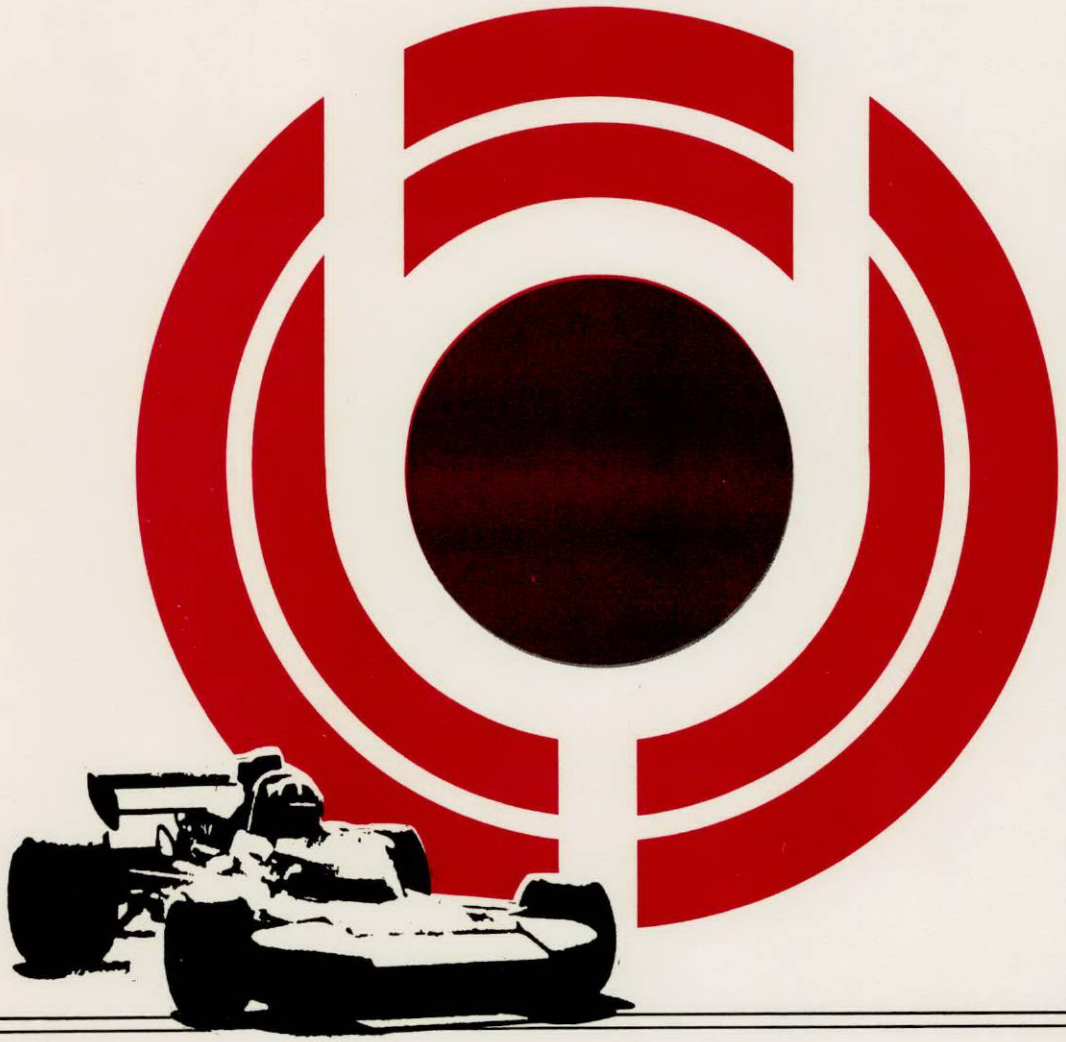
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SUR/FIN

American Electroplaters' Society SUR/FIN '83

70th Annual Technical Conference



June 27-30, 1983
Hyatt Regency Indianapolis and
The Indiana Convention - Exposition Center
Indianapolis, IN

SESSION M

AMERICAN ELECTROPLATERS' SOCIETY, INC.

70TH ANNUAL TECHNICAL CONFERENCE - INDIANAPOLIS, IN

ELECTROFORMING

SESSION M

Page No.

Flexible Circuits Manufactured by an Electroforming Process.....M-1

Glenn R. Schaer, Battelle, Columbus Labs., Columbus, OH

Precious Metal Electroformed Reflectors.....M-2

David Epner, Cohan-Epner Co., Brooklyn, NY

Electroformed Nickel, "The Modern Tool".....M-3

Rich Edwards, Electroformed Nickel Products, Brea, CA

Electroformed Boiling Surfaces.....M-4

Clarence Albertson, George Nichols and John Rasmussen,
Roy C. Ingersoll Research Center, Borg-Warner Corp.,
Des Plaines, IL

Electroforming in Japan.....M-5

Osamu Nakamura and Kuniko Nishimura, The Eftech Co. Ltd.,
Tokyo, Japan

M-1

Electroforming
Session M

Flexible Circuits Manufactured by an Electroforming Process

Glenn R. Schaer
Battelle, Columbus Labs.
Columbus, OH

FLEXIBLE CIRCUITS MANUFACTURED BY AN ELECTROFORMING PROCESS

Glenn R. Schaer
Battelle, Columbus Laboratories
Columbus, Ohio 43201

ABSTRACT

Flexible copper circuits called wiring harnesses are becoming more common in consumer products such as automobiles, business machines, and cameras. Flexible circuit manufacture by conventional substractive processes is a well established process. A new production process for making flexible circuits by an additive process is described. Copper circuits are electrodeposited on a metal strip, masked appropriately, and transferred to an adhesive-coated, plastic film in a continuous operation. Equipment and process steps are described.

INTRODUCTION

Processes for manufacturing one- and two-sided flexible circuitry are well known in the industry including a method for electroforming circuits continuously (1-4). This paper describes details for the flexible circuitry manufacturing method not yet disclosed. Process steps for manufacturing one-sided flexible circuitry by this additive process include (1) conditioning a stainless steel belt, (2) applying an ultra-violet light cured resist, (3) electroforming the copper, (4) transferring the circuits to the flexible base and (5) separating the circuits from the stainless steel belt. A solution maintenance system is used in combination with insoluble anodes to replenish the copper in the electroforming solution.

PROCESS DETAILS

Mandrel Preparation

In this process a thin, 0.20 to 0.25 mm (0.008 to 0.010 inch) stainless steel belt is reused many times. After each use it is cleaned to remove the resist remaining from the last operation then polished with a fine abrasive such as 320 grit silicone carbide. The choice of grits depends on the pressure and speed of the mechanical polishing system. High speed and low pressure conditions might require the use of 240 grit or coarser abrasive to develop enough microroughness on the strip to provide the required mechanical bonding of both the resist and electroformed copper. In the printing industry, this is called graining. Figure 1 shows the equipment for cleaning and polishing. The copper must adhere during electroforming, rinsing and drying. It must release after the adhesive is applied and the strip bent during the bonding and separating steps which are shown in Figures 2 and 3, respectively.

Resist Materials

There are many resist materials which can be used for electroforming copper circuits. However, the ultra-violet cured resists were chosen for use because of a short cure time, freedom from pin holes, and adequate adhesion to the grained stainless steel. Figure 4 shows the equipment for applying the UV cure resist. Because the line speed is typically about 2 meters per minute, a relatively inexpensive step and repeat process using mechanical silk screen equipment was used. Continuous printing process could be used but might be much more expensive for the initial equipment costs.

Electroforming Cell

The electroforming cell described previously (3) contained two insoluble anodes with the electrolyte flow introduced between these anodes. Figure 5 is a drawing illustrating the flow paths. The stainless steel strip is held against a contact block of graphite by a partial vacuum. The solution flow entering the two plating zones between the moving strip and the two anodes had some nonuniform turbulence, and low current density zones. These conditions were eliminated by the improved cell design.

Improvements (5) have been made and are illustrated in the drawing shown in Figure 6. A single anode is used with an inlet at one end which directs the flow parallel to the strip movement. This inlet also acts as an electrical shield to prevent deposition of copper at low current density on the stainless steel strip until the full turbulent solution flow impinges on the strip. Thus electroforming is initiated at ideal conditions of high flow and high current density. Solution flows out the end opposite the inlet and returns to the reservoir. A vacuum on the carbon block electrical contact insures a low resistant contact between the stainless steel strip and the carbon block. More details of the cell design are contained in Reference 5.

Solution Maintenance

The electroforming cell uses an insoluble lead-tin (93 Pb-7 Sn) alloy anode to insure that the gap between the surface of the anode and the stainless steel strip (mandrel) remain the same. The use of soluble anodes would cause non-uniform dissolution across the anode because the circuit pattern is seldom if ever uniform in density. Those areas, such as lines parallel to the travel direction, require more current and cause a corresponding larger local current on the anode causing non-uniform electrochemical attack (corrosion).

A solution maintenance problem was introduced with the use of an insoluble anode. However, a system (6) was developed for replenishing the copper using the reaction products of the electrolysis to chemically dissolve scrap copper metal. The reactions are:

Electrolysis

$$CuSO_4 + H_2O + 2e \rightarrow Cu + H_2SO_4 + 1/2\ O_2\ (gas)$$

Chemical Replenishment

$$1/2\ O_2\ (gas) + Cu\ (scrap) + H_2SO_4 \rightarrow CuSO_4 + heat.$$

The reactions are basically simple. The required rate was obtained by contacting scrap copper with both the electrolyte containing the excess acid and the atmosphere in the enclosed cell containing the liberated oxygen. As shown in Figure 7, the electrolyte is sprayed over scrap copper while the oxygen enriched gas is blown through the make-up tank. The driving force for the reaction is the oxygen and the copper metal. The reaction is exothermic and proceeds spontaneously. It is important to maximize the contact between the atmosphere and the scrap copper and a fine spray is used.

If complete immersion of the copper in the electrolyte were used, the reaction rate would be reduced because of the low solubility of oxygen in the electrolyte. Experimental results confirmed these low reaction rates when air saturated electrolyte was pumped over copper. Based on solubilities of oxygen in water at 40 C, (0.00308 g/100 ml water) 8171 liters (2160 gallons) of water are required to contain enough oxygen to dissolve 1 Kg of copper metal.

The system as shown in Figure 7 lends itself to automatic controls. The oxygen enriched gas is passed through the make-up tank continuously while the acid spray is adjusted as needed to maintain the specific gravity or free acid content, whichever is measured.

Rinse Water Effluents

Because the electrolyte system is enclosed in the electroforming cell, the make-up tank and the settling tank, as shown in Figure 7, considerable heat can build up because of the IR drop in the electrolytic zone, even though the gap between the electrodes is small, about 0.318 cm (0.125 inch). This excess heat is removed by evaporative cooling of the electrolyte. The equipment used was a scrubber normally used to remove entrained mist and fumes from exhaust gasses. The air blown through the scrubber removed the heat and evaporated water. The water removal rate was high enough to make room for all the rinse water used to rinse the electroformed circuits. Multiple rinses, as shown in Figure 8, reduce the water volume. This early pilot plant rinse system has been replaced with an improved one. This enclosed system does require that deionized water be used for rinsing to avoid build up of unwanted salts. The electrolyte system and atmosphere is maintained at a slight negative pressure to avoid leakage of mist containing air.

