



The William Blum Lectures

#25 - Harold Weisner - 1984



**The 25th William Blum Lecture
Presented at the 71th AES Annual Convention (SUR/FIN 1984)
in New York, New York
June 27, 1984**

Engineering Properties of Various Coatings

**by
J.W. Dini, W.C. Cowden and W.K. Kelley
in Honor of
Dr. Harold J. Wiesner
Posthumous Recipient of the 1983 William Blum
AES Scientific Achievement Award**





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Editor's Note: Originally published as *Plating & Surface Finishing*, **71** (10), 56-61 (1984), this article is re-publication of the 25th William Blum Lecture, presented at the 71st AES Annual Convention, SUR/FIN 1984, in New York, New York on June 27, 1984. The principal scientific contributions of Dr. Harold J. Wiesner, posthumous recipient of the 1983 AES Scientific Achievement Award, are recounted in this lecture. The authors, his former colleagues, summarize the award winner's work in the areas of plating rhodium, lead, lead-tin dispersion alloys, and copper, as well as electroforming of gold-copper and hard anodizing of aluminum.

Introduction

Dr. William Blum, in whose name this paper was prepared, was one of the pioneers in applying the principles of materials science to electroplating.¹ He stressed the importance of studying the metallurgical structures and properties of electrodeposited metals and alloys. As Dr. Harold Read, the 1965 AES Scientific Achievement Award winner, noted: "Some of the Blum papers in the 1920s and 30s presaged the investigations of the last three decades that have shown the remarkable usage of structures and properties that can be achieved by electrodepositing a given metal in a variety of ways."²

Dr. Blum's book³ contains information on the properties of electroplated metals, and one of the first AES-sponsored research projects at the National Bureau of Standards dealt with the properties of electrodeposited nickel.⁴ Several recipients of the Scientific Achievement Award, including Hammond,⁵ Fischer,⁶ Read² and Weil¹ discussed aspects of the materials science of electrodeposits in their William Blum lectures.

So, like many of his distinguished predecessors, Dr. Harold J. Wiesner, who received the Scientific Achievement Award in 1983, spent his career studying the materials science of coatings. Dr. Wiesner died in 1980, but not before making important contributions in the investigation of electroforming, hard anodizing, precious metals plating, gold-copper electroforming, lead dispersion plating and hard copper deposition. We, his colleagues at Lawrence Livermore National Laboratory, summarize his most important work in this paper.

Rhodium

Some of Dr. Wiesner's pioneering work on heavy rhodium plating was published in 1952 and 1956.^{7,8} He studied the effects of metal concentration, acid content, temperature, and inorganic and organic impurities on the production of heavy rhodium deposits (2.5 to 10 μm). Figure 1, which shows the influence of metal content on deposition rate for two rhodium plating solutions, is representative of the data obtained. As a continuation of this work, a quality control program was instituted to minimize rejects during plating. It was shown that quality control measures, including spectrographic analysis of each lot of rhodium sulfate, plating efficiency tests, stress tests, and bend tests, were essential if relatively heavy deposits of rhodium were desired.

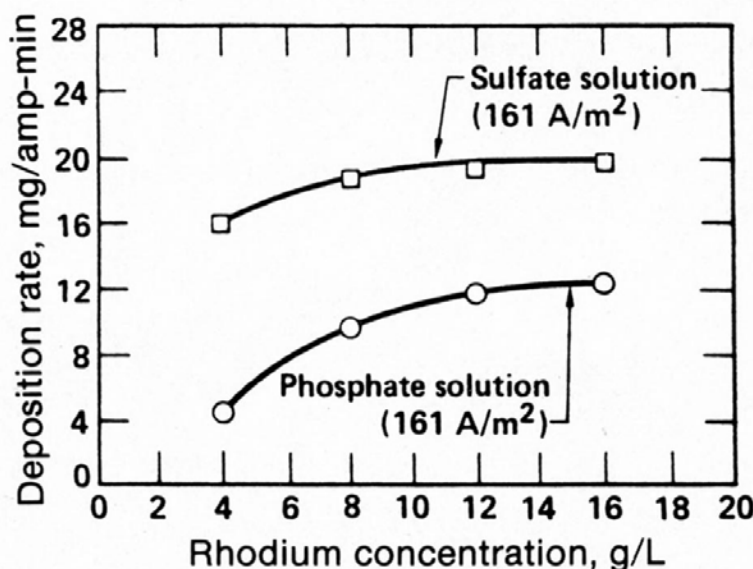


Figure 1 - Influence of metal content on the deposition of rhodium.

