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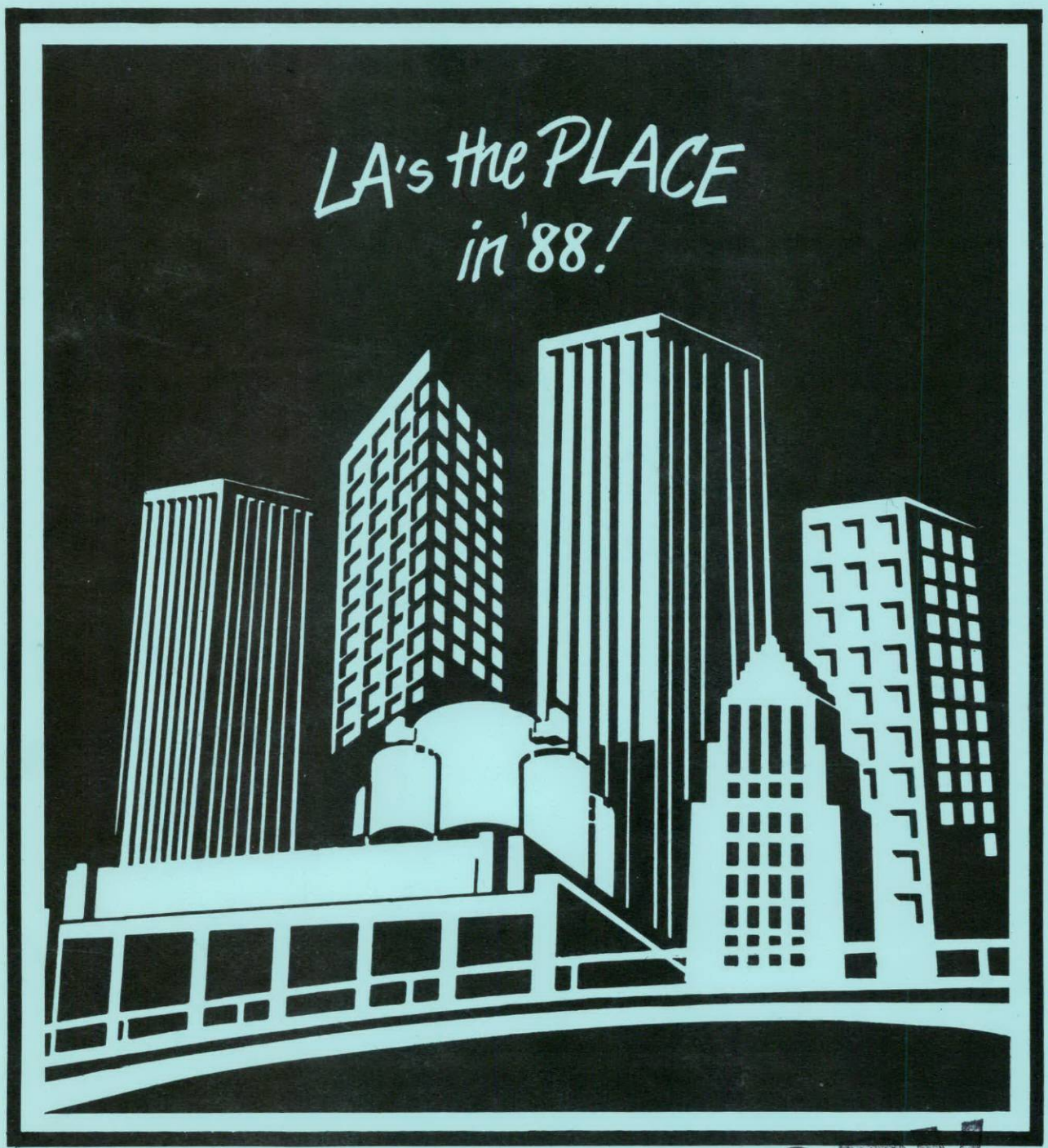

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Electronics I
Session C

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C.A. Holden, H.H. Law,
C.A. Mattoe and J. Sapjeta
AT&T Bell Laboratories
Murray Hill, NJ 07974

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C.A. Holden, H.H. Law
and R.L. Opila
AT&T Bell Laboratories
Murray Hill , NJ 07974

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Engelhard Corp.
Electronic Products Group
One West Central Ave.
East Newark, NJ 07029

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Electronics I
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Murray Hill, New Jersey 07974

ABSTRACT

Since a 40 year life is no longer an overall criterion for all electrical contacts, there has been a relaxation in electrical requirements in some project designs which allows contact resistance (R_c) values up to 50 mΩ. This is a range over which non-precious metal deposits may be effective as replacement coatings. One promising candidate is the nickel phosphorus alloy (Ni/P).

A neutral pH ammoniacal plating bath has been developed that produces low phosphorus content gray colored Ni/P deposits that have favorably low R_c (2-7 mΩ) after exposure to several accelerated tests. The internal stress of the Ni/P deposit is comparable to that of the typical hard gold plate used on plug-in type electrical connectors. The ductility of the Ni/P deposit is less than either pure nickel or hard gold. Preliminary wear results show that lubricated Ni/P deposits appear to perform well for nearly 100 wear cycles. A flash of gold (≤5 μin) improves its wear resistance by at least an order of magnitude.

Although this low R_c gray Ni/P alloy has been successfully plated in the laboratory, it is necessary to demonstrate conclusively that this Ni/P bath can withstand the rigors of everyday use that an industrial bath incurs. With appropriate nickel anodes, the neutral pH ammoniacal Ni/P plating bath can be operated continuously to deposit the Ni/P alloy at >95% cathode efficiency. With only minimal maintenance, the bath continues to function effectively for at least 35 bath turnovers. The current investigation also indicates that the bath chemistry is rather complex and that all of the constitutents are required for proper operation. Based on its adaptability to a flow cell operation, this Ni/P plating bath is a good candidate for use in a production strip-plating machine.

1. Introduction

Precious metals, such as gold and palladium, have been and will continue to be the premier electrical contact materials for low voltage operations in critical areas where interruptions of service cannot be tolerated or where access to initiate repair of faulty connectors is impractical. However, there are many non-critical areas where a 40 year life is no longer an overall design criterion. Thus in some project designs, there has been a relaxation in electrical requirements which allows contact resistance (R_c) values up to 50 mΩ. This is an area where non-precious metal deposits may be able to replace gold.

One candidate is the nickel phosphorus alloy (Ni/P). A survey of the literature pertaining to the electrodeposition of Ni/P alloys shows that most of the work has been with low pH acid systems. There exists little information pertaining to ammoniacal systems. This is perhaps due

to the fact that the low pH baths produced electroplated deposits having a broad range of P contents, while the ammoniacal baths yielded only deposits with the low P content.

Robbins et al. [1] reported that the Ni/P deposits with a P content of 3-8 a/o, plated from a low pH bath, have favorable R_c values. This finding supports the present approach of considering low P content Ni/P deposits as contact materials. The Ni/P deposits from the low pH bath and from the neutral bath are likely to be very different.

The purpose of this work is to report that low P content Ni/P deposits plated from a neutral pH ammoniacal bath are a promising contact material for replacing gold in some applications. This is demonstrated by the R_c data obtained after accelerated environmental tests and the stress, ductility, and wear resistance properties of the Ni/P deposits. Although this low R_c gray Ni/P alloy has been successfully plated in the laboratory, it is necessary to demonstrate conclusively that this Ni/P bath can withstand the rigors of everyday use that an industrial bath incurs. Since the bath chemistry of this neutral ammoniacal Ni/P solution is not simple, to obtain optimum performance it is necessary to determine the operating parameters such as solution flow rate, type of nickel anode, and pH range and to monitor the concentrations of bath constituents, which include nickel, chloride and phosphite ions. It was decided that a flow cell operation would be the best choice for generating high bath turnover, and a flow cell arrangement that simulates a strip plating machine operation was employed.

2. *Experimental*

Contact resistance was measured at a 50 gram load, which was applied using a converted microhardness tester [2]. A pure gold wire (0.02 inch diameter) makes contact at the prescribed load with the test sample, and the R_c is measured using a four wire instrument whose open circuit voltages were low enough (<20 millivolts) to prevent electrical breakdown of any film that might be present on the test sample.

Internal stress was obtained with a modified SEL-REX IS meter based on the principle of measuring the deformation of a thin plane specimen plated on both sides. The detail is described

elsewhere [3]. Ductility was measured with a method of Nakahara et al. [4]. The thickness of all deposits was 2.5 microns. The annealed copper foil substrate was 50 microns thick and has a ductility of about 8% elongation.

In the wear testing, the Ni/P plated wires (80 mil diameter) were mounted on the apparatus with their axes at right angles. The setup has been described elsewhere [5]. The top wire is held rigid while the bottom wire moves back and forth at a 45° angle so that the wear products are pushed to the sides of the wear track instead of piling up at the ends. The load (0-1500 g) can be varied by applying pressure to the lower wire through a balanced beam arrangement and a load of 200 g was used in the present study.

The bath composition during operation of the flow cell (Fig. 1) that simulates a strip plating machine operation was monitored extensively. Plating bath samples were prepared by taking one ml of bath, adding one ml of ammonium hydroxide to prevent precipitation on standing, and diluting to a final volume of 50 ml. These samples were then analyzed for nickel, chloride, and phosphite. The concentration of nickel was determined by atomic absorption spectrophotometry using a calibration curve. The concentrations of chloride and phosphite were determined by ion chromatography using Dionex HPIC-AG3 and HPIC-AS3 columns with an anion suppressor and conductivity detection. Plating bath samples were diluted 1:10 before injection. With 1 mM sodium carbonate as eluent and a flow rate of 1.8 ml/min, chloride and phosphite showed retention times of approximately 5 and 20 minutes, respectively. Concentrations were determined by running a daily calibration curve for each ion, with an error of about 5%.

3. Results and Discussion

3.1 Contact Resistance

A typical Hull cell panel from the Ni/P bath is shown in Fig. 2A. The good deposit is the light gray deposit at the lower current density (C.D.) region. The R_c is much lower than that of the bright area (higher C.D.). The Hull cell pattern is opposite to that obtained from a typical Watts nickel plating bath without any H_3PO_3. Figure 2B shows the latter pattern, which is

common in electrodeposition: matte and bright deposits in the lower C.D. region (0-80 mA/cm^2) and gray deposits in higher C.D.(>80 mA/cm^2). However, the gray deposits are not the same. After an exposure to 50°C and 95% relative humidity (R.H.) for 86 hours, the R_c of the gray-colored Watts nickel deposit at 100 mA/cm^2 (Fig. 2B) was 100 mΩ, compared to the R_c of 5 mΩ for the gray Ni/P deposit at 60 mA/cm^2 (Fig. 2A). This clearly established the difference in R_c between the pure nickel deposit and the Ni/P alloy.

A longer exposure period to the warm humid environment showed similar R_c values. After 26 days the Ni/P deposit plated at a lower C.D. of 35 mA/cm^2 (gray area) has a R_c of 2-2.4 mΩ, while the R_c in the the high C.D. region (200 mA/cm^2) Ni/P deposit has a very high R_c (20-4000 mΩ) similar to bare nickel (700-3800) after 9 days exposure to the same environment.

The R_c of the gray Ni/P deposit also remained low when the deposit was exposed to other accelerated tests. After 90 days exposure to a dry heat of 205°C, the R_c values of Ni/P deposits plated at C.D. of 25-50 mA/cm^2 were 3-7 mΩ. In another test the Ni/P deposits, bare nickel, and copper were subjected to moist sulfur vapor, generated from flowers of sulfur, at 50°C and 75% R.H. for 72 hours. As expected, the R_c of the copper was that of an insulator, while the R_c of three Ni/P deposits were 1.0-2.8 mΩ and the R_c of bare nickel was of 60-2000 mΩ.

3.2 Stress and Ductility

The change of the internal stress with the deposit thickness of Ni/P plated at 35 mA/cm^2 is shown in Figure 3. When the deposit is more than 0.05 mil thick, the stress reaches a constant value of 25 kg/mm^2. The current density does not affect the stress. The stress of Ni/P deposits obtained at both 25 and 35 mA/cm^2 is 25 kg/mm^2. This is lower than the stress of 35 kg/mm^2 found with Ni deposited from a $NiCl_2$ bath (pH 4.8). The stress of the Ni/P is in the range of the reported values for nickel from a chloride bath (21-60 kg/mm^2) and for cobalt hardened gold (22-29 kg/mm^2) [6]. Thus the internal stress of the Ni/P should not cause any problem if the alloy is used as a contact material.

The ductility of Ni/P plated at different current densities is compared to that of the cobalt

hardened gold and to nickel plated from a $NiCl_2$ bath in Table I. Within the experimental accuracy, the ductility of Ni/P deposited at 25 and 35 mA/cm^2 is the same. The value is less than that found for both hard gold and nickel. This is expected because Brenner et al. [7] reported that Ni/P alloy with less than 2% P is strong and slightly ductile. Although no specific data were given, the deposits become more brittle as the phosphorus content was increased. It is clear that the Ni/P prepared with the present method is not appropriate for applications requiring ductile material. For such applications and the ones where lower stress is desirable, the use of an alternating current to plate the Ni/P should be considered. Kendrick [8] reported that nickel deposits obtained from an all-chloride solution have higher ductility and lower stress when the plating is performed at frequencies of 500 c/s with relatively large amounts of deplating during each cycle. The use of AC plating for depositing Ni/P is being explored.

3.3 Wear Resistance

The wear resistance of the gray Ni/P deposit was evaluated using a crossed wire wear test method [5] that simulates the wear that develops on plug-in type printed wiring boards. This wear testing method has been used since 1963 to evaluate gold plating from proprietary hard gold baths prior to their acceptance for connector use in by AT&T Technologies. After 100 cycles, the wear resistance of the lubricated Ni/P deposit was comparable to that of a typical hard gold plate. However, some type of organic lubrication, which is necessary for the initial wear-in of any material, including hard gold, appears to be limited in its effectiveness in preventing appreciable wear of the Ni/P deposit after 150-200 cycles with this wear apparatus. One method that is likely to provide excellent wear resistance (similar to hard gold) is to put a flash of gold ($\leq$5 μin) on the deposit. The gold will also act as a lubricant in the initial "break-in" during wear. A flash of gold over rhodium has been used as a lubricant since at least 1967 [5].

3.4 Operation of Flow Cell

In the first run, nickel sheet anodes (200 series Ni) were used and the desirable gray Ni/P deposit was obtained. However, the depletion of nickel from the solution was rapid, and within 1.5 bath turnovers the nickel concentration was about 80% of the initial value (Fig. 4). An

addition of nickel chloride brought the nickel concentration to the initial value and increased the chloride concentration by 4 g/L. The rate of nickel depletion remained the same. Thus, the anodic current efficiency is about 87% of the cathodic current efficiency (~92%). Over a longer period, it can be expected that an excessive amount of chloride will accumulate and subsequently imbalance the complex chemistry of the Ni/P bath. If the anodic current efficiency were not improved, the life of the plating bath would not be long enough for practical operation.

The reason for this nickel depletion was the passivation of the nickel anodes that initiated the formation of a heavy slimy green precipitate of nickel hydroxide. Although an increase in pH from 7.8 to 8.0-8.3 considerably reduced the precipitation on the anodes, the nickel concentration in the solution continued to be depleted, though at a slower rate. It appears that the anodic reaction consists of not only nickel dissolution but also oxygen evolution. Since hydronium ions are produced with oxygen, the pH at the anode surface would be in the range of 5-7, where the precipitation of nickel hydroxide would occur. Once the surface is coated with the nickel hydroxide, the anode, for all practical purposes, ceases to dissolve and the oxygen reaction dominates, resulting in a heavy precipitate. By increasing the pH to the range of 8-8.3, the oxygen evolution was slowed down, but not sufficiently to maintain constant nickel concentration. Thus it was reasonable to try the depolarized nickel anodes.

After confirming that the depletion of nickel still occurred in a new bath, the nickel concentration was brought to the initial value by adding nickel chloride, and sulfur-bearing depolarized anodes were substituted. It was found that the passivation that occurred on the original nickel anodes was prevented. However, when the pH was allowed to drift below pH 8 for an extended period of time, nickel hydroxide did appear, though to a lesser degree. Hence, the anodic efficiency of nickel dissolution using sulfur depolarized anodes was about the same as the cathodic current efficiency, i.e., the amount of nickel dissolved into the solution was the same as the amount plated out.

Over four months the same Ni/P bath was used with only minor additions of ammonium citrate, phosphorous acid, and ammonium chloride being made as necessary to compensate for the

normal dragout and to maintain bath chemistry. No further addition of nickel salts was made since the depolarized nickel anodes were dissolving sufficiently to maintain an adequate nickel concentration. The concentrations of nickel and phosphite were maintained to within 20% of the initial values, whereas the concentration of chloride was within 10%.

When the cathodic efficiency fell below 90%, analysis by ion chromatography showed that the chloride and phosphite ions were low, indicating a slight imbalance in bath chemistry. Although the citrate ion was, unfortunately, not clearly detected by our ion chromatography set-up, its concentration was assumed to be proportionately lower than its initial value. Small additions of phosphorous acid, ammonium citrate, and ammonium chloride were made with subsequent improvement in cathode efficiency. Of course, with these additions ammonium hydroxide was added to insure that the optimum complex chemistry existed and to maintain the pH at 8-8.3. Thus the cathodic current efficiency is a good indicator of whether the bath components are within the desirable range.

