Research and Development

EPA/600/SR-93/201

December 1993



Project Summary

Carbon-Black Dispersion **Preplating Technology for Printed** Wire Board Manufacturing

Dale W. Folsom, Arun R. Gavaskar, Jody A. Jones, and Robert F. Olfenbuttel

This project compared chemical use, waste generation, costs, and product quality between electroless copper and carbon-black-based preplating technologies at the printed wire board (PWB) manufacturing facility of McCurdy Circuits in Orange, CA. The carbon-black-based preplating technology evaluated is used as an alternative process for electroless copper (EC) plating of through-holes before electrolytic copper plating. The specific process used at McCurdy Circuits is the BLACKHOLETM1 (BH) technology process, which uses a dispersion of carbon black in an aqueous solution to provide a conductive surface for subsequent electrolytic copper plating. The carbon-black dispersion technology provided effective waste reduction and long-term cost savings. The economic analysis determined that the new process was cost efficient because chemical use was reduced and the process proved more efficient; the payback period was less than 4 yr. McCurdy Circuits found that the product quality achieved was equal to that achieved with EC plating. Thus, the new carbon black dispersion process was found to be a viable alternative to EC.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

This study, performed under the U.S. Environmental Protection Agency's (EPA) Waste Reduction and Innovative Technology Evaluation (WRITE) Program, was a cooperative effort between EPA's Risk Reduction Engineering Laboratory (RREL) and McCurdy Circuits. The goal of the WRITE Program is to evaluate, in a typical workplace environment, examples of prototype or innovative commercial technologies that have potential for reducing wastes and to provide this information to potential users. The objectives of the carbon-black dispersion technology study were to evaluate (a) the waste reduction potential of the technology, (b) the economic feasibility of the technology, and (c) the product quality of the PWBs.

McCurdy operates two process lines for the through-hole plating of PWBs: one uses EC and the other uses the carbonblack dispersion process. The EC process at McCurdy Circuits consists of the following 18 operational steps:

- 1. Acid cleaner
- 2. Rinse (to discharge line)
- 3. Microetch (sodium persulfate solution)
- 4. Rinse (to ion exchange line)
- 5. Activator--pre-dip
- 6. Catalyst
- 7. Rinse (to discharge line)
- 8. Rinse (to discharge line)
- Accelerator
- 10. Rinse (to discharge line)
- 11. EC



¹ Mention of trade names or commercial products does not constitute endorsement or recommendation for

- 12. Rinse (to separate ion exchange system)
- 13. Sulfuric acid 10%
- 14. Rinse (to ion exchange system)
- 15. Anti-ox
- 16. Rinse (to discharge line)
- 17. Deionized (D.I.) water rinse (to discharge line)
- 18. Forced air dry

In the first 17 steps, racks of PWBs are moved from tank to tank with an automated hoist. All the rinses are single flow through, which generates more wastewater than does cascading or multiple-use rinses. Because of dragout, the rinse following the EC bath (Step 11) receives complexed copper from the bath. This complexed copper, which is discharged with the rinse water, is hard to treat by typical metal hydroxide precipitation. Rinse water from the EC process is collected in one of three drain lines; one to a discharge line, another to the first ion-exchange collection system, and the third to an ion-exchange system for the EC rinse. Whereas the EC process is essentially a batch process, the carbon-black process is a continuous system in which parts are placed on a roller conveyor. This carbon-black dispersion technology, termed BLACKHOLETM technology by the vendor/

- ing 11 process steps: 1. BH™ cleaner
 - 2. Rinse (water from step 4, to discharge line)

inventor, consists of fewer baths and a

simplified process. It has only the follow-

- 3. BH™ conditioner
- 4. Rinse (fresh tap water, to rinse #2)
- 5. BH™ bath
- 6. Dryer
- 7. Microetch
- 8. Rinse (water from step 10, to ion exchange system)
- 9. Anti-tarnish
- 10. Rinse (fresh tap water)
- 11. Dry

The BH™ bath (Step 5) is an aqueous, carbon-black dispersion, which eliminates the need for electroless copper metallization before electrolytic plating. The steps before and following Step 5 are similar to those used in the EC copper process.

Unlike the EC process, with BH™ technology the rinse after the microetch process step is the only rinse water stream that goes to the ion-exchange system, which is shared with the first ion-exchange system for the EC process. The rest goes to the discharge line. The carbon-black dispersion process uses only two rinse

water flows, and the process solutions contain nonhazardous materials.