Electroforming gold-copper alloys

Dr. Wiesner developed solutions for producing thick deposits (0.5 to 1.5 mm) of gold-copper alloys and analyzed their engineering properties.^{9,10} Initially, he and his colleagues investigated an all-cyanide solution and a potassium gold cyanide bath with copper chelates. Table 1 gives the initial formulations and operating conditions.

The cyanide bath (Solution 1) gave rough deposits at thicknesses greater than 7.5 μm , and the alloy composition was highly dependent upon critical control of free cyanide. Consequently, this bath was abandoned in favor of the $\text{KAu(CN)}_2\text{-Na}_2\text{Cu EDTA}$ bath (Solution 2). With the latter, much smoother, brighter deposits were obtained, although they were brittle and stressed. The alloy composition was very dependent upon current density. Under the operating conditions shown for Solution 2, an alloy of about 93 wt% gold was obtained. However, when the current density was raised to 1 to 1.5 A/dm^2 (10 to 15 A/ft^2), alloys of about 70 to 80 wt% was obtained. After these encouraging results, several baths of varying compositions were tested to obtain one suitable for plating deposits as thick as 1.5 mm without cracking or burring. Two typical baths (Solutions 3 and 4) are shown in Table 2.

Table 1 - Initial Solutions and operating conditions.

Item	Solution 1	Solution 2
Potassium gold cyanide (67 percent Au), g/L	19	18
Copper cyanide, g/L	28	—
Copper EDTA,* g/L	—	8
Potassium cyanide, g/L	56	—
Temperature, ° C	60	60
Current density, A/dm^2 (A/ft^2)	0.35 (3.25)	0.35 (3.25)
pH	7.0	8.0
Anodes	Separate Au and Cu	Separate Au and Cu

*Ethylenediaminetetraacetic acid.

Table 2- Compositions and operating conditions for Au-Cu electroforming solutions.

Item	Solution 3	Solution 4
Gold as potassium gold cyanide (67-68 percent Au), g/L	6-6.5	6.0-6.5
Copper as disodium copper EDTA, g/L	16-18	—
Copper as trisodium copper DTPA,* g/L	—	16-18
PO ₄ expressed as 85% H ₃ PO ₄ , mL/L	25	25
Sodium sulfite, g/L	—	6-8
pH	7.0-7.5	7.5-9.0
Temperature, °C	65	65
Current density, A/dm ² (A/ft ²)	0.6-1 (6-10)	0.6-1 (6-10)
Deposition rate, g/A-hr	2.3-2.5	2.3-2.5
Deposition rate, mil/hr	0.4-0.5	0.4-0.5
Anodes	Platinum	Platinum

*Diethylenetriamine pentaacetic acid. Versenex-80, purchased from Dow Chemical Co., was used to form the copper chelate.

The relationship between alloy composition and current density for Solution 4 is presented in Fig. 2. A broad range of alloys can be produced simply by varying the current density. Figure 3 shows the typical banded structure characteristic of gold-copper deposits produced from Solutions 3 and 4.

A major effort was made to extend solution life and to control stress through the use of additives; however, no satisfactory stress-relieving agent was found. In all cases heat treating the deposits for 3 hr at 300°C as soon after plating as practicable gave favorable results.

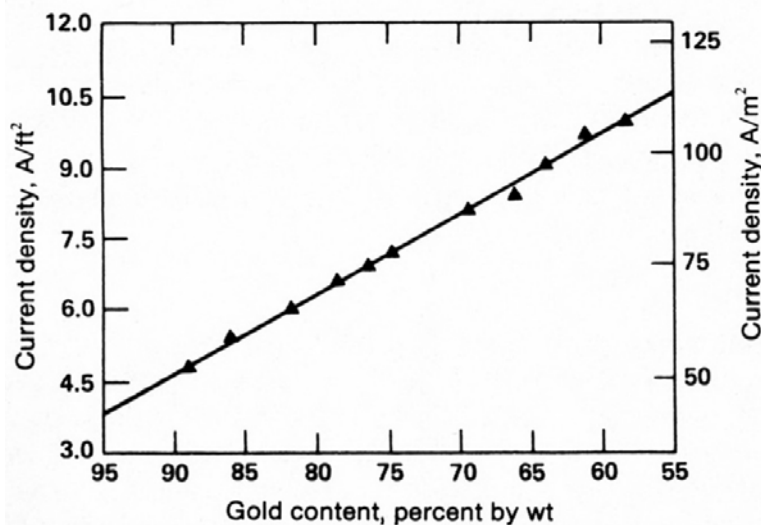


Figure 2 - Relationship of current density to gold content of alloy.