Laminating

Commercially available electrolytic copper foil is made by electroforming and it has excellent mechanical properties. In addition one side typically has a microscopically nodular surface texture to promote adhesion during lamination. The electroformed flexible circuitry made by the process

described in this paper uses a polyester type adhesive with a coupling agent to promote bonding between the copper and the flexible backing. Because the coupling agent was so effective, it was not necessary to electrodeposit a micro-modular surface to promote adhesion. The adhesive is applied to the polyester backing using commercially available coating equipment. A view of this equipment is shown in Figure 9.

When soldered contacts are required to the flexible circuits then a Kapton base and a different adhesive system is required to resist the elevated temperatures. Details of this adhesive system are not available at this time.

Circuit Separation

After the circuits are made and a coating applied to the second side to seal the copper circuits, the individual flexible circuits are separated by a punching operation. Figure 10 shows a punch and die set for separating the circuits.

SUMMARY

The process for electroforming flexible circuitry has been shown to be commercially competitive. Much of the cost advantage for the process is because scrap copper can be dissolved in a completely enclosed system to maintain the electroforming solution composition. The maintenance system depends on oxidizing the scrap copper with excess oxygen generated in the process.

An improved cell design provides a more uniform flow and current density in the electroforming zone.

Effluents needing expensive waste treatments are eliminated by using a completely enclosed copper plating system. The only effluents from the copper plating system are warm air and water vapors. There is an effluent generated when the resist is removed from the stainless steel when the steel strip is cleaned for reuse.

ACKNOWLEDGMENT

The authors wish to thank Koito Seisakasho Company, Ltd., Tokyo for permission to publish this information and for supplying the pictures of the equipment.

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(1) K. Yamashita, T. Wada, Y. Okamura, and W. Safranek, U.S. Patent 4,053,370, October, 1977.

(2) S. Yamaguchi, et al., U.S. Patent 4,119,516.

(3) G. Schaer, T. Wada, "Electroformed Flexible Printed Circuitry", Plating and Surface Finishing, Vol. 69, July, 1981.

(4) E. Brooman, G. Schaer, "A New Manufacturing Technique for Flexible Circuitry", Electronic Packaging and Production, Vol. 21, August, 1981.

(5) G. Schaer, et al., U.S. Patent 4,323,441, April, 1982.

(6) G. Schaer, U.S. Patent 4,324,623, April, 1982.

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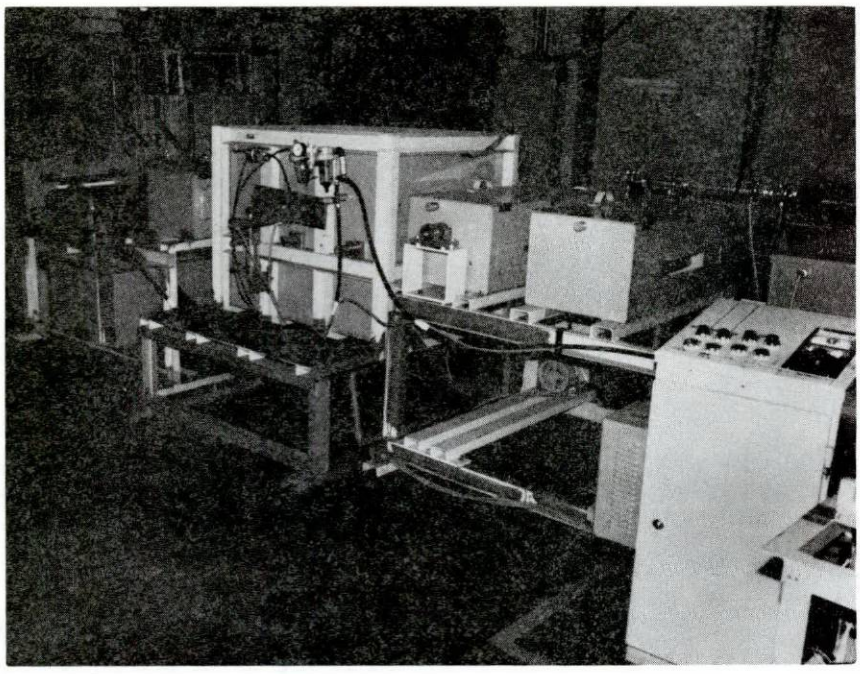


