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TITLE: **REDUCING THE EMISSION OF OZONE DEPLETING CHEMICALS THROUGH USE OF A SELF-CLEANING SOLDERING PROCESS**

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REDUCING THE EMISSION OF OZONE DEPLETING CHEMICALS THROUGH USE OF A SELF-CLEANING SOLDERING PROCESS

by

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ABSTRACT

Motorola has joined with Sandia and Los Alamos National Laboratories to perform work under a Cooperative Research and Development Agreement (CRADA) to reduce the use of CFC's and other ozone depleting printed wiring board (PWB) cleaning solvents. This study evaluated the use of a new soldering process that uses dilute adipic acid in lieu of rosin flux. The process consumes the adipic acid in lieu of rosin flux. The process consumes the adipic acid during the soldering process and precludes the need for subsequent cleaning with ozone depleting solvents.

This paper presents results from a series of designed experiments that evaluated PWB cleanliness as a function of various levels of machine control parameters. The study included a comprehensive hardware reliability evaluation, which included environmental conditioning, cleanliness testing, surface chemical analysis, surface insulation resistance testing, along with electrical, mechanical and long term storage testing.

The results of this study indicate that the new process produces quality, reliable hardware over a wide range of processing parameters. Adoption of this process, which eliminates the need for supplemental cleaning, will have a positive impact on many environmental problems, including depletion of the ozone layer.

INTRODUCTION

The destruction of the Earth's protective ozone layer is one of today's largest environmental concerns. Printed wiring board (PWB) cleaning solvent emissions have been identified as a primary contributor to this destruction. Industry has responded to this threat by developing new self-cleaning soldering processes, which eliminate the need for subsequent PWB cleaning. However, these processes have not yet been approved for military hardware applications. This paper describes a task designed to evaluate a new self-cleaning soldering process, and to prove that hardware produced by the process is acceptable for military applications.

The program is a joint effort undertaken by Motorola Inc., along with Sandia and Los Alamos National Laboratories. This work is being accomplished as part of a Cooperative Research and Development Agreement (CRADA) under the Department of Energy (DOE) Industrial Waste Reduction Program (IWRP). The objective was to evaluate the new process, solder hardware thereon, subject the hardware to environmental screening, and perform appropriate reliability testing and analysis. The data from these tests will be used to support approvals of the process for military hardware applications.

The program was approximately 75% complete in early December 1991. This paper describes the events that led to the undertaking of this program; the experimental approach and testing methodologies employed; the results from the experimentation and analysis thereof; and the conclusions based on the results-to-date. Post test analysis and supplemental testing was still in-process, the results there from will appear in a final report at the end of the program.

BACKGROUND

The impact of the emission of ozone depleting chemicals (ODC's) on the ozone layer is well documented. It has been estimated that one-fifth of these ODC emissions come from cleaning processes for PWB's and other electronic gear (Reference 1). In response to this environmental problem, industry has started using alternate solvents with lower ozone depletion potentials (ODP's); developed new, non-ozone depleting solvents such as terpenes; installed conservation techniques to reduce the emission of ODC's where alternate solution have not been discovered; and developed self-cleaning soldering processes. Conservation techniques and the use of lower ODP solvents are only short term solutions, as environmental legislation and cooperative efforts, such as the Montreal Protocol, are striving to eliminate all ODC usage by the year 2000.

Alternate cleaning solvents are not the optimal solution, as they still have negative environmental and economic impacts. These negative factors include: 1) the environmental impacts of procuring raw materials for cleaning equipment fabrication; 2) the large amount of energy consumption for conversion of these raw materials into fabrication materials, cleaning machine fabrication, cleaning solvent production and cleaning equipment operation; 3) the environmental impacts of disposal or reclamation of these alternative solvents; and 4) the economic impact of equipment purchase and operation, and solvent purchase, storage and handling.

There are several self-cleaning soldering processes that have been developed over the past few years. The process utilized in this study uses a dilute adipic acid board preparation solution, coupled with a formic acid vapor in a nitrogen cover blanket in the soldering zone.