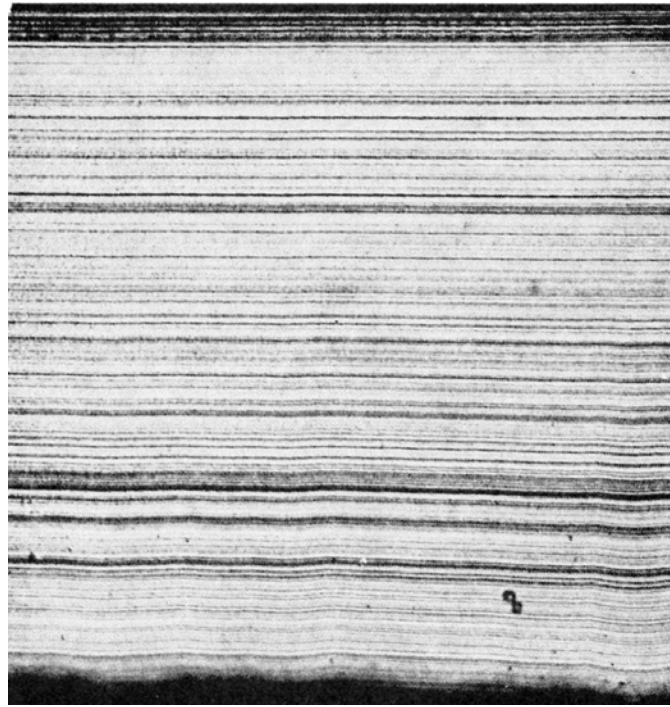


Figure 3 - Banded structure of gold-copper deposit (250×)

Wiesner and Distler¹⁰ extensively studied the mechanical properties of electroformed Au-Cu alloys. Ultimate and yield strengths as a function of heat treatment and alloy composition were determined for alloys from 65 to 90 wt% gold. Ultimate strengths as high as 170,000 psi (1173 MN/m²) were obtained when alloys of about 75% gold were heat treated for 3 hr at 300°C (Fig. 4). As gold composition increased beyond 85%, the strength of the alloy decreased rapidly. Heat treatment above 300°C lowered the ultimate and yield strengths but increased elongation. The electroplated specimens responded to heat treatment in essentially the same manner as alloys prepared by conventional metallurgical methods. Electron microscopy studies of the alloy showed extremely fine grain size.

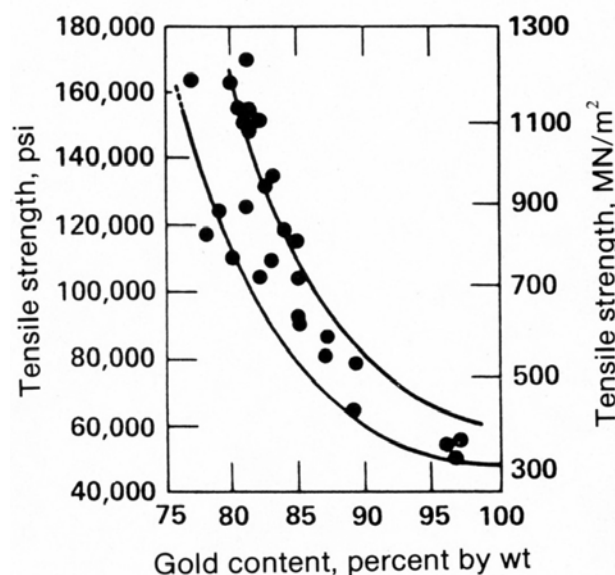


Figure 4 - Effect of heating for 3 hr at 300°C on tensile strength of electroformed gold-copper alloys.

Lead and lead-tin alloys

Prior to Dr. Wiesner's reports^{11,12} published in 1970, relatively little data had been recorded on the electrodeposition of heavy (2.5 to 10 mm) coatings of lead. In addition, although the solutions and operating conditions for lead and lead-tin alloys were well defined, almost no work had been reported on improving the strength and creep resistance of lead by electrodeposition.

