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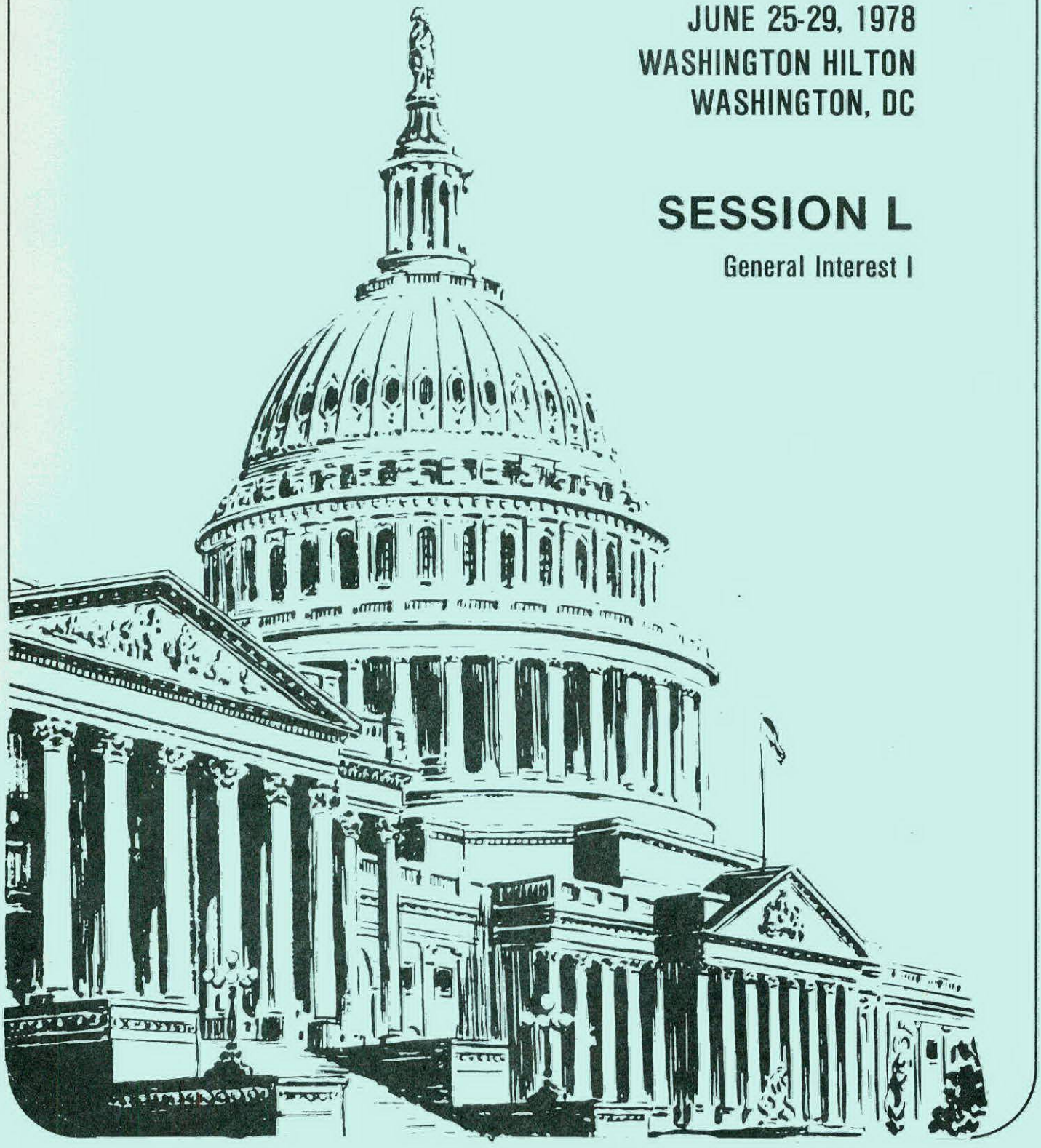
SESSION L

General Interest I



AMERICAN ELECTROPLATERS' SOCIETY, INC.

65TH ANNUAL TECHNICAL CONFERENCE -- WASHINGTON, D.C.

PROCEEDINGS -- SESSION L

"GENERAL INTEREST I"

Papers included in this proceedings:

Precision Etching of Thick-Film Circuits of Aluminum and Aluminum-0.1 wt% Copper*

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ABSTRACT

In certain high-current applications the resistance of the aluminum conductors is an important design parameter. Such a case is the aluminum exploding-bridge used in some nuclear detonators. The resistance of the network must be accurately known so that the individual bridge will receive the proper firing current. Vapor-deposited, thick aluminum films (0.011 mm) are often used to produce the necessary circuitry. These films are suitably masked and etched to make the conductors.

Conventional etching methods for aluminum or aluminum-0.1 wt% copper do not yield conductors with a well-defined, reproducible cross section. This results in unacceptable variations in electrical resistance. For this application, we have developed a new etching solution that contains 25 to 50 vol% polyphosphoric acid, 75 to 50 vol% orthophosphoric acid, and 10 to 30 g/l ferric chloride.† Etching may be done at 55 to 65°C, but for precision etching the temperature should be controlled to ±1°C. The solution is useful for dip etching of aluminum circuits. The paper describes some limited production experience with this etch.

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†Patent applied for.

INTRODUCTION

Vapor-deposited, thick aluminum films (0.011 mm) are often used as conductors in high-current applications where the resistance of the aluminum conductors is an important design parameter. An example of such a high-current application is the aluminum exploding-bridge used in some nuclear weapon detonators. In this application, the resistance of the network must be accurately known so that the individual bridge will receive the proper firing current.

Conventional etching solutions for aluminum do not yield conductors with a well-defined, reproducible cross section, which results in an unacceptable variation in electrical resistance. Etching can leave aluminum conductors with a trapezoidal or curved cross section or foot, or can undercut the photoresist (see Fig. 1). The ideal etch leaves a perfectly rectangular cross section. Thin-film aluminum circuits are usually etched with a mixture of phosphoric acid, nitric acid, and water, at 50 to 55°C[1]. However, for thick films we found that this etchant was unsatisfactory with the Shipley AZ-340* photoresist. The resist lifted badly during the etching; furthermore, this solution produced tapered edges on the elements.

Several other etching solutions were considered. In industry, ferric chloride-water-phosphoric acid solutions have been used for etching thick films, but usually only for cases where edge definition was not critical. These solutions were not suitable for narrow (0.18 mm) elements.[2] An etching

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*Reference to a company or product name does not imply approval or recommendation of the product by the University of California of the U.S. Department of Energy to the exclusion of others that may be suitable.

solution containing concentrated hydrochloric acid, phosphoric acid, and a small amount of ferric chloride has also been tried.[2] Although this solution gave good, straight edges, the bath was unstable and, therefore, not suitable for production applications.

We have recently developed a simple etching solution consisting of orthophosphoric and polyphosphoric acids and a small amount of ferric chloride. This solution gives good edge definition and is stable over a relatively long period. Wide variations in the concentrations of the constituents do not seem to affect the etching rate or edge definition.

DESCRIPTION OF OUR EXPERIMENTS

In the initial phases of development, The Bendix Corporation, Kansas City Division, supplied thick films that had been made by physical vapor deposition of pure aluminum, or aluminum-0.1 wt% copper, onto Kapton. Deposits were produced using equipment manufactured by Davis and Wilder, and Endurex. After deposition the aluminum or aluminum alloy was cleaned and dried and the photoresist (Shipley AZ-340) applied and baked. The pattern was then exposed and developed. After drying, the circuits were ready for chemical etching. The circuit boards were cut into small pieces (approximately 2.5 cm by 5.0 cm) and etched in baths that contained 500 to 2000 ml of solution.

The etching solution was stirred with a magnetic stirrer and the parts were moved back and forth in the etching solution by hand. Initially the end point for removal of the excess aluminum was determined by eye; subsequently, the pieces were examined microscopically at 20X. If there were areas where the aluminum was not completely removed and the elements were not undercut, the parts were etched for an additional period. Finally,

observations were recorded relative to the edge condition, a typical element was photographed, and its width was measured. Circuits with 0.18-mm-wide elements were photographed at 150X; those with 0.75-mm-wide elements were photographed at 75X.

PHOSPHORIC ACID-NITRIC ACID ETCHING SOLUTION

Samples of pure aluminum and aluminum-0.1 wt% copper alloy were etched at 53°C in a phosphoric acid-nitric acid solution composed of:

Orthophosphoric acid	500 ml
Water	125 ml
Nitric acid	50 ml
Sodium lauryl sulfate	0.1 g/l.

After etching, we examined the circuits and found them to be unsatisfactory. Their edges were severely tapered, as shown by the pure aluminum sample in Fig. 2, and the resist had washed off during the rinsing operation. Spotting on the surface of the elements is additional proof that the resist had broken down during etching. The aluminum-0.1 wt% copper alloy had been undercut badly during the 14-min etching (Fig. 3), yet traces of unremoved aluminum were still visible near the element.

When we added 200 ml of polyphosphoric acid to the bath and etched a pure aluminum circuit at 56 to 57°C for 12.5 min, we found less tapering on the circuit edge. However, some debris still remained on the Kapton, and the resist washed off again during the rinsing operation.

Additional experiments were performed using higher concentrations of polyphosphoric acid and nitric acid:

Orthophosphoric acid	850 ml
Nitric acid	100 ml
Water	225 ml
Polyphosphoric acid	400 ml
$CoCO_3$	3.5 g.

We also added $CoCO_3$ to accelerate the etching of the aluminum; however, its effect was not clear. With this etching solution, the tapered edges were essentially removed from the pure aluminum circuit, but the alloy circuit still displayed feathered edges. Because strict tolerance for the width of the element had been exceeded, no further tests were made with etching solutions containing nitric acid.

ORTHOPHOSPHORIC-POLYPHOSPHORIC ACID ETCHING SOLUTION

We have investigated a wide range of orthophosphoric-polyphosphoric acid combinations. We find that circuits etched in orthophosphoric-polyphosphoric acid solutions show vertical rather than tapered edges on the elements in contrast to the circuits etched in nitric acid solutions. However, a slight foot still remains (Fig. 4). For pure aluminum, the polyphosphoric acid may range from 25 to 75 vol% without appreciable change in the etching results. With 75 vol%, the solution is quite viscous and requires a long rinse. Because considerable heat is generated when polyphosphoric acid and orthophosphoric acid are mixed, caution must be exercised in preparing the etching solutions. For etching aluminum-0.1 wt% copper circuits, a mixture of 1 part orthophosphoric acid and 1 part polyphosphoric acid appears to give the best results.

Adding ferric chloride to the bath improved the edges. Samples etched in solutions containing between 6 and 30 g/l $FeCl_3 \cdot 6H_2O$ produced satisfactory edges (Figs. 5-7).

PILOT-LINE STUDIES OF ETCHING SOLUTIONS

The performance and resolution obtained with the polyphosphoric acid etching solution (25 vol% polyphosphoric, 75 vol% orthophosphoric acids, 20 g/l $FeCl_3 \cdot 6H_2O$) was studied at The Bendix Corporation, Kansas City Division, for four photoresist exposure times and four photoresist development times. A pure aluminum deposit was whirl-coated with AZ-340 photoresist to a thickness of approximately 5 μm, and the measured photomaster image was exposed on the part using a high-pressure mercury lamp at an intensity of 2.9 mW/cm^2. Exposure times of 40, 60, 80, and 100 s were used. Images were then developed for 2, 3, 5, and 8 min to produce a matrix of 16 data points. The width of the bridge was measured before and after etching, and the bridge-width reductions were calculated. In Figs. 8 and 9, bridge-width reduction after development and etching is shown as a function of developing and exposure time for the 127- and 254-μm patterns, respectively.

The data show that exposure time is the less critical variable in terms of bridge-width reduction after etching. The optimum of the two variables is reached at an approximate 3-min development time and a variable exposure period. The bridge-width reduction is in accord with data obtained from etched parts indicating good repeatability.

EFFECT OF VARYING THE RATIO OF POLYPHOSPHORIC ACID TO ORTHOPHOSPHORIC ACID

In beaker-scale experiments, the polyphosphoric acid was varied from 25 to 75 vol%, with acceptable etching results. However, from a practical point of view, a solution containing 75 vol% polyphosphoric acid would not be feasible in a spray etcher. In fact, we found that a centrifugal pump attached to a 3/4 hp motor caused the motor to overheat, even when we used 25 vol% polyphosphoric acid. From this we concluded that a positive displacement pump would be required for spray etching. Because this pump was not immediately available, we evaluated the possibility of dip etching the circuits. The circuits were attached to a polypropylene disk by tape, and rotated for 2 min in each direction for the required etching period. A schematic of the equipment is shown in Fig. 10.

Two 40-l solutions were made up, as shown below:

	I	II
Polyphosphoric acid, vol%	25	50
85% Orthophosphoric acid, vol%	75	50
Ferric chloride ($FeCl_3 \cdot 6H_2O$), g/l	20	20
Temperature °C	60-62	60-62

A number of aluminum circuits were processed in each solution to establish an etching rate for pure aluminum and aluminum-0.1 wt% copper. These rates are shown below.

	Etching Solution	
	I	II
Etching rate, μm/min for aluminum	1.0	1.0
Etching rate, μm/min for aluminum-0.1% copper	—	1.35

Using this information, we etched 30 pure aluminum circuits in solution I for 10.5 min and examined the bridge wires at 50X magnification on a TV screen. All bridge wires were clean, had sharp edges, and were within the width-tolerance band (see Fig. 11 for typical bridge elements).

The two baths can be operated satisfactorily on an intermittent basis for several months. We were originally concerned that because the baths were hygroscopic, moisture absorption might cause deterioration in the edge acuity. To date, we have not seen problems in this area, and the baths have been left uncovered for 30 to 45 days. In beaker-scale experiments, up to 10 vol% water has not caused detrimental effects. However, we have not determined the maximum amount of water that can be added to the 40-1 solutions without causing problems.

CONCLUSIONS

1. We have developed an etching solution that is satisfactory for thick-film aluminum circuit boards. It contains 25 to 75 vol% polyphosphoric acid, 75 to 25 vol% orthophosphoric acid, and 20 g/l ferric chloride.

2. The solution produces vertical rather than tapered edges on elements.

3. The solution can be used either for dip etching or spray etching, but, for spray etching, a positive displacement pump must be used.

ACKNOWLEDGMENTS

The author wishes to acknowledge the assistance of Cheryl McCaffrey and Stanley McInturff of the LLL Metallurgical Analysis Group in preparing the photographs. John Stein, William Nicholson, and Tom Murray of The Bendix

Corporation, Kansas City Division, performed the line-width studies and evaluated the etching solutions in a pilot-line setup. Their assistance is gratefully acknowledged.