Adipic acid is a white crystalline dicarboxylic acid material that is dissolved in anhydrous isopropyl alcohol for use as a flux. The typical concentration of the adipic acid for use as a board preparation material ranges from 1 to 3 percent. Adipic acid has been used as a fluxing material for several years within the commercial electronics industry.

The physical and chemical properties of adipic acid have been evaluated by a number of researchers to characterize the effects of the material after wave soldering (References 2, 3 and 4). The material has been used in commercial electronics assembly for several years, generally in modes that have not used cleaning after wave soldering operations. These applications range from under-hood automotive applications to cellular radio communications.

The adipic acid material used in this study was applied to the PWB's by an ultrasonic spray process. Much of the adipic acid is consumed during the soldering process. At the end of the process only a small percentage of the original amount of material remains on the circuit. During the preheat stage the adipic acid reacts to reduce the tin and lead oxides on the surface of the solder, like normal rosin fluxes. During the preheat period a small amount of the adipic acid is driven off and condenses on the cooler surfaces of the machine. Adipic acid is also driven off during the wave soldering operation.

Formic acid vapor is added to the process by bubbling nitrogen through a liquid formic acid solution. The amount of formic acid vapor introduced to the machine is governed by the nitrogen flow rate. The formic acid in the nitrogen cover blanket acts as an oxygen getter, thereby further reducing oxide formation in the soldering zone. The formic acid decomposes into CO_2 and H_2O due to the heat of the soldering process. An additional benefit of the inert atmosphere is the reduction of dross on the solder pot.

The wave soldering machine used during this program has several key features including three independent conveyors (flux, preheat and solder), a dual wave (turbulent chip and laminar), and an ultrasonic spray head for the board preparation fluid. This soldering process has many controllable parameters which influence visual solder quality and ionic cleanliness. These parameters include:

- flux conveyor speed
- preheat conveyor speed

- solder conveyor speed
- solder pot temperature
- wave angle
- turbulent wave on/off
- adipic acid percentage
- formic/nitrogen flow rate

Motorola uses several of these machines in their commercial divisions with very good success. In addition to improved solder quality, they are seeing improved product reliability. Figure 1 illustrates the reduction in failures observed in accelerated life testing of a commercial product.