Dr. Wiesner and his co-workers were pioneers in improving the mechanical properties of lead and lead alloys by codepositing dispersoids during plating.^{11,12} The first phase of this was the development of addition agents for producing hard, smooth, fine-grained lead and lead-tin electroforms up to 3.2 mm (0.125 in.) thick. The best results were obtained using 2 g/L of a very pure lignin sulfonic acid (or sodium lignin sulfonate) and 1 g/L of coumarin in the lead fluoborate solution described in Table 3. Anticipating that the introduction of fine particulates into the solution might result in deposit roughness, particularly if agglomeration of the particles occurred, an apparatus that could provide mechanical burnishing during plating using Teflon fingers was designed and built. Evaluation of a number of dispersoids revealed that only TiO₂ having an average particle size of 0.01 to 0.03 μ m gave improved results.

Mechanical property data were obtained for electroformed lead and lead alloys containing small amounts of: Sn; Sn and TiO₂; Sn and BaSO₄; and BaSO₄. In addition, the mechanical properties of 99.99% lead and a commercially available, high-strength lead alloy containing 1.5% PbO were determined for comparative purposes.

Table 3 - Solution and operating conditions for electroplating lead.

Item	Detail
Lead fluoborate concentrate	1:1 dilution
Lead as metal	250 g/L
Free boric acid	30 g/L
Free fluoboric acid	20-30 g/L
Lignin sulfonic acid	2 g/L
Coumarin	1 g/L
Temperature	Room
Cathode current density	5.4 A/dm ² (50 A/ft ²)
Anode	99.99 percent Pb

Engineering stress-strain curves for these materials are shown in Fig. 5. Significantly, the yield and ultimate strengths of electroformed lead and lead alloys are greater than those for a large majority of lead alloys fabricated by conventional methods. Typical creep curves are illustrated in Fig. 6. The creep curves for electroplated lead and the electroplated lead alloys were distinctly different. Primary creep strain for the lead was generally 6 to 8% and the primary region of creep lasted for about 10 hr after application of load. On the other hand, primary creep strain for all the lead alloys was 0.5 to 2.0% and steady-state creep occurred after 1 to 2 hr under load. As indicated in Fig. 6, the lead-tin and lead-tin-TiO₂ alloys had the greatest creep resistance.

Correlation of chemical analysis and microstructure with the mechanical property data revealed that the strengthening effect in the electroformed alloys was principally associated with carbon content. The origin of the carbon was the lignin sulfonic acid and coumarin, both of which had been added to the solution to enhance the production of smooth deposits. The manner in which the carbon was incorporated in the deposits is uncertain, but absorption of individual or small groups of organic molecules on the surface of the deposit during plating is a likely mechanism.

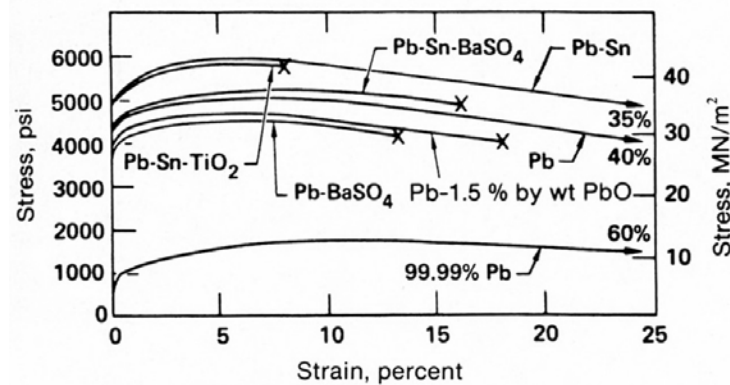


Figure 5 - Engineering stress-strain curves for electroformed lead alloys and 99.99% lead.