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1. S. Wernick and R. Pinner, Surface Treatment of Aluminum (Robert Draper Ltd., 1964), 3rd ed., p. 105.

2. W. H. Knopf and J. W. Chesney, Aluminum Etchant Studies, The Bendix Corporation, Kansas City Division, Rept. BDX-613-1105 (1974).

HJK

FIGURE CAPTIONS

Fig. 1. Conceptual drawing showing cross sections that can be obtained when thick-film circuits are etched. In the ideal case, the cross section forms a perfect rectangle.

Fig. 2. Pure aluminum circuit etched in a bath containing nitric acid. The photographs are taken from the top; the thick black outline indicates severe tapering.

Fig. 3. An SEM photo of aluminum-0.1 wt% copper alloy circuit etched in a bath containing nitric-acid. The photo shows severe undercutting and traces of aluminum near the element.

Fig. 4. Aluminum and aluminum-0.1 wt% copper alloy circuits etched in a 1:1 mixture of orthophosphoric and polyphosphoric acids. The edges are much better than those shown in Figs. 2 and 3, but there is still a slight foot.

Fig. 5. Aluminum and aluminum-0.1 wt% copper alloy circuits, etched with 1:1 orthophosphoric and polyphosphoric acids and 6 g/l ferric chloride. Both circuits were etched for 10 min at 59°C. Note the reduction in the foot compared to Fig. 4.

Fig. 6. Aluminum and copper alloy circuits etched with 350 ml each of orthophosphoric and polyphosphoric acids, 70 ml water, and 13 g/l ferric chloride. Both circuits were etched at 58°C. The pure aluminum circuit was etched for 12 min and the copper alloy circuit for 15 min. Compared with Fig. 4.

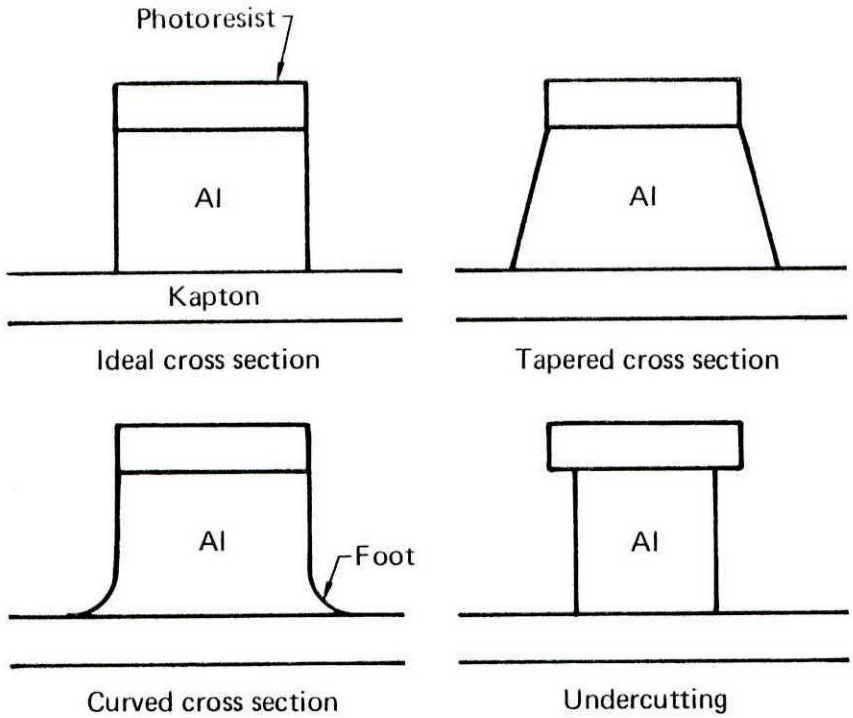
Fig. 7. Aluminum circuit etched with 1:1 orthophosphoric and polyphosphoric acids and 30 g/l ferric chloride. The circuit was etched at 64°C for 7.5 min. Note the clean, straight edge.

Fig. 8. Width reduction for 127-μm-wide bridges as functions of exposure and development times, and etching. Measurements were made after exposure and development and again after etching.

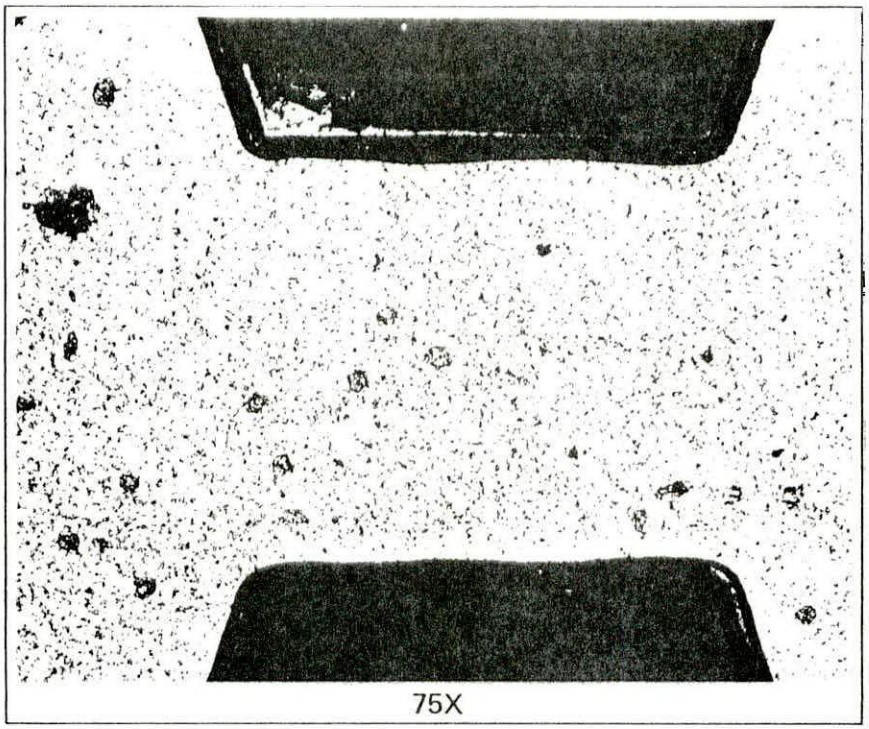
Fig. 9. Width reduction for 254-μm-wide bridges as functions of exposure and development times, and etching. Measurements were made after exposure and development and again after etching.

Fig. 10. Schematic (top view) of pilot-line tank for etching aluminum circuits. The part to be etched is mounted in a polypropylene ring. The ring is placed in guide slots in the tank. A drive wheel rotates the ring at approximately 2 to 3 rpm for 2 min. Then, the direction of rotation is reversed. This process is repeated until the part is etched.

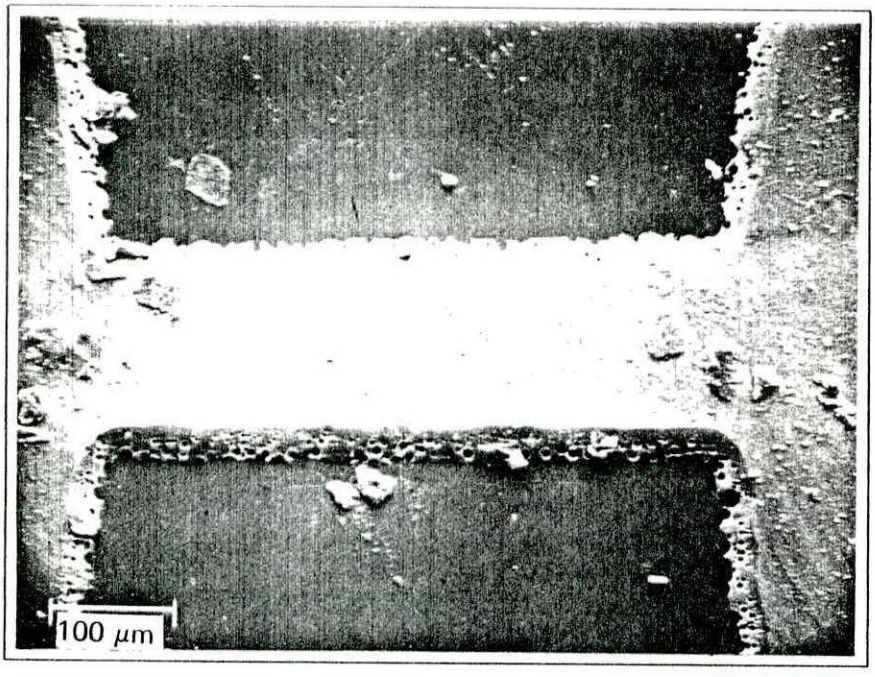
Fig. 11. Typical bridge wires from three circuits etched in pilot setup. There is no evidence of outlining, which would indicate a foot or tapering.



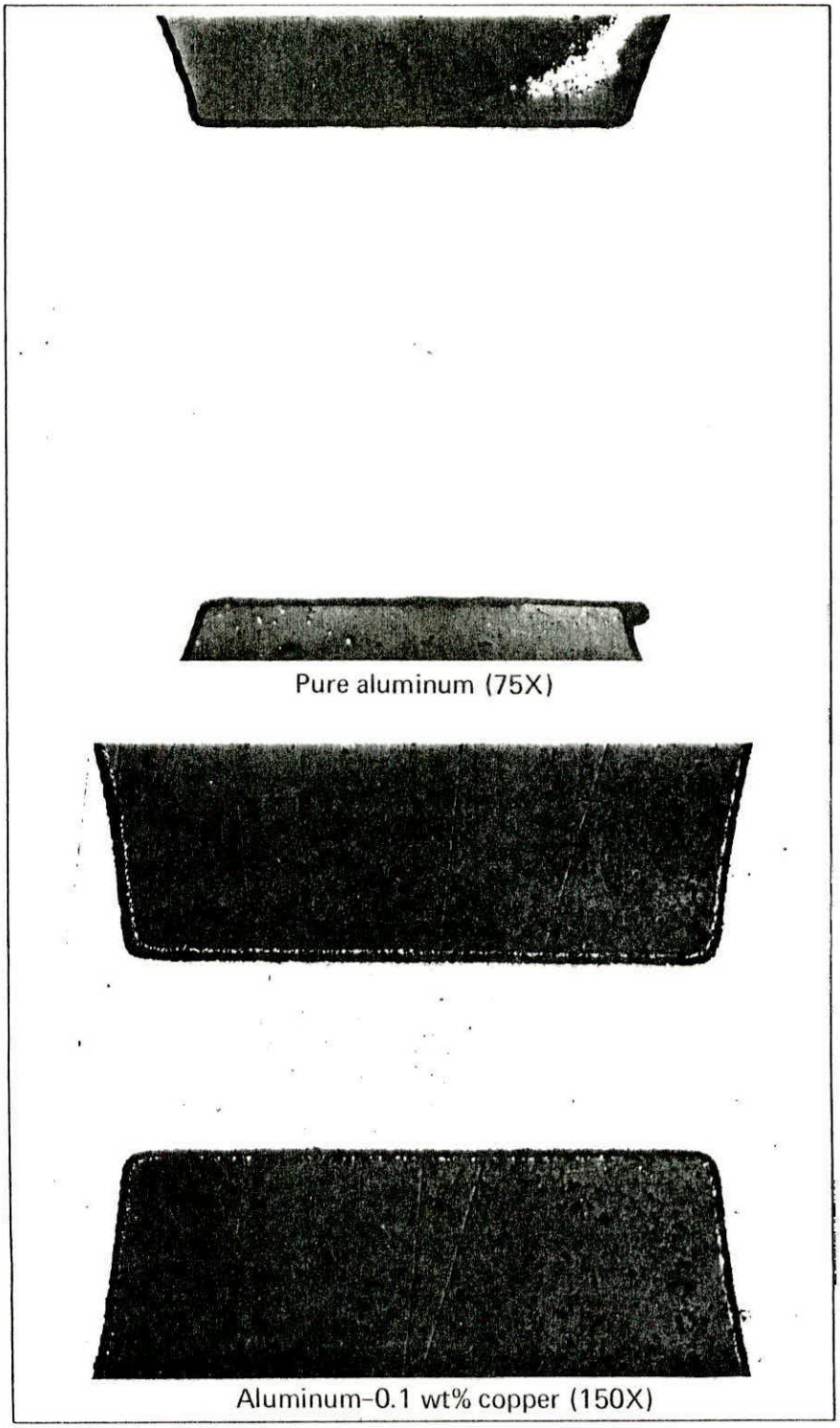
Wiesner - Fig. 1



Wiesner - Fig. 2



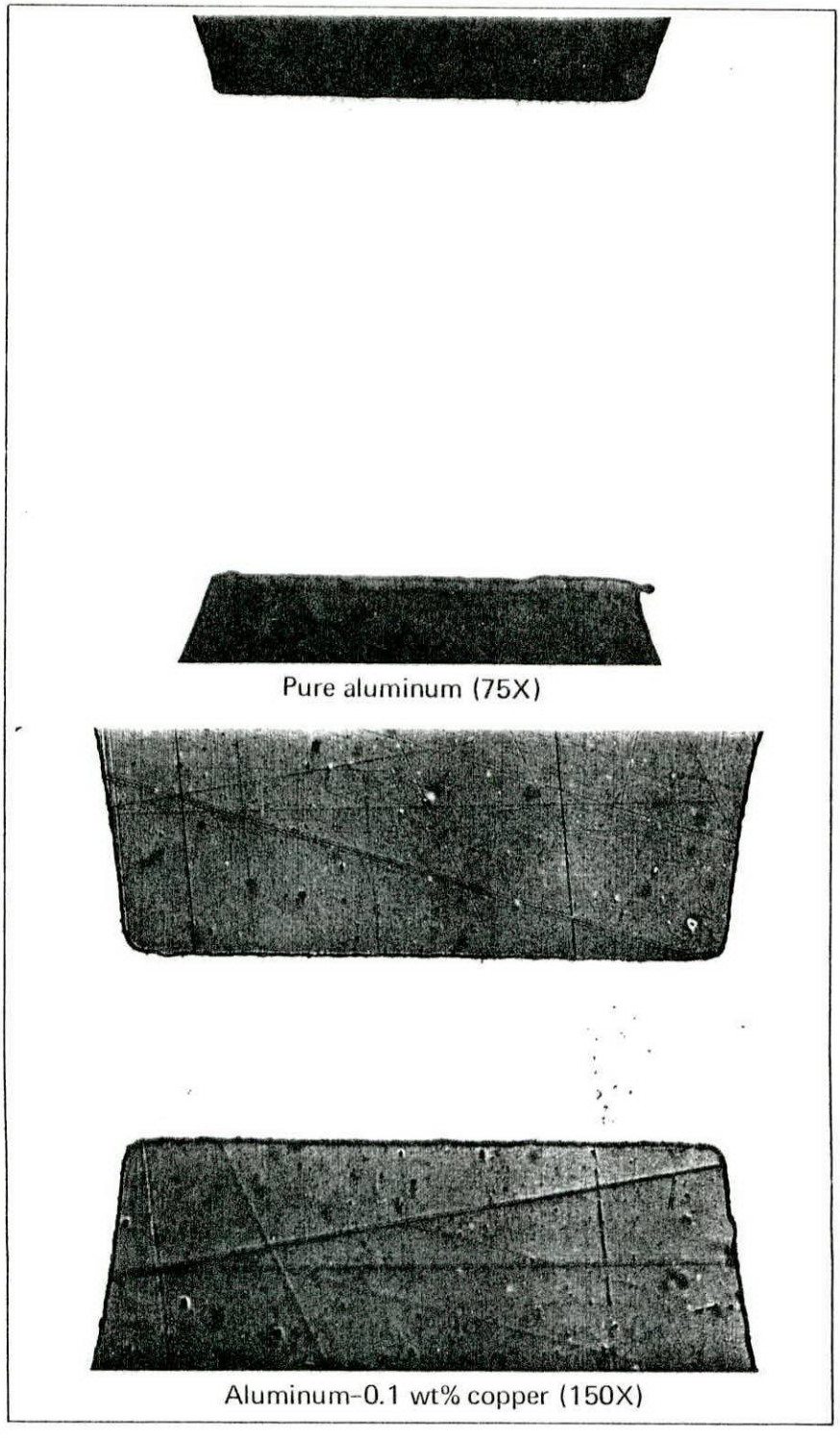
Wiesner - Fig. 3



Pure aluminum (75X)