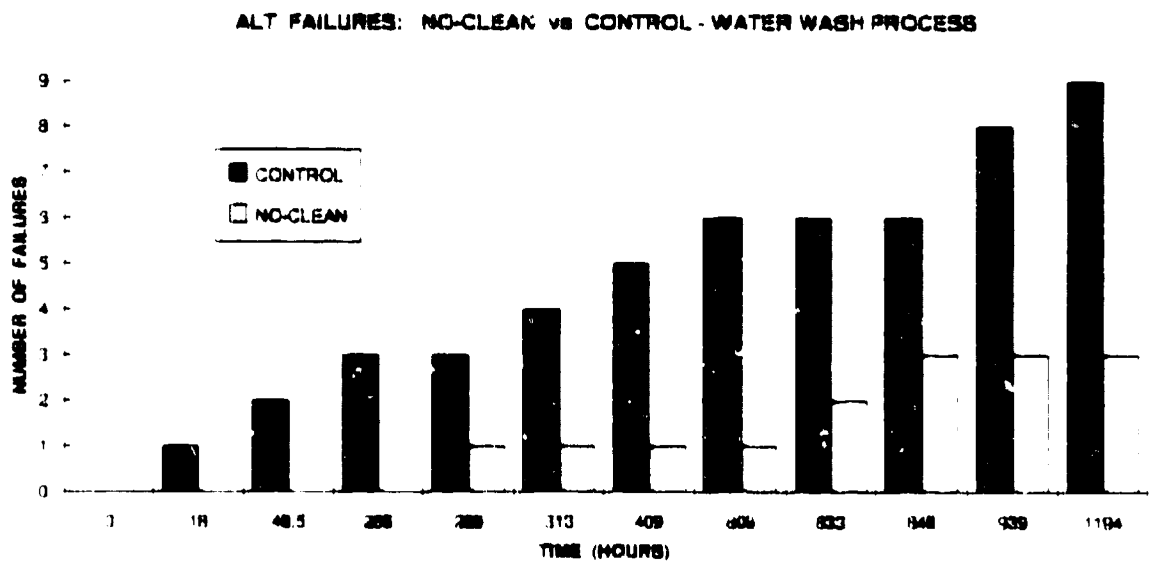


FIGURE 1. Self Cleaning Process Reduces Accelerated Life Test Failures

Military specifications and standards do not allow adipic acid as a fluxing material and mandate that PWB's be cleaned after soldering. Thus, in spite of the successes demonstrated by commercial entities, military contractors are currently prevented from using this new self-cleaning soldering process.

The purpose of the program described in this paper was to evaluate the new self-cleaning soldering process and produce data to show the process produces hardware that is as reliable as hardware solder with existing rosin flux/solvent cleaning processes. This data will be used to support requests for Government approval to use this process in the self-clean mode.

EXPERIMENTS

Recognizing that every different PWB design may have a different combination of soldering parameters to achieve optimal visual solder quality, experiments were performed to define a range of parameters that represented a broad process window. The objective was to understand how the combination of parameters within this window affected solder quality and ionic cleanliness. Hardware was fabricated and tested to demonstrate that any hardware soldered within the process window would be as reliable as the existing rosin flux process.

Specific test objectives were to demonstrate that the process could produce hardware that:

1. Meets the military specification limits for ionic cleanliness and surface insulation resistance;

2. Does not degrade during typical product environmental conditioning; and

3. Does not degrade with long term storage.

The multi-functional Motorola, Sandia and Los Alamos team personnel designed a series of experiments to meet these objectives. These experiments required three different PWB's: a general purpose board, a comb pattern board, and a functional test board. Details of how these boards were used in their respective experiments are described hereafter.

EXPERIMENT 1 – LONG TERM STORAGE VALIDATION

This experiment required a functional board whose performance could be physically measured, and visually inspected, after being subjected to simulated long-term storage testing. An FMU-139 PWB was selected for this purpose.

The FMU-139 is a general purpose bomb fuze, currently being built at a rate in excess of 500 fuzes per day, for Navy and Air Force applications. This is an 0.093 inch thick double-sided board, currently being soldered with a rosin flux/solvent cleaning process.

An initial screening experiment was performed to understand the impact of process parameters on the solder quality and ionic cleanliness of the 0.093 inch thick board. The five soldering process parameters evaluated in the experiment are shown in the following table.

Table 1. Initial Screening Experiment Parameters for 0.093 Inch Thick PWB

Factors	Levels	
	Low	High
Flux conveyor speed	0.8	1.1 meter/min.
Preheat temperature	80	120 deg C
Time in solder pot	3	6 sec.
Adipic acid concentration	1	2 %
Presence of Formic acid	none	7 liter/min.

Please note that the time in the solder pot and preheat temperature are governed by their respective conveyor speeds. The wave angle, solder pot temperature and turbulent wave status were held constant. A half-fraction of a 2^5 factorial experiment was designed, yielding a 16 cell experiment (a cell is a unique combination of process settings). One board per cell was used to gather this preliminary data. The data from this experiment was analyzed using several statistical software packages. The output from these analyses provided information that helped define the soldering parameters for the long term storage test boards.

An analysis of variance (ANOVA) was calculated for those factors influencing visual and cleanliness of the boards after wave soldering. The most significant effects influencing cleanliness and visual defects are reported in the order of their listing:

Cleanliness influence:

Single factor effects:

- Preheat (high level)
- Time on solder pot(high level).

Two factor interaction effects:

- Flux conveyor speed (low level) and preheat (at high level)
- Preheat and adipic acid concentration (both at high level).

Visual defects influence:

Single factor effects:

- Time on solder pot (high level)
- Preheat (high level)
- Adipic acid concentration (high level).