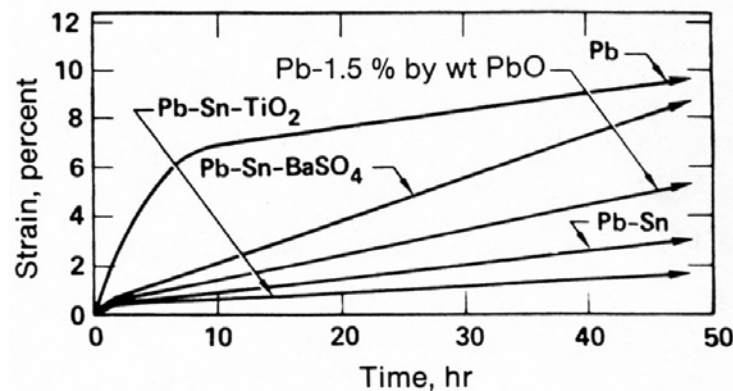


Figure 6 - Creep curves for electroformed lead and some electroformed lead alloys at 23°C and 21 MN/m² (3000 psi).

Room temperature is approximately one-half the melting point (in degrees Kelvin) of lead, and lead will deform under a constant load at ambient conditions. Thus, the creep strength is probably the most important design parameter for using lead in structural applications at room temperature. Accumulation of long-term creep data at strain rates of less than $10^{-3}/\text{hr}$ for many alloys requires a large number of creep units and extensive periods of time. When limited equipment is available, a screening test is highly desirable. Correlations between the short-term mechanical properties of hardness and yield strength with the steady-state creep rates for the electroformed lead and lead alloys are shown in Figs. 7 and 8. These correlations were reasonably good. Yield and tensile strengths can be predicted fairly well from the hardness numbers, and creep rates can be predicted fairly well from the yield strength, tensile strength, or hardness results.

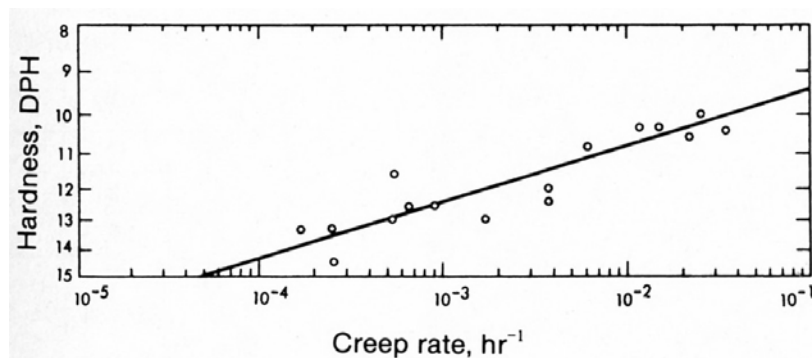


Figure 7 - Relationship between steady-state creep rate at 21 MN/m² (3000 psi) and 23°C hardness for electroformed lead and lead alloys.

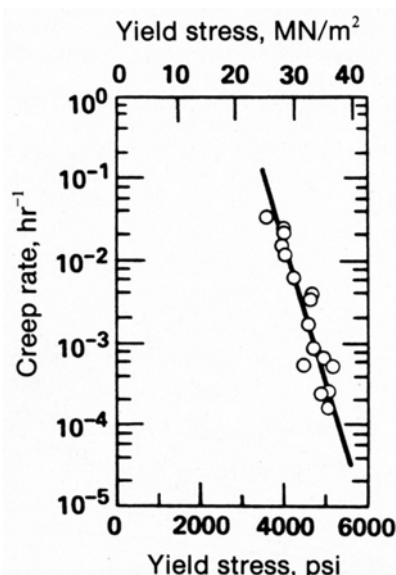


Figure 8 - Relationship between steady-state creep rate at 21 MN/m² (3000 psi) and yield stress for electroformed lead and lead alloys.

Acid and pyrophosphate copper

Acid and pyrophosphate copper solutions were investigated to identify conditions yielding copper deposits that would retain yield strength and hardness after heating.^{13,14} This was desired for certain electroforming applications. Data based on deposits from commercial acid and pyrophosphate copper solutions clearly showed that mechanical properties varied widely as a function of addition agent concentration. The degree to which electroplated copper softened with either room-temperature aging or high-temperature baking appeared related to the amount of brightener in solution, and consequently to the amount of codeposited brightener (or its breakdown products). This is demonstrated in Table 4.

Table 4 - Property data for deposits produced in a pyrophosphate solution containing varying amounts of addition agent.