Waste Reduction Evaluation

The amount of waste resulting from the EC operation, run at full production, was evaluated to represent baseline data. The amount of waste from the carbon-black dispersion process using BHTM technology, run at full capacity, was then compared with this baseline. The wastestreams from both processes consisted of the bath solutions (discarded periodically) and the rinse water. The volumes of these wastestreams were obtained from plant records (bath volumes) and field measurements (rinse-water flow). The pollutant content of the bath solutions was estimated from plant records of the chemical makeup of the baths. The pollutant content of the rinse water was obtained by analyzing samples collected during field testing. Measurable factors in analyses to characterize the rinse water included copper, pH, and total solids content.

Samples from both processes were obtained to analyze the pollutants in the rinse water. Six sample sets for the electroless copper line and 11 sample sets for the carbon-black dispersion process line were taken over 4 days of operations. Composite samples were required to allow for the cyclic concentration swings of the rinse water caused by the batch rinsing operations of the racks used in the electroless copper line. In contrast, the carbon-black process was continuous and reached steady state rather quickly, allowing for shorter composite sampling times.

The copper content in rinse water was measured with the use of inductively coupled plasma spectrometry by employing EPA Method 6010. Total solids were measured by EPA Method 160.3. Only pH measurements were taken in the field; these were taken with a pH meter.

Rinse tanks were used as receiving vessels to determine the rinse-water flow rates of the two processes. After the rinse-tank outlet had been plugged, a stopwatch measured the time required to raise the water level by 2 in. The flow to each rinse tank in the process was totaled for all rinse-water flows listed in Table 1. This total flow and the material concentrations were used to determine the quantity of waste discharged in the rinse water from each process.

The production rate on the carbon-black dispersion process line using BH™ technology (i.e., 3.3 ft²/min) was found to be 2.1 times as fast as the production rate on the electroless copper (EC) process line

(i.e., 1.6 ft²/min). Production rates were timed during field testing and compared with production schedules maintained by McCurdy Circuits. The production rate of 8 hr/dav. 5 dav/wk, for 50 wk/vr assumed for this study is the approximate rate at McCurdy Circuits. McCurdy Circuits operates the electroless copper process at approximately the full capacity of 1.6 ft²/min, which yields 200,000 ft²/yr. The carbonblack process line, installed in response to increased demand, is currently operated at only about 11% of its capacity. Equivalent productions must be used to compare the waste types and quantities generated by both processes. In this study. because we assumed that the carbonblack process could completely replace the electroless copper process, the waste reduction estimates reflect the potential production of the carbon-black process at McCurdy Circuits, not the actual production. Tables 2, 3, and 4 generally show the chemicals used, costs incurred, and wastes generated as if each process were operated at capacity for 1 yr; the figures given for the carbon-black process are, therefore, adjusted to account for the fact that the carbon-black process would have processed twice the number of PWBs as the electroless copper process. In this way, wastes generated can be compared for equivalent annual productions.

As seen in Table 1, the BH process uses much less water than does the EC process. These water volume figures indicate that a smaller quantity of wastewater treatment chemicals would be needed because less wastewater would be generated.

Waste averages and standard deviations for copper and total solids were calculated, and a t-test was performed with a 95% level of confidence. The test statistic, which takes into account the standard deviations, indicated that the levels of both copper and total solids discharged by the BH process are significantly lower than those for the EC process. The average reduction in copper is 76 mg/ft², a reduction of 23%. The average reduction in total solids is 19,300 mg/ft², a reduction of 81%.

The BH process thus releases significantly less copper into the wastestream. If approximately 200,000 ft² of PWB (the operating capacity of the EC process) were run on both processes, the difference in copper waste would average 15.2 kg (33.4 lb)/yr.

The total solids discharge is reduced when the BH process is used. Although the higher solids composition of the BH baths would lead one to expect that this

Table 1. Rinse Water Flow Rates

Process	Operation Step	Flow Rate (gpm)	Destination
Electroless copper	2	2.5	To discharge line
• •	4	0.9	To ion exchange
	7	1.4	To discharge line
	8	6.0	To discharge line
	10	4.6	To discharge line
	12	1.6	To complexed ion exchange
	14	1.5	To ion exchange
	16	3.8	To discharge line
	Total	22.3	Ū
Blackhole™	2	2.9	To discharge line
	8	2.6	To ion exchange
	Total	5.5	•

process would discharge more solids, the faster production rate and fewer process baths containing chemicals apparently offset this effect when the data are normalized

Formaldehyde (a suspected human carcinogen that poses a significant health hazard when inhaled or ingested or through direct physical contact) is completely eliminated in the BH process, whereas approximately 200 gal/yr are used in the EC bath. Palladium and trace amounts of cyanide, also used in the EC process, are not present in the carbon-black dispersion process.