During these four months, there were approximately 35 bath turnovers with an average cathode efficiency >95%. The desirable gray colored Ni/P deposit, as determined by SEM micrographs and Auger electron spectroscopy, was consistently obtained.

4. Conclusions

A neutral pH ammoniacal plating bath has been developed that produces low phosphorus content gray nickel deposits that have favorably low R_c (2-7 mΩ) after exposure to several accelerated environmental conditions: a temperature of 50°C and 95% R.H. for one month, a dry temperature of 205°C for three months, and sulfur vapor at 50°C and 75% R.H. for 72 hours.

Stress, ductility and wear resistance of the Ni/P deposit have been evaluated. The stress of the Ni/P deposit is comparable to nickel from a chloride bath and to cobalt-hardened gold (used for wear). The ductility of the Ni/P deposit is less than that of nickel or hard gold. For applications where high ductility is desired, the use of an alternating current to plate the Ni/P should be considered.

Preliminary wear results show that lubricated Ni/P deposits appear to be limited to <100 wear cycles with this wear apparatus. A flash of gold (≤5 μin) appears to improve its wear resistance by at least an order of magnitude.

It has been demonstrated that, with sulfur bearing depolarized nickel anodes, the neutral pH ammoniacal Ni/P plating bath can be operated continuously to deposit a gray colored Ni/P alloy at >95% cathode efficiency. With only minimal maintenance, the bath still works perfectly after 35 bath turnovers, which is considered to be a good lifetime for a commercial bath. The current investigation also indicates that the bath chemistry is rather complex and that all of the constituents are required for proper operation. Based on its adaptability to a flow cell operation, this Ni/P plating bath is a good candidate for use in a production strip-plating machine.

5. Acknowledgment

We wish to acknowledge our appreciation for the help from our colleagues: J. A. Abys and V. Lambrecht for the ductility measurements, and R. Opila for his analysis of the phosphorus content of the Ni/P deposits. We are also grateful to Mr. P. C. Milner for stimulating discussions.

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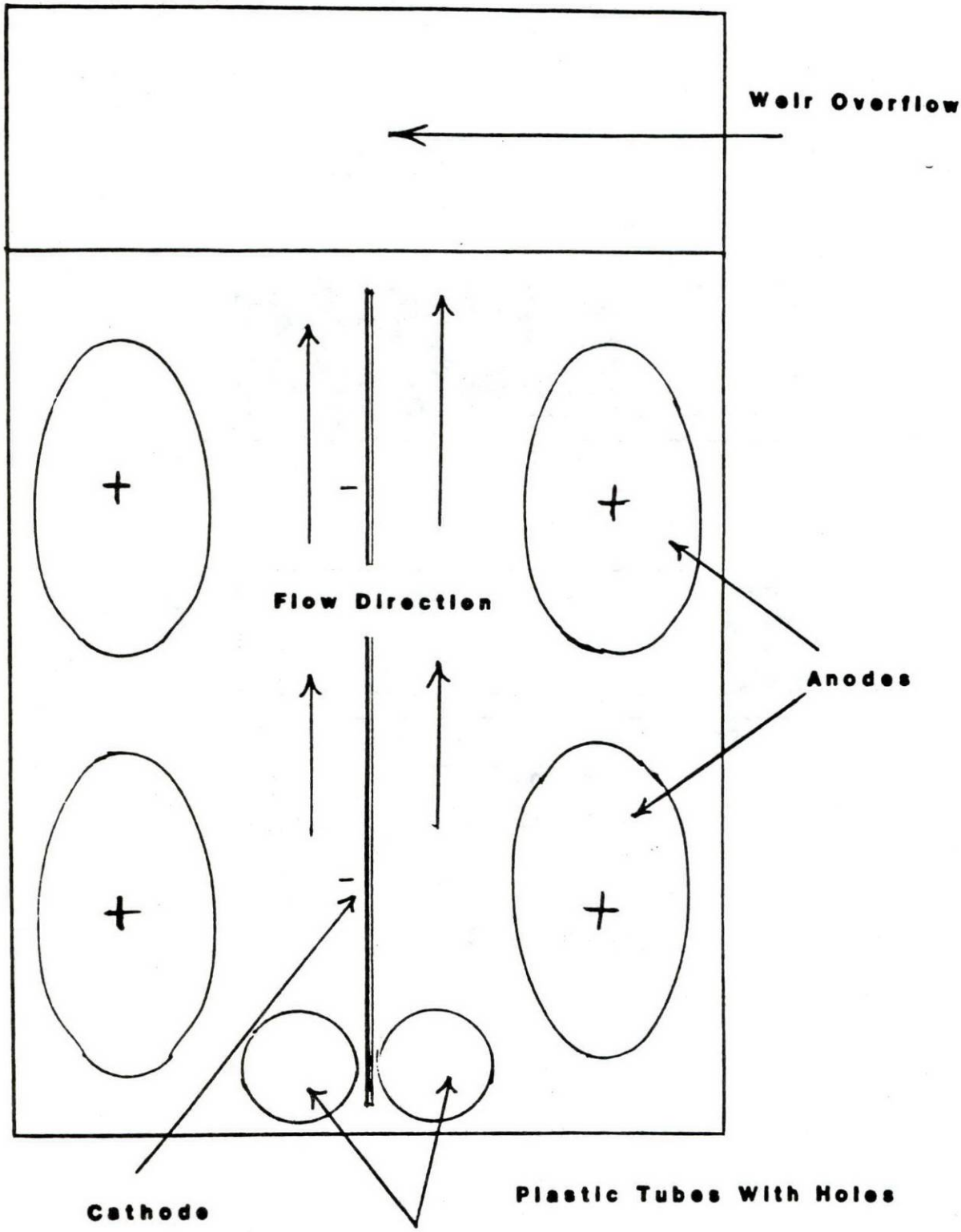
Table I. Ductility of Electrodeposits

Deposit	% Elongation
Ni (Ni Chloride bath)	1.4
Au (Co hardened)	2.4
Ni/P (25 mA/cm^2)	0.3
Ni/P (35 mA/cm^2)	0.5

FLOW CELL DESIGN



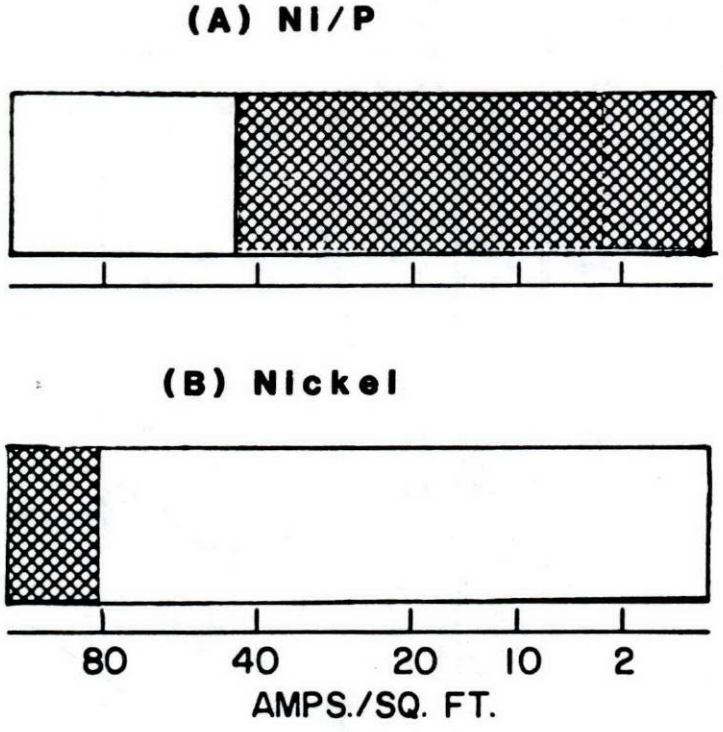
TOP VIEW OF THE PLATING FLOW CELL.

FIGURE 1

HULL CELL PANELS

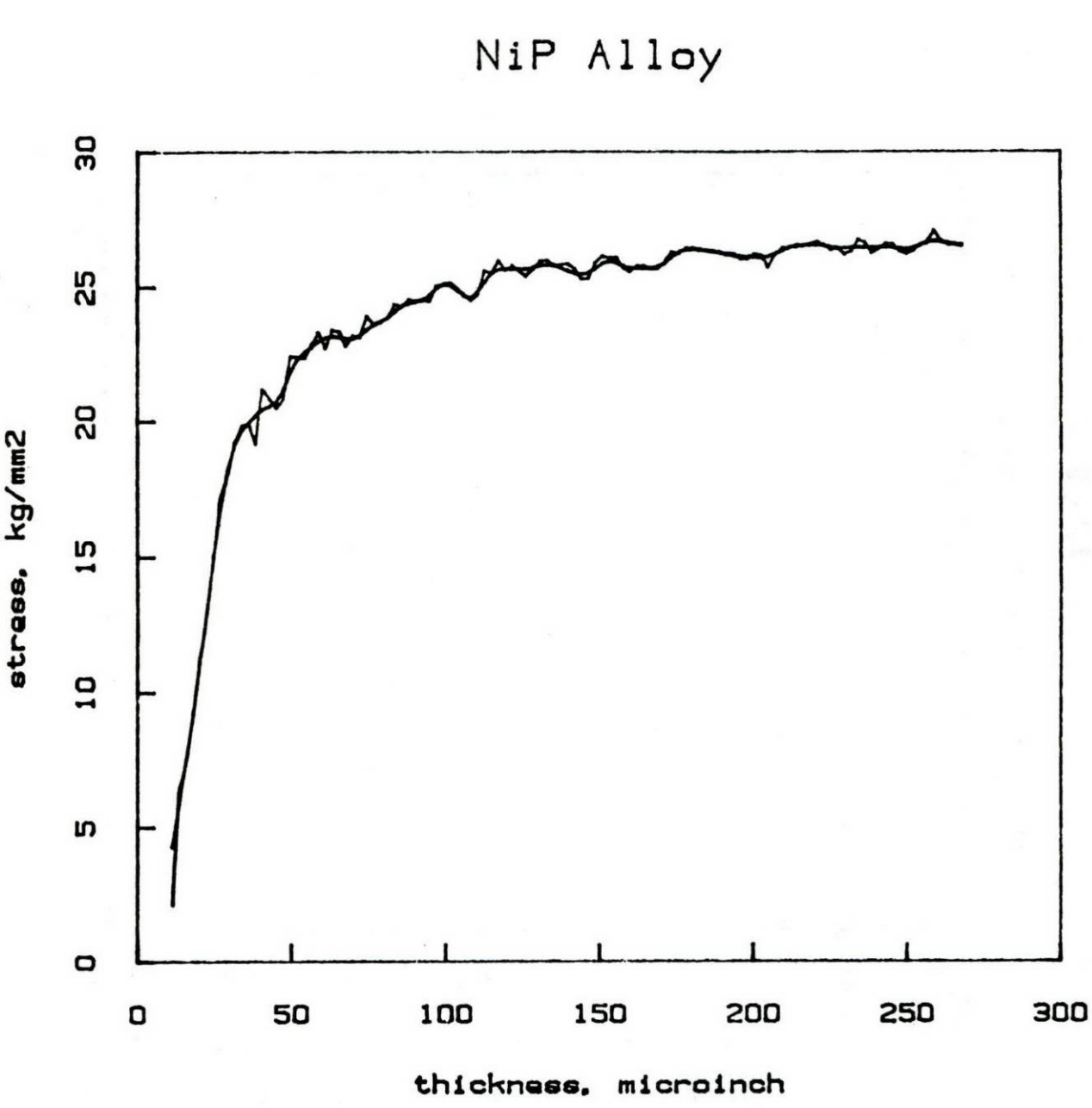
Gray

Bright



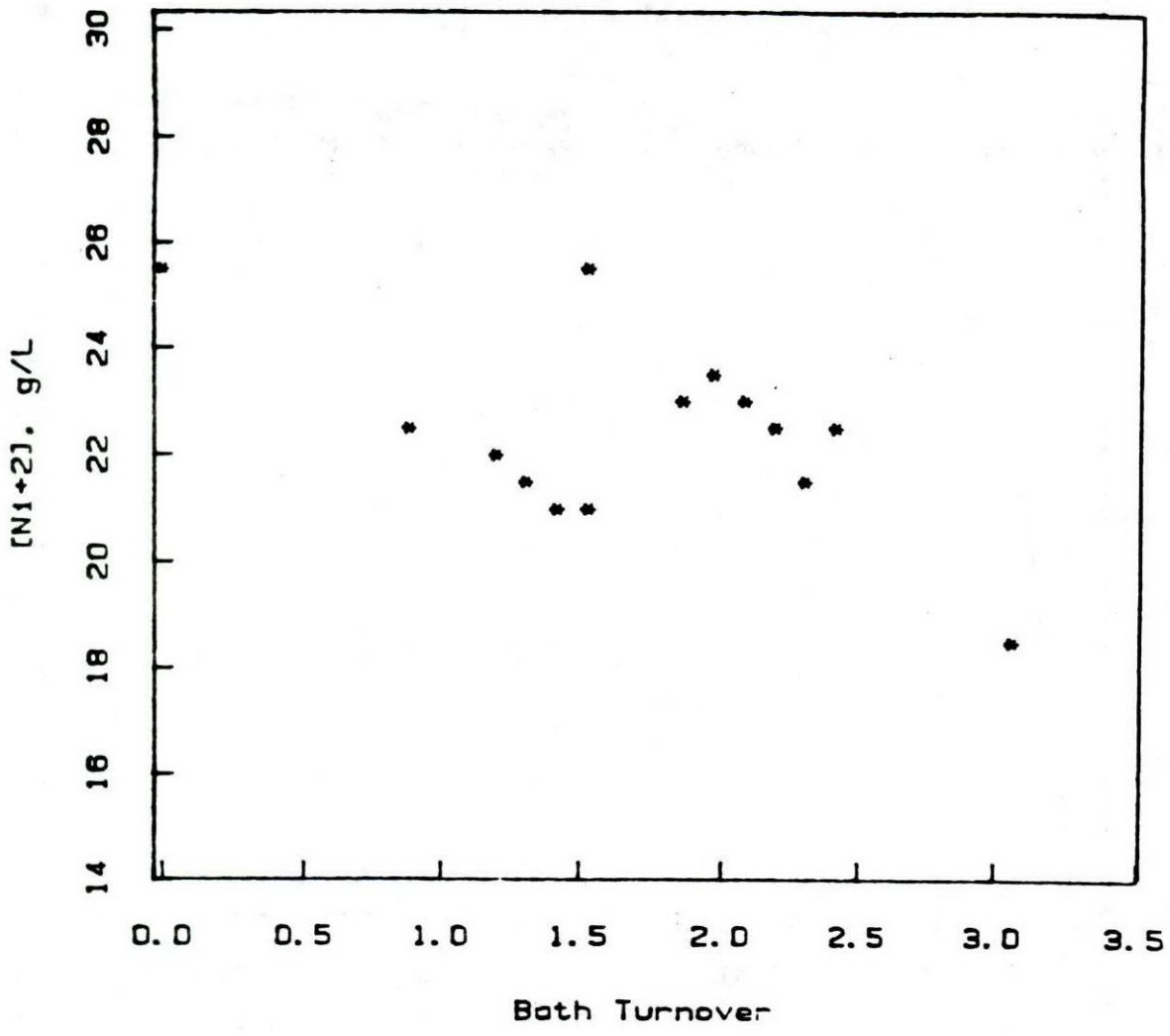
HULL CELL PANELS OF NI/P AND NICKEL DEPOSIT.

Figure 2



INTERNAL STRESS OF NI/P DEPOSIT VS. THICKNESS.

Figure 3



CONCENTRATION OF NICKEL VS. BATH TURNOVER SHOWING THE DEPLETION OF NICKEL FROM THE SOLUTION DUE TO ANODE PASSIVATION.

Figure 4

C-2

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Session C

Factors for Producing Low Contact Resistance Of Nickel Phosphorus Alloys

C.A. Holden, H.H. Law
and R.L. Opila
AT&T Bell Laboratories
Murray Hill, NJ 07974

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C. A. Holden
H. H. Law
R. L. Opila

AT&T Bell Laboratories
Murray Hill, New Jersey 07974

ABSTRACT

As more electronic products become disposable because it is cheaper to replace than to repair, the product life cycle becomes shorter and shorter and the need for a low cost electrical contact material for use in separable connectors in these products becomes greater. One promising candidate is a nickel phosphorus alloy (Ni/P) plated from a neutral ammoniacal bath. The objective of the present investigation was to determine the factors that produce the low contact resistance (R_c) because an understanding of these factors should define the reliability of this Ni/P coating.

The surface morphology of the gray colored Ni/P deposits appears to be the predominant factor in producing low R_c. The gray deposit consists of a multitudinous number of tightly spaced microscopic star-like asperities of relatively uniform height when viewed at a magnification of 2000X. This structure may assist in breaking through any oxide or other insulating film on the base metal deposit and in inhibiting the subsequent ingress of oxygen or other contaminants that would affect the intimate a-spot contacts provided by the protrusions. The presence of the phosphorus in the Ni/P deposit also seems to retard the oxidation rate to a level appreciably less than that typical of pure nickel.