FIGURE 1. CLEANING AND POLISHING EQUIPMENT FOR CONDITIONING THE STAINLESS STEEL BELT

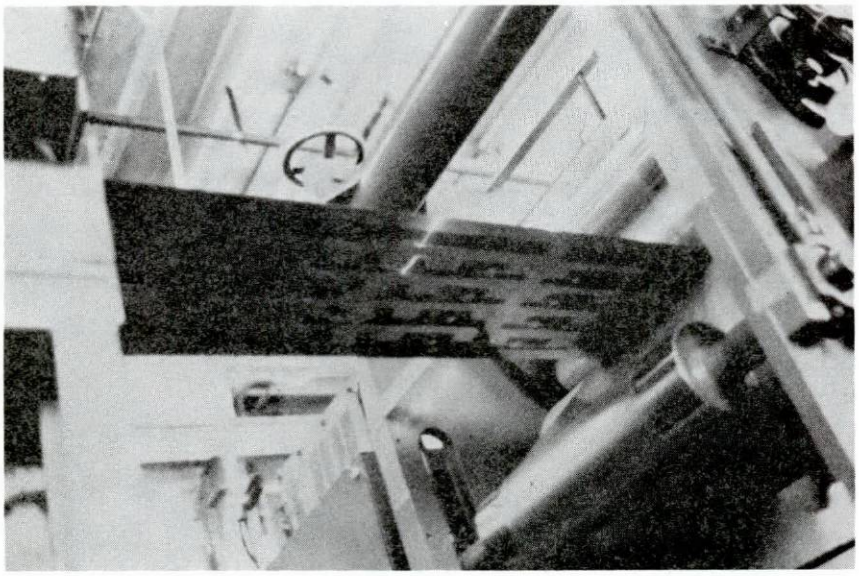


FIGURE 2. BONDING THE PLASTIC FILM TO THE ELECTROFORMED CIRCUITS

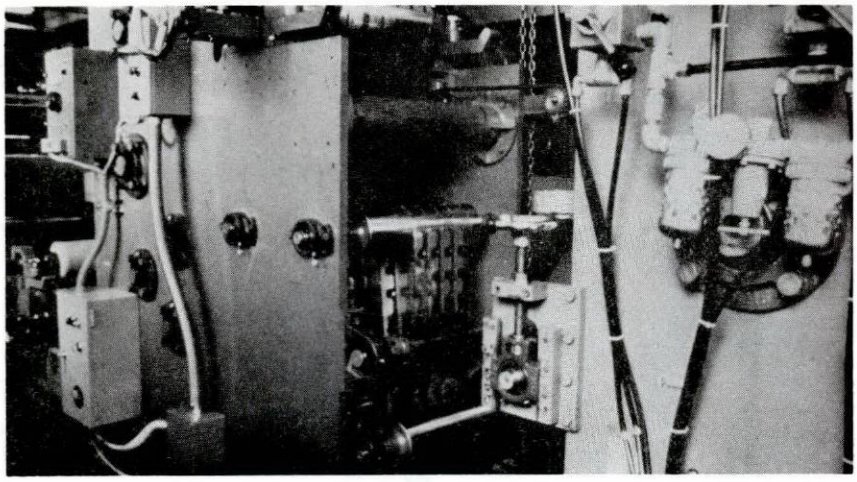


FIGURE 3. SEPARATION OF COPPER CIRCUITS AND PLASTIC FILM FROM STAINLESS STEEL STRIP

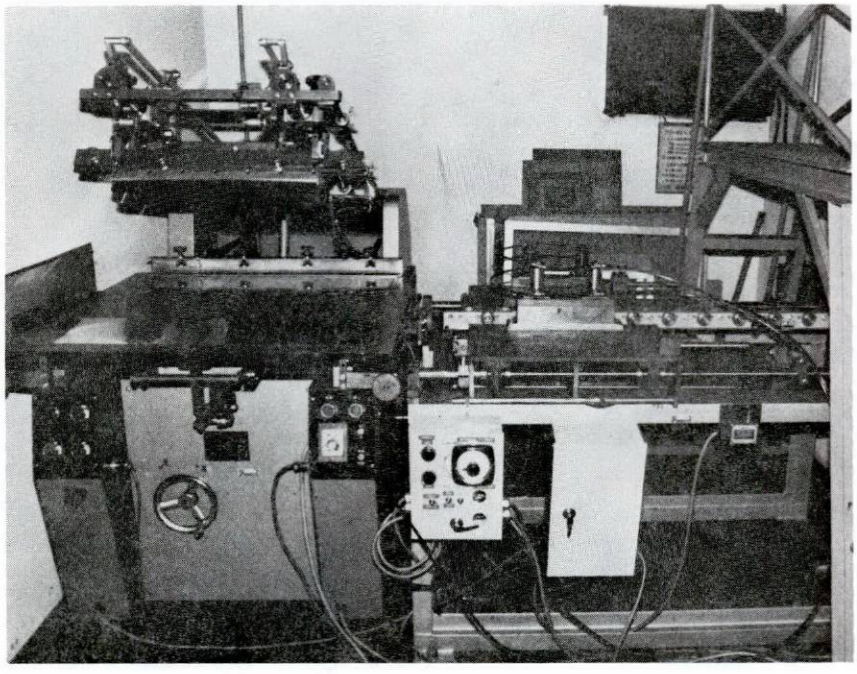


FIGURE 4. SILK SCREEN PRINTER FOR APPLYING UV CURED RESIST

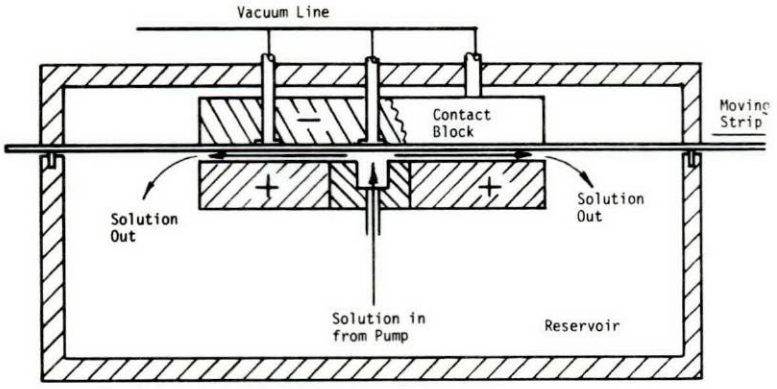


FIGURE 5. DOUBLE ANODE CELL FOR ELECTROFORMING COPPER FLEXIBLE CIRCUITS WITH SOLUTION INTRODUCED BETWEEN THE TWO ANODES

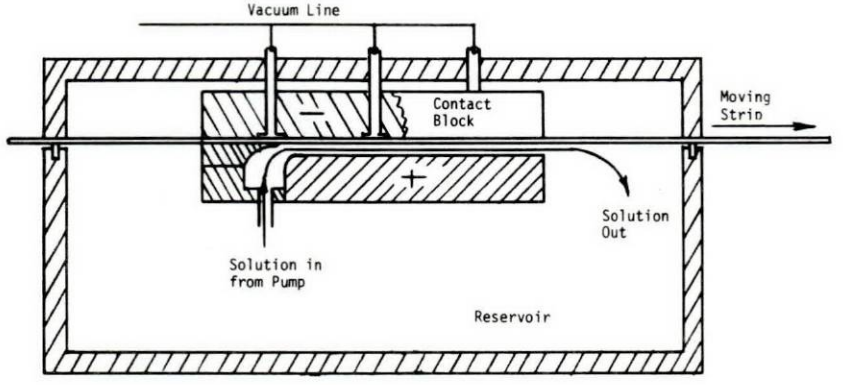


FIGURE 6. SINGLE ANODE CELL WITH SOLUTION INTRODUCED AT UP-STREAM END OF ANODE SYSTEM

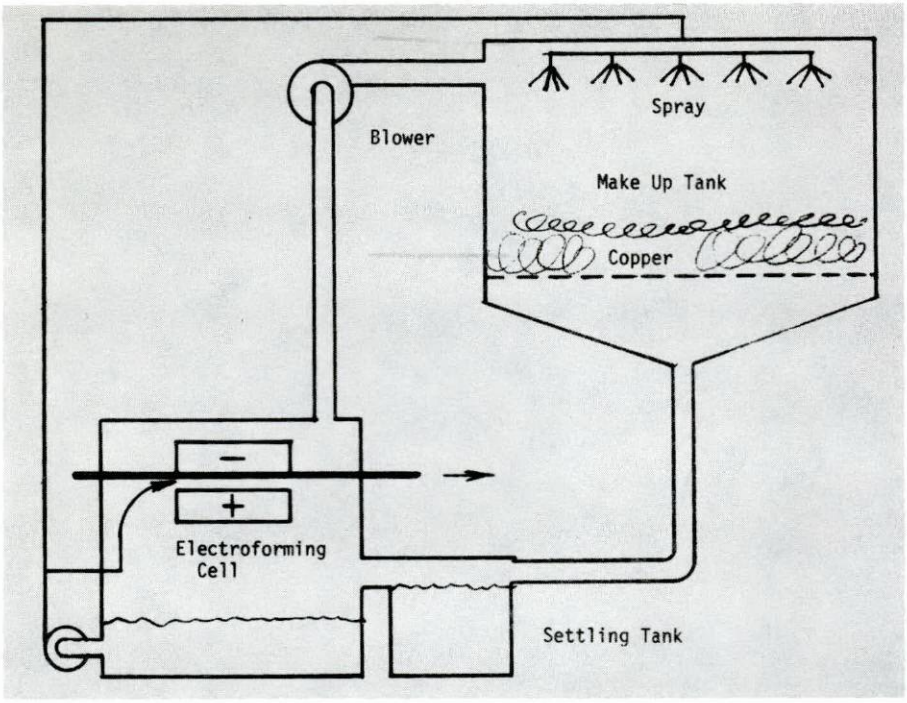


FIGURE 7. SOLUTION MAINTENANCE SYSTEM FOR REPLENISHING COPPER

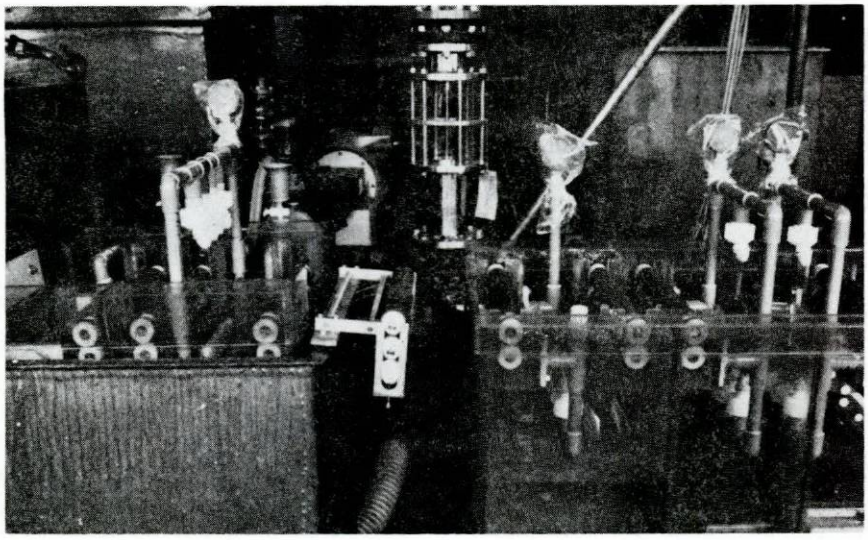


FIGURE 8. MULTIPLE RINSE SYSTEM TO MINIMIZE WATER USAGE

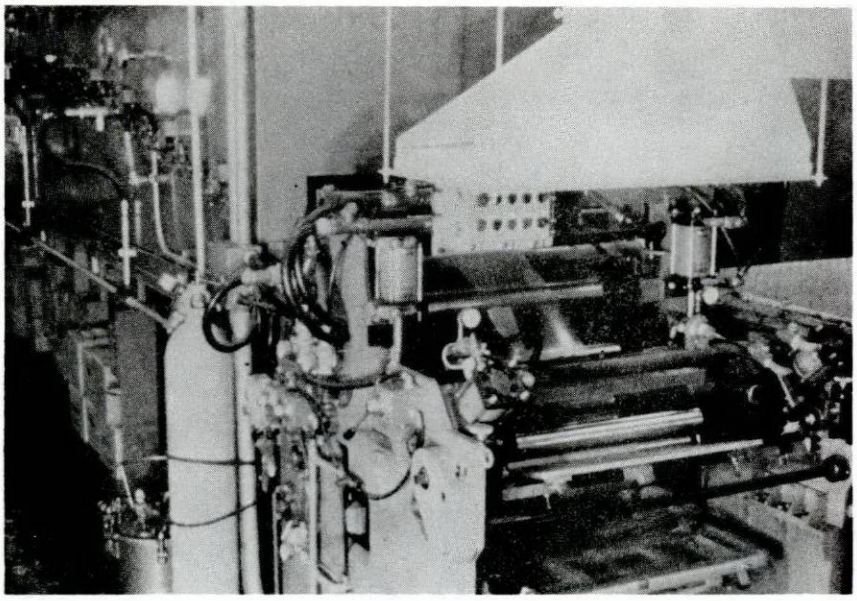


FIGURE 9. COATING EQUIPMENT FOR APPLYING ADHESIVE TO PLASTIC FILM

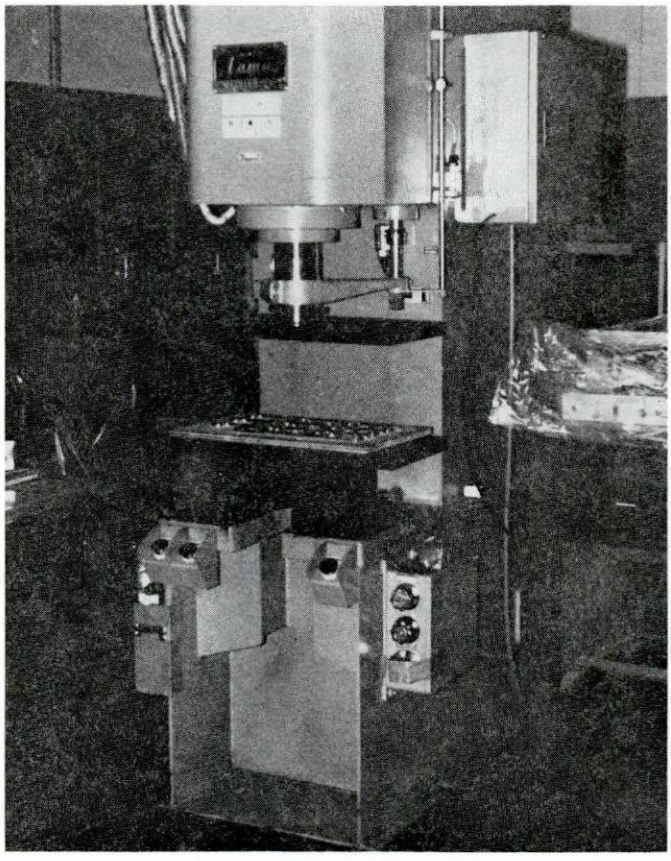


FIGURE 10. PRESS WITH PUNCH AND DIE SET FOR SEPARATING INDIVIDUAL CIRCUITS

M-2

Electroforming Session M

Precious Metal Electroformed Reflectors

David Epner
Cohan-Epner Co.
Brooklyn, NY

PRECIOUS METAL ELECTROFORMED REFLECTORS

DAVID EPNER
COHAN-EPNER CO.
25 DIVISION PLACE
BROOKLYN, N. Y. 11222

This paper will discuss Cohan-Epner Company's development of techniques and processes required to electroform pure silver optical reflectors.

Cohan-Epner is a small job plating Company in New York (30 employees). It was incorporated in 1913.

The company specializes in unusual and often difficult plating projects, primarily in the precious metals, with many programs first undertaken through an R&D contract.

Such was the case when our company was approached by an overseas manufacturer to develop a pure silver electroformed elliptical reflector.

The manufacturing process was to be designed with techniques that would be appropriate for a high production commercial product.

The reflector design was a rather simple elliptical shape approximately 1/2" wide and 1/2" deep x 3-1/2" long. There were dimensional tolerances on the width, the height and length. These were held to within .001 after machining. The thickness of the silver was .025 to .030.

Because the functional surface of the part was not an imaging optical surface but rather a reflector, the mandrel quality also need not have been that of imaging optics.

Cohan-Epner had had experience some years back with a disposable aluminum mandrel. Combining this knowledge with some recent experience in the fabrication and plating of aluminum extrusions particularly with the surprisingly low cost of tooling the extrusion dies, it was decided to go in that direction with the mandrel, that is, an aluminum extruded mandrel. The extrusion die would have a polished surface in the area of the ellipse to increase the quality of the mandrel. This surface of the mandrel would be polished and buffed prior to plating as well.