Aluminum–0.1 wt% copper (150X)

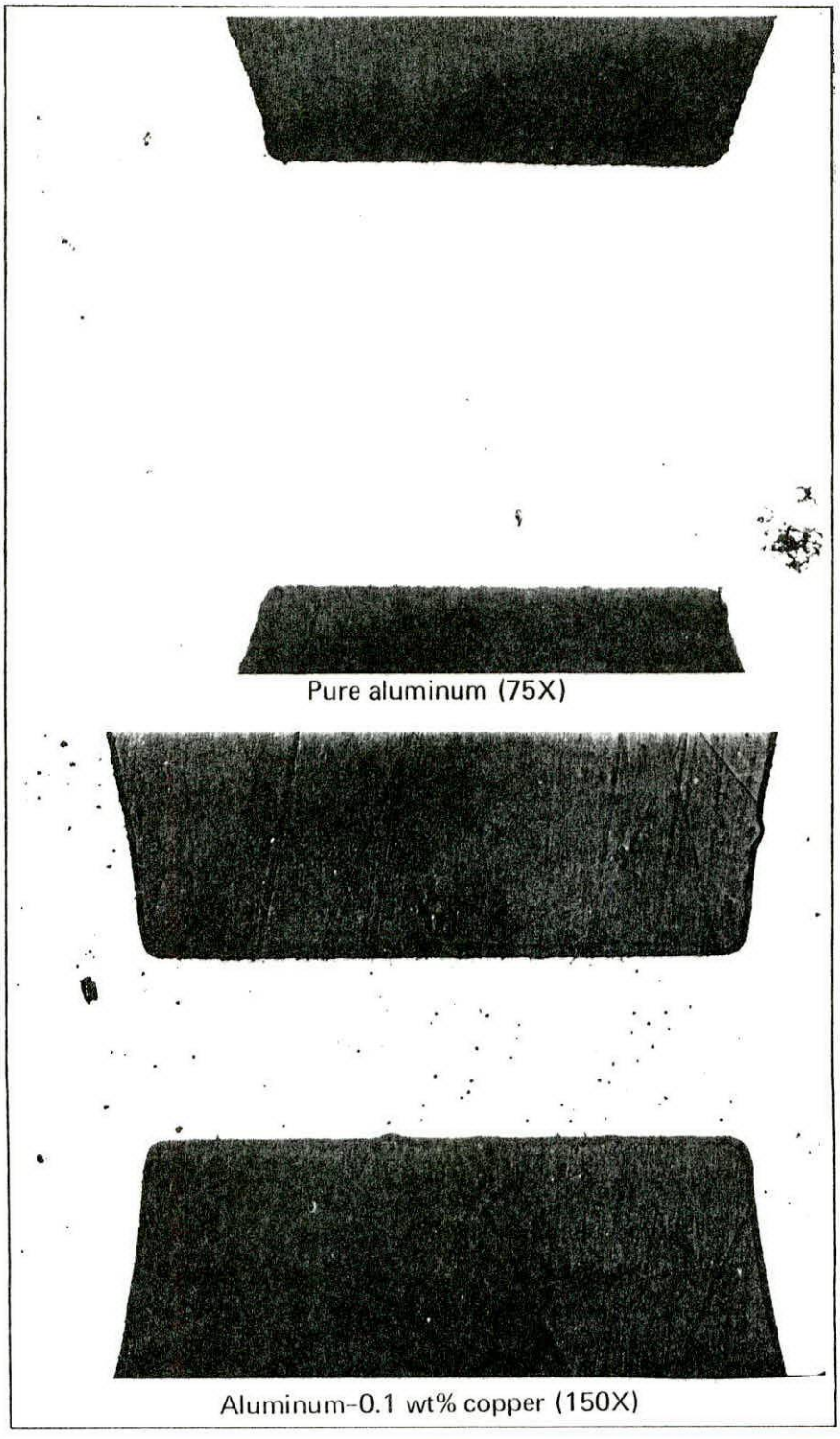
Wiesner - Fig. 4



Pure aluminum (75X)

Aluminum-0.1 wt% copper (150X)

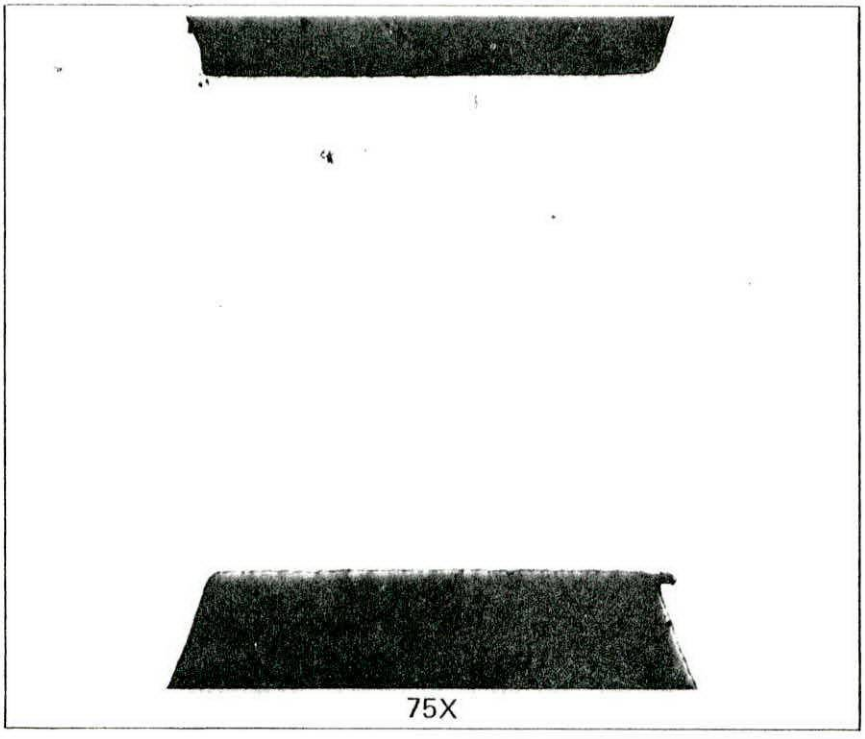
Wiesner - Fig. 5



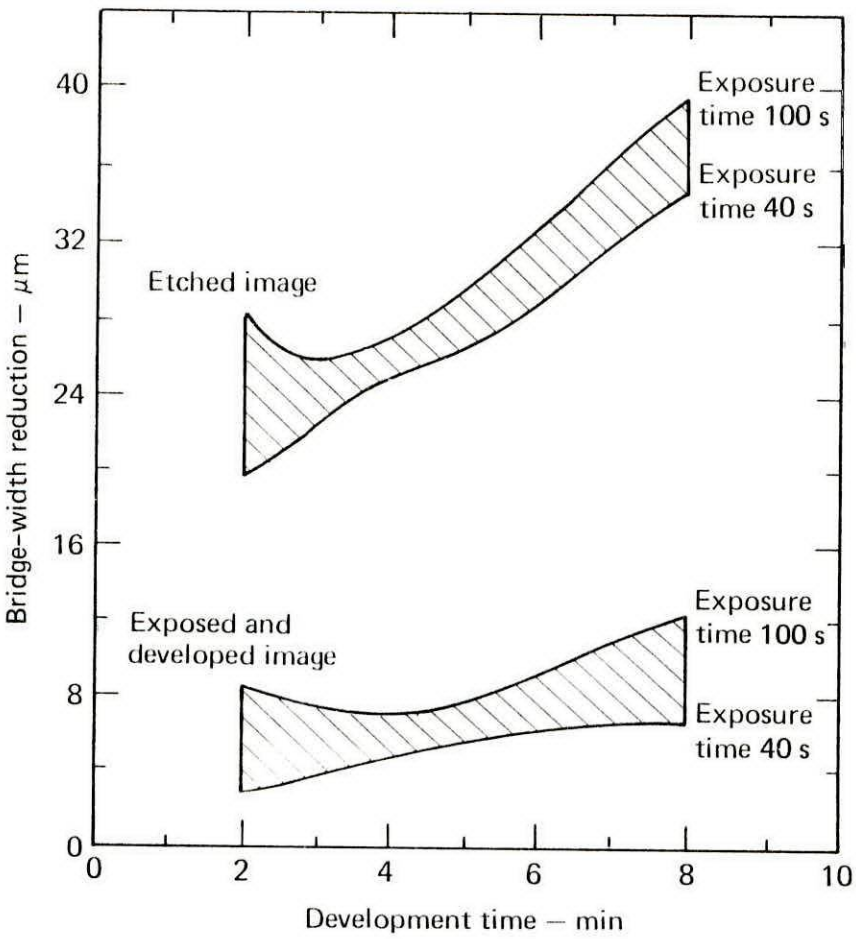
Pure aluminum (75X)

Aluminum-0.1 wt% copper (150X)

