techniques as current reversing, superimposing either ac or dc current, salt bridges, and ultrasonic vibration.

TEST LABORATORY INVESTIGATIONS

OBSERVATIONS

The Bell Laboratories paper revived Test Laboratory interest in the phenomena of a polymer being co-deposited with gold plated from acid cyanide baths. Using gold plate from the 1962 investigations and more recent gold plate from acid cyanide baths, the investigation was continued.

When acid cyanide gold plate was dissolved in aqua regia, a transparent film of the same size and shape of the gold fragment being dissolved was observed. Dilute aqua regia was used to make the reaction slower and less violent. This enabled the reaction to proceed at a fairly slow rate and the reaction could be observed with a low power microscope. Observations made in the Bendix Test Laboratory confirm the Bell Laboratories findings.

POSSIBLE EFFECT OF BARREL PLATING SMALL PARTS AND COMPONENTS

A problem currently being investigated is the poor solderability or wettability of certain small gold contact pins. Although the gold plate was apparently deposited from a pure gold acid cyanide bath (no metal hardeners), trade-named "Temperex," many of the pins exhibited the co-deposition of polymer in the gold plate when dissolved in aqua regia. The apparent quantity of polymer film varies from pin to pin, some pins seeming to have much more polymer than others.

The most economical method of plating small parts is to barrel plate them. Due to the large quantities this is usually satisfactory for most items. However, in the case of acid gold plating some complications may arise.

In the barrel plating operation, the parts in the plating barrel are only intermittently conducting an electrical current. Also, there is undoubtedly a large fluctuation in cathode efficiency because of this intermittent type current flow through the part. One source lists the current efficiency as being between 50 and 90% for barrel plating gold operations. (It is not possible to determine cathode efficiency of this type plating because of the variables involved.)

The logical explanation for the formation of a co-deposited polymer from an acid cyanide bath containing no metal hardeners is that the effective cathode efficiency in the barrel plating operation is too low. Low cathode efficiency would favor the formation and co-deposition of the polymer observed in parts plated in the barrel.

SUMMARY

The cause of poor solderability or failing to wet gold electroplated from acid cyanide solutions has been shown to be, at least in part, the co-deposition of a polymer-like substance. The presence of this organic film prevents the effective action of solder fluxes.

The comprehensive Bell Laboratories paper has shown that a polymer is co-deposited with gold plated from acid cyanide baths with the following conditions:

- a. The solution must be an acid cyanide solution (one exception).
- b. The solution must have a metallic hardener such as nickel or cobalt to reduce cathode efficiency.
- c. Any condition that reduces the cathode efficiency of the plating bath contributes to the formation of a co-deposited polymer.

Both the Bell Laboratories paper and Test Laboratory investigations show that the co-deposited polymer exists throughout the deposited gold and is present in multiple layers.

Barrel plating, with its lower current efficiency, is thought to contribute to the co-deposition of a polymer from an acid cyanide bath containing no metal hardeners.

Only gold plate substantially free of co-deposited polymer will properly wet and produce an acceptable solder joint.

The polymer-like film co-deposited with the gold plate would result in high resistance problems in electrical contact applications. Bell Laboratories noted that an orange-brown deposit of the polymer occurred on the surface of gold plated contacts (plated from acid cyanide solutions) that led to high contact resistance.