The proposed manufacturing approach would build up .025" to .030" of silver on the elliptical surface of a two foot length of extrusion. These two foot lengths would then be sliced into 4" long lengths and machined to final dimensions. Indeed this was the key idea of this fabrication process, that is, to combine electroforming with machining to create the finished product.

To do this the mandrel was designed, of course, to replicate the desired elliptical shape. But more "body" was added to the mandrel than just this elliptical form. These additional surfaces would be kept free of plating.

After the silver ellipse was roughly formed on that functional part of the mandrel, the machinist would use the unplated surfaces of the mandrel for chucking and a datem plane for final dimensioning.

Because of the high purity requirements of the reflector the choice of the silver plating bath was somewhat limited. The bath finally decided upon was made up as follows:

$KAg(CN)_2$	9.45 oz/gal	(2.5 oz/liter)
Free CN	5.00 oz/gal	(1.3 oz/liter)
K_2CO_3	7.5 oz/gal	(2.0 oz/liter)
Current Density:	8 amps/sq. ft.	

The plating rack held 5 bars vertically and was rotated during a 24 hour plating cycle. Periodic reverse was used.

After inspecting for proper silver thickness, a sample of the deposit and of the plating solution was analyzed in our lab for purity. Atomic absorption spectroscopy was used to determine the presence and quantity of metallic impurities.

The plated electroform was then machined to size while still on the mandrel. A hole was bored down the length of the mandrel to speed the dissolving. A 50% hydrochloric acid solution at room temperature was used for dissolving the mandrel. When the silver reflector was freed from the mandrel, it was placed in a conforming buffing fixture and the reflective surface color buffed to a high finish.

The final process step was electro cleaned an enhancement of the silver surface to reflectance of 98% at 700 nm. The measurement of this reflectance value was made on an in-house Beckman DK-2A Spectrophotometer with an Integrating Sphere.

Final cleaning requires that all surfaces in the reflector show no water break when sprayed with an atomized solution of 5 megohm deionized water.

The part is packed in dry nitrogen to maintain reflectance and freedom from impurities during its overseas shipment.

M-3

Electroforming Session M

Electroformed Nickel, "The Modern Tool"

Rich Edwards
Electroformed Nickel Products
Brea, CA

ELECTROFORMED NICKEL, "THE MODERN TOOL"

By Rich Edwards
Electroformed Nickel Products
Brea, California

Introduction

Electroforming provides a precise means of economically replicating a surface or shape of complex geometry. The ability of nickel electroforming to faithfully reproduce large composite forming tools or aircraft/aerospace component parts has been demonstrated with excellent results. This paper will deal with the processes required to produce composite tooling, component parts and the reproduction of holographic, video and fine line images from laser exposed photo resist.

Reinforced Plastic and Advanced Composite Tooling

The aircraft industry today is faced with major changes in manufacturing techniques. In an effort to reduce weight, surfaces that were formerly made of aluminum are now being manufactured of graphite/epoxy or kevlar composites. Composites have replaced up to 40% of aircraft exteriors resulting in a weight reduction of 10%

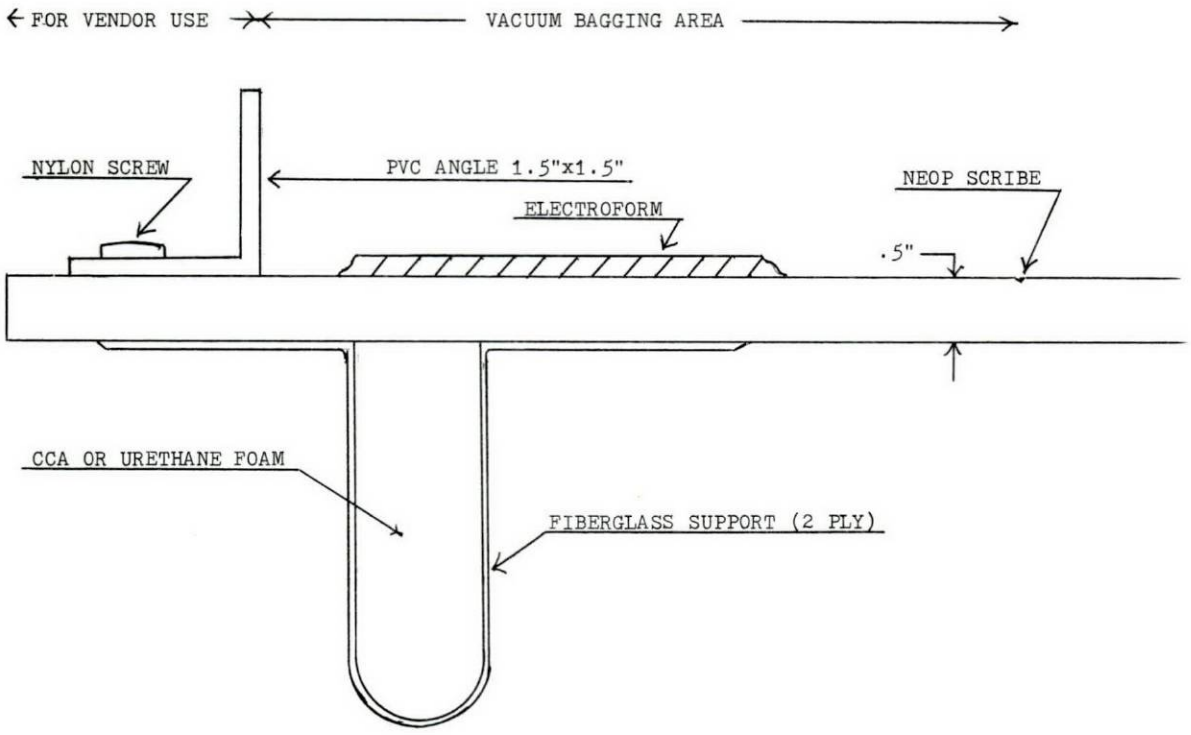
Tool design engineers encouraged to reduce cost, increase production and design hard tooling that will last the full production run of a program have been turning to electroformed nickel tooling. After cycling in an autoclave hundreds of times, electroformed nickel form tools manufactured in the mid 1960's are still maintaining vacuum integrity while producing composite parts.

An electroformed tool begins with the building of a wood model. The model is built to the exact contour of the part including net end of part (NEOP) scribe lines, locating holes and vacuum bagging area. The wood model is painted with a seal coat, sanded and treated with a release wax. (Silicone bearing release agents are not to be used under any circumstances). Next a reinforced plaster reverse is made directly off the wood model. The plaster model, referred to as a splash, is used as an intermediate for development of the plating mandrel.

Most often the mandrel is supplied by the buyer; however, the electroformer must insist that the mandrel is constructed of materials that will remain stable during the electroforming process. The strength designed into the mandrel is dictated by the size and configuration of the electroformed tool. Laminates of epoxy surface coat, epoxy laminating resin and fiberglass up to 1/2" thick are recommended. An egg crate stiffener made of closed cell foam

covered with fiberglass is strategically placed on the back of the laminate to insure that the mandrel will maintain integrity. After the mandrel is separated from the splash, it is inspected for flaws, repaired if necessary, sanded and shipped to the vendor electroformer.

FIBERGLASS REINFORCED PLASTIC (EPOXY) MANDREL



At the electroforming facility the vendor will inspect the mandrel and process for electrodeposition in the following manner.

1. Gently sand entire surface of the mandrel with 400 grit wet or dry silicon carbide paper. This will tend to remove entrapped dust and residual release agent.

2. Attach hangers, electrical connections, weights (if required), PVC angle and shielding.

The PVC angle used at the edge of the tool will serve several purposes. First and most important it will reduce the nodules that grow at an accelerated rate robbing metal and consuming current. It also serves to attach shielding. The PVC angle may be so placed as to define the edge of the tool eliminating the need for subsequent machining.

3. Remove all shielding and PVC angle.

4. Solvent clean mandrel using IPA or acetone.

5. Wash front and back with commercial detergent, rinse well, allow to dry.

6. Mask all surfaces that do not receive electrodeposited metal.

7. Spray surface to be electroformed with colliodal silver paint to form a uniform continuous electrically conductive film. Allow paint to air dry for two hours before testing for conductivity.

8. Conductivity test - attach the common lead of a volt/ohm meter to one electrical connection. With the other lead, touch the silvered surface at various spots. The resistance should be no more than 50 ohms. If resistance is more than 50 ohms, repeat step 7.

9. Remove masking and reattach PVC angle and shielding.

10. Rinse silvered mandrel with D. I. water.

11. Set rectifier at two volts.

12. Submerge mandrel in electroforming tank, increase rectifier amperage to 20 ASF.

13. After one hour lift part from bath to inspect for complete nickel coverage. During this operation a jumper cable should be attached to the cathode to maintain a current flow.

14. When the electroform reaches approximately 50% of its desired thickness, remove it from the tank.

15. Remove nodule growth, grind as required, attach boss blocks and adjust shielding.

16. Activate the exposed surface of the electroform to insure a bond when the mold is returned to the tank.

17. Electroform at 20 ASF until tool reaches its specified thickness.

This completes the electroforming phase of manufacturing a composite form tool.

The last manufacturing operation is to mount the electroform on a stress relieved steel weldment. This is accomplished by attaching the weldment to the electroform before the electroform is released from the mandrel. This is the recommended procedure because it will hold the electroform rigid until the mandrel is removed. Remove the mandrel by forcing wood wedges between the plastic face of the mandrel and the electroform.

With the mandrel removed, the completed tool is inspected for vacuum integrity. Electroforms rarely have vacuum leaks; however, if there is a vacuum leak, it may be corrected with one of several low melting alloys. Before shipping the tool to the buyer, the surface of the tool is sanded with 400 grit wet or dry silicon carbide paper. This operation serves to remove the colliodal silver paint and to give the electroform an improved appearance.

Aircraft/Aerospace Component Parts

When conventional manufacturing methods prove costly or impractical, the electroformer is often called upon to build component parts such as aircraft fuel lines, complex ducting, precision I.D. ball bearing tubes, and abrasion resistant helicopter rotor blade strips.

The routine for making component parts is basically the same as the procedure followed for manufacturing aircraft tooling. A wood or plaster model is made to engineering drawing specifications. This part is called the pattern. From the pattern a two part mold is made. This mold, most often made of fiberglass reinforced plastic, has flanges for clamping and locating pins to register both sides of the mold. This part is referred to as the master.

The master is used to generate the plating mandrel which may be fabricated of epoxy, wax or plaster. The most common material used today is a special wash out plaster. Plaster mandrels must be sanded to remove mold flash lines and the surface must be sealed. Several coats of sealer are used but not so much as to influence the dimensions.

Electroforming Procedure

1. Wash mandrel thoroughly with a commercial detergent
2. Rinse well with D. I. water
3. Air Dry
4. Spray paint with colliodal silver paint.
5. Allow to dry 24 hours. Test for conductivity.
6. Attach shielding if required.
7. Rinse well, D. I. water.
8. Electroform at 20 A.S.F. for predetermined length of time.
9. Remove from bath, check thickness, grind, mask, or adjust shielding as required.