Economic Evaluation

The economic evaluation was based on data obtained from McCurdy Circuits, including the unit costs and amounts used of chemicals and water, and from suppliers. The current capital cost of carbon-black dispersion equipment was obtained from an equipment vendor. The calculations are based on the production rate of 200,000 ft² of PWB per year, approximately the rate of the current EC system. The BH process cost basis is half a year, running at capacity, i.e., the time it would take to process approximately 200,000 ft² of PWB.

Annual chemical usage and cost for both processes are shown in Table 2. As seen in Table 3, the summary of major operating costs, BH has lower operating costs than does EC in all cost categories that could be obtained from company data. The major savings accrued through lower chemical and labor (time) costs, and the total savings added up to more than 50%.

BH equipment having the capacity of the system tested at McCurdy Circuits currently costs \$212,000 (in 1992 dcllars), with an estimated installation cost of \$9,000. The payback period is less than 4 yr, with an assumed cost of capital of 15%.

Product Quality

The ability of the carbon-black dispersion process using BH technology to meet product quality and performance requirements was evaluated based on results of previous tests done in accordance with the Military Standard MIL-P-55110D requirements for through-hole plating and internal testing done by McCurdy Circuits. No additional testing was conducted during this evaluation because the tests involve destructive testing of a number of PWBs and are time consuming.

McCurdy Circuits routinely conducts internal quality checks of 10% of the PWBs. During these checks, small coupons are punched from selected PWBs, cast in resin, and polished to allow visual inspection of through-hole plating and layer bonding. Also, the PWBs are placed on a test grid that checks continuity of the circuits. These quality checks made by McCurdy Circuits and inspections by their clients verify product quality.

Discussion

In this study of waste-reduction potential of the carbon-black dispersion process using the BH technology, the process was found to reduce waste by reducing the number of process steps and the number of hazardous chemicals used in and wasted from the process as compared to the EC process. Table 4 summarizes the waste reduction achieved.

Rinse water use was reduced by a factor of eight. Chemical usage dropped considerably, and copper waste in the rinse water was reduced 23%. The only copper found in the carbon-black dispersion rinse

water was that removed from the PWBs during microetching. No additional copper was introduced in the carbon-black dispersion baths during processing. This does not take into account the copper lost due to replacement of the electroless copper solution. Each day, 20% of the 100-gal electroless copper bath is replaced. A copper solution concentration of 2 g/L removed from the bath results in a loss of 83.4 lb copper/yr, based on a 50-wk yr.

The quantity of total solids leaving with the rinse water was reduced by a factor of five because of the reduced use of rinse water and the fewer number of process baths. The reduced solids indicate that fewer bath chemicals are lost and that fewer chemicals are discharged to the wastewater treatment system.

The carbon-black dispersion process uses five chemical process baths and four rinse baths that do not introduce the hazardous metals and materials found in the EC process baths (formaldehyde, cyanide, palladium, and complexed copper). In addition to the positive long-term environmental aspects of carbon-black dispersion, eliminating the use of formaldehyde diminishes health risks to personnel and reduces industry's potential environmental liabilities. Reducing the number of process steps and quantities of chemicals reduces storage and transportation requirements, minimizes the possibility of leaks and accidental spills during storage and transportation, and results in economic savings too varied and intangible to be included in the analysis of economic fac-

The BH technology proved to be cost effective with the annual operating cost determined to be less than half that of the EC process and a payback period of less than 4 yr. Further, the option of converting electroless copper equipment to the carbon-black dispersion process would reduce the capital cost and result in an even faster payback period.

The energy costs were assumed to be almost equal for the two process lines.

The actual waste treatment costs at the test site were unavailable. In both processes, copper-containing wastewater is passed through an ion-exchange resin to remove the copper before entering the discharge line. The copper is eluted from the resin, recovered by electrowinning, and given away as scrap. A plant that operates a conventional wastewater treatment system consisting of pH adjustment and precipitation should realize a significant savings in treatment costs with the carbon-black process because of the reduced