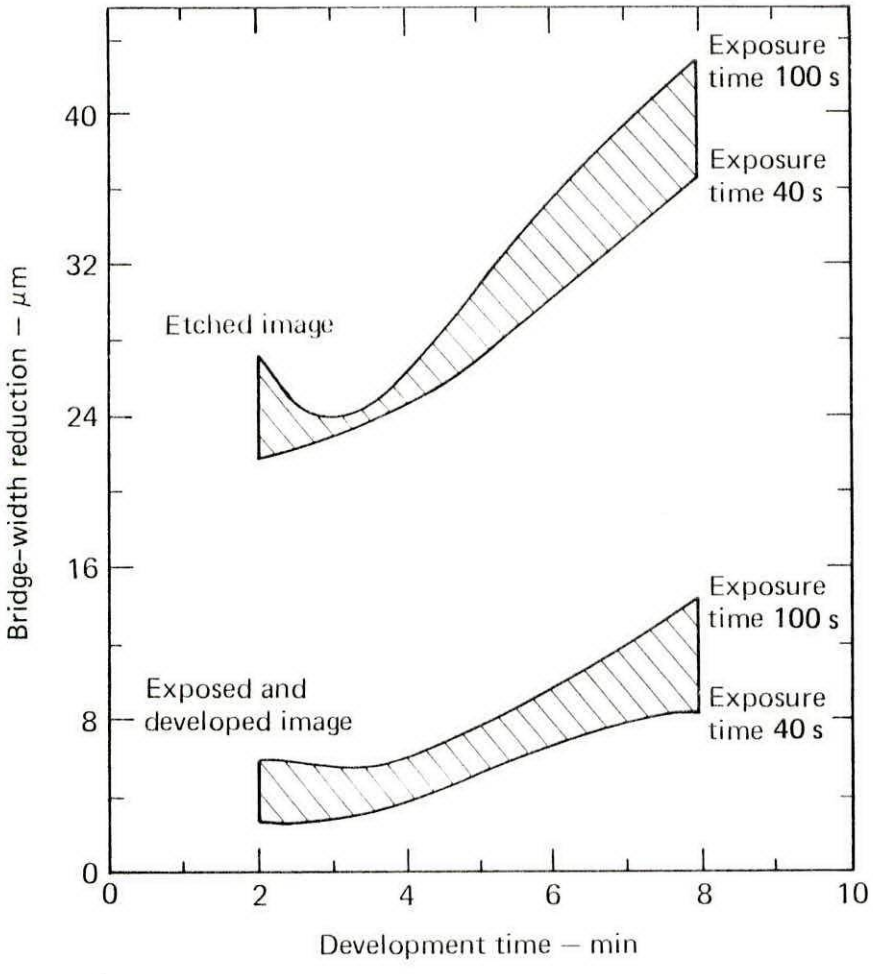
Wiesner - Fig. 6



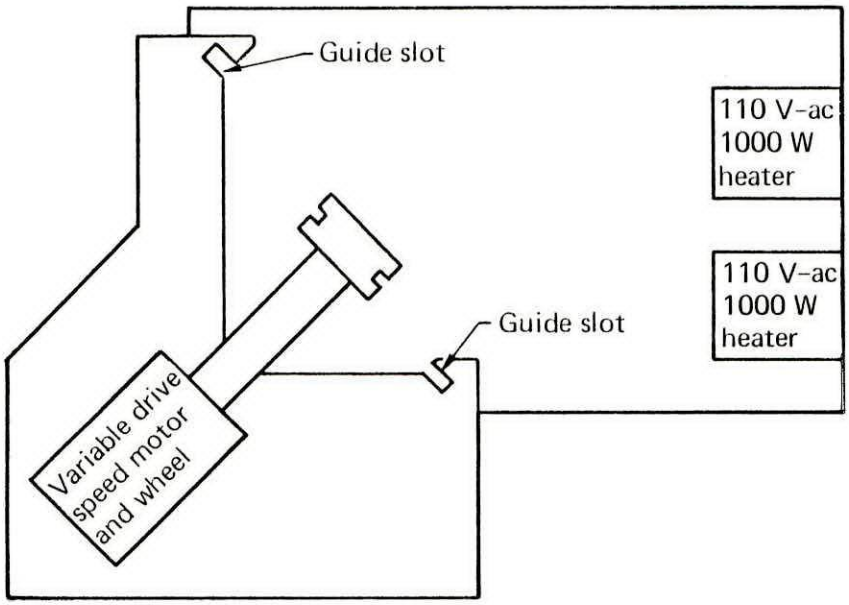
Wiesner - Fig. 7



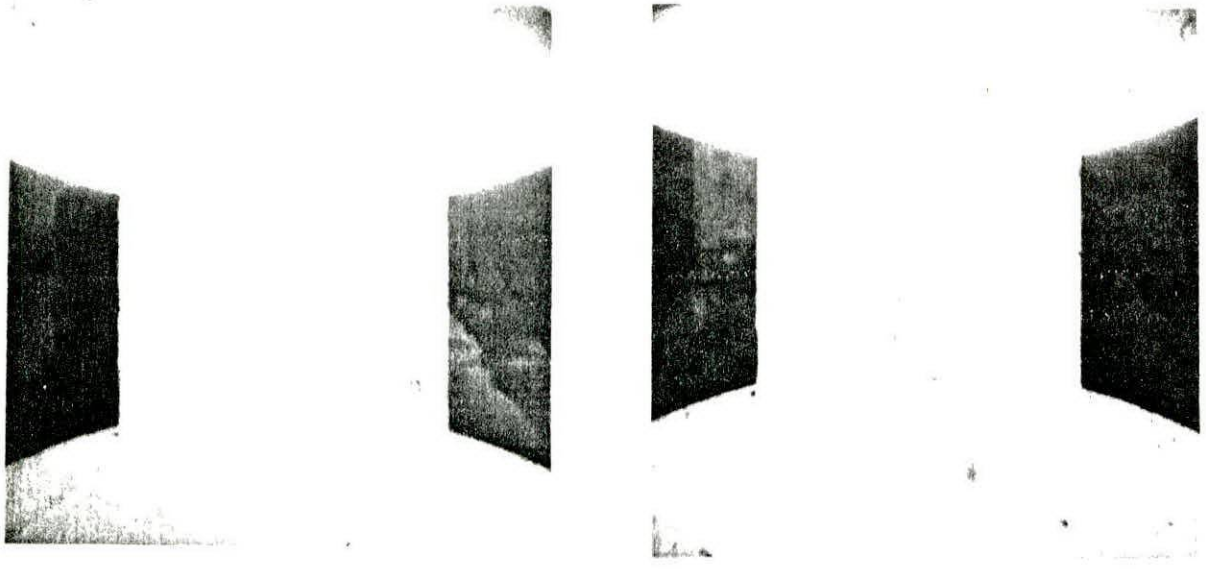
Wiesner - Fig. 8



Wiesner - Fig. 9



Wiesner - Fig. 10



Wiesner - Fig. 11

Corrosion Resistance of Electroless Nickel by Food Constituents

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Enthone, Inc.

The use of electroless nickel deposits for their protective value has increased through the years. This deposit, a nickel-phosphorus alloy, has acquired the reputation of having a chemical resistance superior to pure nickel (1, 2, 3). The excellent wear resistance and relative ease of deposition on complicated shapes and structures of various substrates has enhanced its image.

Protecting food processing equipment is an area where electroless nickel deposits appear to be gaining acceptance. This present paper reflects a growing interest and need to establish guidelines for using electroless nickel when in contact with food products.

Several authors have reported that processing equipment containing nickel can be a source of contamination for food materials (4, 5, 6). Other authors (7, 8) indicate that the possible injurious effects of such ingested contamination are negligible. While the toxicological and epidemiological effect of nickel have not been completely established, the oral intake of nickel has been considered relatively innocuous (4). Table I gives an indication of the tolerance to oral intake.

Table 1

Test Animal	Ni Compound	Dosage ppm	Effect
Rats	$NiCO_3$, catalyst	250 - 1000	No effect
Monkeys	Ni soaps, catalyst	250 - 1000	No effect
Calves	$NiCO_3$	250 - 1000	Retarded growth
Chicks	$NiSO_4$, Ni acetate	300 - 1300	Same

However, the relatively high tolerance to orally ingested nickel contrasts with other forms of nickel intake such as inhalation, percutaneous absorption and parenteral absorption or injection (Table 2).

Table 2

Intake	Toxicology or Epidermiology
Oral	Non toxic
Inhalation	Possible carcinogen
Percutaneous	Allergenic
Parenteral	Allergenic and carcinogenic effects reported
Intravenous/intramuscular	Toxic

A possible reason for the innocuity of orally ingested nickel is the very low absorption of nickel in the digestive tract. More than 90% of such ingested nickel is excreted in the feces. The normal oral intake of nickel by American adults has been estimated at 300-600 µg/day.

While presently available information indicates no harmful effects from the ingested nickel, the principal of reducing the contamination of food products should be considered whenever possible. Previous reports (1, 6, 9) indicate that various acids contained naturally or as additives in food products can corrode nickel and nickel-phosphorus alloys (Fig. 1). With this potentiality in mind and because of the number of electroless nickel formulations in use today that deposit nickel-phosphorus alloys of varying degrees of corrosion protection, further review and investigation appears to be justified.

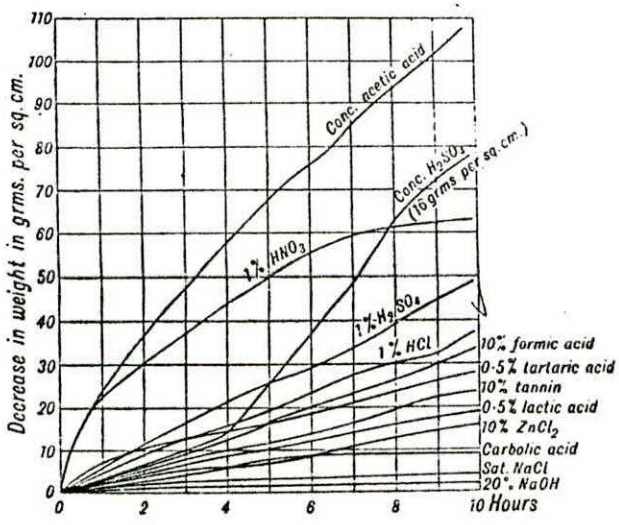

Fig. 1 - Dissolution of Nickel in Various Solutions (from Mellor)

It has been recognized for some time that the protective value of electroless nickel deposits are enhanced with increasing phosphorus content especially in conjunction with heat treating the deposit.

In this work we investigated the following factors influencing the corrosion process.

A. Reaction conditions and their influence on attack of the deposit.
B. Composition and metallurgical conditions and their influence on attack of the deposit.
C. Corrosion of nickel-phosphorus alloys by food products.

EXPERIMENTAL

A. Reaction Conditions

A high phosphorus-nickel alloy was selected for the preliminary study of the reaction variables. The selection was based on the relative resistance of this nickel-phosphorus alloy to chemical attack. An indication of this is its increased resistance to nitric acid. In industrial application this deposit is resistant to two minutes of immersion time in concentrated nitric acid. Most commercial electroless nickel deposits fail this test. Also, the resistance to staining by handling is of consideration for food applications. This high phosphorus-nickel alloy is more tolerant to such handling.

Mild steel panels were coated with 25 µm of nickel-phosphorus deposit containing 10-11%/wt. P. The deposit was obtained from an electroless nickel bath containing no other alloying metals or additives such as sulfur commonly used for stabilizing the bath or brightening the deposit. The plated panels used for the tests were allowed to age at least a week to provide more homogenous conditions.

Individual panels, 129 cm^2 were immersed in 500 cc of reagent solution with and without aeration respectively. Citric, lactic, acetic, hydrochloric, and phosphoric acids as well as sodium chloride were used as reagents. These acids occur in food products both naturally and as additives and have been reported as mg/l of nickel in reagent solution. Analyses was by atomic absorption spectrophotometry. The results of these tests are shown in Table 3.

Table 3

Reagent	Conditions	Exposure Times 3 hrs	6 hrs	24 hrs
6% citric acid	50°C. - no aeration	8 mg/l	9 mg/l	32 mg/l
	50° C. - aeration*	10 mg/l	20 mg/l	83 mg/l
	50° C. - 2 x aeration	11 mg/l	21 mg/l	124 mg/l
	100°C. - no aeration	--	--	18 mg/l
	100°C. - aeration	--	--	4 mg/l
6% acetic acid	50°C. - no aeration	9 mg/l	14 mg/l	27 mg/l
	50°C. - aeration	17 mg/l	30 mg/l	114 mg/l
	50°C. - 2 x aeration	18 mg/l	33 mg/l	112 mg/l
6% HCl	50°C. - no aeration	7 mg/l	10 mg/l	20 mg/l
	50°C. - aeration	6 mg/l	7 mg/l	26 mg/l
	10°C. - 2 x aeration	9 mg/l	12 mg/l	36 mg/l

*rate of aeration 3 ml/min.

The results indicate aeration increased the attack on the nickel-phosphorus alloy. The results are in accord with those expressed in the literature (1, 2). Increasing the aeration accelerates this attack. Figure 2 shows that this reaction becomes lineal with aeration for the period of 24 hours. The subsequent experiments are based on this time period. Elevated temperatures apparently cause reduced corrosion because of passivating effects. For this reason, the temperature condition of 50°C. was selected for the subsequent experiments.

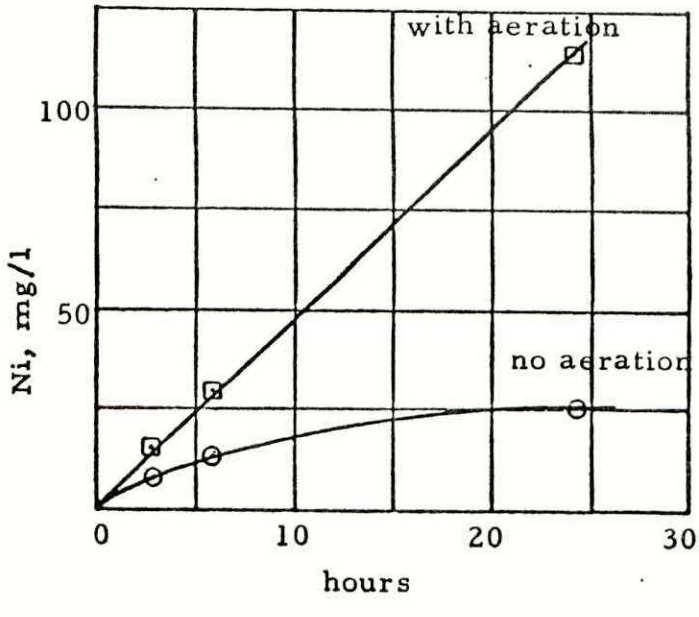

Fig. 2 - Dissolution of Nickel from Ni-P Alloy in 6% Acetic Acid @ 50°C.

The preceding results are interesting inasmuch as carboxylic acids are more aggressive than hydrochloric acids under the testing conditions.

The effect of the reagent concentration was the next variable studied (Table 4).

Table 4

Reagent	pH	Conditions - 24 hrs	Ni - P	Ni (99.9%)
0.6% citric acid	2.3	50°C. - aeration	97 mg/l	91 mg/l
6% " "	1.8	50°C. - aeration	84 mg/l	104 mg/l
18% " "	1.4	50°C. - aeration	91 mg/l	48 mg/l
0.6% acetic acid	2.9	50°C. - aeration	72 mg/l	132 mg/l
6% " "	2.3	50°C. - aeration	114 mg/l	152 mg/l
18% " "	1.9	50°C. - aeration	72 mg/l	97 mg/l
0.6% HCl	0.9	50°C. - aeration	29 mg/l	152 mg/l
6% "	0.25	50°C. - aeration	26 mg/l	292 mg/l
18% "	<0.0	50°C. - aeration	29 mg/l	1320 mg/l

These results indicate that the attack is not solely dependent on reagent concentration nor pH. While the corrosion of electroless nickel and pure nickel is similar in the carboxylic acids, hydrochloric acid attacks pure nickel significantly more than the nickel-phosphorus alloys.

Other reagents were tested as indicated in Table 5.

Table 5

Reagents	pH	Conditions - 24 hrs.	Ni - P	Pure N
6% Lactic acid	1.9	50°C. - aeration	100 mg/l	63 mg/l
6% Phosphoric	1.2	50°C. - aeration	54 mg/l	75 mg/l
6% NaCl	5.7	50°C. - aeration	2 mg/l	2 mg/l
6% NaCl in 0.6% acetic acid	2.6	50°C. - aeration	23 mg/l	73 mg/l

Note again that the carboxylic acid is more corrosive than the mineral acid and the inorganic salts.

B. Composition and Metallurgical Influences

Several different types of electroless nickel deposits were compared using 6% citric acid as reagent. Prior reports indicate that the attack of nickel-phosphorus coatings will be influenced by the phosphorus content as well as by the composition of the electroless solutions including additives used for stabilization and brightness. Results of these observations are shown in Table 6.

Table 6

Deposit	Reaction Condition	Attack
Corrosion resistant high P (10-11% P)	50° C. 6% citric acid, aerated 24 hours	84 mg/l
General purpose semibright (8% P)	same	137 mg/l
General purpose bright, low P (5% P)	same	176 mg/l

In these experiments all the test specimens were aged 8 days before testing to obtain a uniform condition. The results indicate that the composition of the deposits had a significant effect on the extension of the attack and verifies that increasing phosphorus content reduces the rate of attack.

The effects of heat treatment were also investigated as shown in Table 7.

Table 7

Deposit	Heat Treatment	Reagent	Attack-24 hrs
corrosion resistant high P (10-11% P)	no HT	6% citric acid aerated	84 mg/l
	in air, 750°C., 1 hr.	same	1 mg/l
	in vacuum*, 750°C., 1 hr.	same	50 mg/l
	no HT	6% acetic acid	114 mg/l
	in air, 750°C., 1 hr.	same	1 mg/l
	in vacuum, 750°C., 1 hr.	same	86 mg/l
	no HT	6% HCl	13 mg/l
	in air, 750°C., 1 hr.	same	9 mg/l
	in vacuum, 750°C., 1 hr.	same	965 mg/l

*0.1 μm vacuum, nitrogen purged

The results strongly indicate that the higher protection of heat treated nickel-phosphorus deposits in our work is related to the formation of passive surface layers, rather than by the sole transformation of the deposit from an amorphous structure to a crystalline state.

The protective surface layers could also explain this increased corrosion resistance of the deposits after aging them at ambient room temperatures. This phenomenon was observed in the work as is reported in Table 8.

Table 8

Deposit	Reaction Conditions	Treatment	Attack
Corrosion resistant high P (10-11% P) 8 days old	6% citric acid aerated	none	84 mg/l
same, 34 days old	same	none	1 mg/l
same, 34 days	same	activation in 50% HCl	53 mg/l
nickel (99.9%)	same	none	104 mg/l
same	same	activation in 50% HCl	103 mg/l

The durability of the passive layers was investigated. The nickel-phosphorus alloy as compared to pure nickel, develops a more durable surface layer, which appears to offer protection for extended periods. Results are in Table 9.