NOTE: Step 9 may have to be repeated several times.

10. Activate nickel to insure bond.

11. Electroform to final thickness.

12. Attach mounting flanges or supports using silver solder.

13. Trim and sand to final dimensions.

14. Inspect to specifications, package and ship.

Replication of Laser Exposed Photoresist Images

Successful replicating of holographic images from photoresist surfaces requires a specialized technology. The photoresist must be applied in a clean room to avoid particulate contamination.

To manufacture a master for the electroforming process, an optical quality glass substrate is coated with an adhesion promoter followed by positive photoresist. The coated glass is mounted in a complex computer controlled laser cutting machine. By exposing the photoresist with ultraviolet light from the laser, an image is encoded on the photoresist. The encoded glass/photoresist master is developed to remove the exposed portions of photoresist, and then forwarded to the electroformer for permanent metal replication. The laser generated image has a depth of 1/4 to 1/2 micron. Holographic images are a series of lines containing variations in depth and width, video discs are a series of billions of tiny pitts. At the electroforming facility, which must be a reasonably clean facility, the glass is mounted in a fixture that has been fabricated to include edge guards and electrical connections.

Electroforming Process

1. Clean photoresist using proprietary cleaners, conditioners and procedures. Do not use solvents, solvents disolve photoresist.

2. Render entire surface conductive using reduced silver technique. Proprietary silvering solutions that will not damage photoresist surface should be used.

3. Preplate in a closely controlled low stess, low temperature electrolyte to avoid images distortion.

4. Plate at 20 A.S.F. to desired thickness (0.040")

5. Remove from bath, carefully seperate electroform from fixture. The photoresist will come off the glass sticking to the electroform.

6. Strip photoresist with proprietary stripper, acetone, M.E.K., or 4-6 oz/gal caustic soda. Extra caution, do not touch, the fine surface of the electroform can be scratched by a cottonball.

7. Mount master electroform in electroforming fixture.

8. Clean and passivate silver faced electroform.

9. Electroform at 20 A.S.F. to desired thickness (0.040").

10. Remove from bath, carefully seperate electroform (matrix) from the master. At this time, temporarily submerge the matrix in a tray of D.I. water. This will protect the matrix while the master is being prepared for storage. Rinse master with D.I. water, blow dry (do not touch), cover with protective coating.

11. Mount matrix in electroforming fixture.

12. Clean and passivate.

13. Electroform at 20 A.S.F. to desired thickness (0.004" - 0.015").

14. Carefully seperate electroform (stamper) from the matrix.

15. Rinse all parts with D.I. Water.

16. Blow dry and protective coat all image surfaces.

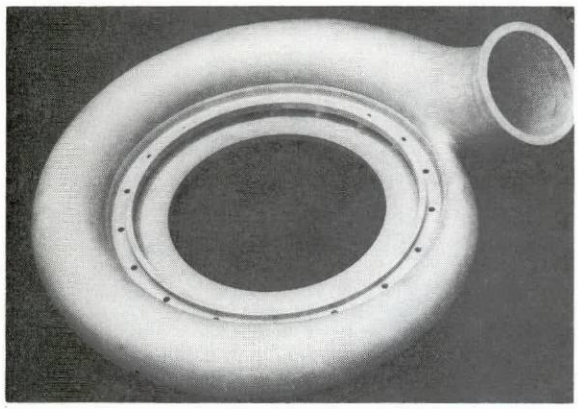
Considerable research and development in this process has yielded consistant results with excellent quality. This is not a simple process and minor variations in process, chemistry, environment, water quality and photoresist will yield inconsistant quality.

Conclusions

The advantages of electroforming with nickel has proven that it is a valuable method of producing high quality permanent tooling. When properly designed, electroforming is an economical method for manufacturing hard tooling and/or complex component parts.

Acknowledgements

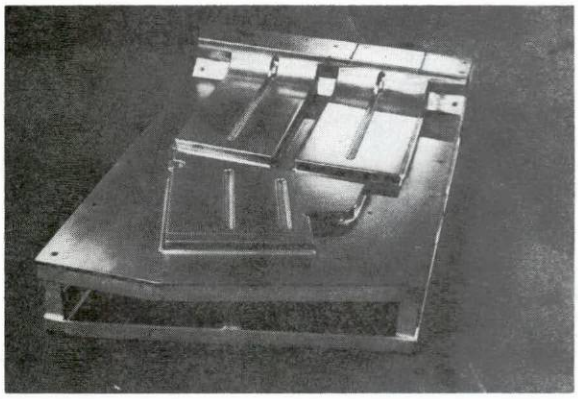
The author would like to take this opportunity to thank the following individuals for their contributions to this paper. Rick Schneck, Consulting Engineer; Tom Henderson, Electroforms, Inc.; Carol Fite, Executive Secretary.



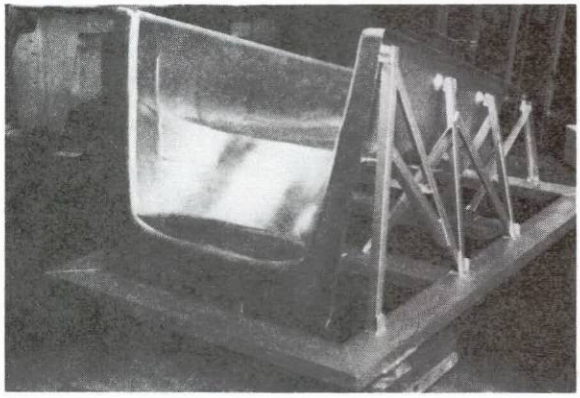
Electroformed nickel duct with mounting ring and stiffeners brazed in place.



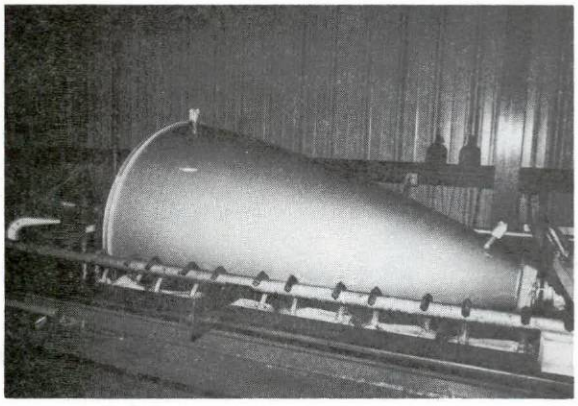
Tri-vent duct includes grown on flanges.
Photos by Electroforms, Inc.



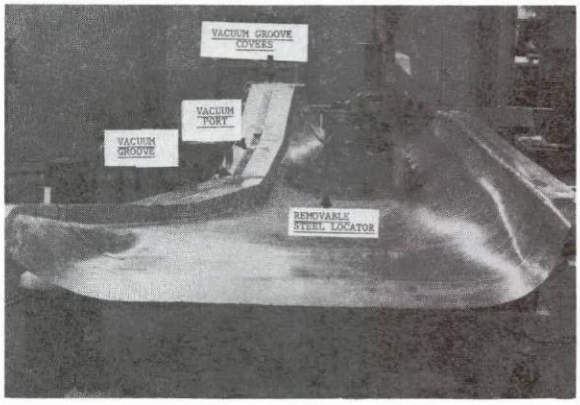
Electroformed nickel tool will form composite parts to inside mold line.



Completed nickel form tool with welded support structure.
Photos by Mafix, Inc.



In process nose cone form tool includes encapsulated vacuum ports.



Electroformed nickel facing sheet with removable locator.

M-4

Electroforming Session M

Electroformed Boiling Surfaces

Clarence Albertson, George Nichols and John Rasmussen
Roy C. Ingersoll Research Center
Borg-Warner Corp.
Des Plaines, IL

ELECTROFORMED BOILING SURFACES

Clarence Albertson, George Nichols and John Rasmussen

Roy C. Ingersoll Research Center, Borg-Warner Corporation

Des Plaines, Illinois

Introduction

I would like to describe the development of electroformed high heat flux boiling surfaces, using an aqueous copper sulfate-sulfuric acid plating bath. We will describe what a high heat flux boiling surface is, show the various types of boiling surfaces, and review process work on electroformed copper surfaces conducted in our laboratory.

Boiling Surfaces

Vapor-filled, interconnected, re-entrant cavities on a heated surface promote bubble nucleation and boiling, with a smaller temperature drop, compared to plain and finned surfaces. Fig. 1 illustrates re-entrant cavities of this type. The boiling performance of a surface is related to the number, size and shape of these cavities, thermal conductivity of the coating material, surface tension, heat of vaporization, viscosity and vapor pressure of the boiling fluid[1]. A high flux boiling surface is defined as a surface which will transfer more than 1000 Btu/hr/ft^2/^{o}F. One of the first high flux boiling surfaces was a 0.007" thick, 60% porous, matrix of copper particles brazed on the OD of a tube[2] (see Fig. 1). More efficient heat exchangers for petroleum refineries were made of this tubing, starting about 1967. Another paper[3] reported that flooded evaporators for centrifugal refrigeration equipment can be made with about half the length of high flux surfaced tubes compared to finned tubes, due to the higher boiling efficiency of the porous surface.

Types of High Flux Boiling Surfaces

Porous, high flux boiling surfaces can be classified as metallurgically-bonded metal powders[4,5], mechanically formed surfaces[6,7] and electroformed surfaces[8,9,10,11,12,13,14]. An example of each type is shown in Fig. 1. Fig. 2 shows a variety of boiling surfaces made by electroplating, composite plating, electroforming around an open cell sponge, and electroless coating of magnetically-aligned iron particles.

Rolled Copper Nodule High Flux Boiling Surface

Exploratory tests were run to see if adherent, copper-nodule surfaces could be plated which would enhance boiling heat transfer. A commercial plating bath[15] was used containing 225 g/L hydrated copper sulfate, 56 g/L sulfuric acid and additives. Copper tubes 3/4" OD x 7-1/2" long were alkali cleaned, uniformly etched in 50% nitric acid, air dried, sanded with 60 grit emery cloth and plated at room temperature in a verticle position, in a 2" ID copper tube anode plating cell. Dendrites were grown at high current density and then reinforced and bridged by continuing to plate at normal current density. Plating conditions, which yielded a dense, adherent, porous, nodular coating were:

Tube No. Buildup		Dendrite Growth
1	15 sec at 100 A	3/4 hr at 5 A
2	12 sec at 100 A	1/2 hr at 3 A

Hydrogen gas evolved strongly from the cathode during the dendrite growth step. Nodule heights were not uniform, producing a rough surface. Tube 1 was resistant to light abrasion, but Tube 2 lost some copper particles when abraided. The plated tubes were rolled between the three rolls of a sheet metal bender to partially compact the nodules, give the tubes a more uniform OD, and improve abrasion resistance by work hardening. The rolled coating was about 0.005" thick on Tube 2, shown in Fig. 3.