Table 2. Annual Chemical Use and Costs

Description	Chemical Usage (gal/yr)	Unit Cost (\$/gal)	Cost (\$/yr)	Adjusted Cost (\$/yr)*
Electroless Copper		A / 7A	0.450	0.450
Acid cleaner Microetch:	145	21.70	3,150	3,150
Sulfuric acid	195	0.08	15.26	15.6
Sodium persulfate	1,800 lb	1.00 lb	1,880	1,880
Activator Catalyst:	2,500	3.35	8,380	8,380
Predip	15.9	3.35	<i>53.3</i>	53.3
Catalyst	21.8	280	6,100	6,100
Accelerator Electroless Copper:	393	18.65	7,330	7,330
Copper	3,950	10.35	40,900	40,900
Sodium hydroxide	2,250	2.50	<i>5,630</i>	5,630 1,220
Formaldehyde	199	6.20	1,230	1,230
Sulfuric Acid	<i>308</i>	0.08	24.6	24.6
Anti-Ox	1,250	11.95	14,900 Total:	14,900 \$89,600
Blackhole™				
Cleaner	41.2	400	16,500	<i>8,250</i>
Conditioner	41.4	400	16,600	8,280
Blackhole [™]	68.0	595	40,500	20,250
Microetch Sodium persulfate	1,130 lb	1.00	1.130	565
Sulfuric acid	13.2	0.08	1.06	0.5 3
Copper sulfate	50.0 lb	6.62	331	166
Anti-Tarnish				
CTCS 501	6.60	12.00	<i>79.2</i>	39.6
Sulfuric acid	3.30	0.08	0.26	0.13
			Total:	\$ 37,500

^{*} Because the BLACKHOLETM process has a production rate approximately twice that of the electroless copper process, costs were adjusted to compare a half year of processing for BLACKHOLETM to a full year for electroless copper.

Table 3. Comparison of Annual Adjusted Major Operating Costs*

Description	Electroless Copper	Blackhole™	Blackhole™ Savings, %
Chemicals	\$89,600	\$37,500	58
Tap water	3,200	403	<i>87</i>
D.I. water	503	<i>38.3</i>	92
Energy (b)	N/A	N/A	0
Labor	50,000	<i>25,000</i>	50
Waste disposal	N/A	N/A	0
Waste treatment labor	10,000	<i>3,330</i>	<i>67</i>
Totals	<i>\$153,000</i>	<i>\$66,300</i>	<i>57</i>

^{*} Because the BLACKHOLE™ production rate is approximately twice as fast as that of the electroless copper process, the costs are adjusted to take this into account. The BLACKHOLE™ costs reflect a half year of processing, whereas the electroless copper costs represent a full year.

Table 4. Summary of Waste Reduction

Waste Types	Electroless	Blackhole™	Net Change
	Copper Process	Process	in Waste
Rinse water	13.8 gal/ft²	1.7 gal/ft ²	12.2 gal/ft ²
Chemical use	11,755 gal + 38 lb	90 gal + 611 lb	not calculable
Copper waste	324 mg/ft²	248 mg/ft ²	76 mg/ft ²
(in rinse water) Total solids	23,800 mg/ft²	4,510 mg/ft²	19,300 mg/tt²

amount of copper waste. This option was not included in our evaluation.

In tests conducted by McCurdy Circuits, product quality of the carbon dispersion processed boards was similar to that of the electroless copper processed boards—boards from both processes were of acceptable product quality. In addition, PWBs using the BH carbon dispersion technology have passed MIL-P-55110D qualification and performance standards for plated through-holes.

Conclusions

Because the carbon-black dispersion process reduces wastes, avoids many hazardous chemicals and metals, is cost effective, and yields an acceptable product, it should be considered a viable alternative to the EC process. If the shop involved is a job shop, client input and requirements would be important in determining the feasibility of incorporating the carbon-black dispersion process. Although this study provides generalizations for com-

panies considering carbon-black dispersion, it is recommended that each company examine its specific requirements to determine the suitability of this alternative technology for specific applications.

The full report was submitted in fulfillment of Contract No. 68-CO-0003 by Battelle under the sponsorship of the U.S. Environmental Protection Agency.

D.W. Folsom, A.R. Gavaskar, J.A. Jones, and R.F. Olfenbuttel are with Battelle, Columbus, OH 43201-2693

Teresa Harten is the EPA Project Officer (see below).
The complete report, entitled "Carbon-Black Dispersion Preplating Technology for Printed Wire Board Manufacturing," (Order No. PB94-114 790/AS; Cost: \$17.50, subject to change) will be available only from:

National Technical Information Service

5285 Port Royal Road Springfield, VA 22161 Telephone: 703-487-4650

The EPA Project Officer can be contacted at: Risk Reduction Engineering Laboratory U.S. Environmental Protection Agency

Cincinnati, OH 45268

United States Environmental Protection Agency Center for Environmental Research Information Cincinnati, OH 45268

Official Business Penalty for Private Use \$300

EPA/600/SR-93/201

BULK RATE POSTAGE & FEES PAID EPA PERMIT No. G-35