Addition agent conc., ^b mL/L	Sulfur, ppm	Carbon, ppm	Hardness, ^c DPH _{100g}	Ultimate strength, ^c MN/m ²	Elongation, ^c percent
0	~20	93	80 (81)	236 (233)	28 (30)
0.23	~20	68	113 (98)	572 (276)	6 (34)
0.45	~20	50	181 (104)	601 (303)	9 (24)
0.9	30	77	193 (128)	629 (378)	8 (10)
4.5	180	75	225 (213)	628 (628)	7 (5)
9.0	268	160	225 (221)	613 (621)	4 (4)

^aDeposits were plated at 20 mA/cm² and 53°C.
^bPY-61-H, M&T Chemicals Inc., Rahway, NJ.
^cNumbers in parentheses were obtained after heating for 2 hr at 250° C.

Deposits with high levels of brightener could withstand heating at 250°C without loss of mechanical properties. Another important observation was that hardness measurement alone did not give sufficient information to predict the strength of a copper deposit. This is particularly evident in Fig. 9.

This was not the first time a Scientific Achievement Award winner had made an observation such as this regarding hardness. Dr. Read published considerable data supporting the fact that hardness determinations provided little consistent or useful relationship to important properties such as tensile strength or ductility.²

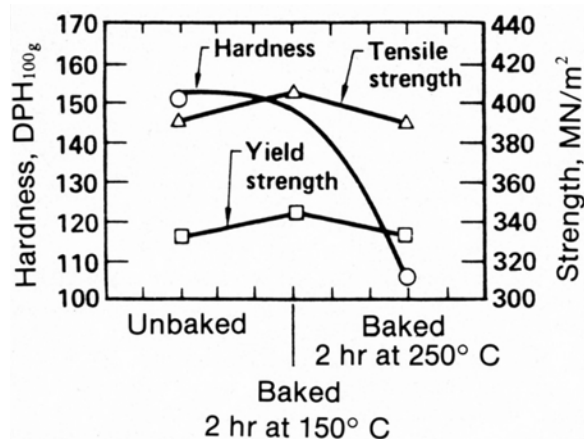


Figure 9 - Hardness and strength data for as-deposited and aged(2 years) UBAC-1 copper (Udylite Division, OMI, Warren, Michigan).

Hard anodizing of aluminum

Dr. Wiesner studied and reviewed several important properties of hard anodized aluminum, including salt-spray resistance, hardness, wear or abrasion resistance, and dielectrics. It was shown that this hard, wear-resistant coating with excellent corrosion resistance and dielectric properties can extend the use of aluminum in many aircraft applications.

Investigations were conducted to determine the most suitable solution composition for hard coating various alloys. Figure 10 presents the data obtained for 6061 alloy. The dashed line is a theoretical plot assuming a hardcoating rate of 25 μm per 20 min at a current density of 387 A/m². In the case of alloys such as 6061 and 7075 with a low copper content, the points were reasonably close to this theoretical line at the lower thicknesses (less than 63 μm). In the more concentrated solutions, particularly at lower temperatures, 7075 appeared to hardcoat at a faster rate. Cast alloys such as 355 and 356 hardcoated at a considerably faster rate than that predicted by the theoretical curve. Again, the increased rates were favored by higher concentrations of sulfuric acid and lower operating temperatures. High-copper aluminum alloys (2017, 2024 and X2219) were hardcoated satisfactorily only in a 385-g/L sulfuric acid solution.

In an attempt to determine the effects of processing variables on wear resistance, tests were performed on a Taber abraser. Some results are summarized graphically in Fig. 11. In general, 6061 panels showed the best wear resistance while 7075 and 2024 were about equal. Subjecting the unsealed, heavy hard-coat to a second cycle appeared to reduce the wear resistance of 7075 and 2024 alloys.

Achievement and dignity

The AES Scientific Achievement Award recognizes outstanding contributions that have advanced the theory and practice of electroplating and allied arts, raised the quality of products or processes, or advanced the dignity of the profession. Dr. Wiesner qualified in all three areas. His work helped identify the wide range of properties that are obtainable and controllable by electrodeposition. He showed that deposits such as rhodium, gold-copper, lead dispersion alloys, and hard copper can be reproduced in sound fashion.

With regard to advancing the dignity of the profession, Harold Wiesner had few peers. He was a loyal friend, an enthusiastic and effective co-worker, a trusted advisor, and a tireless volunteer for the AES. Those of us who were privileged to know and work with him can truly say we were enriched both personally and scientifically.