1. Introduction

As more electronic products become disposable because it is cheaper to replace than to repair, the product life cycle becomes shorter and shorter and the need for a low cost electrical contact material for use in separable connectors in these products becomes greater. Table I shows the current cost of three of the electroplated metals commonly used for separable connectors and the cost of nickel, which is relevant to this discussion. Gold is about four times more expensive than gold flashed palladium and about three hundred times more expensive than base metal finishes such as tin-lead. Although the cost of the noble metal may be only a small fraction of the total cost of a connector, these figures give a clear idea of the magnitude of the savings possible when a much lower cost contact material is substituted in high volume production.

Tin-lead solder plate, a common base metal finish, is recommended[1] for usage in benign environments and at moderate ambient temperature, when the number of insertions required is small, when life requirements are relatively short, and when reliability requirements are modest. In the case of connectors that mate with wiping contacts, the number of contacts per connector is

restricted to about 20-30 due to the high friction forces. Tin-lead solder plate is therefore quite limited in application, and a better base metal finish is desirable.

One candidate is a nickel phosphorus alloy (Ni/P) plated from a neutral ammoniacal bath[2]. Low (<2 atomic %) phosphorus content gray colored Ni/P deposits have favorably low contact resistance (R_c) (less than 10 mΩ) after exposure to several accelerated environmental tests. This R_c is well below the relaxed electrical requirements in some project designs which allow R_c values up to 50 mΩ. The engineering properties of the Ni/P coating further support its study as a promising low cost contact material.

The objective of the present investigation was to determine the factors that produce the low R_c because an understanding of these factors should also define the reliability of this Ni/P coating. In order to understand the mechanism for low R_c, it is useful to review briefly electrical contact phenomena and the attributes that lead to low contact resistance.

2. *Electrical Contact Phenomenon*

When two stationary contacts come together, the ideal "welded" condition will give the lowest R_c. Since contact surfaces are microscopically rough, the ideal condition does not exist. The actual contact is provided by the asperities (a-spots) on both surfaces (Fig. 1). If a film is present, the contact resistance consists of the constriction resistances R_1 and R_2 in the two members, respectively, as well as the film resistance R_f. Thus

$$R_c = R_1 + R_2 + R_f$$

According to this definition,[3] the R_c is a surplus resistance in the body of the contact members, caused by the narrowness of the paths through the a-spots, to which may be added the resistance of a film on the a-spots. For two identical metals, the total constriction resistance is $\rho/2\alpha$ where ρ is the resistivity of the metal and α is the radius of the equivalent circular contact area. These a-spots that touch and deform to support the applied load are the only places through which electrons can flow. The observed resistance is then the parallel sum of the resistances associated with these a-spot contact areas, which typically are on the order of 10^{-3} to 10^{-4} of the apparent

contact area.

On gold or freshly cleaned base metal surfaces such as copper or nickel, only a few elastically or plastically deformed a-spots are necessary to provide low R_c. However, once a resistive tarnish film forms on a base metal, even heavy plastic deformation of a typical contact surface may not create sufficient metal-to-metal a-spot contacts to carry the current through the film. The R_c is increased because of the higher film resistivity. If the thickness of the film remains at a level where electron tunneling can occur, the R_c would, on the other hand, not be high. Thus, a reasonable strategy to achieve low R_c with base metals is: (1) increase the number of a-spots on the surface, and (2) use a contact material that has an oxide layer or tarnish film with low resistivity and that is resistant to further oxidation or tarnishing so that the film remains thin.

3. Experimental

Contact resistance was measured at a load of 50 grams with a modified Kentron microhardness tester. The set-up has been described elsewhere.[4] The R_c is obtained using a Hewlett Packard micro-ohmmeter, Model 4328A, a four wire instrument with a low open circuit voltage (<20 mV) to minimize electrical breakdown of any film that might be present on the test sample. All the R_c measurements were made with a pure gold wire (0.02 inch diameter) except where a gray Ni/P alloy plated copper wire (0.018 in dia.) was specified.

For the humidity testing, the samples were placed in a quart size mason jar and suspended above a saturated salt solution of potassium sulfate. The jar was then placed in an oven where the temperature was controlled at 50°C for various time periods. The salt, potassium sulfate, was chosen because it can maintain a constant relative humidity of about 95 % within a wide temperature range of 40°C to 100°C.

4. Results and Discussion

It appears that the surface morphology of the gray colored Ni/P deposits is the predominant factor in producing low R_c. The gray deposit consists of a multitudinous number of tightly spaced microscopic asperities of relatively uniform height when viewed at a magnification of

2000X. Fig. 2 shows clearly the surface morphology of the gray deposit and a bright Ni/P deposit after an exposure for 26 days to a warm humid environment.

The upper left SEM micrograph (Fig. 2A) shows a bright Ni/P deposit (R_c>400 mΩ). It has a "rolling hills" structure with some scattered relatively large protrusions. This is typical of bright deposits obtained from most plating baths. The lower left micrograph (Fig. 2B) shows a matte-white to very light gray Ni/P deposit (R_c>200 mΩ). It shows considerable smoothing of the "rolling hills" seen in the bright deposit (2A). Also, there is a hint of the surface morphology of the full gray colored Ni/P deposit (R_c <10 mΩ) shown in the lower right micrograph (2C). In this Ni/P deposit the "rolling hills" are no longer evident and only the tightly spaced microscopic asperities that are suggested to be the predominant factor in providing low R_c are observed. It may also be pertinent that the tips of these protrusions are star-like in structure. However, this tip structure is not as clear-cut in the upper right micrograph (2D) of a dark gray Ni/P deposit (R_c <10 mΩ). Here, the microscopic asperities are even more closely packed, which may account for the lack of clarity in determining the structure at the tips.

This star-like structure, which is clearly visible in the micrograph (2C) of the gray Ni/P deposit, may assist in breaking through any oxide or other insulating film on the base metal deposit and in inhibiting the subsequent ingress of oxygen or other contaminants that would affect the intimate a-spot contacts provided by the protrusions. As a consequence, the constriction resistance of the mating contact surfaces should be very low, with only the bulk resistance (resistivity) of the Ni/P deposit affecting the observed R_c.

Further evidence substantiating the influence of the a-spot asperities in the gray Ni/P deposit on reducing the constriction resistance between two mating surfaces is the data obtained from studies in which a gray colored Ni/P plated copper wire was substituted for the gold wire used in the probe of the apparatus for making R_c measurements. Initially, whether a gold or a Ni/P panel was tested with the Ni/P wire at a 50 gram load, the R_c values were low (1-2 mΩ). However, after approximately 150 R_c measurements, the R_c between the gray Ni/P wire and a clean gold panel was considerably higher (40-45 mΩ). When a Ni/P panel was substituted for the gold

panel, the R_c decreased to 2-3 mΩ. This alternation of Ni/P and gold panels in contact with the Ni/P wire was repeated several times with the same result: high R_c with gold and low R_c with Ni/P.

A plausible explanation for this unexpected result is that after the ~150 R_c measurements, the asperities on the Ni/P plated wire had been flattened considerably, thereby reducing the number of points capable of intimate (a-spot) contact with the gold substrate. This flattened Ni/P wire had become a typical oxidized base metal which no longer had an atypical surface that could make pin point intimate contact. As a consequence, high R_c between the Ni/P wire and the gold panel would be predicted.

When the Ni/P panel was substituted for the gold panel, the multitudinous number of microscopic protrusions, each with a high unit load, were able to penetrate the oxidized layer on the Ni/P wire, thus making intimate contact and reducing the constriction resistance between the mating surfaces. In this respect, the unique surface morphology of the gray colored Ni/P deposit is better than that of gold.

If the surface morphology is the predominant factor, then smoothing the top layer of a Ni/P deposit should result in higher R_c Table II shows that after 20 cycles of abrasion with a Taber Abraser at a 200 gram load, the R_c of the gray Ni/P deposit had increased approximately eightfold to 33-35 mΩ. This R_c change occurred after exposure to 50°C and 95% R.H. for 17 days. A view of the abraded surface at a magnification of 2000X showed that the tips of the closely packed protrusions were flattened considerably. Many of the protrusions had been completely worn away. However, these were only a small fraction of the area of the abraded surface. In all likelihood, the flattened asperities account for the increase in R_c as in the case of the Ni/P wire in contact with the gold panel.

After 50 cycles of abrasion at a 200 gram load, the R_c increased to >1000 mΩ after exposure to 50°C and 95% R.H. for 17 days. This increase in R_c is similar to that of bare nickel after a similar exposure to a warm humid environment. A view of the 50 cycle abraded surface at 2000X shows that only a small percentage of asperities remain. Most of the microscopic

protrusions are completely worn away. Since the surface morphology of the Ni/P has been, for all practical purposes, obliterated, the large increase in R_c after exposure to high temperature and humidity is predictable.

The results of these abrasion tests appear to substantiate the theory that the surface morphology of tightly spaced asperities with star-like tips is the predominant factor in achieving low R_c with the gray colored Ni/P deposit. This leads to the important question of whether the surface morphology is the only factor.

It has been known since 1950 that at least some Ni/P deposits have higher corrosion resistance than nickel[5]. Electroless Ni/P deposits with 14% P were considerably more resistant than nickel to attack by acids, being corroded only about 1/100 as much in hydrochloric acid. Marton and Chan[6] reported that, at temperatures below 280°C, electroless Ni/P deposits containing 16 atomic % (a/o) P are "practically inoxidizable, at least in terms of a surface oxide film." In studying the catalytic activity of electroless deposited Ni/P substrates (2-3 wt % P) in electroless nickel plating, Fils and Duquette[7] attributed the observed higher activity to thinner, less stable, or discontinuous oxides on the surface. From these studies, it appears that Ni/P would have the desirable properties of a good contact material, and yet no work has been reported on these materials until recently at AT&T Bell Laboratories. A low pH bath was developed[8] and it was found that the resulting bright Ni/P deposits with a P content of 4-7 a/o also have favorable R_c values. Hauser, Robbins, and Plewes[9] investigated the mechanisms for improving the R_c of nickel and found that an exposure test at 75 °C and 95% R.H. for 65 hours produces a top layer of oxide only 25 Angstroms thick on selected nickel alloys.

To distinguish the effect of surface morphology and the intrinsic properties of the Ni/P alloy with low P content, different nickel coatings with similar surface structures were prepared. Gray colored nickel deposits produced by constant current and pulse plating at high current density from low pH acid nickel chloride solutions were compared with gray Ni/P deposits produced at low current density from neutral pH ammoniacal baths where low R_c gray deposits have been consistently obtained. Table III shows that after 14 days of exposure to 50°C and 95% R.H., the

R_c of gray deposits pulsed-plated from the low pH NiCl bath is significantly higher than that of Ni/P deposits. SEM micrographs show that the pulse-plated deposit also has a similar star-like structure (Fig. 3b) to the gray Ni/P deposits. Thus, alloying with phosphorus does influence the R_c behavior.

As also shown in Table III, the R_c of high current density plated deposits from the low pH nickel chloride bath is high, being about 40 mΩ after only 7 days of exposure. An SEM micrograph (Fig. 3c) shows that, even though it is gray, the microstructure is nodular rather than the star-like structure as found with the Ni/P deposits from the neutral ammoniacal bath (Fig. 3A). Not all gray deposits yield low R_c.

In the relatively long time period (9 weeks) of the tests reported in Table III, the R_c of the gray Ni/P deposit was not greater than seven mΩ. The results of this exposure test continue to substantiate previous data indicating that the gray colored Ni/P deposit is unique in its consistently low R_c values, since the pulsed-plated acid NiCl gray deposit appears to have a similar surface structure. It seems likely that the phosphorus content of the Ni/P deposit retards the oxidation rate to a level appreciably less than that typical of pure nickel. However, further testing of gray deposits produced by pulse plating from NiCl baths (with and without P) appears to be necessary to provide a clearer insight into the effect of P content on the low R_c of the gray colored Ni/P deposit.

One important observation from these long term and previous short and long term temperature and humidity tests (50°C and 95% R.H.) is that a one week exposure is not sufficient for definitive results (see Table III). It appears that at least a minimum of three weeks is necessary before definitive R_c data are obtained under these test conditions that sharply differentiate the various coatings. A cumulative percentile plot (Fig. 4) strongly suppports this observation. The R_c of the Ni/P deposit is <10 mΩ after 9 months.

5. Conclusions

The surface morphology of the gray colored Ni/P deposits appears to be the predominant

factor in producing low R_c. The gray deposit consists of a multitudinous number of tightly spaced microscopic asperities of relatively uniform height. This star-like structure may assist in breaking through any oxide or other insulating film on the base metal deposit and in inhibiting the subsequent ingress of oxygen or other contaminants that would affect the intimate a-spot contacts provided by the protrusions.

The phosphorus content of the Ni/P deposit also seems to retard the oxidation rate to a level appreciably less than that typical of pure nickel. Gray deposits pulsed-plated from the low pH NiCl bath without P also have the star-like structure, but the R_c is significantly higher than that of Ni/P deposits after 14 days of exposure to 50°C and 95% R.H. Thus, alloying with phosphorus does influence the R_c behavior.

6. Acknowledgment

We are grateful to Mr. T. A. Palumbo and Mr. P. C. Milner for stimulating discussions and Mr. G. R. Crane for interpreting SEM micrographs.

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Table I. Cost of Metals

Metal	Cost ($/cm^2)	Thickness (μinch)
Au	1.3E-2	25
Pd	3.1E-3	25 + 2 (Au)
Sn/Pb	4.5E-5	300
Ni	2.5E-5	200

Table II. Contact Resistance of Abraded Ni/P Panels (mΩ)

Abrasion Number of revolutions	0.1 mil Coating	0.2 mil Coating
0	5	4
10	11	19
20	33	36
50	>1000	>1000

Taber Abraser at 200 gram load.
Contact Resistance (mΩ) measured after exposure at 50°C and 95% RH for 17 days.

Table III. Contact Resistance of Gray Ni and Ni/P Coatings (mΩ)

Days Exposure**	7	14	21	42	63
Ni/P	5	6	4	6	7
Ni, Pulse*	5	23	29	24	56
Ni, High I*	42	43	57	88	>1000