Table 9

Deposit; HT @ 750°C., air	Reaction condition	Exposure 24 hrs.	168 hrs.
Corrosion resistant high P alloy (10-11% P)	6% citric acid 50°C. - aerated	1 mg/l	4 mg/l
same	6% acetic acid 50°C. - aerated	1 mg/l	1 mg/l
Nickel (99.9%)			
Nickel (99.9%)	6% citric acid 50°C. - aerated	6 mg/l	45 mg/l
same	6% acetic acid 50°C. - aerated	5 mg/l	35 mg/l

C. Corrosion of Nickel-Phosphorus Alloys by Food Products

The non-heat-treated nickel-phosphorus alloy was tested with a number of commercial food products by immersing test panels for 24 hours @ 50°C. with aeration. Results are in Table 10.

Table 10

Reagent	pH	Ni-P deposit appearance	Ni-P mg/l Ni	Pure Ni mg/l Ni
Coffee	5.6	Black discoloration	73.0	24.5
Sauerkraut juice	4.0	No discoloration	6.9	--
Tomato juice	4.3	No discoloration	0.6	--
Orange juice	3.6	No discoloration	4.2	2.7
Tea	4.9	Yellow discoloration	14.5	31.3
Beef consomme	5.8	Cloudy discoloration	12.0	20.0
Cola beverage	2.8	No discoloration	75.0	71.5
Beer	4.4	No discoloration	22.5	22.5
Red wine	3.6	No discoloration	26.5	45.0
Milk	5.7	No discoloration	3.4	5.7

The above data is interesting from several viewpoints. The effects of such juices as orange, tomato, and sauerkraut had less effect in corroding the deposit than anticipated. This is attributed to the overall chemical composition of these juices rather than to pH and carboxylic acid concentration alone.

On the other hand the severity of attack by coffee on the nickel-phosphorus deposit was surprising. The appearance of the test panels after testing showed severe discoloration. This discoloration is very reminescient of the appearance of the low-phosphorus nickel deposit after nitric acid treatment. Based on published analyses of coffee, we have no obvious explanation for our results.

Since much food processing equipment will be subjected to handling the chemical resistance of nickel to such handling that might cause staining and/or potential dermatitis was investigated.

Nickel-phosphorus and pure nickel test panels were exposed to an artifical perspiration (10) environment at 50°C. with aeration for 24 hours. A significant amount of nickel wasfound inthe test solutions, 30 and 58 mg/l respectively. The same test was performed on electroless nickel-phosphorus alloys containing various amounts of phosphorus that were obtained from baths having addition agents. The results show a dramatic difference in appearance of the panels. The deposits obtained from baths having additives and lower phosphorus content, 5 and 8%/wt. were noticeable discolored; the deposit from an additive-free bath, 10%/wt. P, was not discolored at all.

As a separate corrosion experiment a practical cooking procedure was used. A 5 liter electroless nickel plated pot was used to prepare tomato sauce. The sauce contained tomatoes, tomato paste, tomato puree, shallots, terragon, thyme, rosemary, oregano, parsley, fennel, salt and pepper. This mixture was analyzed for nickel prior to cooking and again after 4 hours of cooking. The amount of nickel found by analyses was:

a) before cooking - 2.5 ppm
b) after cooking - 5.0 ppm

The total area exposed to the sauce was of 1319 cm^2 and the volume of the sauce was of 5000 cc.

Summary and Conclusion

The purpose of this work was to investigate the use of electroless nickel for food applications. The results show that nickel-phosphorus alloys are not inert to corrosive environments associated with food products. Some of the test conditions might be considered extreme but were selected to accelerate the corrosion process.

In view of these results and the present information as to the toxicity of electroless nickel to humans via ingestion, the use of electroless nickel deposits for food processing applications seems feasible in many cases.

The extent of the corrosivity is influenced by the nature, concentration and temperature of the corroding environment. Furthermore such conditioning as aging and heat treating the deposits as well as the metallurgical and compositional variables should be considered in selecting a particular electroless nickel deposit. The data and results re-enforce the concept that electroless nickel deposits should be subjected to a comprehensive evaluation in order to determine its functionality for a particular application.

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UNIQUE CHARACTERISTICS

OF CADMIUM ELECTROPLATING

by

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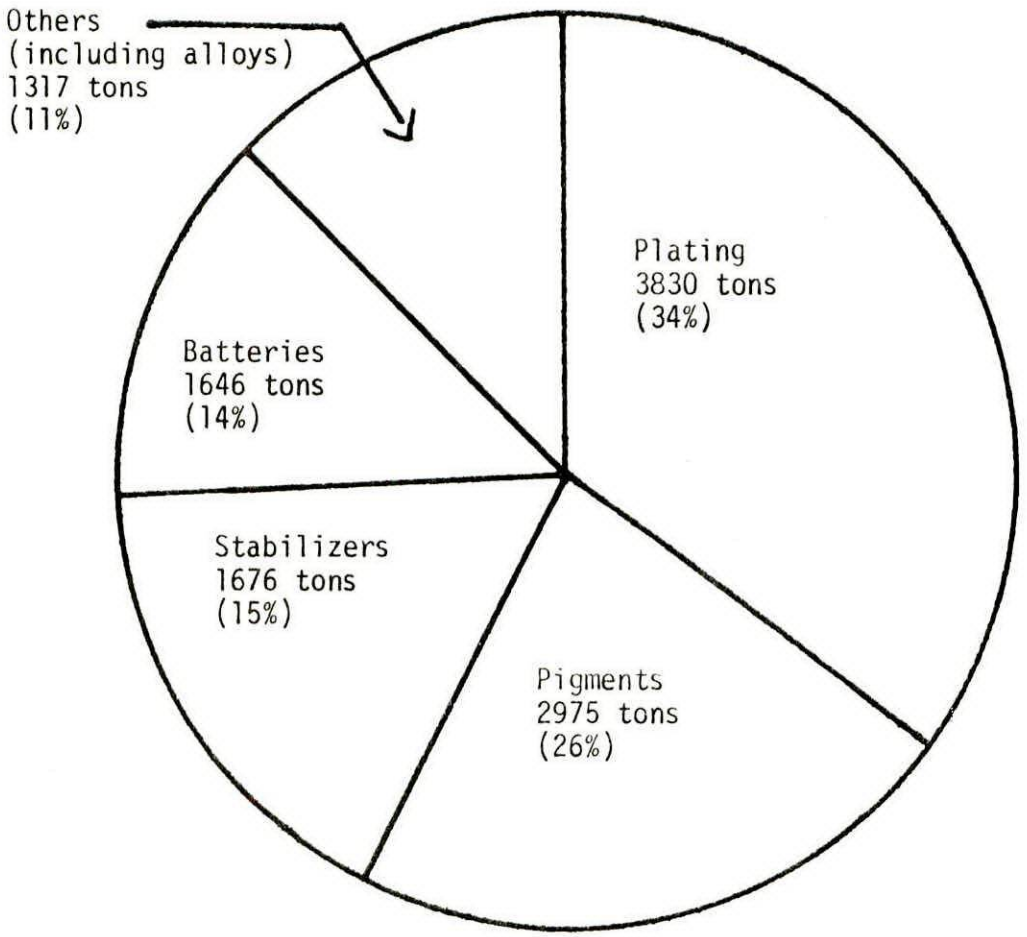
Cadmium metal, a byproduct of zinc production, is of vital importance to industry.

The end uses of cadmium for five major industrial nations* in 1974 are shown in this pie chart in metric tons(1).

1974 Total: 11444 metric tons



These 3,830 tons of cadmium used for electroplating would be sufficient to provide corrosion protection for 700 million sq. ft. of steel.

* Germany F.R., Japan, United Kingdom, United States and France.

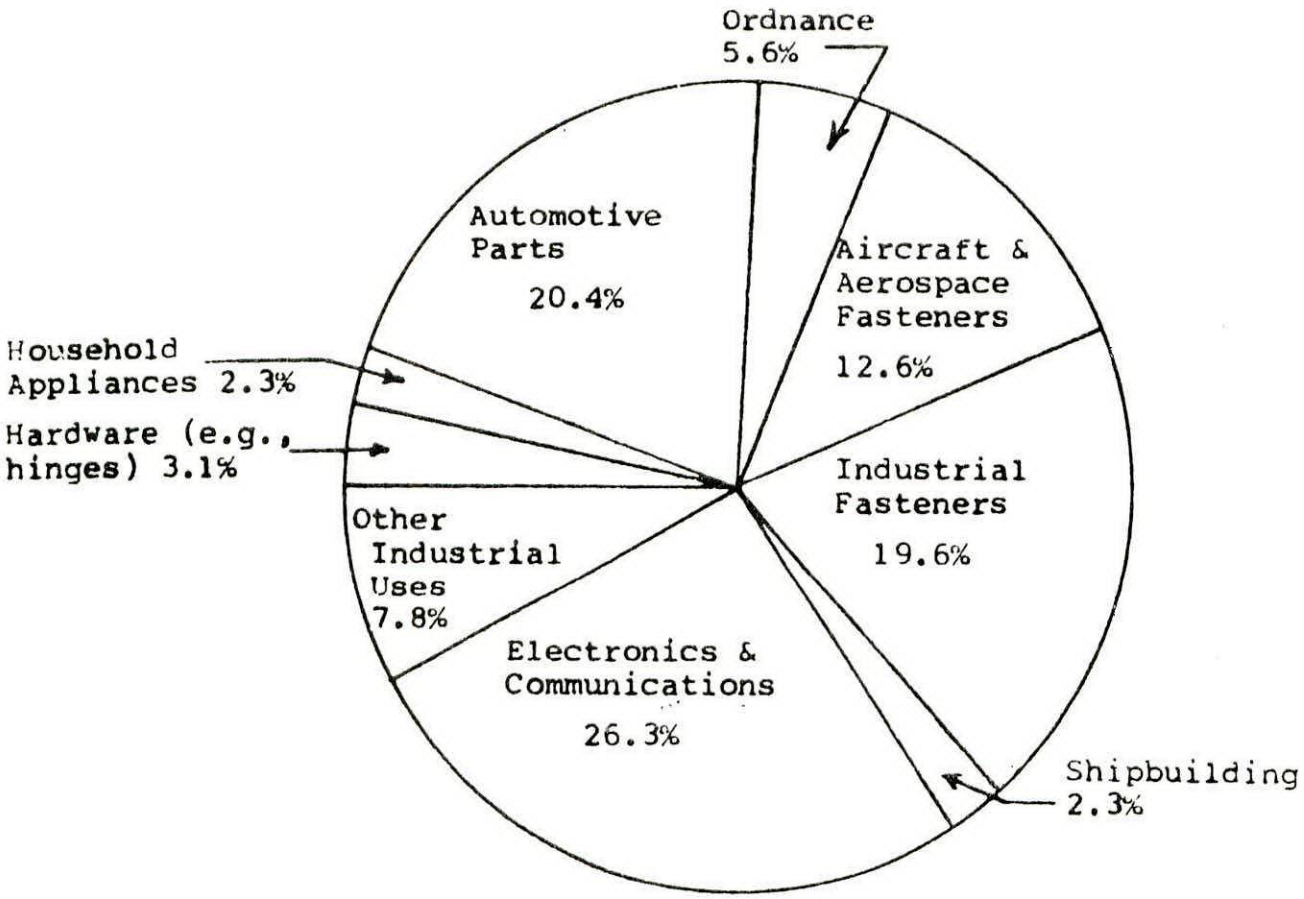
That was the position in 1974, and it can be seen that electroplating is an important application for cadmium. This is a rapidly changing world, but we must do what we can to ensure that any changes are made for the better. Changes hastily made and for the wrong reasons can have disastrous consequences. This workshop is entitled "Alternatives to Cadmium Plating." The purpose of this paper is to point out some of the unique characteristics of cadmium plating and to demonstrate that cadmium plating should retain an important place as a unique cost effective protective coating for metals.

Preservation of the environment is a matter of the greatest concern to us all. The metals-producing and electroplating industries have demonstrated their ability to meet the increasingly stringent environmental controls now being imposed. The cadmium plating industry is no exception. The industry is meeting its obligations as regards effluent control and the cadmium plating process is compatible with high standards for the environment. We can therefore confine ourselves to making a cost-benefit analysis to determine what may be the result of using a particular alternative to cadmium plating. Some of the benefits of using cadmium are not immediately obvious, and ill-considered changes can be hazardous or costly.

What of the present uses of cadmium plating in the U.S.A.? The following pie chart shows how an average annual consumption of 5,400,000 lbs. was utilized in the U.S.A. from 1965-1974.

CADMIUM USAGE - PLATING IRON AND STEEL PRODUCTS FOR CORROSION PROTECTION

Consumption of Cadmium in Electroplating By End Use [2-11]



Average Values for Consumption from 1965-1974

of 5,400,000 pounds

Taken from Cadmium Utilization Environmental Impact Materials and Process Specifications and Substitutes by E. J. Dyckman, Naval Ship Research and Development Center, June 26, 1975

In order that you may have an appreciation of the diversity (and essentiality) of the use of cadmium plating, here is a list of components which are typically cadmium-plated.

Fasteners
Nuts
Bolts
Screws
Washers
Rivets
Nails
Fittings
Tools
Electrical connectors
Rifle barrels
Mortar Tubes
Carburetor Parts
Magnet parts
Clutch throw out plungers
Aircraft undercarriage components
Diode holders
Voltage regulators
Electrical relays
Textile machinery
Metal cutters
Turbine engine blades
Vanes and cases
Piano wire
Catapult hooks
Marine hardware
Pole line hardware
Metal cutting machinery
Cast and Malleable iron components
Low alloy steel heat treated below 200 K psi
Actuator arms
Be-Cu bushings and bearings
Compressor blades
Dissimilar metal faying surfaces
Gears
Shafts
Splines
Shrouds
Stainless steel bushings
Tools

* Where the aircraft will meet extreme temperature conditions.

Following are some of the U.S. specifications and standards calling for the use of cadmium.