Tube 2, containing a tubular heating element, was tested for heat transfer in a pool of R-12 refrigerant. It caused vigorous boiling of R-12 with only a $2^{o}F$ temperature difference between R-12 liquid and the copper tube, at a heat input of 10,000 Btu/hr/ft^2 of surface. For comparison, a commercial 3/4 in. OD tube with 26 fins/in. required a $7^{o}F$ temperature rise to dissipate the same heat flux (Fig. 4). Looking at Fig. 4 another way, for a $2^{o}F$ temperature rise, the finned tube transferred 700 Btu compared to 10,000 Btu for Tube 2. About 14 times more heat was transferred by electroformed Tube 2. In a life test, Tube 2 maintained its high heat transfer for 15,000 hrs of boiling in R-12 containing 1/2% lubricating oil, and remained in good mechanical condition. This exploratory work demonstrated that a dendritic copper nodule surface can promote boiling heat transfer at high heat flux.

Factors in Process Optimization

It was decided to optimize this electroforming process to economically produce refrigeration tubing for flooded evaporators. The tube surface must be abrasion-resistant for insertion through header holes, stiff enough not to sag between supports, and fatigue resistant to the bumping vibration of boiling liquid. Work hardened, 3/4-in. OD copper tubes up to 20-ft long are used commercially. An inexpensive plating process is needed to plate the tube with

a porous, abrasion-resistant boiling surface. Effective pore cavity diameter is over 2 mils for R-11, and 1/2 mil for R-12 and R-22[3]. Quality control is needed to achieve consistent pore size and structure for high heat transfer, and to meet abrasion and fatigue requirements.

Plating Setup

A plating fixture (Fig. 5) was built to rotate the tube in a horizontal position to allow scale-up of tube length, more even evolution of hydrogen, uniform plating around the tube and bath agitation. Heavy wall 3/4-in. OD tubes about 8" long of Type 122 copper alloy, specified by our heat transfer group, were used for better boiling heat transfer tests. Solid commercial phos-copper anode sheets 5 in. x 8 in. were positioned on each side of the tube in a rectangular plastic tank. Frictional electric contact was made between the end of the tube and a copper plate. The tube was rotated at 11 rpm unless otherwise specified, with an "O" ring belt and pulley. A 15 V, 100 A, DC power supply was used.

Experimental Work

Runs were made to evaluate the performance of the rotating tube fixture and to learn how electrolyte ingredients influence the structure of the plated coating. Eight-inch tubes were cleaned, acid etched, sanded with emery cloth and plated at room temperature, with one-inch anode to tube spacings. Dendrites were grown at high current density and then built up for 1-hr at 5 A in the same electrolyte used for growing the dendrites. Test data are given in Table I.

Uniform, densely-packed nodule or hole coatings plated on the tubes. The fixture performed satisifactorily and was used for continuing work. Dendrites were grown for about 1 minute at 100 A; however, anode polarization caused current to drop in several of the runs in Table I. Anodes were immersed about 3-1/2 in. deep in these runs. Anode area was insufficient to prevent polarization. Anode polarization was avoided, after these runs, by using a tank deep enough to fully submerge the 5-in. deep anodes.

Dendrite Growth Conditions

Exploratory tests indicated that dense, adherent nodular coatings would be built up on 8-in. tubes when dendrites were grown at 30 A to 100 A for at least 4000 A-sec in a (210-75)* plating bath. Poorly developed nodular coatings formed on smaller dendrites grown with less than 4000 A-sec of current. A couple of dendrite growth and buildup cycles yielded a dense, nodular coating structure, for example, 60 sec at 40-A growth, 3/4-hr at 5-A buildup, 45 sec at 40-A growth, 3/4-hr at 5-A buildup.

*(210-75) 210 g/L copper sulfate and 75 g/L sulfuric acid.

Tube Rotation Rate

The effect of tube rpm on coating structure was observed in a (210-75) bath. Dendrite structure was unaffected from 7 to 11 rpm. At increasing speeds, from 16 to 56 rpm, dendrite tips were progressively broken off, producing a more dense, less porous coating after the buildup step. Subsequent work was done at 11 rpm which is about the highest speed the fragile dendrites can withstand.

Bath Composition Effects

In the first set of runs, copper sulfate concentration was held constant at 210 g/L and acid concentration varied from 25 to 100 g/L. In the second set, acid concentration was constant at 75 g/L and copper sulfate varied from 120 to 240 g/L. One extreme electrolyte contained 92.5 g/L copper sulfate and 341 g/L sulfuric acid. The results are summarized in Table 1.

In the first four runs at 210 g/L, copper sulfate, dendritic nodular surfaces formed in all cases. Coating adhesion was good in all but the highest acid concentration run. Although anode polarization occurred in the four runs, good, dense, nodular deposits were formed.

In the next four runs at 75 g/L sulfuric acid, good nodular deposits formed at copper sulfate concentrations of 200 and 240 g/L. At concentrations of 160 g/L copper sulfate and lower, the character of the plated coating changed significantly. A smoother, abrasion-resistant, porous coating formed instead of the more fragile rougher nodular dendrite coatings. This new structure was called a honeycomb coating (see Fig. 6). It was decided to optimize this honeycomb structure for boiling heat transfer because it does not require a rolling step to improve abrasion resistance.

Coating density was estimated by dividing the g/cm^2 columns in Table 1 by the corresponding thickness. Coating density ranged from 1.7 g/cc for Tube 17 to 5.2 g/cc for Tube 13. The density of copper metal is 8.9 g/cc. Highly porous surfaces were produced.

Holes and spaces between nodules varied from 0.5 to 8 mils in diameter. Electrolyte composition, dendrite growth current and the amount of buildup all influence the size of surface holes or pores.

Surface Conditioning

An automatible, reproducible surface conditioning method is desired for a production process. Sand blasting with a controlled abrasive and knurling were evaluated for making a reproducible starting surface. Tubes were cleaned in an alkaline cleaner and then either sand blasted with silicon carbide particles or knurled. The tubes were etched in a dilute-nitric-sulfuric acid

bath, rinsed and plated in a (160-60) plating bath. Dendrites were grown for 1 min. at 500 A/ft^2 and built up for 1 hr at 40 A/ft^2 into a honeycomb coating[12]. Boiling heat transfer data are tabulated:

Tube Treatment	Btu/ft^2/^{o}F in R-12
100 mesh SiC	1192
60 mesh SiC	1150
30 mesh SiC	1100
240 Tpi Knurl	1122

The honeycomb structure forms on the knurled ridges, with a beautifully uniform pore structure, approximately 57,600 pores/in^2. On sand blasted surfaces, the number of pores increased as grit size decreased.

Effect of Bath Temperature

Eight-inch tubes, sand blasted with 60-mesh silicon carbide and acid etched were plated from 10^o to 40^{o}C at dendrite growth currents of 50 to 80 A in a (170-60) plating bath with 1-hr buildup at 5 A to learn which plating conditions give better honeycomb coatings. Test data are given in Table 2. More adherent coatings were produced by growing the dendrites at 80 A for 1 min. dendrite growth, compared to 50 A for 2 min. The coating formed at 10^o had smaller visible pores than 25^o and 40^o coatings. Coating structure changed from predominately honeycomb to predominately nodular as temperature increased to 40^{o}C. Coating adhesion decreased as temperature increased. Based on these results, bath temperature was held between 20^o and 25^{o}C and higher dendrite growing current densities were used in subsequent work.

Effect of Process Conditions on Structure & Heat Transfer

Boiling heat transfer tests and coating inspection were used to evaluate the electrolyte composition and plating conditions which gave good performance in the honeycomb coating range, i.e. copper sulfate content, less than 180 g/L in the plating bath. Eight-inch tubes were cleaned, sand blasted with 100-mesh silicon carbide, etched for about 15 seconds in a solution containing 12% nitric acid and 25% sulfuric acid, rinsed and plated at 11 rpm at 23^{o}C. Data are given in Table 3.

Baths containing from 160 to 120 g/L copper sulfate and 25 to 75 g/L sulfuric acid all yielded fair to good honeycomb coatings. Adhesion was generally good, excepting Tubes 131 and 144, which appeared to have insufficient buildup, only 1/2 hr at 5 A. Tube 133 also had poor adhesion. Visual hole diameter in the honeycomb surfaces was about 0.002 in. Tubes with well-formed, adherent coatings were generally made at higher dendrite forming A-sec. conditions followed by 1-hr buildup at 5 A. The best looking tubes, Nos. 118 and 156, were made in a (140-50) plating bath.

Dendrites were grown on Tube 156 by slowly cycling the current manually from 30 to 100 A for a 1-min. period. For Tube 118, the dendrite growth current was gradually reduced from 95 to 70 A at 50 to 60 sec. A scanning electron microscope photo of Tube 156 (Fig. 7) shows the fine structure in the coating.

Tubes 118 and 156 were evaluated for heat transfer in R-12 and R-11 in the pool boiling rig; see data in Table 4. These tubes have very good boiling heat transfer. Temperature differences of less than $1^{o}F$ were required to transfer 1000 $Btu/hr^{1}/ft^{2}$ in R-12 and less thant $2^{o}F$ difference to transfer 10,000 $Btu/hr/ft^{2}$. Refrigerant 11 does not transfer heat as well as R-12. Temperature differences of 5^{o} to $7^{o}F$ were required to obtain 10,000 $Btu/hr/ft^{2}$ in R-11 with these boiling surfaces. Also, Table 4 shows that the heat transfer of these surfaces compares favorably with that of commercial, brazed granule boiling surfaces[4].

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14. S.Oktay, et al to IBM, U.S. 3,706,127.
15. Cubath #2, Sel-Rex Corp.

Table 1

Effect of Bath Composition on Coating Properties

Tube No.	Electrolyte Composition (g/l) $CuSO_4.5H_2O$	H_2SO_4	Dendrite Formation	Tube Length (cm)	Weight Gain(g)	Coating Thickness (cm)	Coating Weight (g/cm^2)	Coating Properties
13	210	25	40 sec @ 95-100 A 20 sec. @ 95-55 A	20.9	5.64	.0085	.044	Dendrites vary in height from short to very tall. Uniform plating all over. Fairly well developed - looks good.
9	210	52.5	1 min. @ 100A	20.95	5.55	.024	.043	Good nodule development at each end, but light in the middle.
16	210	75	40 sec @ 95-100A 20 sec @ 95-30A	20.7	5.60	.010	.0445	Good combination of holes and dendrites.
17	210	100	40 sec @ 95-100A 20 sec @ 95-30A	20.6	4.50	.021	.036	Rather heavy deposit of well developed dendrites (nodules) but adhesion is zero.
21	240	75	25 sec @ 95-100A 35 sec @ 95-30A	20.6	3.92	.011	.0315	Fairly uniform dendrite formation and development. Slightly heavier plating at one end with poor adhesion at that end.
23	200	75	30 sec @ 95-100A 30 sec @ 95-25A	20.6	4.51	.008	.036	Small diameter holes in dendrite coating. Light plating uniformly distributed over entire surface.
25	160	75	1 min @ 95-100A	20.6	5.20	.016	.041	Uniform plating all over. Holes are prominent.
27	120	75	1 min. @ 95-100A	20.5	4.19	.0075	.034	Holes predominate over dendrites. Plating is uniform.
11	92.5	343	20 sec @ 95A 20 sec @ 90-60A	20.85	4.66	.032	.037	Fairly uniform hole development. Not nodular. Holes are small in diametermeter (ca. 2.2 mil diameter) and uniform in size.