** 50°C and 95% RH
* Ni Chloride bath; low pH.

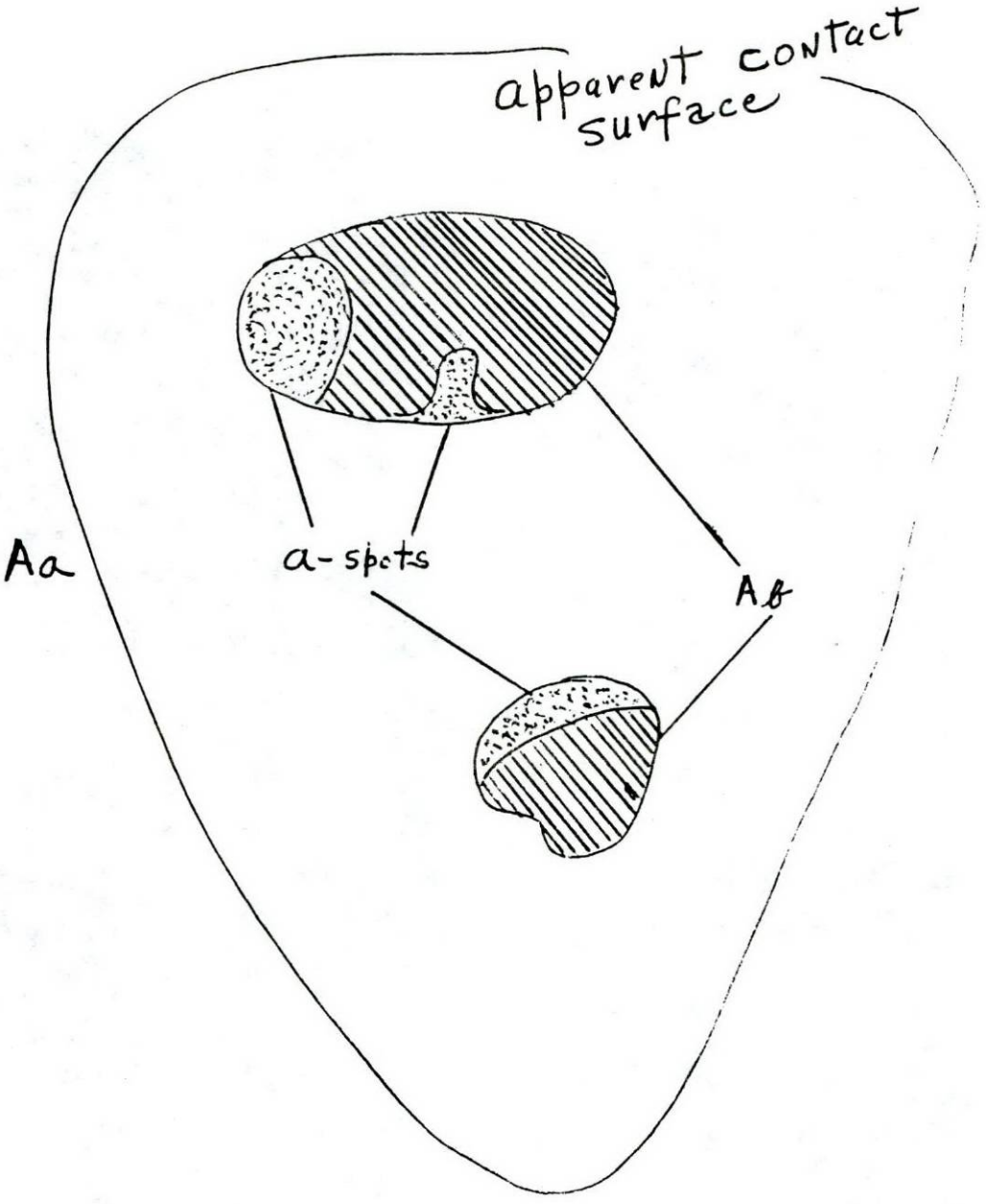
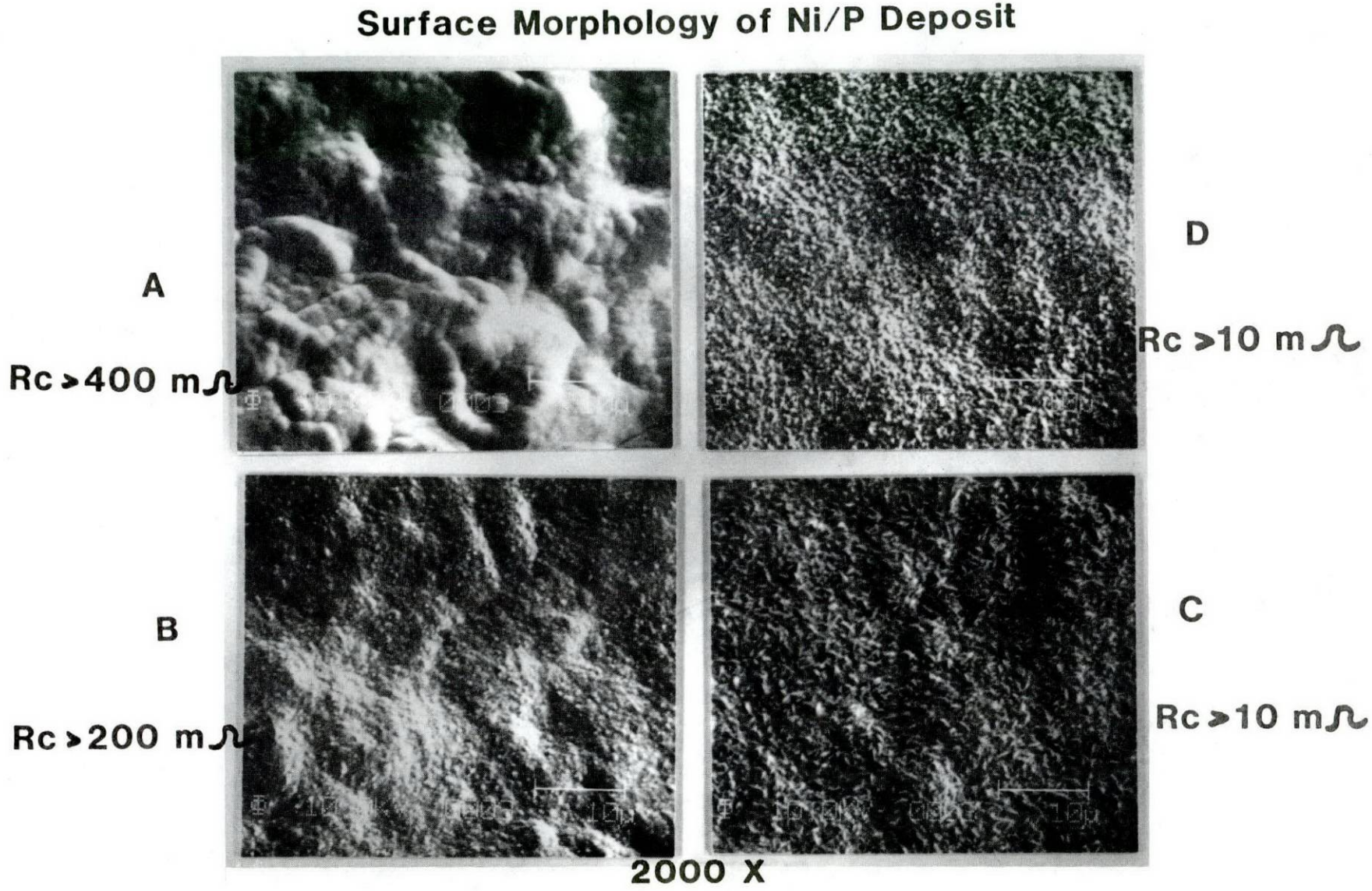


Figure 1

Apparent contact surface, A_a, load bearing contact area, A_b, containing insulating spots, shaded, and conducting a-spots, dotted.

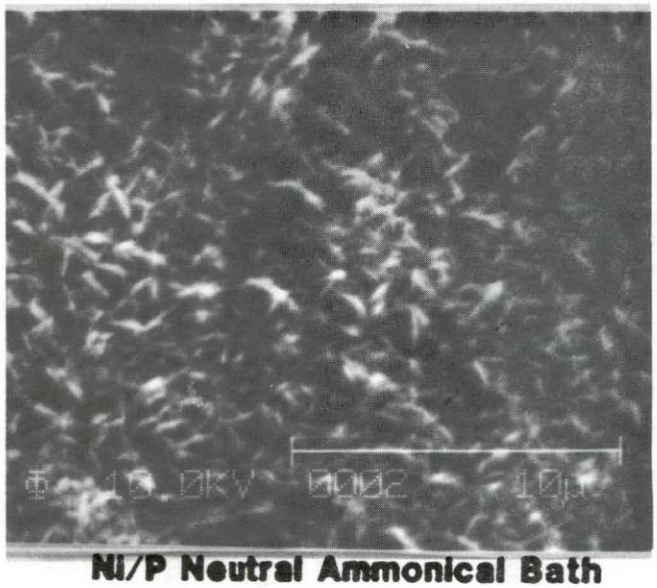


SEM micrographs of gray and bright Ni/P deposits with corresponding R_c values.

Figure 2

Surface Morphology of Gray Colored Deposits

5000 X



Ni/P Neutral Ammonical Bath

A

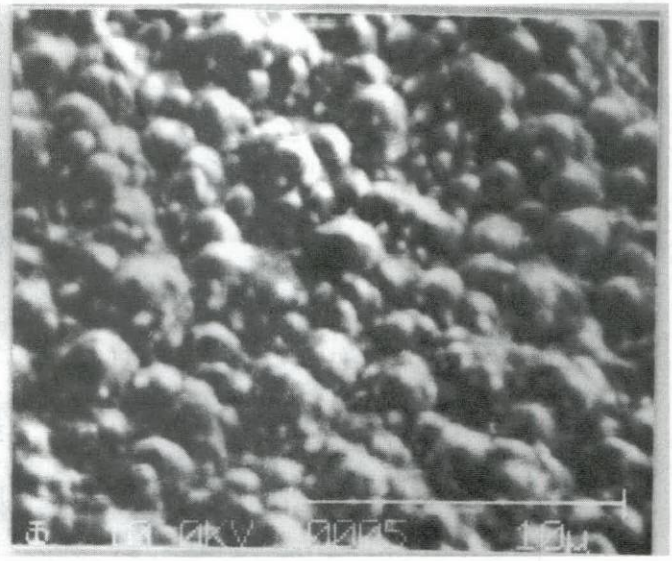
5000 X



Acid NICl Bath - Pulse-Plated

B

5000 X

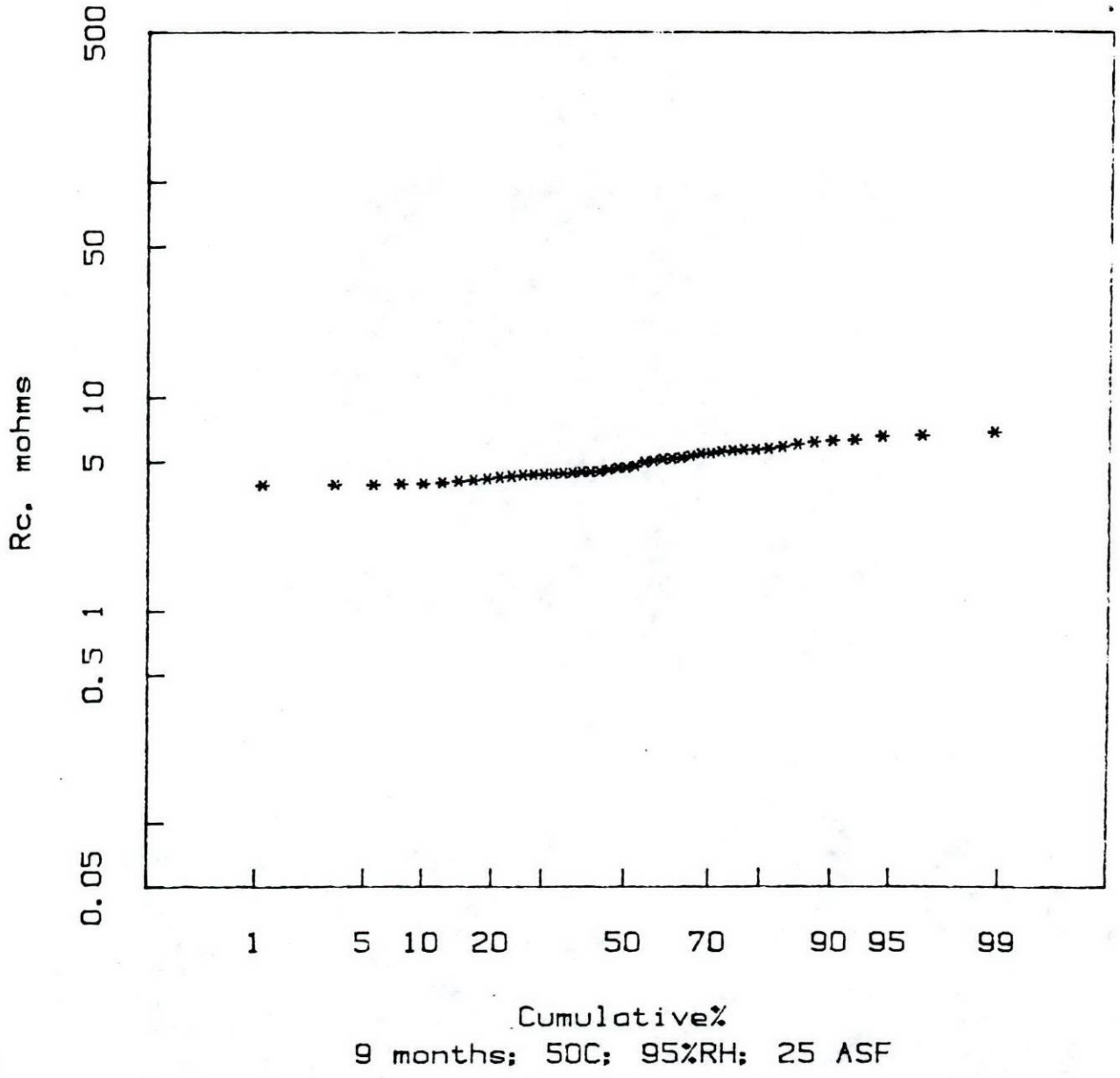


Acid NICl Bath - Constant Current

C

SEM micrographs of gray Ni and Ni/P deposits.

Figure 3



Cumulative plot of R_c of Ni/P deposits.

Figure 4

C-3

Electronics I
Session C

Effectiveness of Electrodeposited Coatings in Reducing Atmospheric Corrosion of Copper Substrates

James E. Voytko and Terry R. Guilinger
Sandia National Laboratories
Albuquerque, NM

EFFECTIVENESS OF ELECTRODEPOSITED COATINGS IN REDUCING ATMOSPHERIC CORROSION OF COPPER SUBSTRATES

James E. Voytko and Terry R. Guilinger
Sandia National Laboratories
Albuquerque, New Mexico

Abstract

Coatings of gold, nickel, palladium, and nickel with 20 at% phosphorus were electrodeposited on copper substrates at thicknesses of 50 and 150 microinches. These coated samples were exposed in an atmosphere of 100 ppb nitrogen dioxide, 100 ppb hydrogen sulfide, and 10 ppb chlorine, with a relative humidity of 60% and a temperature of 38°C for 332 hours. Weight gain of the samples was monitored to determine corrosion rate. Pore densities and sizes were measured after exposure to compare the performance of each deposit. Although the number of pores in the nickel coatings were fewer than in the other samples, pore sizes were significantly greater. Gold over nickel exhibited smaller pores but a higher density. Palladium at 50 and 150 microinches showed low pore densities. Surface analyses on the pores of the various coatings showed Cu and S as the principal species. The presence of these corrosion products affected the solderability of the samples. Gold plated on nickel over a copper substrate retained its solderability better than the other coating combinations.

Introduction

Electrodeposited coatings are used to provide corrosion protection and to enhance the physical and electrical properties of copper-based high reliability electronic contacts and interconnections. Typically, these coatings are chosen to be various thicknesses of gold over nickel[1]. The nickel provides a diffusion barrier between the gold and the underlying copper or copper alloy substrate. Also, the nickel improves the hardness and wear resistance of the contact. The gold layer provides good electrical conductivity with long term stability in corrosive atmospheres.

Recently, palladium[2] and palladium alloy[3,4] electrodeposits have found increased use as a replacement for the nickel/gold combination. The impetus for such substitutions has been the increased cost of gold. Studies of palladium and palladium alloys, such as palladium-silver and palladium-nickel, indicate that these materials exhibit low contact resistance, particularly when a gold flash (2 to 5 microinches) is used over the palladium layer.

Besides low and stable contact resistance, the coating layer must also exhibit good solderability. When soldering gold contacts, it is necessary to limit the thickness of the gold layer to control the amount of gold/tin intermetallic formed. Typically, gold layer thicknesses are limited to approximately 50 microinches in these soldered contacts. The porosity of gold

layers at these thicknesses allows access to the underlying nickel and/or copper substrate. Corrosion products from the nickel and copper layers may then form in the pores and creep over the surface of the gold. The existence of corrosion products in, or on, the gold surface impedes solder wettability and may require the use of activated solder fluxes. In critical applications, the use of active fluxes is discouraged since inadequate removal of the flux leads to further corrosion problems.

The requirements of providing good solderability and quality solder joints led to a study aimed at evaluating the effectiveness of alternate materials to coat copper and copper alloy substrates. Such materials must have good electrical conductivity, low porosity, high corrosion resistance, and good solderability. We identified several possible contact materials for comparison with the standard gold over nickel combination including palladium and palladium alloys, nickel with 20 at% phosphorus and duplex gold over nickel. This preliminary report discusses the corrosion behavior of gold, nickel, palladium, gold over nickel, and nickel-phosphorus electrodeposits on copper substrates. The full scope of this study will include other contact materials.

Experimental

OFE grade copper panels were prepared by photo-imaging and etching to provide test coupons. A matrix of 30 samples, measuring approximately 3/4 inch by 1 inch, was plated as a panel to ensure uniformity in plating thickness. No special polishing of the copper substrates was performed since it was our intent to examine surfaces which are representative of those found in actual contacts.

The panels were degreased in 1,1,1 trichloroethane, soak cleaned in an alkaline cleaner, and immersed in 10% (volume) H_2SO_4 prior to electroplating. With the exception of the Ni-P deposit, all plating was done in commercial plating solutions as prescribed by the operating conditions provided by the manufacturer. Gold was deposited from a high purity acid gold solution, nickel was deposited from a sulfamate solution, and palladium was deposited from a non-ammonia alkaline phosphate solution. Make-up and operating conditions for the Ni-P deposits are listed in Table 1. The Ni-P deposits were plated on individual coupons after degreasing in acetone and immersing in concentrated HNO_3 followed by concentrated HCl.

During panel plating, a rack located the panels equidistant from the two platinized titanium parallel anodes, thus allowing plating to occur on each side of the panel. After plating, all samples were thoroughly rinsed in deionized water, dried, and stored in dry nitrogen until use. Thickness measurements were taken on each side of the panel-plated coupons by X-ray fluorescence. Composition of the Ni-20P deposits was verified by X-ray fluorescence. Thicknesses of the Ni-20P deposits were determined by weight gain during deposition. Table 2 shows the plating conditions and resulting thicknesses of each deposit.

Samples were also examined metallographically and by scanning electron microscope (SEM) to verify deposit quality prior to exposure to a corrosive atmosphere.

The plated samples were exposed in a chamber to an atmosphere which accelerates aging in a carefully controlled environment[5]. Atmospheric conditions in the chamber, shown in Table 3, were selected to accelerate both nickel and copper corrosion[6,7]. Each coupon was weighed prior to, during, and after exposure. Additional characterization was done microscopically to determine pore density and pore size by examining corrosion spots on the surface of the deposits. Some corrosion spots were analyzed by Auger electron spectroscopy and SEM. Solderability tests were performed on coupons not used for surface analysis using a mildly activated flux followed by a 60-40 tin-lead solder. Solderability analysis followed the procedure described by Jellison et al. [8].

Results

Table 4 contains the weight gain and pore density and size data. Although weight gain measures corrosion rate accurately in uniform samples, the highly localized corrosion behavior of the test coupons lessens the significance of the weight gain measurements. For electronic contact performance, pore density and pore size are more important indicators of corrosion behavior.