MATERIALS AND PROCESSES SPECIFICATIONS AND STANDARDS CALLING FOR THE USE OF CADMIUM

Military Specifications

MIL-STD-171
MIL-STD-454C
MIL-STD-870
MIL-STD-889A
MIL-STD-1500 (CdTi)
MIS-S- 5002C
MIL-P- 23408A
QQ-P- 416C
MIL-C- 8837
MIL-C- 81562
MIL-C- 0026482F (Navy)
MIL-C- 005015F (Navy) Contact plating
MS Sheet Forms including:

Nuts MS-9882, 9881, 51968C, 51967D, 27040B

Bolts MS-9088-91, 9146-51, 9441-48, 9451-57, 9458A, 9459A, 9942, 9926, 9941, 9927, 9928, 9946, 9929, 9947, 9944, 9932, 9937, 9933-36, 9914-18, 9688, 9689, 9691, 9693, 9924, 9518-26, 9530-37, 9217, 9222, 9681, 9938, 9920, 9919, 9208-14, 9219, 9221, 9223, 9680, 9682, 9683, 9218, 35754B, 9400-02, 9397-99

Washers MS-27183D

Screws 90728C, 90727D, 51095E, 18153C, 18154C, 51106C, 90725C, 90726B, 35458B, 35457B, 16998D, 16997C, 24667A, 24677A, 24678B, 21318A, 9449, 9940, 9939, 9930, 9931, 9913, 9921 9527, 9516, 9517, 9216, 35206F, 35207F, 9215, 9206, 9207, 9528, 35190D, 35223B, 9184, 9183A, 51975A, 24629C.

Industrial Specifications

ASTM-A-165
AMS-2400M
AMS-2401
AMS-2416
AMS-2419
AMS-2426

Let us now consider the special qualities of cadmium plating which led to its use for these components and very widespread presence in military and aircraft industry specifications.

Plateability

Cadmium plating requires only very simple control of plating solutions. It is less demanding as regards surface preparation as compared to zinc. Cast and malleable iron components are easily plated with cadmium in barrel plating, because cadmium electroplate offers unusual ability to bridge pores in the basis metal, cadmium's hydrogen overvoltage favors the deposition of cadmium rather than hydrogen.

Corrosion Resistance

More resistant to some corrosive environments than zinc, cadmium's corrosion products are always less voluminous, reducing the possibility of cracking bolted joints or binding sliding surfaces. It shows greater resistance to wet storage stain.

In bimetallic couples, the following table allows comparison of cadmium's role[2]. Metals with a relatively large difference in electrode potential can be effectively separated by cadmium. The electrode potential of cadmium in sea water is 0.43V; lying between aluminum, 0.52V; and mild steel, 0.34V. That of zinc is 0.76 volts.

Cadmium and zinc are the only two plating materials which can provide the benefit of galvanic protection for steel. The position of cadmium in the electromotive series means that it is able to provide galvanic protection to steel but since the difference in potential is relatively small there is no tendency for cadmium to "overwork." Thus, while it will not cover a large expanse of bare steel with its protection, it will provide long term protection, and without

undue production of corrosion products. Tin plated steel, when exposed to the atmosphere, will rust overnight because tin is cathodic to steel and will induce severe corrosion because a large area of tin (cathodic) is related to a small area of steel. Plating with cadmium before application of tin will prevent this problem and provide a corrosion resistant bright finish.

Cadmium plating of copper alloys, stainless steel and aluminum provides a long lasting finish because the galvanic couple does not stimulate aggressive action from the cadmium.

In general, cadmium is the preferred galvanically active coating for use in "factory" atmospheres.

Effects of metallic contacts on atmospheric corrosion

Number	Investigated metal	Affected metal 1	2	3	4	5	6	7	8	9	10	11
1	Carbon steel, cast iron	-	B	B	B	B	B	A	A	A	B	B
2	Stainless steel	A	-	A	A	A	A	A	A	A	A	A-B
3	Nickel and nickel alloys	A	A	-	A	B	A	A	A	A	A	A-B
4	Chromium	A	A	A	-	A	A	A	A	A	A	A
5	Copper and copper alloys	A	B	B	B	-	A	A	A	A	A	B
6	Aluminum and aluminum alloys	B	B	B	B	C	-	A	A	B	A	C
7	Zinc and zinc alloys	C	C	B	B	C	B	-	B	B	B	C
8	Cadmium	B	B	B	B	B	B	A	-	A	A	B
9	Magnesium and magnesium alloys	C	C	C	C	C	B	B	B	-	C	C
10	Lead, tin and their alloys	A	B	A	B	B	A	A	A	A	-	B
11	Silver, gold, platinum (rhodium, palladium, osmium, iridium)	A	A	A	A	A	A	A	A	A	A	-

Columns 1 to 11 correspond to the description on the row with the same number.

A: There is no effect of contact of the metals on the corrosion of the investigated metal.

B: There is a small effect of contact of the metals on corrosion of the investigated metal, but is is significant only in very aggressive atmospheres.

C: Strong effects in outdoor exposures, and also exceptionally, in aggressive indoor climates.

One alternative to cadmium plating is zinc plating. V. E. Carter of the British Non-Ferrous Metals Research Association (now BNF Metals Technology Centre) has compared the corrosion resistance of the two[3]. Greater coating thickness of zinc can be used on account of its lower cost but cadmium performs better in contact with aluminum and in enclosed spaces in high humidity[4, 5, 6, 7], especially at elevated temperatures (tropical conditions). Where coating thickness must be kept to a minimum, say 5 μm, cadmium performs better than zinc under marine and alkaline conditions[8]. It is 2 or 3 times more resistant to organic vapors from electrical insulation[9] and is more resistant to the formic acid from paint films.

In the textile industry, zinc corrosion products can cause deterioration of some fabrics whereas cadmium has no adverse effect. In the weaving industry in the U.K. cadmium plating is regarded as essential for protection of fasteners and pins in water jet looms. High humidity in the conventional shuttle loom weaving shed can lead to corrosion which can jam machinery solid over a weekend. Cadmium plating provides better protection and a necessary supplement to the lubrication used. Parts which are to be disassembled after service in a corrosive environment should preferably be plated with cadmium. Bolted connections will not seize and electrical conductivity will be maintained.

When codeposited with nickel, a corrosion resistant coating of unusual quality is created[10]. P. S. Willcox of ITT has commented that the intermetallic compound formed between nickel and cadmium seems quite unique as it has a high melting point and is quite low on the electromotive series. Ni-Cd

diffused coatings are used for compressor parts in low alloy steel (max. U.T.S. 140 Kg/mm), 12-14% Cr, 18-8 Cr Ni steels and nickel based alloys. These materials are less susceptible to hydrogen embrittlement and permit the use of dense cadmium deposits[11].

Low-alloy steel parts which operate in jet engines at temperatures up to 1000°F have been protected from corrosion with 0.0003 in. (7.6 μm) of nickel plus 0.0001 in. (2.5 μm) of cadmium diffused at 630°F (332°C)[12] for one hour. This coating could withstand 100 hours salt spray without rusting even after 23 hours at 700°F (372°C) and one hour at 1000°F (539°C) prior to exposure.

Three independent studies have shown that chromate-treated cadmium over nickel offers the best conductive corrosion-resistant finish for aluminum.

Recent work by McDonnell-Douglas has shown that for aluminum a diffused cadmium over nickel coating, proprietary to Stanford Applied Engineering[13], meets conductivity requirements and successfully passed 816 hours of salt spray exposure (salt spray tests to ASTM B117-73). This may be a development of the R.W. Moeller technique[12, 14].

Jankowsky[15] found cadmium with chromate conversion coating over nickel to be a superior coating for aluminum (6061 T6 panels) and advocated its use. His testing involved 25 cycles, each cycle consisting of 16 hours at 200°C (392°F) followed by 32 hours of salt spray exposure. That is 800 hrs. salt spray plus 400 hrs. elevated temperature exposure.

Willcox has shown that cadmium, with chromate conversion coating, over nickel on a variety of aluminum alloys, 2024, 2011, 7075, die cast A380, and 6061, has successfully withstood 500 hours of salt spray exposure[16].

Torque Resistance

Cadmium-plated components have an inherent lubricity and demonstrate lower torque resistance than zinc plated components[17, 18] and exhibit a more constant torque resistance than is the case with lubricants. In some cases, this will be a vital consideration. A cadmium plated part will not gall when in sliding contact. On this account, if an assembly is to be subject to corrosion and then dismantled for maintenance, it is necessary that cadmium plating be used.

Formability

More ductile than zinc, cadmium plate allows easy forming after plating.

Electrical Resistance

Cadmium has a relatively low electrical resistance[7] even when provided with a chromate conversion coating for additional corrosion protection.

Jamming

Cadmium corrosion products are closely adherent and not voluminous. This reduces the danger of fouling switches and relays and makes cadmium plating ideal for the return springs in automobile brakes and clutches and for hydraulic rams used in the coal industry.

Solderability

Cadmium surfaces are excellent for soft soldering[7, 8, 17].

Appearance

Cadmium retains brightness for excellent decorative appeal.

Hydrogen Embrittlement

After cadmium plating from cyanide solutions, high strength steel, such as is used for aircraft landing gear, can be baked to eliminate hydrogen embrittlement. In general, hydrogen can be baked out through an initial flash of cadmium of thickness about 2.5 microns (.00005 mils). Because

cadmium can be plated at approaching 100% efficiency, subsequent cadmium plating can be carried out over this initial flash without danger of hydrogen embrittlement[19].

High Temperature Operation

Cadmium plated steel parts can operate under stress at temperatures up to 900°F (482°C) provided that a nickel undercoat is applied before cadmium plating followed by a diffusion baking operation.

Compatibility with Adhesives

Cadmium provides an excellent bond when adhesives are used, this is true even for passivated coatings. Problems may occur when passivated zinc coatings are used and expensive adhesives may become obligatory. A decal placed over cadmium plating will not be displaced by any corrosion products.

Conclusions

When considering whether an alternative for cadmium plating can be justified, it is not only necessary to consider carefully what cost penalty may be incurred, but to pay particular attention to some of the above vital and beneficial characteristics which are not always apparent at first sight.

Cadmium electroplaters can comply with needed pollution control regulations. We, therefore, question the need to develop "Alternatives to Cadmium Electroplating in Metal Finishing."

Cadmium electroplating need not be a threat to the environment and we must be sure that we do not risk failure of life supporting components because we have not given careful thought to the implications of finding alternatives to cadmium plating.

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ION VAPOR DEPOSITED ALUMINUM COATINGS

by

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Abstract

A process for the application of dense, uniform, and very adherent aluminum coatings has achieved production status and can be used to replace cadmium almost exclusively. The process is a vacuum metallizing process and is referred to as ion vapor deposition. Aluminum coatings can be used at temperatures up to 925°F (496°C), whereas cadmium is limited to 450°F (232°C). The process can be used to coat high strength steel without fear of hydrogen embrittlement. It can also be used in contact with titanium without causing solid metal embrittlement. Cadmium is prohibited for this application. Finally, ion vapor deposition is a clean process and does not contribute to any ecology problems.

Details of the ion vapor deposition process, performance data, and current production applications at McDonnell Aircraft Company on both Navy and Air Force Programs will be discussed.

Introduction

Cadmium electroplating was the favored method for protecting steel on aircraft structure for many years. Obvious problems with its use were minimal prior to the use of high strength aluminum and steel alloys. Cadmium plated fasteners installed in high strength aluminum alloys helped promote exfoliation corrosion in the countersinks and hydrogen embrittlement often occurred when electroplating cadmium on high strength steel. More recently it has received further disfavor because it was found to cause solid metal embrittlement of titanium structure and because of its toxicity and harmful effects on the environment.

However, it was mainly for the first two reasons that we at McDonnell Aircraft Company (a division of McDonnell Douglas Corporation) started looking for a viable alternate for cadmium in the early 1960's. After extensive paper studies, aluminum coatings were selected as the best substitute. Being the least dissimilar to aluminum alloy structure, it is ideally compatible. Furthermore, aluminum is anodic to steel and provides galvanic protection as does cadmium.

It was quickly found that available processes for applying aluminum coatings such as metal spraying, electroplating, cladding, hot dipping and others had severe limitations such as thickness control, adhesion, size and shape of product that could be coated, and effect on substrate properties.

During this same period we had selected vacuum deposited cadmium as the coating for solving the problem of hydrogen embrittlement of high strength steel. Our production experience with the vacuum cadmium coating process was very favorable. For this reason we started looking at vacuum coating processes for aluminum. This included physical vapor deposition, ion vapor deposition, and chemical vapor deposition. Ion vapor deposition provided the best adhesion and most uniform coating thickness and with other considerations was selected for further development.

The performance advantages of ion vapor deposited (IVD) aluminum have since been confirmed in both laboratory and service tests and the process has reached production status. This high performance protective coating is also environmentally clean. The following is therefore a description of the process, the equipment, the coating performance, and illustrations of typical applications.

Discussion

Description of the Equipment and the Process

The basic equipment required for ion vapor deposition, called Ivadizer[R] at McDonnell, is a steel chamber, a pumping system, an evaporation source, and a high voltage power supply. A schematic of a typical IVD unit is shown in Figure 1.

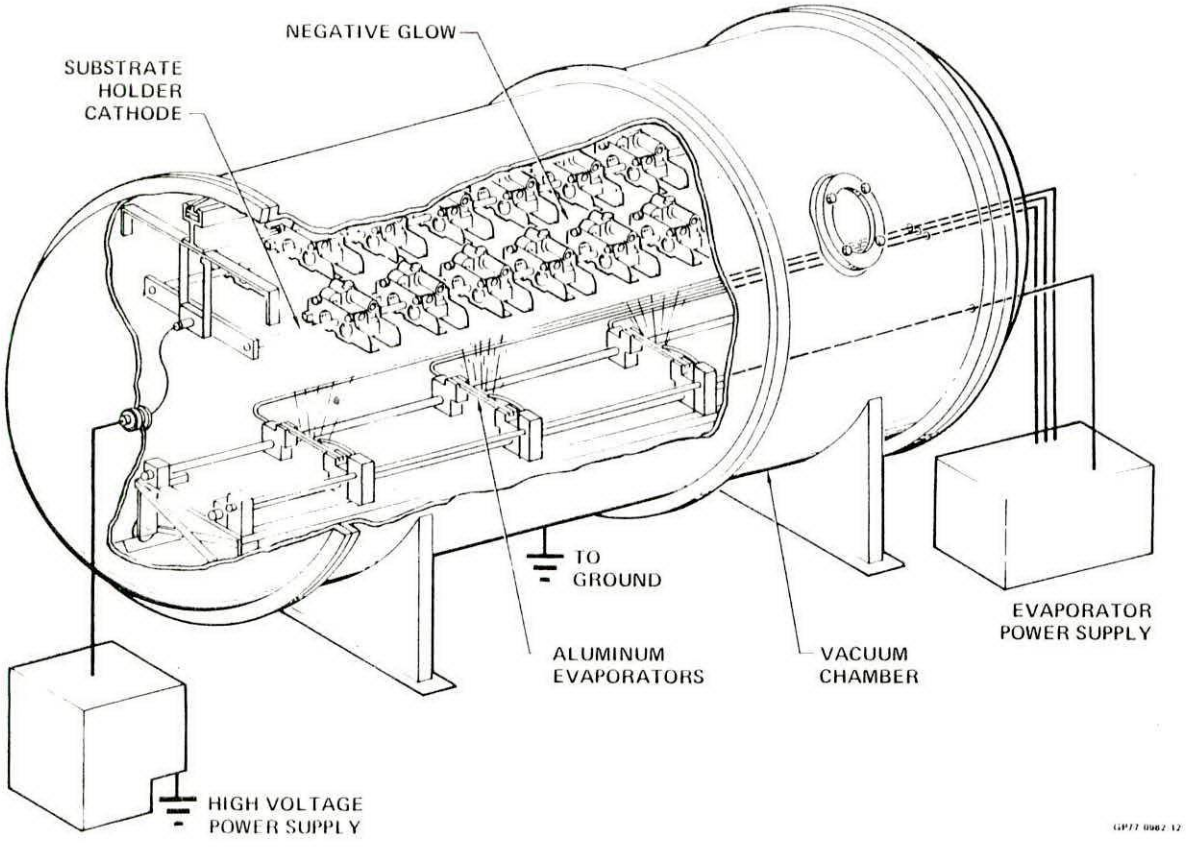


FIGURE 1
SCHEMATIC OF AN ION VAPOR DEPOSITION SYSTEM

The process sequence consists of pumping the system down to about 10^{-4} Torr. The chamber is then back-filled with an inert gas to about 10 microns and a high negative potential applied between the parts being coated and the evaporation source. The gas becomes ionized and creates a glow discharge around the parts to be coated. The positively charged gas ions bombard the surface of the parts and perform final cleaning. The clean surfaces resulting are essential for good coating adhesion.