Table 2

Effect of Bath Temperature on Coating Structure

Tube No.	Temp. °C	Dendrite Growth Current-Time	Coating Properties			
			Adhesion	Microstructure	Uniformity	Pore Size, in.
15	10	80A-1 min.	Good	Some dendrites Honeycomb, fine porosity	Good	0.0002-0.001
16	10	50A-2 min.	Fair	Honeycomb with some columnar on the top of the honeycomb	Good	
4	25	80A-1 min.	Good	Honeycomb	Good	0.001-0.003
12	25	50A-2 min.	Poor	Honeycomb and columnar	Poor	
6	40	80A-1 min.	Fair	Mostly columnar, some honeycomb	Good	
14	40	50A-2 min.	Poor	Mostly columnar	Poor	

Table 3

Effect of Process Conditions on Honeycomb Coatings

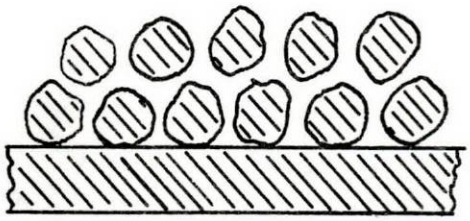
Tube No.	Electrolyte Composition (g/L) $CuSO_4.5H_2O$	H_2SO_4	Dendrite Formation Conditions in Seconds @ Amperes	Buildup in Hrs @ 5A	Coating Wgt. (g)	Coating Thick. (in.)	Structure Development	Adhesion	Average Hole Dia(in)	No. of Holes per in^2
108	160	75	50 @ 95-100+ 10 @ 95-35	1	6.08	.0069	Fair	Good	.0020	-
109	160	75	50 @ 95-100+ 10 @ 95-30	1	6.18	.0077	Fair	Good	.0020	-
118	140	50	50 @ 95-100+ 10 @ 95-70	1	5.18	.0085	Good	Good	.00276	55,000
131	140	25	60 @ 80	1/2	-	-	Good	Bad	.0026	
132	140	25	30 @ 85	1	5.03	.0054	Poor	Good	.0014	52,000
133	120	75	40 @ 100	1	5.76	.0079	Good	Bad	.0020	
144	120	75	40 @ 70	1/2	-	-	Poor	Bad		
150	120	75	40 @ 70	1	4.28	.0049	Fair	Good		
156	140	50	60 @ 20-100 Fluctuating	1	5.64	.0061	Good	Good		
157	140	50	60 @ 20-100 Fluctuating	1	6.31	.0061	Good	Good		

Table 4

Pool Boiling Heat Transfer Data

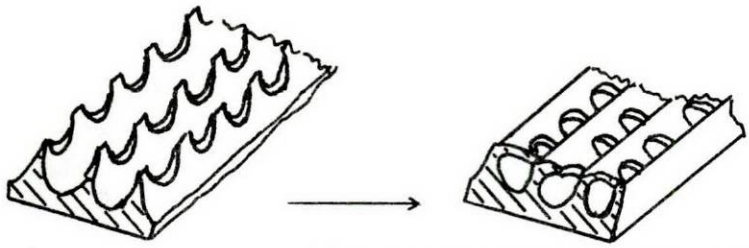
Heat Flux Density Btu/hr/ft^2	T(^{o}F) for Various Tubes					
	Tube 118		Tube 156		Brazed Granule Tube	
	R-12	R-11	R-12	R-11	R-12	R-11
1,490	0.65	--	0.68	--		
1,785	0.72	--	0.70	--		
2,980	0.95	--	0.81	4.58	0.53	3.08
4,470	1.15	--	0.90	--	0.82	3.42
5,960	1.30	4.66	0.98	4.86	1.06	3.86
8,940	1.50	5.54	1.08	4.74	1.43	4.44
11,900	1.70	6.36	1.25	4.91	1.91	5.01
14,900	1.90	7.29	1.50	5.39	2.44	5.69