Data in Table 4 show that the gold over nickel combinations performed better than gold or nickel alone since they have both small pore densities and pore sizes. Palladium at a thickness of 150 microinches combined very small pore densities with among the smallest pore sizes of any deposit. The thinner palladium deposit exhibited larger pores at a density about the same as the thicker palladium.

Table 5 summarizes the solderability results on the various coating combinations. Following the procedure of Jellison et al. [8], we report several solderability parameters: t_{90}, wetting rate, and contact angle from meniscograph tests as well as meniscus height. The t_{90} and wetting rate parameters are best understood by examining Fig. 1 which shows a typical meniscograph for a 50 μin Ni coating which was not exposed to the corrosive atmosphere. The t_{90}, or time to 90° turnaround, describes the time for the solder meniscus to become perpendicular to the sample. The wetting rate is a function of the slope of the force-time meniscograph and, as recommended by Jellison et al., was the parameter we used to compare the solderabilities of the electrodeposited coatings.

Not shown in Table 5 are the solderability results for Ni and Cu substrates. In both cases, when these samples were exposed to the corrosive atmosphere, the solderability tests yielded a negative wetting rate.

The solderability parameters in Table 5 should be used to compare exposed with unexposed samples within a particular coating combination. Thus, the 150 μin Au coating soldered better than its 50 μin counterpart when comparing the wetting rates of

the exposed versus unexposed samples. We look first for high wetting rates since this is the most significant soldering parameter [8]. Samples with good solderability should also have a low t_{90} and contact angle with a large meniscus height. Using these criteria, Table 5 shows little change in solderability for all the Au and Au/Ni samples in response to corrosion testing. NiP and Ni alone both showed decreased solderability due to corrosion product formation. The data for Pd are somewhat inconclusive as the solderability data were not reproducible. We are currently examining a 2-5 μin Au flash over the Pd to determine if this flash aids in obtaining consistent solderability data.

We attribute the decrease in solderability to the formation of copper sulfides on the surface of the test coupons as determined by surface analyses. Figure 2 shows a representative SEM-EDS analysis of a Au/Ni 50/150 μin sample. No evidence of Ni was found in the corrosion products of this or any of the Au/Ni samples. In areas of corrosion, Cu and S were always identified with a few occurrences of K, Na, and Cl which could have come from plating bath residue.

Summary

Atmospheric corrosion testing of palladium, nickel, gold, and nickel-phosphorus electrodeposits on copper substrates indicated that palladium and gold over nickel deposits exhibited the smallest pore densities. Analyses of the pores by Auger and SEM-EDS showed Cu and S as the predominant species indicating sulfidation of the underlying Cu substrate through nearly all of the coating combinations tested. Solderability testing of the various coating combinations both before and after atmospheric corrosion testing showed gold over nickel over a copper substrate best retained its solderability. We attributed the decreases in solderability for the various coating combinations to the presence of Cu and S on the surfaces of the exposed samples. We are in the process of expanding the scope of this investigation to include other coating combinations such as Pd-Ni alloys, Au flash over Pd and its alloys, Au over amorphous Ni-P, and Au over Ni-Cr-P amorphous alloys.

Acknowledgments

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Table 1. Composition and Operating Conditions for Ni-P Plating

Component	Concentration(gpl)
$NiCl_2 6H_2O$	200
H_3PO_4	50
H_3PO_3	45

Plated at 163 ASF at room temperature with Pt mesh anode

Table 2. Plating Data for Samples Exposed to Atmospheric Corrosion Testing

Sample No.	Deposit	Current Density (ASF)	Thickness (μin)	Std. Dev.* (μin)
2-1	Ni	20	47.4	1.9
2-2	Ni	20	49.7	1.9
4-1	Ni	20	147.6	5.3
4-2	Ni	20	148.9	7.5
9-1	Au	2	49.5	1.1
9-2	Au	2	49.9	0.9
10-1	Au	2	151.3	3.5
10-2	Au	2	151.2	5.0
11-1	Au/Ni	2/20	50.3/49.5	1.1/5.1
11-2	Au/Ni	2/20	51.3/54.6	1.2/5.1
12-1	Au/Ni	2/20	55.3/155.0	2.2/8.3
12-2	Au/Ni	2/20	56.1/147.4	2.0/9.9
14-1	Au/Ni	2/20	155.4/46.1	6.1/1.3
14-2	Au/Ni	2/20	158.3/43.0	5.4/2.2
15-1	Au/Ni	2/20	148.7/145.0	5.9/6.1
15-2	Au/Ni	2/20	150.1/148.7	5.5/5.4
16-1	Pd	10	51.2	1.9
16-2	Pd	10	53.2	5.8
18-1	Pd	10	162.3	10.9
18-2	Pd	10	134.2	4.3
----	Ni-P	163	50.0**	---
----	Ni-P	163	150.0**	---

* Based on 36 measurements per sample.
**Calculated thickness from weight gain on plating.

Table 3. Atmospheric Corrosion Testing Conditions

Component	Test Condition
NO_2	100 ppb
H_2S	100 ppb
Cl_2	10 ppb
Rel. Hum.	60 %
Temperature	38°C
Duration	332 hours

Table 4. Weight Gain, Pore Density, and Approximate Pore Size for Plated Samples after 332 Hours Exposure

Plate	Thickness (μin)	Weight Gain ($\mu g/cm^2$)	Pore Density (cm^{-2})	Approx. Size (μm)
Ni	bulk	nd*	--	--
Pd	150	nd	13	10
Pd	50	13	13	50
Au/Ni	150/150	nd	21	10
Au/Ni	150/50	nd	25	10
Au/Ni	50/150	nd	26	10
Au/Ni	50/50	5	33	10
Au	150	6	141	10
Au	50	8	87	25
Ni-P	150	25	14	50
Ni-P	50	30	39	75
Ni	150	40	4	30
Ni	50	40	6	100

*none detected

Table 5. Solderability Results for the Electrodeposited Coatings

Sample & Thickness	Exposed*	t_{90}(sec)	Wetting Rate (dyne/cm/sec)	Contact Angle(°)	Meniscus Height(cm)
Ni 50**	N	1.13	163	8.8	0.258
Ni 50	Y	2.44	50	11.6	0.214
Ni 50	Y	3.18	84	12.8	0.234
Ni 150	N	1.68	160	10.8	0.243
Ni 150	Y	3.26	95	15.2	0.214
Ni 150	Y	2.75	63	17.4	0.196
Ni 150	Y	3.03	80	18.7	0.218
Au 50	N	1.03	130	34.6	0.202
Au 50	Y	1.12	105	55.3	0.148
Au 50	Y	1.33	121	52.9	0.164
Au 150	N	1.05	143	10.2	0.259
Au 150	Y	1.18	138	17.7	0.244
Au 150	Y	1.05	138	19.6	0.238
Pd 50	N	1.33	121	67.9	0.128
Pd 50	Y	0.86	47	82.9	0.055
Pd 50	Y	N.A.	11	102.	0.100
Pd 150	N	1.92	145	67.5	0.134
Pd 150	Y	3.86	19	76.0	0.056
Pd 150	Y	2.22	144	81.6	0.079
NiP 50	N	1.55	144	23.2	0.220
NiP 50	Y	N.A.	1	100.	0.100
NiP 50	Y	N.A.	26	125.	0.155
NiP 150	N	0.63	204	38.0	0.211
NiP 150	Y	N.A.	59	121.	0.113
NiP 150	Y	1.22	22	62.9	0.075
Au/Ni 50/50	N	0.92	166	33.0	0.220
Au/Ni 50/50	Y	1.06	130	43.3	0.186
Au/Ni 50/50	Y	0.92	148	49.4	0.171
Au/Ni 50/150	N	N.A.	162	26.2	0.227
Au/Ni 50/150	Y	1.19	134	46.6	0.173
Au/Ni 50/150	Y	0.97	156	49.3	0.178

Table 5. Solderability Results (cont.)

Sample & Thickness	Exposed*	t_{90}(sec)	Wetting Rate (dyne/cm/sec)	Contact Angle(°)	Meniscus Height(cm)
Au/Ni 150/50	N	0.83	165	34.0	0.205
Au/Ni 150/50	Y	N.A.	129	37.0	0.187
Au/Ni 150/50	Y	1.33	122	37.3	0.193
Au/Ni 150/150	N	0.85	160	33.8	0.217
Au/Ni 150/150	Y	1.09	132	34.0	0.189
Au/Ni 150/150	Y	N.A.	124	33.6	0.197

* Exposed indicates if the sample was exposed to accelerated atmospheric corrosion testing.

** Thickness reported in microinches.

N.A. Not available because of the shape of the meniscograph.

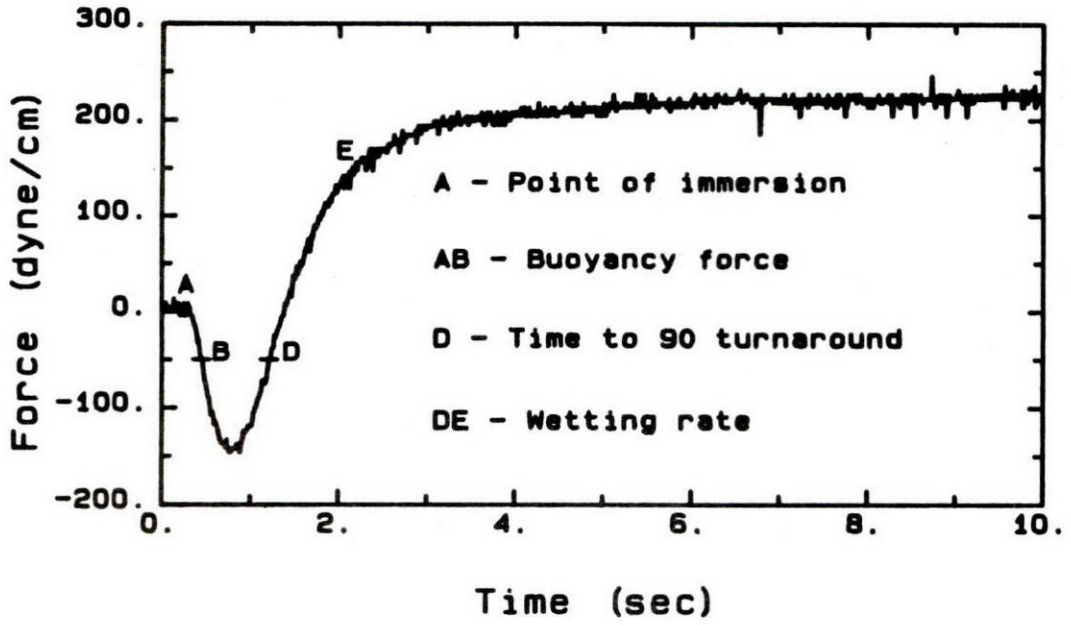

Figure 1. Solderability meniscograph for a 50 μin Ni coating on Cu substrate not exposed to atmospheric corrosion.

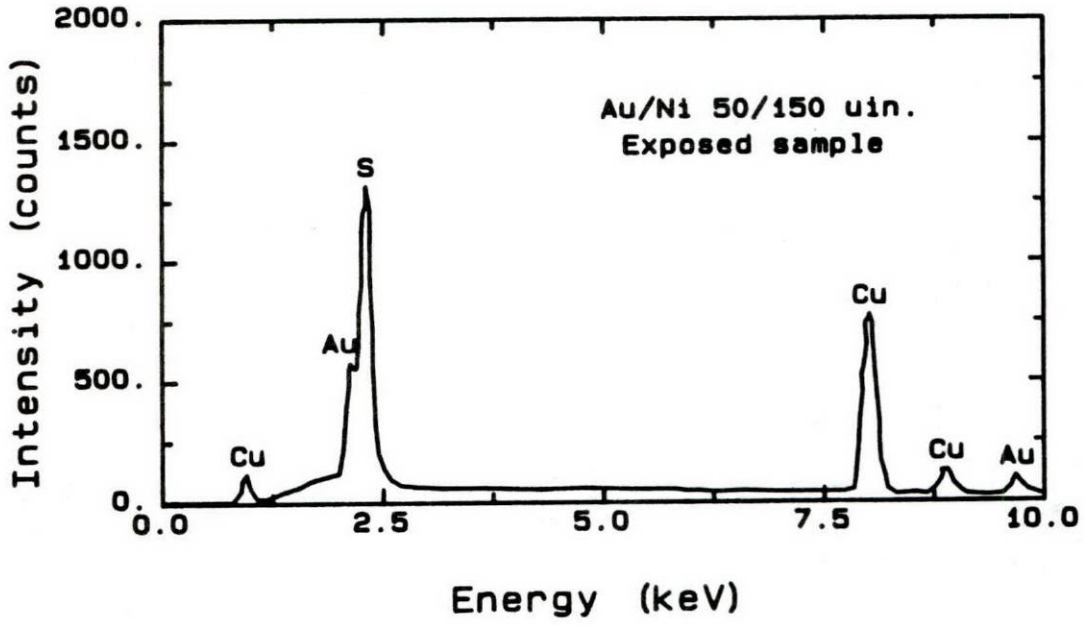

Figure 2. SEM-EDS of sample exposed to atmospheric corrosion showing presence of Cu and S on surface.

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Electronics I
Session C

To Be Sure of the Right Connections—You Must Have a Heart of Gold

John Donaldson, Tech. Dir.
Mesa West, Inc.
Anaheim, CA

TO BE SURE OF THE RIGHT CONNECTIONS
(You Must Have a Heart of Gold)

John Donaldson, Tech. Dir.
Mesa West, Inc
Anaheim, CA

A few years ago the AESF sponsored a special symposium having the well structured and publicised objective of advising electronics engineers and component designers how to make their products work better, last longer, and cost less by utilizing the knowledge and the unique and proven capabilities of electroplaters and the surface finishing industry. A grand total of two, equalling about 5% of those attending, qualified as the target audience, thus underscoring what have long been two major concerns of many "Platers for Electronics".

The first of these concerns is that it seems too many specifiers and users of plated electronic components and devices do not understand that designing appropriately for electroplating, and selecting the correct metal coatings, can significantly improve the quality, reliability and performance of their products, while usually reduce processing costs. The second, and perhaps even more bothersome one is that a number of them don't seem to care. Far too many AESF technical offerings are ignored by those who could really benefit from them, and the events become simply forums for platers and plating suppliers to tell each other what we pretty well already know.

For whatever reason, our "customers", those who require the products of our tanks and bubbling cauldrons, seem strangely hesitant to mingle with, or even be seen with platers. And yet we are that very segment of industry that produces the coatings which actually provide electrical components with the ability to function, and function reliably for as long as the system is needed.

Admittedly this hesitancy to rub shoulders with electroplaters could be due to the peculiar aroma sometimes noted in their immediate vicinity. A more probable and acceptable cause of the poor showing of "non-platers" at our tech sessions is a woeful lack of understanding of the technical importance of plated for electronics coatings.

Carrying that supposition just a bit further - the problem might be even deeper than that! It's conceivable that more than a few of the aforesaid designers and specifiers pay but little heed to the vital role of certain of the components of which electrical devices and equipment are fabricated!

For instance it's a good bet that at least half of the electronics engineers asked to name the principle components of a typical electronic system will fail to mention the one that can with some justification claimed to be the most important of all! Not present in their lists of such exotics as semi-conductors, resistors, integrated circuits and printed circuits will be that 'anything but' exotic device with the mundane pseudonym of "plug" - the electrical connector.

The fact is that no matter how exotic or technically unique they might be, none of the other devices of an electronic system can perform it's electronic miracle if not appropriately "plugged" into a power source and/or suitably interconnected with the other components of the system. And whatever their assignment, commercial, industrial and/or military, connectors must transmit electrical impulses from the terminal end of one conductor to that of another, instantly, repeatedly, and reliably for many, many years. Failure to perform satisfactorily, even when the interval of interrupted function is measured in nano seconds, can result in anything from disruptive irritant to another Chernobyl type disaster to international warfare!

The electrical connector was invented about sixty years ago to permit quick, easy and simultaneous connections of a couple to maybe half a dozen wires. There's no denying that in those days it was truly but little more than what it was officially named, - a plug! But now in this dynamic age of electronics the number of simultaneous connections typically run from fifteen to several hundred. In today's electronics devices and systems the amount of current transmitted is usually so small that a half century ago they'd have had a tough time accurately measuring it. And the connectors used today are required to work in once unimaginable adverse conditions of heat, cold, pressure, humidity and corrosive environments.

The simple "plug" has most certainly evolved into a very sophisticated and complex electronic device. No longer a substitute for a few twisted or soldered wires, connectors are now produced in a seemingly limitless number of sizes, shapes and styles which each year cost U.S. electronics industries about five billion dollars.

Of course there are those who neither ignore, nor are ignorant of, the critical role that electrical connectors play. In a fairly recent publication one went so far as to deem them the "heart" of electronics systems. It was that very statement that inspired the observations and conclusions set forth in this presentation.