Following glow discharge cleaning, commercially available aluminum wire (1100 alloy) is evaporated by continuously feeding into resistance heated crucibles. As the aluminum vapor passes through the glow discharge, a portion of it becomes ionized. This, in addition to bombardment by the inert gas ions, accelerates the aluminum vapor toward the part surface. This results in denser coatings and also improves the coating adhesion. The ionization also provides better throwing power and allows complex shapes to be more uniformly plated.

A typical plating cycle for coating detail parts would consist of the following:

1. Pump down to 10^{-4} Torr - 15 minutes
2. Backfill with inert gas - 2 minutes
3. Glow discharge clean - 15 minutes
4. Plate - 10 minutes
5. Backfill to atmosphere - 3 minutes

The total coating cycle requires about 45 minutes.

After coating, parts are generally chromate treated in accordance with MIL-C-5541 (Reference 1). This provides additional protection against corrosion. It also provides a good base for paint adhesion and is a common requirement for aluminum surfaces.

Technical Advantages

IVD aluminum coatings have several advantages over other coatings used to protect both steel and aluminum alloy parts. Advantages include:

1. Useful temperature to 925°F (496°C). Cadmium is limited to 450°F (232°C) (Reference 2 and 3).
2. Replace diffused nickel-cadmium and provide better corrosion protection at all strength levels. Diffused nickel-cadmium is limited to steels having strength levels below 200,000 psi because of hydrogen embrittlement and has a salt spray requirement of only 100 hours.
3. Does not cause solid metal embrittlement of titanium. Cadmium plating is prohibited.
4. Can be used in contact with fuel. Cadmium is prohibited.
5. Provides galvanic protection to aluminum alloys and does not cause fatigue reduction. Anodize coatings provide only barrier coating protection and cause fatigue reduction.
6. Can be applied thinner than alclad on aluminum alloys resulting in weight savings and is not limited to rolled forms.
7. Neither the process nor the coating create toxic materials and therefore do not present any ecology problems.

Coating Performance

An evaluation of 33 different coatings on fasteners was made by the Air Force and the Naval Air Development Center on service aircraft (Reference 4). IVD aluminum was rated as one of the top three coatings. The other two coatings were also metallic aluminum coatings that outperformed cadmium plated fasteners.

IVD aluminum is a soft, ductile coating and has properties nearly identical to pure aluminum. We use three classes and two types of coatings. The classes reflect coating thickness and the types are I, as coated, and II, as coated with a supplementary chromate treatment. Type II is generally used for reasons previously mentioned. The corrosion resistance requirement for type II coatings is shown in Table 1 for the various class coatings.

TABLE 1
MINIMUM CORROSION RESISTANCE
REQUIREMENTS PER MIL-C-83488 (REFERENCE 2)

Class	Thickness (mils)	Corrosion Resistance (hrs)
1	0.0010 Minimum	672
2	0.0005 Minimum	504
3	0.0003 Minimum	336

Class 1 coatings are used for high temperature and exterior applications where severe corrosion environments are encountered. Class 2 is recommended for interior parts where less severe environments are encountered, and Class 3 is used only when close tolerances are required such as fine threaded parts.

Numerous corrosion tests have been performed on IVD aluminum coatings by McDonnell, the Air Force, the Navy, the Army, and by other companies. As usual with corrosion testing, there is a wide range of results. Some general conclusions can be drawn, however, using cadmium for comparison.

Corrosion testing of bright electroplated cadmium on steel panels along with IVD aluminum of comparable thickness in 5% salt spray per Federal Standard No. 115 will generally show cadmium to be better. However, if a scratch is made through the coatings to the substrates, the cadmium will generally sacrifice itself more quickly and allow red rust to form before the IVD aluminum.

Results obtained in laboratory tests when cadmium and IVD aluminum coated steel fasteners were installed in 7075-T6 aluminum alloy and exposed to SO_2 - salt spray for 168 hours are shown in Figure 2. The cadmium plated fastener heads are more severely rusted. More important is the condition of the countersinks in the aluminum. The IVD aluminum has provided protection to the countersinks while the cadmium coated fasteners appear to have promoted corrosion of the countersinks.

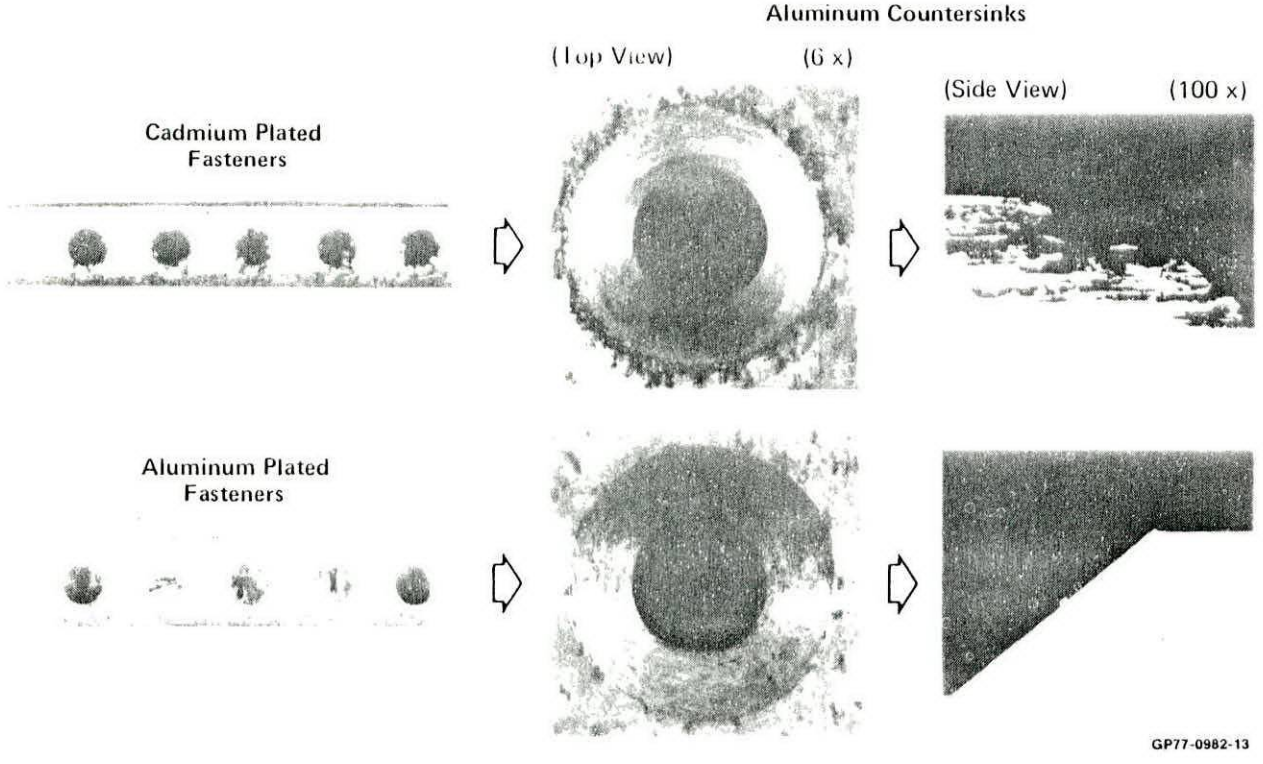


FIGURE 2
IVD ALUMINUM AND CADMIUM COATED STEEL FASTENERS INSTALLED IN 7075-T6 ALUMINUM ALLOY AND EXPOSED TO 168 HOURS OF SO_2 - SALT SPRAY

There are also advantages for IVD coating titanium fasteners installed in aluminum structure. A comparison was made between IVD aluminum coated titanium fasteners installed dry, and bare titanium fasteners installed with wet epoxy primer. The latter is a standard procedure used on aircraft. These fasteners were installed in 7075-T6 aluminum alloy that had been MIL-C-5541 treated. After fastener installation the panel was sprayed with one coat of MIL-C-23377 primer and exposed to SO_2 salt spray for 28 days. Visual examination showed that the blistering

of primer around the peripheries of the fasteners installed with wet primer was more severe than around the IVD aluminum coated fasteners. Examination of the countersinks after fastener removal also showed less corrosion resulted where the IVD coated fasteners were installed (Figure 3). Studies at McDonnell have also shown a cost advantage of using IVD aluminum coated fasteners in lieu of wet installation.

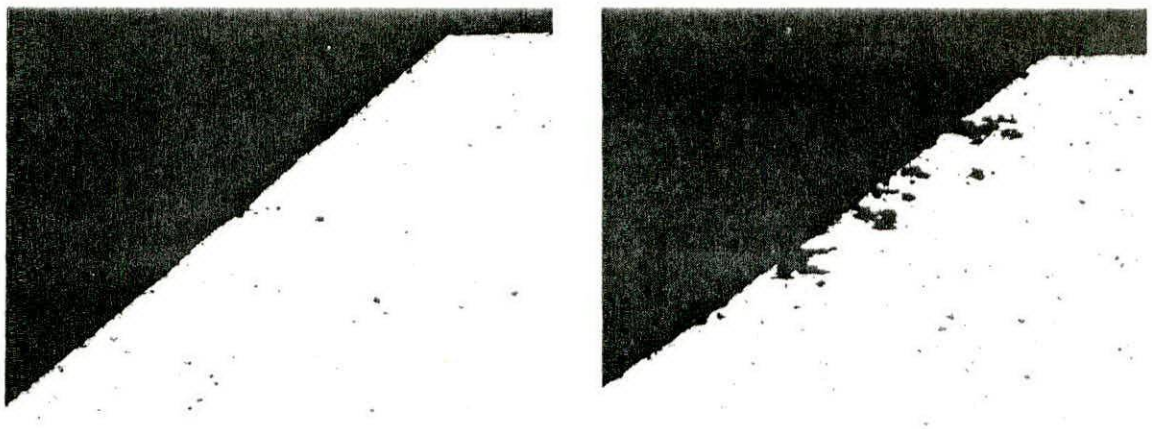


FIGURE 3
CORROSION TESTS OF IVD COATED AND WET INSTALLED TITANIUM FASTENERS IN 7075-T6 ALUMINUM ALLOY COUNTERSINKS

Coating adhesion and thickness uniformity are comparable to electroplating. The adhesion requirements are the same as those specified in Reference 3 for cadmium electroplating. An example of the coating uniformity on a fastener is illustrated in Figure 4.

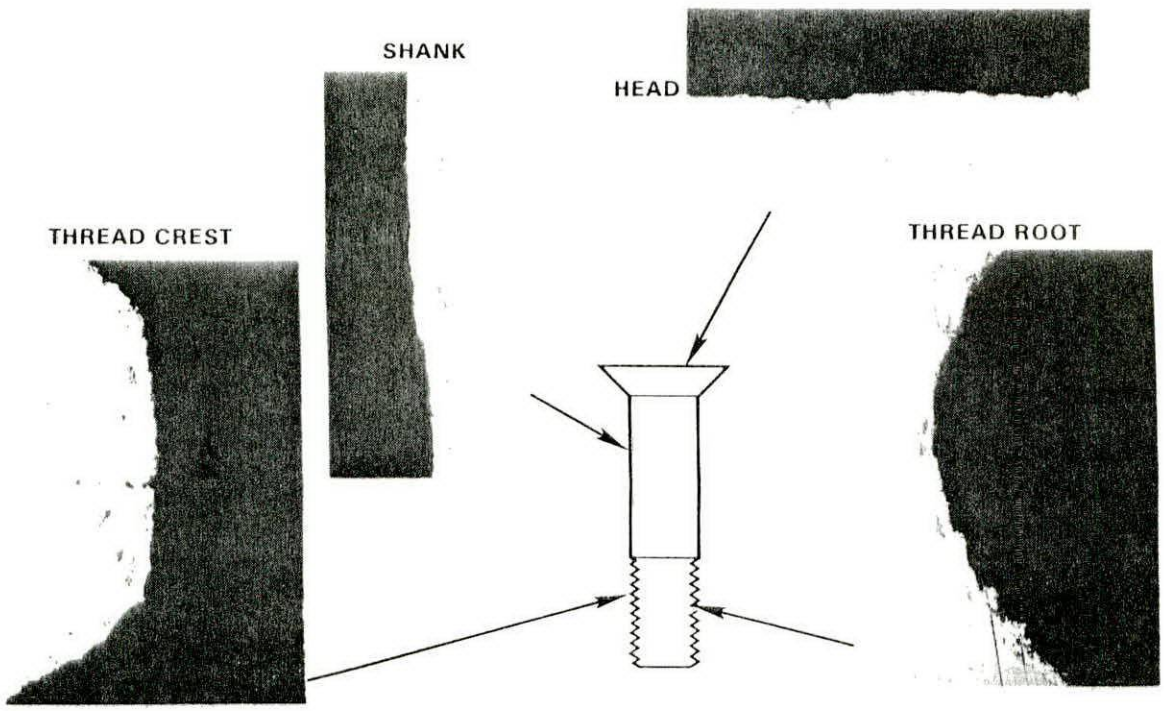


FIGURE 4
IVD ALUMINUM THICKNESS DISTRIBUTION ON A FASTENER

A lot of fastener qualification data has been generated on the use of IVD aluminum (Reference 5). A summary of the tests performed is listed in Table 2. This data is too voluminous to present here, however the conclusions can be summarized as follows:

1. IVD aluminum does not produce any detrimental effects on the mechanical properties.
2. The coefficient of friction of aluminum is higher than cadmium, therefore, higher installation forces are required. These higher values, however, are within the working ranges presently used for cadmium in most cases. Interference fit fasteners may require closer attention to the type of lubricants used.