FIGURE 1
TYPES OF BOILING SURFACES



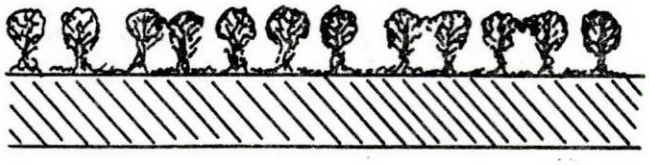
METALLURGICALLY BONDED

Brazed Powder 4



MECHANICALLY FORMED

Bent Fins 6

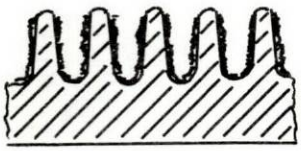


ELECTROFORMED

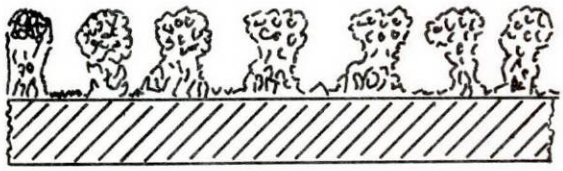
Rolled Dendrites 11

FIGURE 2

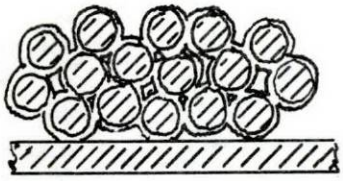
ELECTROFORMED BOILING SURFACES



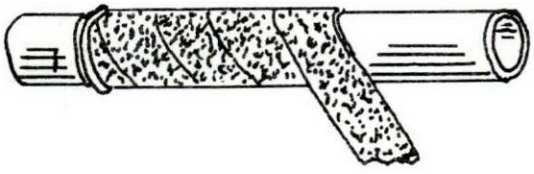
Porous Copper 13



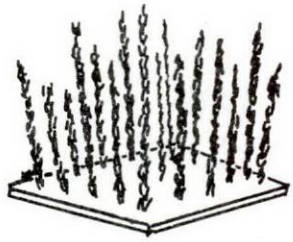
Honeycomb 12



Metal Particles
Plated Together 8

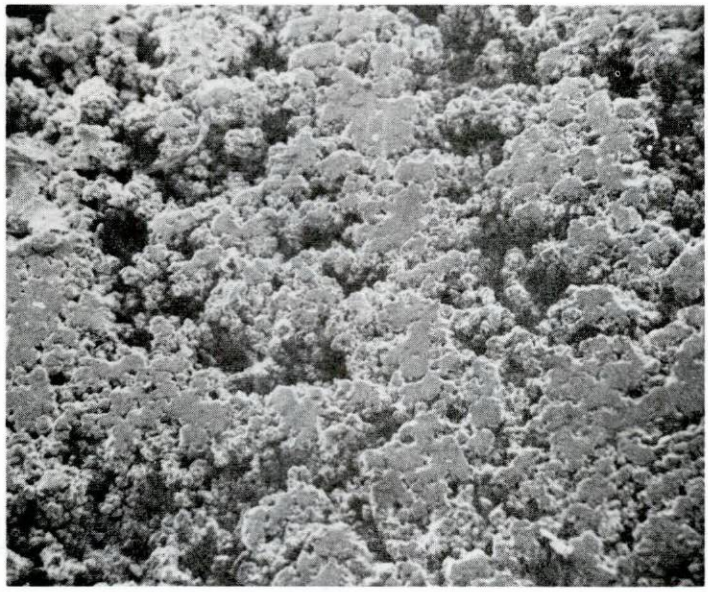


Plated Open-Pore
Sponge 10



Electroless Bonded
Magnet Aligned
Iron Powder 14

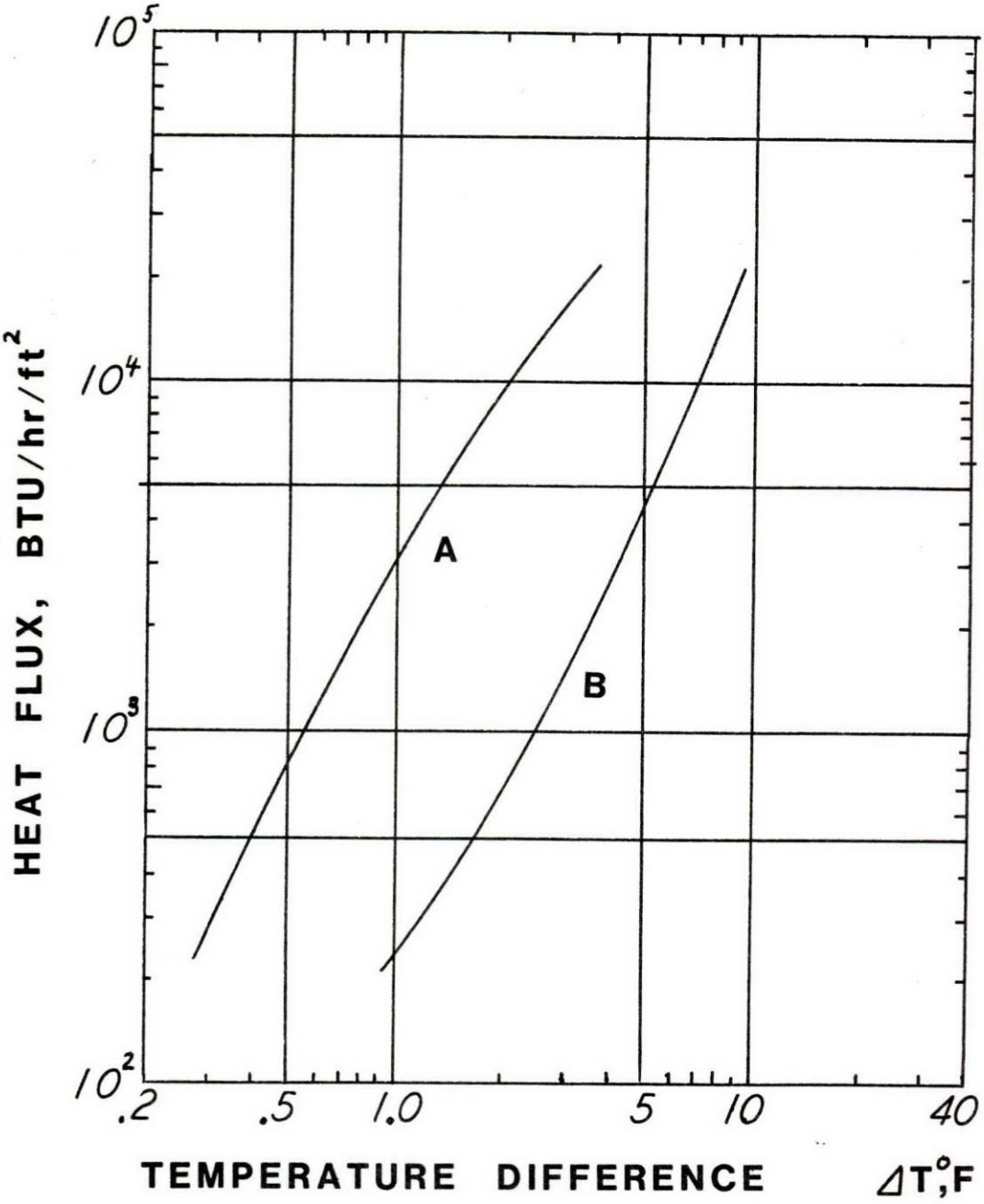
FIGURE 3



ROLLED COPPER NODULE COATING

FIGURE 4

HEAT TRANSFER DATA



A- Rolled, Nodule Coated Tube

B- 26 Fin per inch Tube

FIGURE 5

PLATING APPARATUS

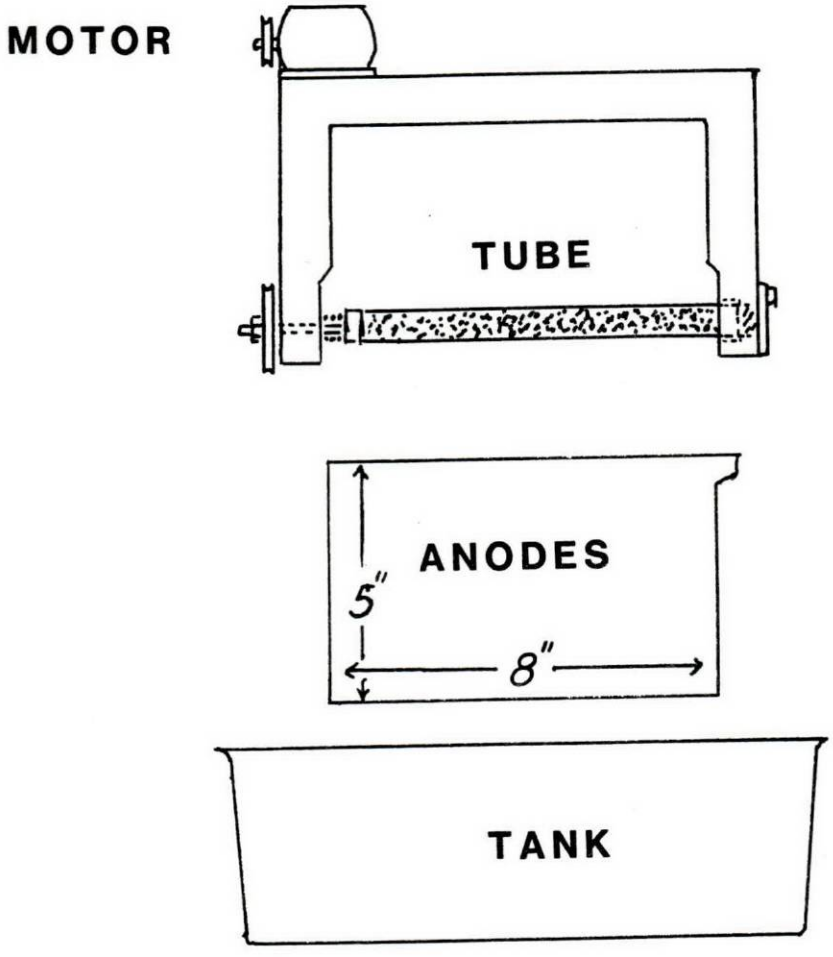


FIGURE 6

HONEYCOMB SURFACE

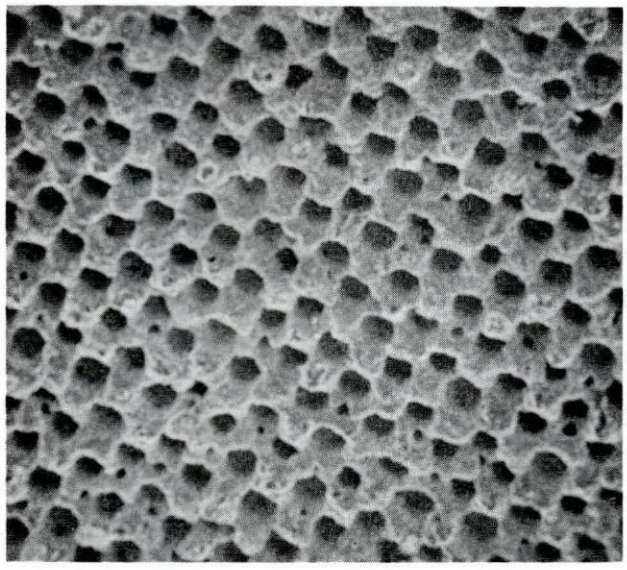
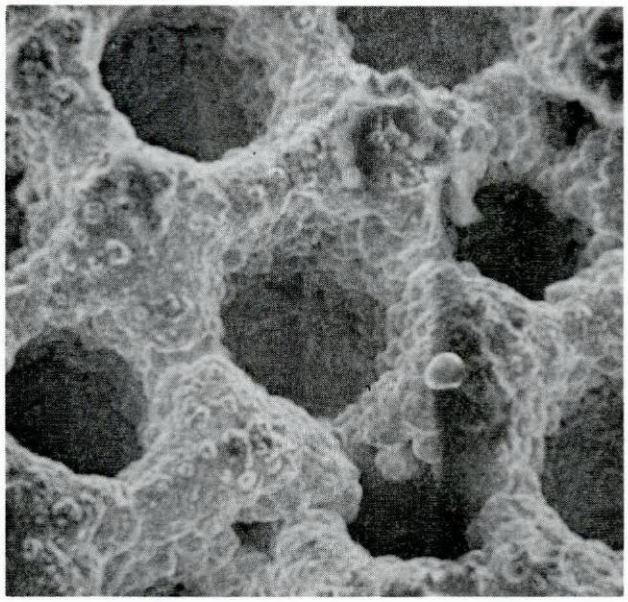


FIGURE 7



HONEYCOMB STRUCTURE

M-5

Electroforming Session M

Electroforming in Japan

Osamu Nakamura and Kuniko Nishimura
The Eftech Co. Ltd.
Tokyo, Japan

ELECTROFORMING IN JAPAN

- A Look Back and a Look Forward -

Osamu Nakamura and Kuniko Nishimura
of The Eftech Co., Ltd., Tokyo, Japan

In Japan, as in other countries, the electroforming industry enjoyed a good start with the production of molds for printing plates, lithography rolls, toys, and matrix tooling for phonograph records. Chrome decorative plating of small parts supplemented the income derived from electroforming.

During the sixties and early seventies, electroforming benefited from the accelerated development of the automobile and electrical appliance industries.

The oil shock of 1983, due to its effect upon major industries, put a halt to the rapid advance of electroforming. Demand for electroformed parts declined; thus the electroformers were unable to expand with new equipment and additional personnel.

During this crisis the mass-production manufacturers were concerned that, in the wake of the oil-shock slow-down, small companies - such as electroformers - would be put out of business and thus deprive them, the large manufacturers, of the requisite electroforms for their tooling.

To solve this imminent problem, some leading manufacturers chose to absorb their supplier - the electroforming company - for relatively small capital outlay.

This absorption was beneficial in several ways. It provided the operating and expansion capital which smaller companies lacked; and, in turn, the electroformers provided the manufacturer with a bonus of high technology in their own specialized field; a combination that helped the larger manufacturers to broaden their capabilities and to look forward with assurance to a renewal of their normal production pace.

During the acceleration years, there had been a resurgence of research and development in high-technology fields - including metal fabrication - with resulting improvements in methods and processes awaiting financial backing and adoption by industry.

However, the economic sag that afflicted America was also severe throughout Japanese industry, deepened significantly by national restrictive policies.

In spite of this full-scale setback, a positive note should be added here to this effect: for major electroformers 1982 electroforming sales were approximately 80% of the 1981 peak. Although total sales decreased, orders for more varieties of molds increased - thus opening up new markets.

It may be of interest to know that, in Japan, electroplaters are now entering the electroforming field. As they do so, they learn anew that the two systems are not identical - neither in chemical structure nor in shop practise; nor do they serve the same markets.

Electroplating can be used as a major mass-production system; whereas electroforming is an electro-chemical system providing precise configuration tooling to serve the mass-production market.

In addition, electroforming is unequalled in its capacity to produce high-precision molds that duplicate complex configurations with unerring fidelity. Examples include medical instruments, optical lenses, rocket engine components and other critical parts required for space and aircraft vehicles.

A current example of the high precision assured by the electroforming method is the development of the artificial heart system. Molds for a recently introduced ventricular assist system were made wholly by electroforming. Minutely calculating the inherent swelling and contraction is a major step in production of a successful mold.

Another development of interest to electroformers is the monolithic molding method now being adopted in Japan. It has been customary to mold parts individually for the vehicular industry, for assembly by others.

The single monolithic mold may obsolete many types of multiple molds. It also presents new problems of its own. The molding dies equipped with heating and cooling pipes are becoming larger and more intricate, often presenting such problems as expansion of the scale of the equipment. The successful reproduction of a monolithic mold requires the technical expertise of veteran electroformers who have consistently kept abreast of every new development of the art and who themselves have enriched their knowledge with their own investigative experiments.

An example of such venture thinking is the cobalt-nickel alloy bath. This sytem of electroforming was originated and developed in the States. It has been reduced to shop practise and has been in successful operation now for almost a decade.

The cobalt-nickel system provides hard-wear surfaces that are almost immune to degradation of any measurement. Its hardness range is from 285 Brinell (machineable) to 550 Brinell (not machineable).

It is our hope that other alloy combinations now being investigated may provide deversified electroforming systems with varying degrees of resistance; perhaps such combinations as Nickel-Manganese; Nickel-Tungsten; Nickel-Cobalt-Manganese; Nickel-Iron.

Another expectation is that the inclusion of fluorine compound will provide necessary lubricity for easier release of a molded product.

We also look forward to development of composites in an original layer containing insoluble particles of aluminum oxide, boron nitride, and other elements providing wear resistance: a prime requisite for space product.

The conclusion to be reached is that, as in any business, problems may beset the electroforming industry; but creative work and venture thinking will help us all meet our shared objective: to solve technological problems and continuously improve the end product.


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