Naming connectors the heart of an electronics system, while certainly a well meant designation, is from a technical view, just a bit off target, and the record needs to be set right. The actual transmission of electrical impulses between connectors is accomplished by the connector's contacts, the pins and sockets. It is the touching or "mating" of the surfaces of these contacts that enables the passage of electrons, and therefore the true heart of electrical systems is really the surface of the contacts in connectors. It follows that this is why electroplaters - and their steaming vats and cauldrons - are of such critical importance to the electronics trade. Most of the several billions of contacts that each year are assembled into connectors are fabricated from copper and copper alloys. Many are made of nickel and its alloys, and some applications may require or allow the use of contacts formed from such metals as molybdenum, tungsten, aluminum, titanium, stainless steel, and even plain steel. None of these metals have all, or even most of the necessary functional and performance characteristics required of an electrical contact. Thus the need to electroplate them with metals that do.

Many types connectors must repeatedly perform their plebeian task satisfactorily and with absolute reliability in whatever type of service in whatever type of environment for whatever length of time. It is particularly on the contacts of these that gold plating is specified, the total amount accounting for close to ten percent of the worth of the connectors annually purchased.

This is about the 25th year of an era that could be named "The ***Golden Age of Electronics.***" Such a designation is due partly to the tremendous proliferation of electronic inventions and innovations during those years; and partly due to the tons and tons and tons of gold used to plate them.

The following gold usage history, often repeated at seminars like this one, is here restated to support a subsequent claim that through scientific endeavor, technical skills, and common

sense the plating industry has done an extremely admirable job conserving gold and improving its utilization. So admirable that it can be claimed that it has been the platers for electronics have been the financiers of the Golden Age.

Between 1960 and 1970 the amount of gold used each year for plating electronics components in the United States increased eight times, from two hundred and fifty thousand to almost two million Troy Ounces. During the 1970's, despite a tremendous increase in the numbers of lead frames, contacts, headers, semiconductors, PC's and other electronics devices being produced, the amount of gold used for electronics plating declined by almost 50% to about one million ounces, dropping even further since 1980 to a level of approximately 850,000.

Several factors contributed to this phenomenal reduction in gold usage that each year saves the electronics trade about Four Hundred Million Dollars (with gold at $ 400.00 per Ounce). The top three, in the probable order of impact, are:

(1) Selective Plating; (2) Reduced Minimum Thicknesses; and (3) Gold Substitutes (replacements)

With respect to factors one and two, it is important to know that even with far less gold being used to plate a far greater quantity of electrical parts, neither function nor reliability have been sacrificed, or even compromised. Actually, quite the opposite is true, with invention and modification of gold plating processes, equipment, and plating techniques having considerably upgraded the quality and performance features of the coatings even at considerably reduced thicknesses. The stressed and brittle deposits, excessive porosity, poor wear, unreliable bondability and solderability and poor heat resistance, once too common defects of gold electrodeposits, no longer "plague the platers. (Or, at least they shouldn't)

As for reason number three, substitutes, or more aptly termed "replacements," this note of caution for those responsible for specifying contact finishes: "Take care!" .... Keep firmly in mind that what you're messing with is the "heart" of electrical systems, and a weak or defective heart is as undesirable in electronic equipment as it is unfortunate in the human body. As in humans, when the heart isn't working too well it weakens the whole system (body); and should it fail all of the other components and devices (organs) are brought to an untimely end.

Just as we don't want our own "tickers" to give out, we are not too enthused about defective or failing hearts in the systems that keep our electronic world 'turned on and tuned in.' This is especially so when it comes to things like fighting wars -or better yet - not fighting them; conquering space, ocean or super highway; and particularly when being transported through the air from city a to city b, an event which most of us fervently hope occurs without serious mishap or undue aggravation.

The best things in life may be free, but the best thing on connector contacts is definitely not. Gold is not called a precious metal just because it looks nice, and when specified it adds much to the cost of manufacturing and using connectors featuring gold plated contacts. In these days of rampant competition from both within and without the United States pressures remain high to minimize processing and material costs. Predictably, gold is a favorite target for cost reductions efforts. The big question, as it has been, continues to be how to use less without sacrificing any of gold's needed attributes and capabilities?

The question will be again answered for the most part by two of the three techniques already identified; reduced minimum thickness specifications and selective plating. There is every reason to believe that these answers have the potential to save even more gold in the coming years than they have here-to-fore!

Consider thickness. About a decade ago connector and semiconductor producers determined that gold thicknesses of 0.0001", 0.000060, and particularly for bonding, even 0.000030 could be halved and more without losing the desired functional capabilities of the deposit. Since then, continued investigation of the effectiveness of barrier layers and post-gold plating processes, along with years of "real time" experience, have resulted in an accumulation of data that should be the basis for a new round of gold thickness reduction efforts.

For instance, increasing the thickness of a nickel barrier coating greatly reduces potential problems of surface films and corrosion by minimizing the effects of porosity, thereby allowing for very thin deposits of gold when wear is not an important consideration. And when it is, wearability can be greatly enhanced by the simple expedient of utilizing a post-plating lubricant or coating graphite type coating.

Another technique that allows a significant reduction in gold thickness by negating the effects of innate porosity, is to employ copper passivation treatments after gold plating. Fairly good and long term corrosion resistance results from chemical conversion of the copper that is present at the base of pores in the plating.

There's been another consequential advancement in plating during recent years that should make the use of thinner deposits even more palatable for electronics engineers. This is the accumulation of a wealth of knowledge pertaining to the equipment and solution parameters that effect plating distribution in batch gold plating processes. Modifications in equipment and some minor adjustments to, and close control over such variables as pH, solution conductivity and metal content, will greatly limit the plating thickness range in any lot plated. Coupled with much more accurate and reliable measurement systems now available at an affordable price, accurate and reliable measurement now possible, this factor helps assure the user that all of the contacts of any plated lot will have more than the specified minimums. Therefore th-ere should be little reason to over specify plating thickness minimums in order to "play it safe."

So reduced gold plating thickness is definitely a viable way for connector users to effect further gold savings without losing gold's valuable properties. And Selective Plating, already described as having been "super effective." is another, especially since "super selective" plating systems can now place extremely small gold spots in once virtually inaccessible locations.

As new methods for obtaining selective deposits have been developed and refined to produce "super selective" deposits, the design of many styles of contacts have been revised (despite previous inferences that this has not generally happened) to take advantage of them. A classic example is the use of a slightly raised area, or bump, on the mating surface of a spring or blade contacts that when selectively plated assures steady and intimate connections at every insertion. Another example is the use of pre-plated gold striped strip which when formed becomes the ID surface of the mating end of female or socket contacts.

Naturally, most of the above statements about selective plating relate to the continuous pre-plating of strip before forming and plating pre-stamped and formed contacts affixed to a carrying strip. However the greatest area for future exploitation of selective gold plating techniques to produce very, very substantial savings actually is in another arena, on "loose piece" or machined contacts.

A minimum thickness of .000050" is typically specified on connector contacts for military applications. Usually formed by cold heading, screw machining, or rolling equipment the contacts are produced "loose" and in large quantities, and have always been plated in bulk processing operations. However the functional areas of these contacts, that is the sites that in service become the "heart" of electronics systems, are but a short segment of the outer surface of the pin and the inner diameter of the socket. Gold is not needed on the rest of the contact.

During the past two years the military has been conducting an in-depth test of contacts that were selectively plated. Approval can revolutionize the manner in how contacts plated to Mil Specs are processed. Connector manufacturers will be allowed the options of continuing to supply over all plated contacts, or ones which have been selectively plated. Competition will most certainly force them to adapt the latter system.

Naturally the heat will be on both in-house engineers and equipment suppliers to develop selective loose piece parts plating capabilities. And this will most certainly cause many platers, plating engineers, department managers and all of the others involved a lot of consternation, bafflement, and sleepless nights.

Several equipment manufacturers and at least two or three major connector houses did invent and develop such equipment a couple years ago anticipating a fairly rapid move into this technology. But two things happened: (1) the very conservative attitude of the government agency(s) charged with evaluating selective plated contacts and the ensuing very extended testing period; and (2) the equipment built either didn't work very well, or if it did, was seriously lacking in versatility and proved too difficult and cumbersome to operate successfully for extended periods of time. (Contacts are made in a whole bunch of shapes and sizes and are not always "perfectly" dimensioned.)

It is predictable that approval of selectively plated machined contacts, if and when it actually happens, will precipitate a flurry of activity - with the dust being blown off a number of existing plating lines and from the plans for several more. Necessity truly being the Mother of Invention, its likely that some firms will be successful in designing equipment that will work and even be at least marginally cost effective.

But its also probable that a couple other techniques will ultimately be utilized for selectively plating most volumes of machined connector contacts. Both are already in use, however both must be improved and refined to handle the large numbers of contacts that will have to be processed.

The most likely candidate is "bandoliering" of the contacts, not a particularly easy thing to do because of their round shape and wide variety of diameters and lengths. But indications are that what was once impossible is now being accomplished, pointing the way for the best technique for loose piece parts platng. Since contacts affixed to a bandolier are plated on conventional continuous strip plating lines, the plating equipment itself is in place, ready and waiting.

The second potentially effective technique is to automatically feed a controlled number of contacts into a magazine, or clip which is then continuously conveyed through a plating lines suspended from a small chain fixture; or is combined with several more clips in a special fixture for "rack" plating. While the potential production rate is a bit slower than bandolier plating, it is a good (and proven) system, particularly because of its versatility, ability to processes small volumes, availability of equipment and the relative low cost of that equipment.

Now to briefly summarizing the essential points of this unabashedly circumlocutory presentation. The primary goal is to explain the need to continue specifying gold plating on electrical contacts used in critical applications requiring highly reliable components. However, recognizing the need for further reductions in production costs in manufacturing connectors, a second purpose is to offer some advice for reducing gold consumption while losing none of its needed characteristics.

It should be pretty clear that the message is directed at those who direct and control product design and specifications, thus the mandate expressed in the title, "***HAVE A HEART OF GOLD -AND YOU'RE SURE TO HAVE THE RIGHT CONNECTIONS***." However it will be the Platers for Electronics who must provide gold deposits that will assure the Right Connections at the least possible cost, so it's important that they too appreciate what it is that is the "true heart" of electronics systems.

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Electronics I
Session C

An Overview of the Ductility Testing of Electrodeposits

Alan A. Halecky and Edward N. Balko
Engelhard Corp.
Electronic Products Group
One West Central Ave.
East Newark, NJ 07029

AN OVERVIEW OF THE DUCTILITY TESTING OF ELECTRODEPOSITS

Alan A. Halecky and Edward N. Balko
Engelhard Corporation
Electronic Products Group
One West Central Avenue
East Newark, New Jersey 07029

ABSTRACT

A review of ductility testing methods is presented with a discussion of the advantages and disadvantages of each method. Special attention is given to the measurement of the ductility of electrodeposits attached to a substrate (composite specimens).

INTRODUCTION

In developing a new palladium electroplating bath in our laboratory, our objective was to have the deposit meet a set of physical properties that our marketing people deemed necessary. One of these target properties was to have the deposit exhibit a ductility of six percent or greater. During our initial screening phase of various electrolytes, we tried to make foils from our palladium deposits for tensile testing. The deposit was plated on a stainless steel coupon and an attempt was made to peel the foil from the substrate. This invariably resulted in broken foils. Furthermore, it is not possible to obtain palladium foils by dissolving away the substrate metal in acid, as it is with gold electrodeposits. This leads to uptake by the palladium of hydrogen formed during the metal dissolution, which, in turn results in embrittlement of the deposit. Therefore the palladium was plated on copper followed by an attempt to remove the copper by dissolution in cyanide with a mild

oxidizing agent. The slow rate of attack on the copper by cyanide rendered this approach impractical. At this point we decided to do our ductility testing on deposits attached to a substrate material of greater ductility than that of the palladium film. At the time we thought that this was a novel approach to the ductility testing of electrodeposits and therefore a discussion of this technique was to have been the focus of this paper. A search of the older literature, however, revealed that tensile testing of electrodeposits attached to the substrate had been performed as early as 1962[1]. Since many knowledgeable people in the electroplating field are unaware of this useful ductility testing method, we decided that it would be useful to transform this paper into a review of ductility testing with emphasis on the testing of composite specimens. The intent of this paper is not to provide a complete review of ductility testing procedures, as there are many fine review articles written on the subject, but rather to provide the electroplater with a brief introduction to the methods available to him in the selection of an appropriate method.

DISCUSSION

The need for the determination of the ductility of electrodeposits arises in a number of instances: 1) when a part is subjected to forming operations after electroplating such as connectors formed from stripe-on-strip; 2) when a plated piece will be subjected to stresses arising from thermal loading, as happens to printed wiring boards during soldering operations; 3) in the fabrication of flexible circuitry or, 4) when a deposit is overplated by a deposit having a large tensile stress, such as chromium plated on nickel. If the deposit is not sufficiently ductile to withstand the applied forces, the deposit will crack and may exfoliate from the piece.

On the surface of things, the definition of ductility as "the ability of a material to deform plasticly without fracturing[2]" seems relatively straightforward. However, the relationship between the means devised for the measurement of ductility and the above definition is anything but straightforward. The technique by which the specimen is

deformed in the test procedure gives rise to the questions of interpretation and accounts for the profusion of methods for the measurement of ductility. Currently, no standard test for the measurement of film ductility exists, although attempts to devise a standard method continue[3]. Further complications arise when it is attempted to transfer bulk ductility measurement techniques to the measurement of the ductility of electrodeposits. Below a thickness of about five microns the mechanical properties of films begin to deviate substantially from that of bulk specimens. Effects due to inhomogeneities and defects that are averaged out in thick specimens become important determinants of material behavior in thin specimens[4]. To collect accurate mechanical performance data, it is therefore prudent to conduct ductility testing on deposits of thickness comparable to that of the application coating thickness.

The four general classes of ductility test methods are categorized by how the specimen is deformed: uniaxial tensile test, bulge tests, bend tests, and fatigue tests[4].

Tension Test

In the uniaxial tensile test, also known as a tension test (**Figure One**), a sample is clamped between two jaws and a force is applied along one axis of the specimen (hence, the name "uniaxial") and it elongates in the direction of the applied force. The internal force that resist this elongation is known as the stress. The change in the specimen length divided by the original length of the specimen is known as the strain. The data obtained from the tensile test is presented as a plot of stress vs. strain as is illustrated in **Figure Two.** The straight line portion of the curve represents the elastic region; over this region, if the stress is removed from the test piece, the specimen would be restored to its original length: No permanent strain results from stresses applied in the elastic portion of the curve. By contrast, if a sufficiently large stress is applied to the material under test to cause an increase in the length of the specimen, which is not reversed when the stress is removed, the piece is said to be plastically deformed. The region of plastic deformation exists on the curve in **Figure Two** from point A to point B. The strain at which fracture occurs multiplied by 100 is called the

percent elongation. It is this value which is most often taken as a measure of the ductility of the material being tested. It should be noted that the percent elongation is easily and directly determined from the graph in the tensile test. In all of the other test methods to be described in this paper, the percent elongation must be derived from an indirect measurement and it is the accuracy of the mechanical model employed that will determine value of the ductility data obtained.

Bulge Tests

Bulge tests are biaxial tensile tests: The forces applied to a specimen to cause it to deform in this type of test are applied along the two axes of a plane (**Figure Three**). The result, as the name implies is the formation of a bulge in an originally flat sample. Many variations on the bulge test exist, depending on what is used to cause the bulge[5]. The hydraulic bulge test[6] is used for testing very thin specimens. In this technique, the sample is tightly clamped over the mouth of a chamber and oil is pumped into the chamber through a small hole as can be seen from **Figure Four**. The force that induces the sample to bulge is transmitted to the specimen by the pressure that the oil exerts on the side of the sample clamped to the chamber. The oil pressure is increased until the bulge ruptures. The elongation is derived, using a great many assumptions, from the measured height of the bulge and the oil pressure at fracture. By far the most common technique used to apply the force that gives rise to bulging is to anchor the flat specimen and to drive a spherical ball into the specimen until a crack appears in the surface (**Figure Five**). This approach is the basis of a very convenient and simple to construct bulge testing apparatus shown in **Figure Six**[7]. Though some investigators in the past have reported problems with accuracy and reproducibility with bulge tests, we have found the apparatus pictured in **Figure Six** to give good results. From the geometrical arrangement depicted in **Figure Five,** one can derive equations which allow one to calculate the percent elongation which the piece suffers at fracture. The bulge tests may be used either on foils or composite samples, though if composite specimens are to be used with this apparatus, our experience has shown that the substrate must be sufficiently thin to transmit the force applied to the attached film. Another disadvantage of the bulge test,

albeit a minor one, is that the strain at fracture is not given directly, as it is in the tension test, but rather must be calculated.

Bend Tests

There are are numerous types of bend test[3], many of which provide only qualitative results, while others provide quantitative data of questionable value. All of the procedures rely on detecting the first appearance of cracks in a specimen which is subjected to bending. The test methods can be differentiated in to two broad groups: 1) the specimen is bent without a support, or 2) the specimen is bent against a mandrel (a supporting structure of well defined geometry) [see **Figure Seven**]. Testing can be performed on either a foil or on composite test pieces in both of these categories. In one of the more frequently used unsupported bend tests[9], a foil is bent into a "U"-shape and placed between the jaws of a micrometer. The jaws are then slowly closed on the piece until the specimen fractures. From the deposit thickness and the size of the opening between the micrometer jaws at fracture, the percent elongation is calculated.