TABLE 2
FASTENER QUALIFICATION TESTS

Mechanical	Installation
Tensile Strength	Torque Tension
Double Shear	Locking Torque
Tension Fatigue	Reuseability
Stress Durability	Interference Fit
Stress Rupture	

Production Status

The first production size coater was sponsored by the Naval Air System Command and delivered to the Naval Air Rework Facility at North Island, San Diego, in April 1974. During this contract period a number of our aircraft parts, both steel and aluminum components, were plated and evaluated. Coating uniformity, adhesion and corrosion performance were all very satisfactory. This unit was 4 feet in diameter and 8 feet long and is shown in Figure 5.

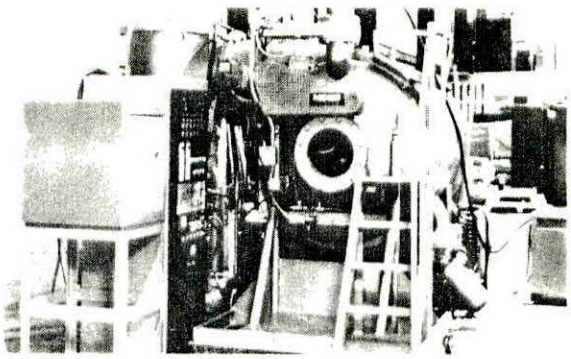
At about this same time a new approach was conceived for coating small parts on a more economical basis. The technique is similar to barrel electroplating in that parts are placed in rotating barrels over the aluminum evaporation source. Following conceptual verification in the laboratory, a 4 foot diameter by 6 foot long system was designed and fabricated. The unit has been used to demonstrate the process and as a test bed for design development. The system has evolved from one barrel to two barrels per unit, doubling the output. Production capacity was increased further by placing vacuum locks on the feed and discharge ends of the system (Figure 6). This allows fasteners to be loaded and unloaded without breaking the vacuum and reduces the total coating cycle by about 50 percent. A similar unit installed this year at a fastener manufacturer, The Voi-Shan Corporation, is also shown in Figure 5.

Early in 1976 a large detail parts coater 7 feet in diameter and 12 feet long was installed in our manufacturing facility (Figure 5). Approval had been obtained from the Air Force to use ion vapor deposited aluminum coatings on the F-15 Eagle. Fatigue improvement and economics were the motivating reasons. Sulfuric acid anodize coatings were replaced on fatigue critical aluminum wing skins. This resulted in a fatigue improvement without a design configuration change. It also eliminated a shot peening operation, resulting in a cost savings. In addition, IVD coated low alloy steel was used to replace higher cost stainless steel components.

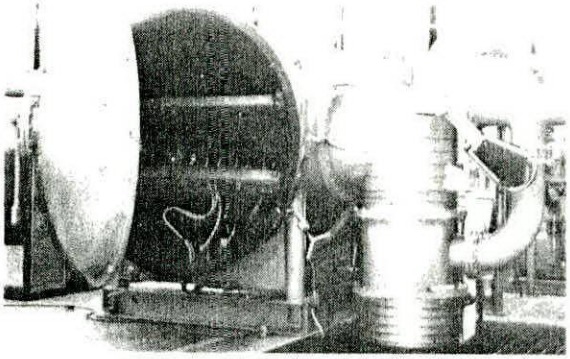
IVD aluminum is presently being used on the F-4 Aircraft and is required for use on the Harrier and the F-18 Hornet. It will be the primary corrosion protective plating on the F-18. On this aircraft it will be utilized on all fatigue critical aluminum structure, all high strength steel structure and on titanium and low alloy steel fasteners.

A unit has also been fabricated under contract with the Air Force Materials Laboratory, Manufacturing Technology Division. This unit is presently at McDonnell and is being used to develop optimum parameters and fixturing for coating both aircraft and engine parts. It will be utilized mainly as a replacement for vacuum deposited cadmium on high strength steel parts. This unit is 6 feet in diameter and 10 feet long (Figure 5).

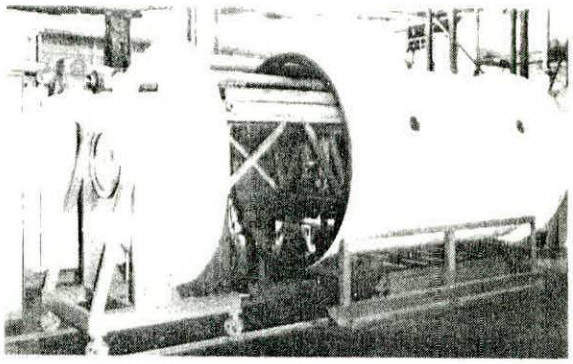
Naval Air Rework Coater



Barrel Coater



McDonnell Production Coater



Air Force Coater

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FIGURE 5
PRODUCTION COATERS

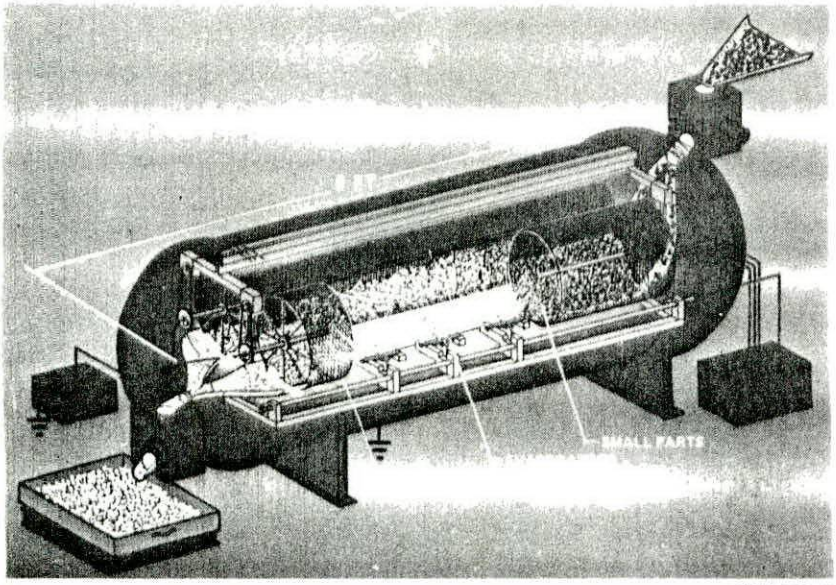

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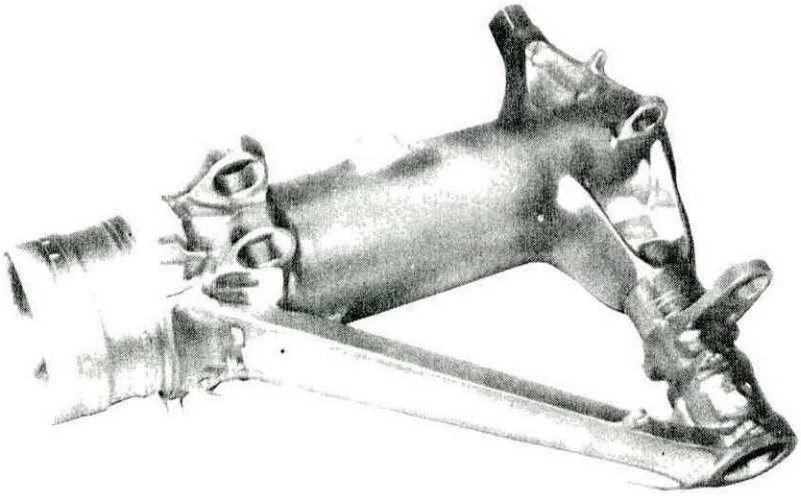
FIGURE 6
SCHEMATIC OF BARREL COATER

A photograph of a few of the aircraft and engine parts that have been coated at McDonnell are shown in Figure 7. There is also a lot of interest in aluminum coatings outside the aircraft industry. A few examples include computer discs, consumer hardware, automotive parts, space systems, electrical components, appliances, etc. Examples of sample parts coated for evaluation are shown in Figure 8.

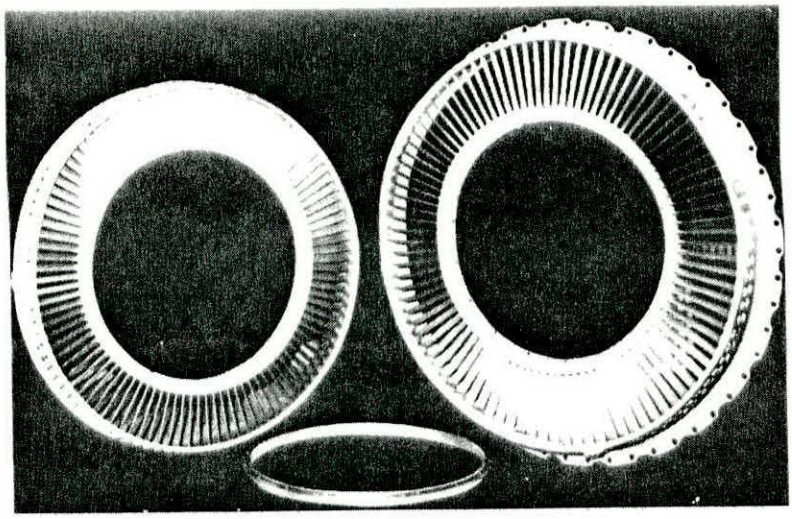
Engine Mount

Bellcrank

Wing Skin



Landing Gear



Stator Vane Assemblies

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FIGURE 7
IVD ALUMINUM COATED AIRCRAFT AND ENGINE PARTS

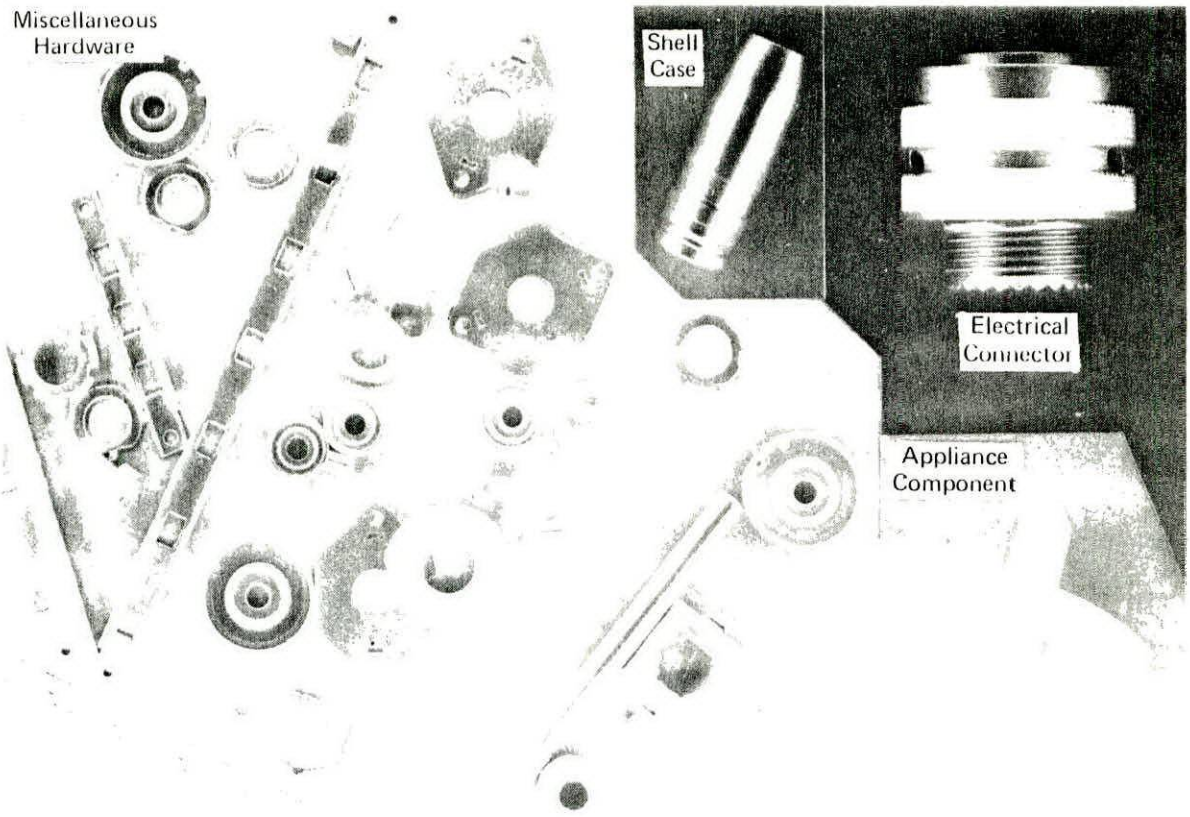

FIGURE 8
IVD ALUMINUM COATED PARTS

Economics of the Coating System

Operating costs of the IVD equipment for the most part can be generalized into three categories—labor, materials and utilities. Labor is the dominant cost factor and each system is designed to be a one man, or less, operation. Materials and utilities costs are a function of coater size and plating requirements, but when combined generally run between $5 and $15 per hour of operation.

In either the barrel or rack coater the plating rate is approximately 0.1 mil per minute.

Plating capacity of a 4 feet by 6 feet barrel coater is approximately 120 pounds of fasteners per hour. Plating capacity for a rack type coater depends upon the size and shape of the parts. A 6 feet by 10 feet coater with a translating evaporation source could coat all of the parts that could be practically racked in one 6 feet by 10 feet plane area. A carriage rack rotating over a fixed evaporation source has higher capacity depending upon part size.

Conclusions

Ion vapor deposited aluminum is a high performance protective coating and is a viable alternate for cadmium plating. It is more compatible with aluminum structure and minimizes the problem of galvanic corrosion when using dissimilar metal fasteners such as stainless steel and titanium alloys. It does not cause hydrogen embrittlement of high strength steel alloys or solid metal embrittlement of titanium alloys. It has a higher useful temperature than cadmium and an all important consideration; it does not contribute to the pollution of the environment.

References

1. MIL-C-5541, Military Specification, "Chemical Conversion Coatings for Aluminum Alloys".
2. MIL-C-83488 (USAF), Military Specification, "Coating, Aluminum, Ion Vapor Deposited".
3. QQ-P-416, Federal Specification, "Cadmium Plating (Electrodeposited)."
4. "Corrosion Performance of New Fastener Coatings On Operational Military Aircraft", Fred H. Meyer, Jr., Edward Jankowsky, International Corrosion Forum, NACE, March 1973.
5. MCAIR M&PD R&D Report No. 118, dated 6 February 1975.