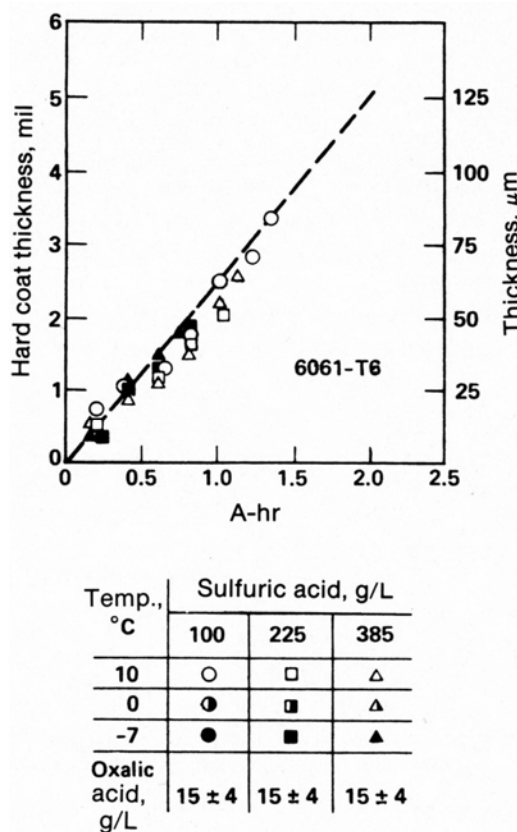


Figure 10 - Effect of acid concentration and solution temperature on anodizing characteristics in 6061 aluminum.

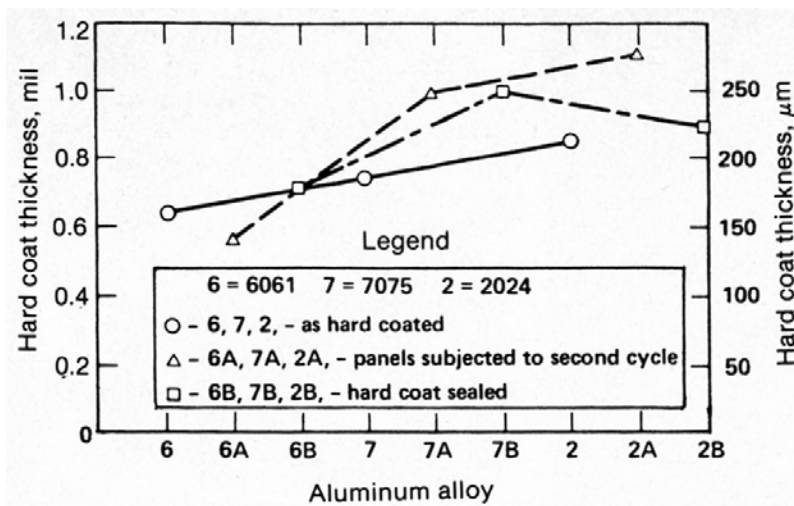


Figure 11 - Taber abraser wear of three hardcoated aluminum alloys using H-10 wheels and 500-g load.

Acknowledgment

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About Dr. Harold J. Wiesner

This piece was written at the time Dr. Wiesner was announced as the recipient of the 1983 Scientific Achievement Award. The biographies of the authors which follow Dr. Wiesner's biography, were written at the time of publication.



Dr. Harold J. Wiesner, who passed away in October 1980, was named the 1983 recipient of the AES Scientific Achievement Award on June 30 during AES SUR/FIN '83, in Indianapolis. The announcement was made by James E. Voytko, CEF, Chairman of the Scientific Achievement Award Committee. It is the first time the award has been presented posthumously. It is presented annually to recognize an individual who has made outstanding scientific contributions advancing the theory and practice of electroplating and allied sciences, raised the quality of products or processes, or enhanced the dignity of the profession. Dr. Wiesner qualified in all areas.

He was born on April 14, 1916, and received his Ph.D. degree from Michigan State University in 1943. He was employed by RCA Victor Division, G.C. Conn Ltd., Bendix Products Division, and, from 1962 until his death, the Lawrence Livermore National Laboratory, Livermore, California.

Dr. Wiesner had more than 24 papers published in the technical literature. He also wrote a chapter in *Modern Electroplating* (3rd edition) and held three patents on subjects relating to surface finishing. The award winner had conducted studies on electroforming, hard anodizing, precious metals plating, gold-copper electroforming, lead dispersion plating and hard copper plating.