The supported bend test procedures can be further subdivided by the shape of the mandrel employed (cylinder, triangle, etc.) and the number of mandrels used (three-point and four-point bend tests); the cylindrical mandrel is the most comonly employed geometry. In a common supported bend test, a composite specimen is bent around mandrels of progressively smaller diameters until fracturing of the deposit is observed. The percent elongation is then calculated from the diameter of the mandrel which first gave rise to deposit fracture and the specimen thickness. This test suffers from poor reproducibility; further, the relationship of the calculated measure of ductility obtained from this test to that of the corresponding percent elongation at fracture measured by a tension test is highly questionable. In fact, in a side-by-side comparison of a the tension test and a popular bend test carried out on nickel deposits, it was demonstrated that a difference of as much as one hundred percent existed between the ductility values obtained from each test[1]. The problem lies in the inability of the test to discriminate fully between the elastic and

plastic deformation experienced by the test piece. A variation of the successive mandrel test uses a conical mandrel so that a continuum of mandrel diameters can be achieved with one bend over one mandrel. An end of the test piece is anchored to the mandrel and the deposit is wrapped in a spiral over the length of the mandrel. The radius of curvature of the support at which a crack is first observed on the deposit is used in conjunction with the film thickness to derive a value for the percent elongation. This test provides better ductility values than the former but also shares the flaws inherent in the simpler bend test.

Fatigue Tests

The final category of ductility tests to be discussed is the fatigue test. This type of test provides the least quantitative value for ductility and exhibits poor reproducibility. At best, they offer only a ballpark estimate of ductility. Invaribly, in fatigue tests, the specimen, either foil or composite piece, is bent, straightened out, and then bent in the opposite direction. This cycle of operations is carried out until fracture is detected. The number of bends to fracture is taken as a measure of the ductility. To ensure a uniform angle of bending from cycle-to-cycle as well as from specimen-to-specimen, one fatigue test procedure uses a vice to bend the specimen[10].

Most ductility determinations on electrodeposited films reported in the literature are performed on foils made either by dissolving the substrate metal away from the film or to a lesser extent by mechanically stripping away the deposit from a substrate to which the deposit has poor adhesion. The reason that testing is so often performed on foils is to obtain ductility measurements that are free from substrate-film interactions. These interactions arise from stresses at the interface between the two metals. For highly ductile metals such as copper or low-stress nickel, the preparation and handling of foils is manageable. The inherent disadvantages in using foils are the time-consuming sample preparation and the tendency of foils to wrinkle. This wrinkling effect gives rise to a value for the ductility which is larger than the true value since some of

the "elongation" recorded is the result of unwrinkling of the foil. Further,the substrate used to generate the foil can influence the mechanical properties of the foil. In one study[12], the percent elongation of a copper electrodeposit over electroless copper was found to be more than double that of the copper plated over stainless steel.

Since the "true" ductility of an electrodeposit is not measured using composite test pieces, owing to the substrate-deposit interactions, it may be asked what is to be gained by the testing of composites. One obvious answer is that no measure of the ductility of brittle films could be obtained if they had to be measured as foils. An even better answer is the fact that if the test substrate material is chosen so that it has mechanical properties closely matched to that of the application material, then realistic conclusions can be drawn about the deposit performance in its intended actual use. Such a test then takes into account the real world fact that the performance of a deposit is intimately linked to the substrate to which it is attached. It also avoids problems caused by artifacts which may appear in the preparation of foils.

The tension testing of composite specimens in our development of a new palladium plating bath proved to be both convenient and well suited to the application. Our test pieces were prepared by plating palladium deposits onto ten mil thickness dog bone-shaped coupons (**Figure Eight**). Copper was chosen because its ductility far exceeds that of the palladium deposit as well as the fact that stripe-on-strip connectors are often made of copper. The requirement that the substrate exhibit greater ductility than the deposit is necessitated by the fact that the deposit must fracture before the substrate does in order to derive any meaningful data.

The specimens were clamped in the jaws of our tension tester and elongated in 0.1 percent increments followed by examination at 50X magnification until lateral cracks extending the width of the panel were first detected. The resolution of the technique could, of course, be improved by conducting the elongations in smaller increments. The

reproducibility of the percent elongation at fracture values is from specimen-to-specimen is about five percent and no significant variation of ductility was observed over the thickness range from fourty to eighty microinches. Test results on the new palladium plating bath are reported elsewhere[13].

The conclusion we draw from our survey of ductility testing methods is that the choice of a testing method should be guided by the end use for the data. If the data are to be used to advance the the scientific understanding of materials behavior, then careful quantitative tests based on accurate physical models are essential. On the other hand, if a practical understanding of how a deposit will perform in an actual application is required, then a test procedure which most nearly models the application environment is what is called for. The tradeoff in simulating the complex physical reality is a loss in exact physical relationships that can only be understood in simplified models. Therefore, all of the tests described above have their place in the spectrum of testing needs.

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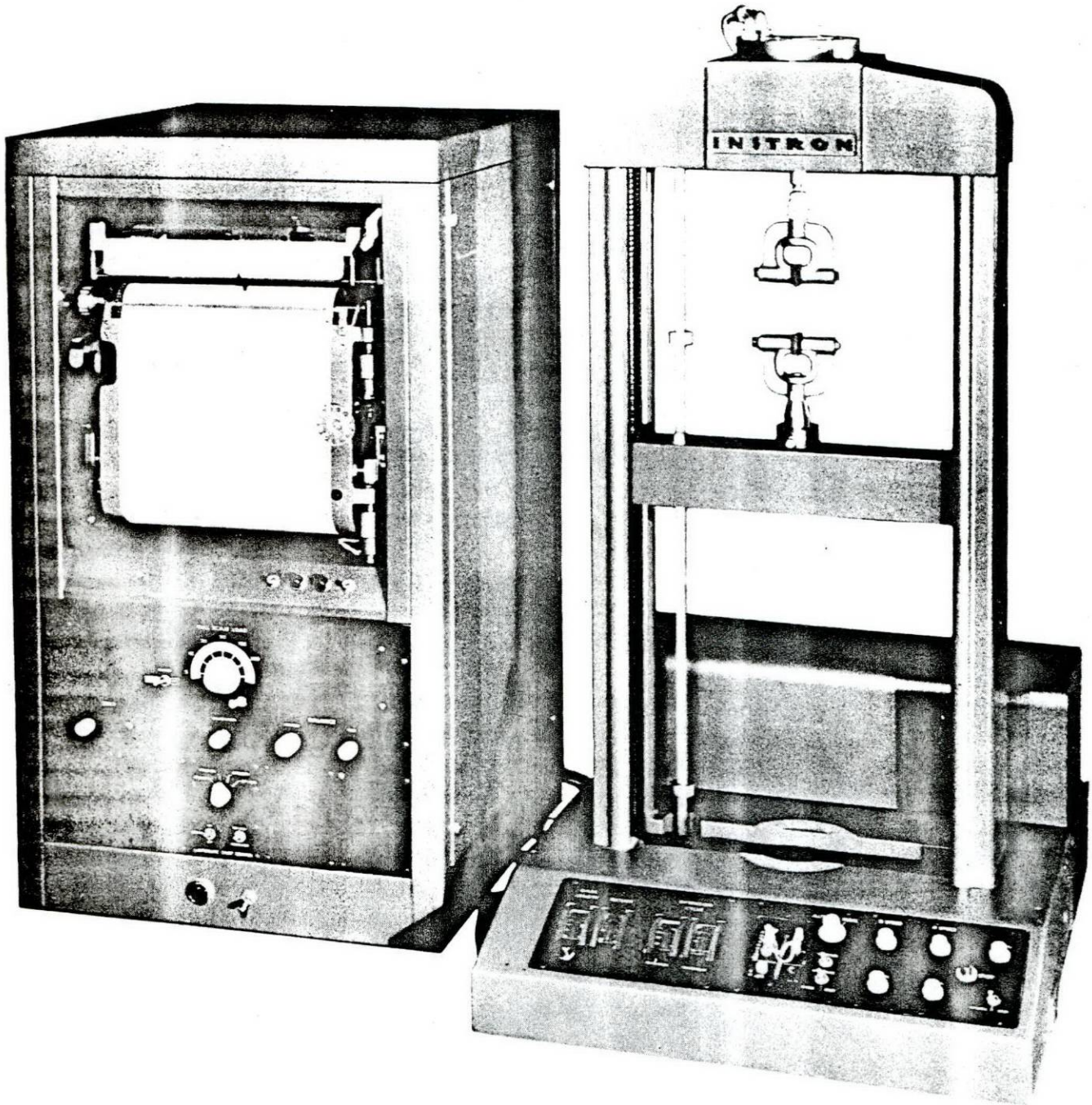
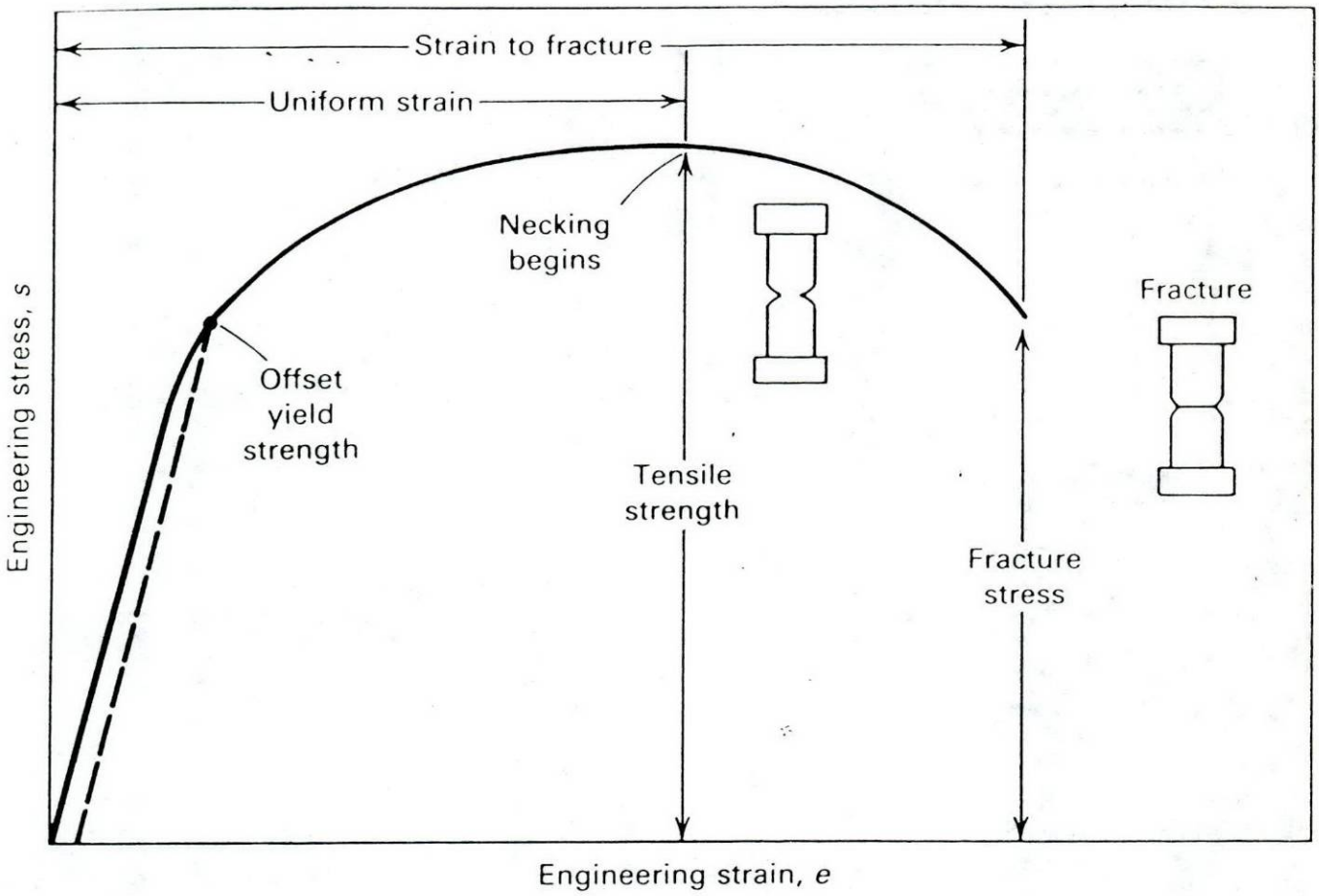
FIGURE ONE



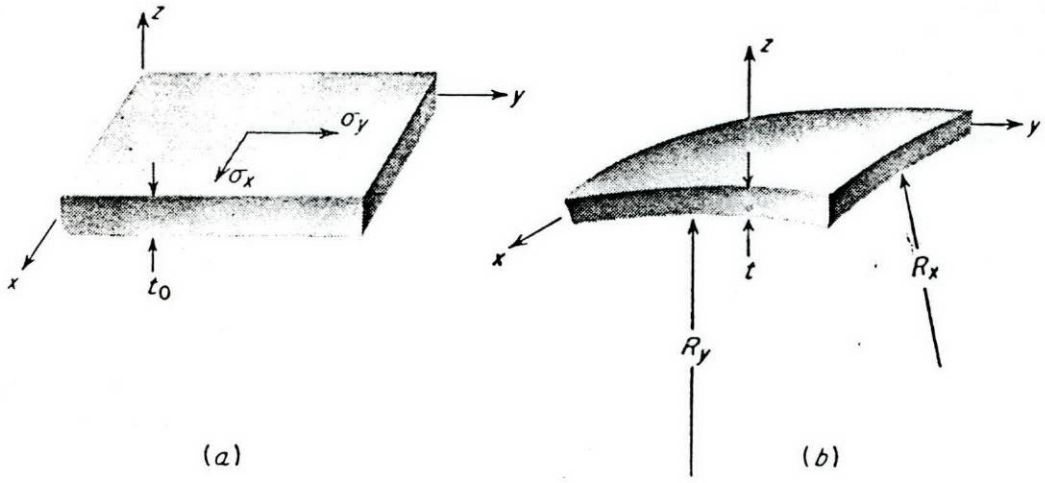
APPARATUS FOR PERFORMING UNIAXIAL TENSILE TESTING

FIGURE TWO



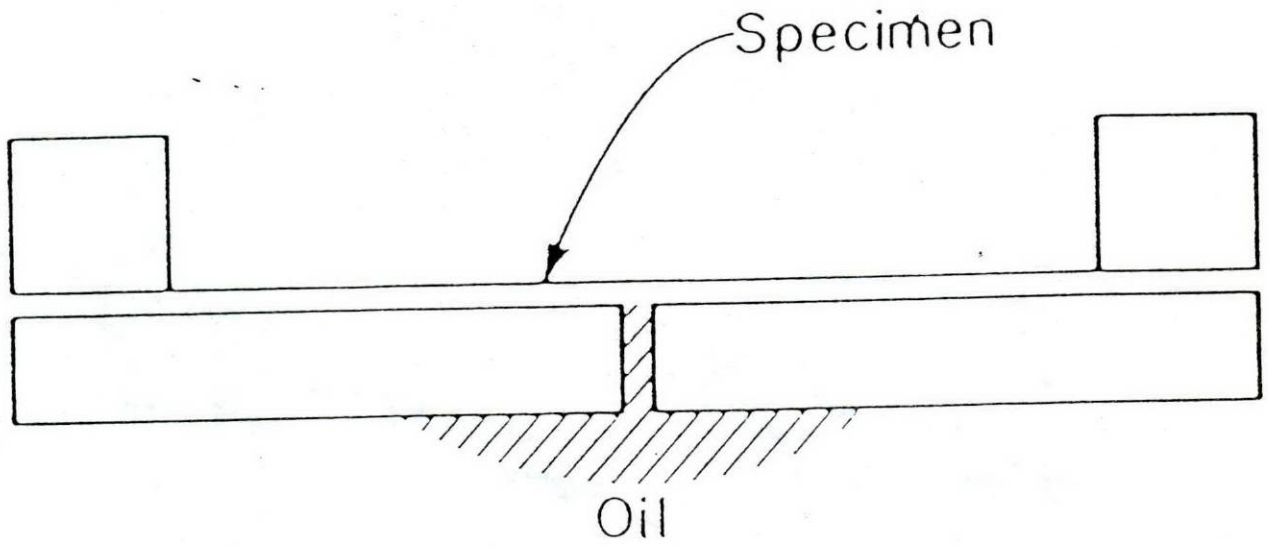
PLOT OF STRESS VERSES STRAIN OBTAINED FROM THE UNIAXIAL TENSILE TEST

FIGURE THREE

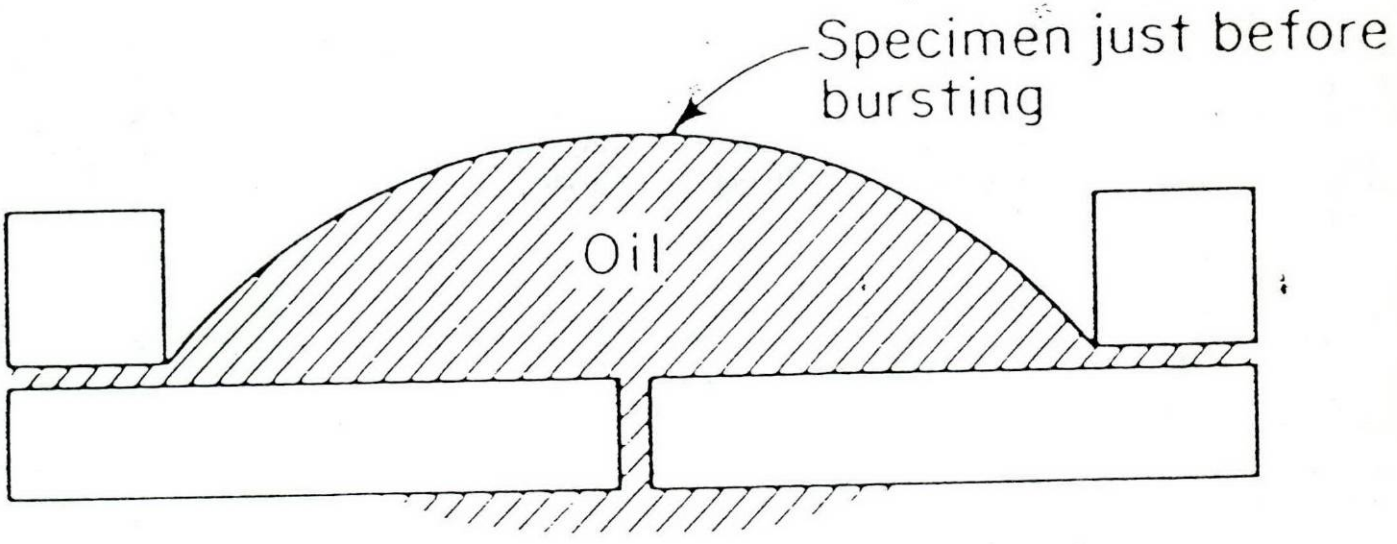


(a) Coordinate system for measuring biaxial stress in thin sheet; (b) curvature produced by removing material from top surface.