Two factor interaction effects:

- Flux conveyor (low level) and adipic acid (high level)

- Preheat (high level) and adipic acid (high level)
- Time on solder pot (high level) and Formic acid (high level)

On the basis of this analysis, three different parameter combinations (three cells) were selected to produce three sets of boards: one with good solder quality and ionically clean; one ionically dirty (cleanliness $\geq$ 20 $\mu g/in^2$) with marginal solder quality; and one with in-between cleanliness and solder quality. The three factors varied were flux conveyor speed, preheat temperature and time in the solder pot. The adipic acid and formic flow rate were held at the high levels. In addition to soldering three cells in the self-clean mode, a control sample of boards was soldered using the existing optimized rosin flux soldering/solvent cleaning process. Sample boards from each cell, including the rosin boards, were measured in the ionograph.

The FMU-139 Fuze was designed for 10 years of storage. However, the long term storage test was designed to simulate 20 years of storage to examine the process margin. A modified Arrhenius rate equation as shown below was used to calculate the test acceleration factors.

$$\frac{t2}{t1} = \text{EXP}\left[\left(\frac{\phi}{K}\right)\left(\frac{1}{T2} - \frac{1}{T1}\right)\right]\text{EXP}\left[\beta\left(\frac{1}{RH2} - \frac{1}{RH1}\right)\right]\frac{A\,E_{C2}}{A\,E_{C1}}$$

Where:

t2	= accelerated test time	
t1	= simulated time (20 years)	
ϕ	= Activation Energy (eV)	
K	= Boltzmann's Constant (8.63×10^{-5} eV/°K)	
T2	= Accelerated Aging Temperature (°K)	
T1	= Normal Temperature (°K)	
β	= Humidity Acceleration Constant	
RH2	= Accelerated Aging Relative Humidity (%)	
RH1	= Normal Relative Humidity (%)	
A	= Voltage Acceleration Constant	
E_{C2}	= Accelerated Electric Field In Corrosion Region (V)	
E_{C1}	= Normal Electric Field In Corrosion Region (V)	

Although temperature, humidity and voltages can be used as acceleration factors, only temperature was selected for this test. This is because the product is a one shot device, that sits dormant in an ammo can with desiccant for storage throughout most of its life.

The boards were suspended vertically on a rack, which was placed in a temperature humidity chamber. The boards were subjected to an acceleration temperature of 80 deg C, and a relative humidity of 40% for 2522 hours, which was designed to simulate 20 years of storage. The boards underwent a production line electrical acceptance test at time = 0, 1, 10, 13.3 and 20 years (simulated).

EXPERIMENT 2 – RELIABILITY EVALUATION:

This experiment required a PWB with through-hole components. The boards were subjected to ionograph testing, visual examination, and electrical and mechanical solder joint testing after environmental conditioning. Figure 2 shows a Motorola test board (MTB) that was selected for this experiment. This board contains axial, DIP, and TO-99 components, along with a connector. The MTB was designed to support soldering process optimization studies, and contains numerous features including various hole-to-lead ratios, and different ground plane-to-solder pad combinations.