His work led to the electroforming of thick layers of gold-copper alloys over a wide composition range. The tendency for deposit cracking was overcome by modifying an existing gold solution to produce an alloy plating bath. Heat treatment of the deposits improved the strength and eliminated cracking. Electron microscopy studies showed gold-copper alloys to be extremely fine grained and responsive to heat treatment, in the same manner as metallurgically prepared specimens. This work with gold-copper also included extensive investigations of the physical and mechanical properties of the alloy and eventually earned Dr. Wiesner and coauthors the AES Silver Medal Award in 1971.

In 1952, he published a pioneering paper on heavy rhodium plating. Effects of a number of variables such as metal content, acid content, and temperature on efficiency were reported, as was information on the effects of inorganic and organic impurities. The



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studies were made in order to establish optimum operating conditions for producing thick rhodium deposits. As a continuation of this work, a quality-control program was instituted in order to minimize rejects during plating. It was shown that quality-control measures, which included spectrographic analysis of each lot of rhodium sulfate, plating efficiency tests, stress tests and bend tests, were essential if relatively heavy deposits of rhodium were desired. The AES Precious Metals Plating Award was presented to Dr. Wiesner in 1952 for this work with rhodium.

He also did fundamental work on strengthening electrodeposited lead and lead alloys. Improved strength was achieved by using specific addition agents and including dispersoids in the deposits. From an evaluation of a number of addition agents, a combination of lignin sulfonic acid and coumarin was chosen as the most suitable to produce smooth, hard and thick deposits. Al_2O_3 , PbO , Pb_3O_4 , W , BaSO_4 , and TiO_2 were tested as dispersoids to increase strength and creep resistance. It was shown that the strength of electroformed alloys was dependent on carbon content and TiO_2 content and that these alloys had higher strength than most lead alloys produced by conventional processes.

Acid copper and pyrophosphate solutions were investigated with the objective of identifying conditions yielding copper deposits that would retain yield strength and hardness after heating. This was desired for certain electroforming applications. The work showed that electrodeposits from either an acid copper or pyrophosphate solution could withstand heating at 250°C (482°F) for up to 8 hr without an appreciable loss of mechanical properties if the addition agents were maintained at higher-than-normal levels. An important observation in this work was that hardness measurements did not reliably predict the yield and ultimate strength of electrodeposited copper when addition agents were used.

Dr. Wiesner developed an etching solution satisfactory for thick-film aluminum circuit boards. This overcame variations in electrical resistance experienced when using conventional etching solutions. The Wiesner solution contained polyphosphoric acid, orthophosphoric acid and ferric chloride, and could be used either for spray or dip etching to produce well-defined, reproducible cross sections.

Harold Wiesner was a leader in the AES for many years. He was national president during 1970-71, served on the AES Technical Education Board and the Publications Board, and was Chairman of The Research Board during 1961-63. He was also a president of two AES branches - St. Joseph Valley and San Francisco - and general chairman of the 1968 AES annual conference, held in San Francisco. In 1975 he was named a National Honorary Member of the society.

A paper summarizing his technical accomplishments was to be written by his colleagues at Lawrence Livermore National National Laboratory and delivered as the William Blum Lecture in New York during AES SUR/FIN 1984 in July.

About the authors



Jack Dini is a leader of the Coating Processes Group, Materials Fabrication Div., at Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94550. Prior to joining LLNL, he was employed by Sandia Laboratories and Battelle Columbus Laboratories. Mr. Dini holds a degree in metallurgical engineering from Cleveland State University and is currently serving AES as national president. He is a former member of the society's Technical Education Board and Research Board.



W.K. Kelley is a senior engineering associate in the Coating Processes Group. He worked for 13 years as a process engineer in metal finishing and heat treating, and, upon joining LLNL in 1964, served as supervisor of the electroplating department for 12 years. He is a member of The Electrochemical Society and the AES Santa Clara Valley Branch.



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Wayne C. Cowden, CEF, is a senior technologist and 13-year veteran at LLNL. For the past 4 years, he has been associated with the Coating Processes Group and has worked on several projects dealing with electrodeposited gold and gold-copper alloys. His prior assignment at LLNL centered on chemical vapor deposition of tungsten alloys. Mr. Cowden previously was employed by General Electric Company. He has a BA degree in education from Colorado State College and is a member of the AES Santa Clara Valley Branch.