FIGURE FOUR



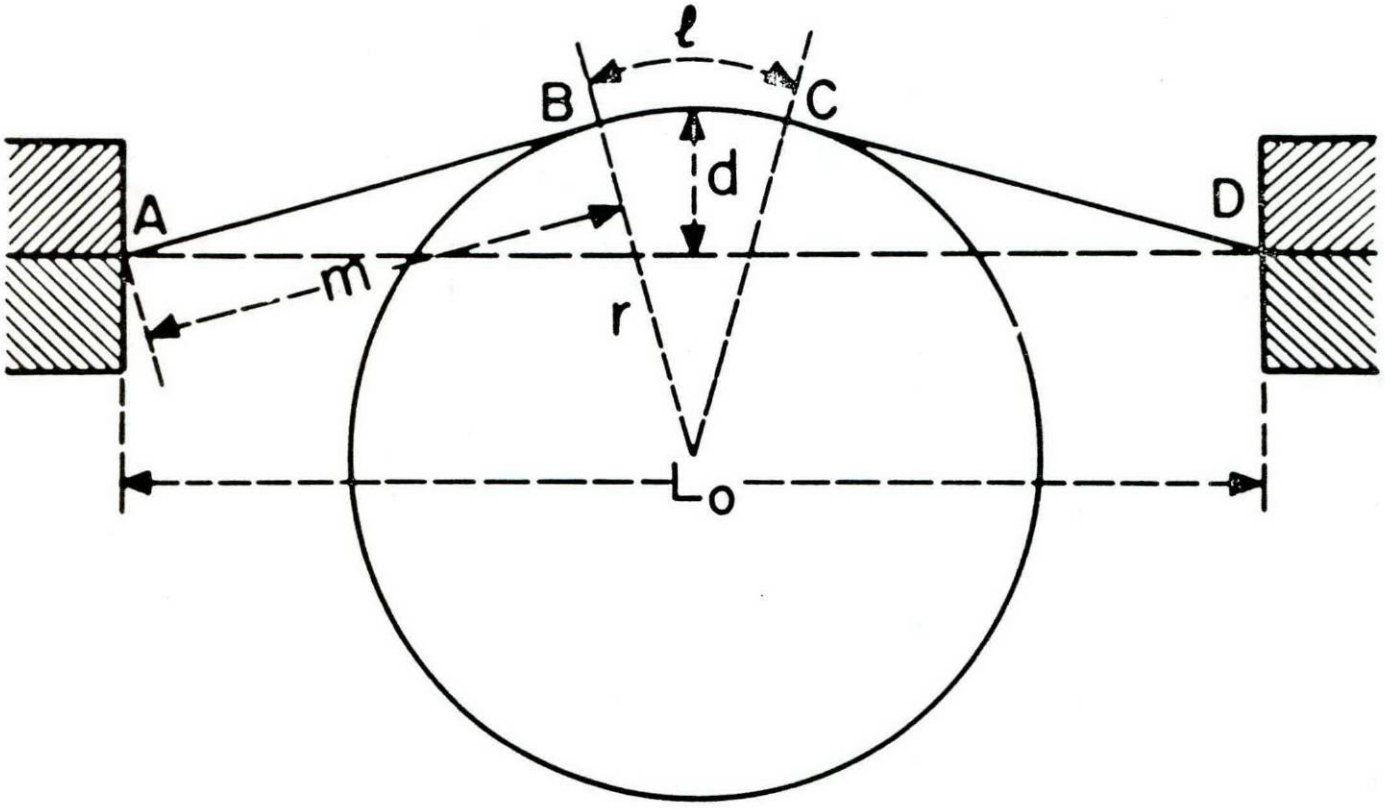
(a)



(b)

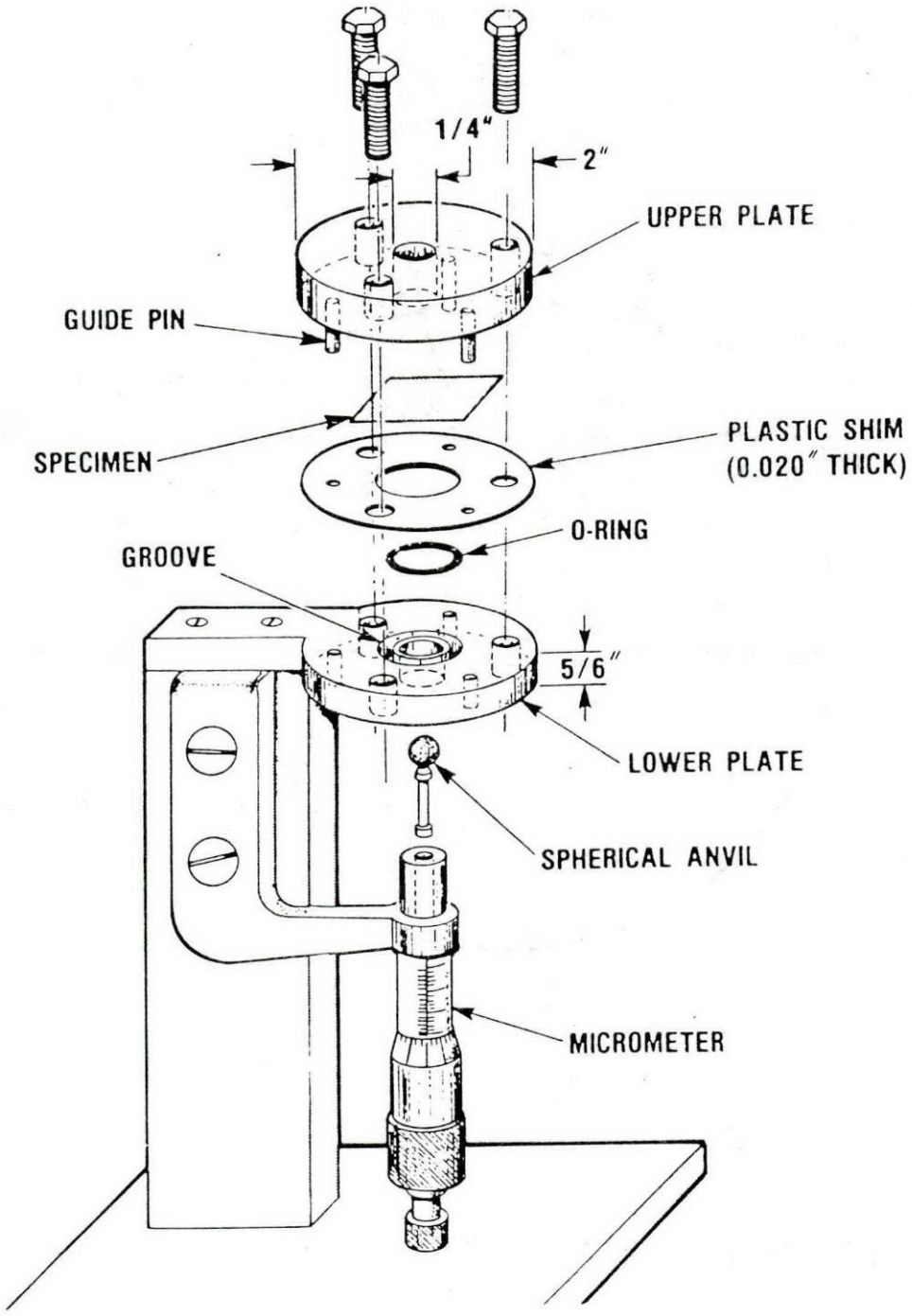
THE HYDRAULIC BULGE TEST

FIGURE FIVE



GEOMETRICAL RELATIONS FOR DETERMINING THE PERCENT ELONGATION AT FRACTURE USING THE BULGE TEST APPARATUS ILLUSTRATED IN FIGURE SIX.

FIGURE SIX



LABORATORY APPARATUS FOR PERFORMING ROUTINE BULGE TEST ON THIN FILM SPECIMENS (FROM REFERENCE 7)

FIGURE SEVEN

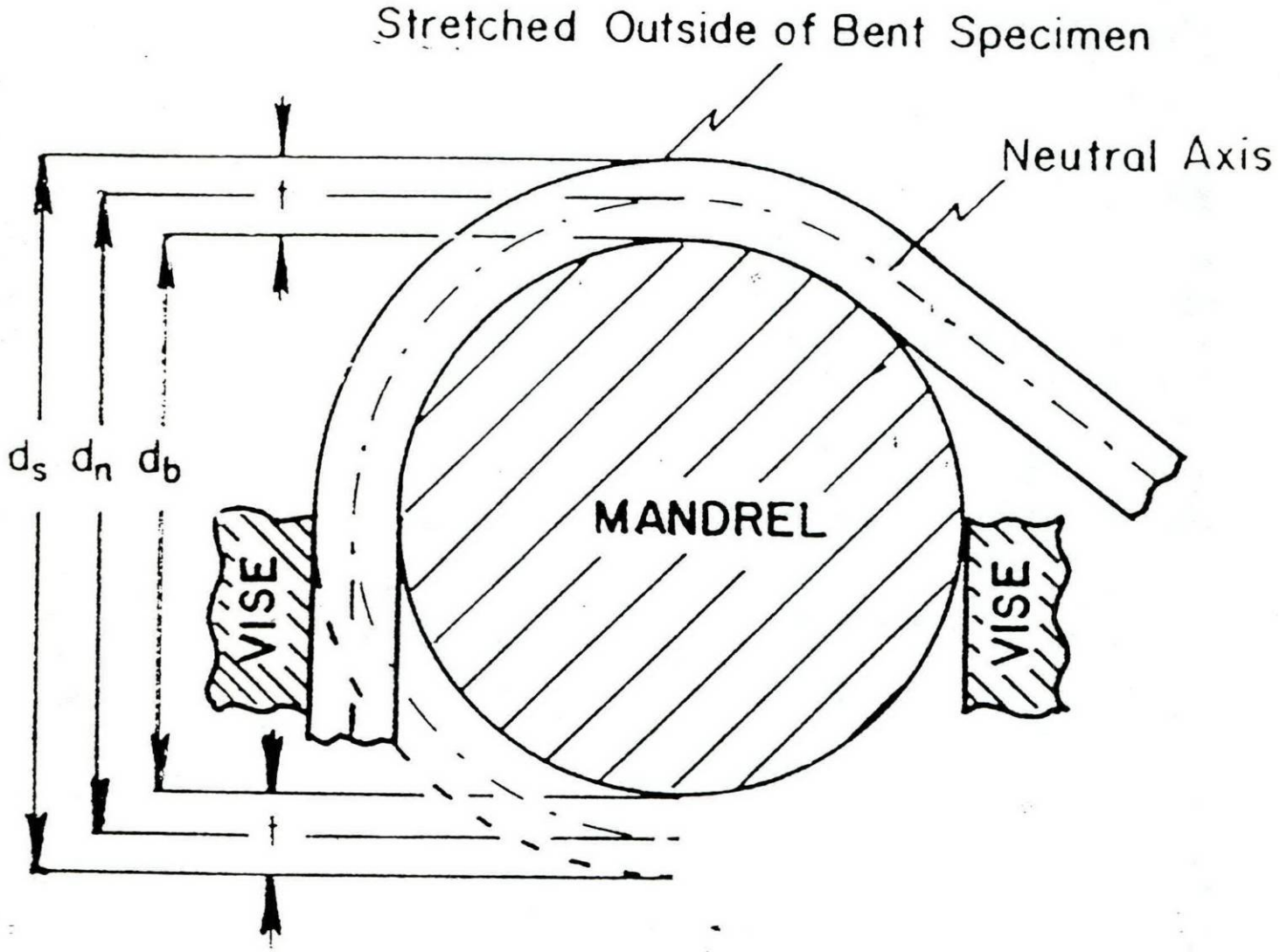
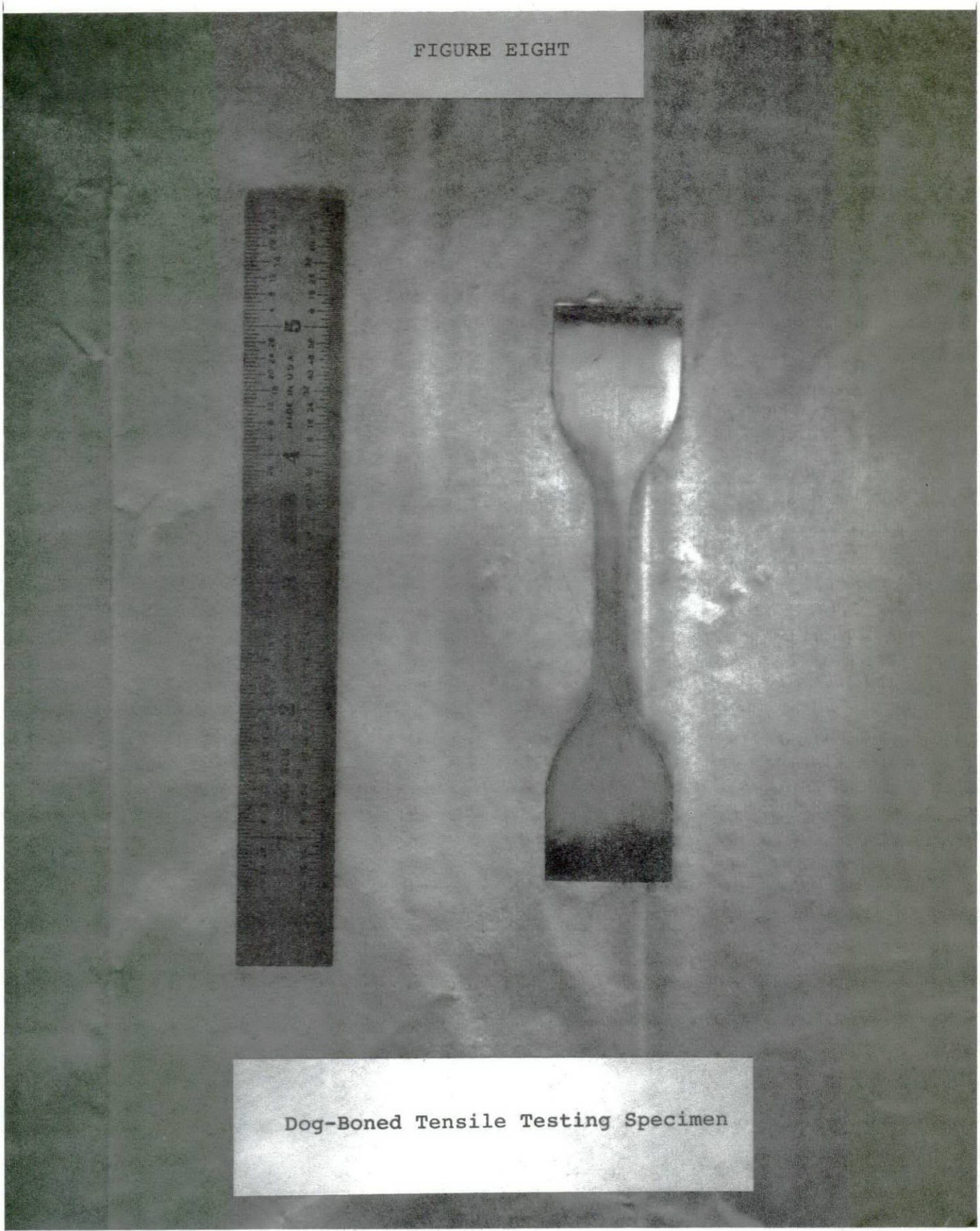


ILLUSTRATION OF THE BASIC SETUP OF ALL SUPPORTED BEND TESTS.

FIGURE EIGHT



Dog-Boned Tensile Testing Specimen