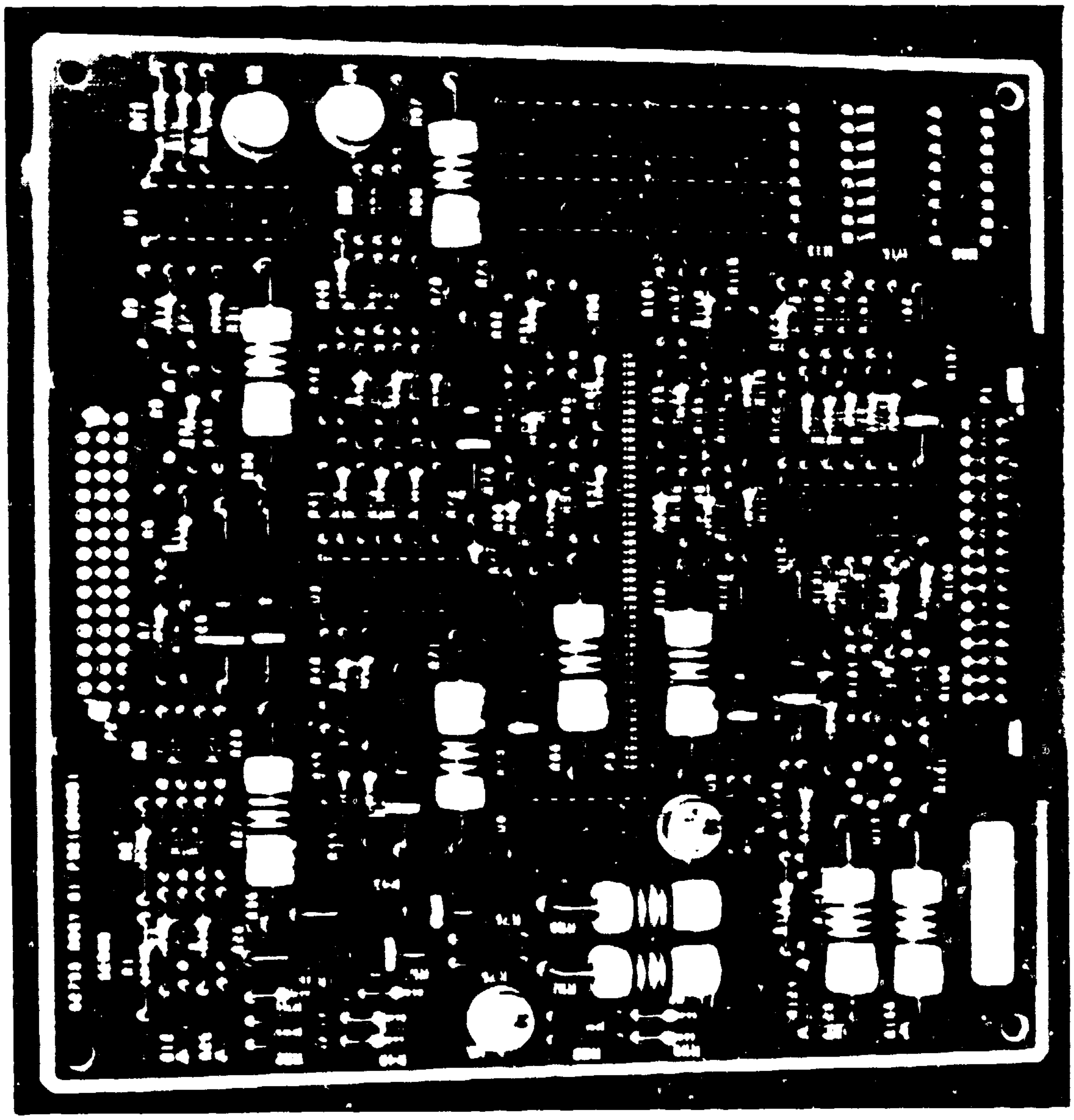


FIGURE 2. Motorola Test Board Used For Reliability Evaluation Testing

An initial screening experiment was performed to understand the impact of process parameters on the solder quality and ionic cleanliness of the 0.062 inch thick MTB PWB. The five soldering process parameters evaluated in the experiment are shown in Table 2. The adipic acid was held constant at 2% and turbulent wave was left on.

Table 2. Initial Screening Experiment Parameters for 0.062 Inch Thick PWB

Factors	Levels	
	Low	High
Flux conveyor speed	0.8	1.2 meter/min.
Preheat temperature	90	130 deg C
Time in solder pot	1.5	4 sec.
Presence of Formic acid	none	7 liter/min.
Wave Angle	5	9 deg
Solder pot temperature	245	260 deg C

A 2^6 full factorial experiment was designed, yielding a 64 cell experiment (a cell is a unique combination of process settings). Two boards per cell were used to gather preliminary data. These boards were visually examined for solder joint quality and had their contaminant levels measured in an ionograph. The data from this experiment were analyzed using several statistical software packages. The output from these analyses provided information that helped define the soldering parameters for the Reliability Evaluation test boards.

An analysis of variance (ANOVA) was calculated for those factors influencing visual and cleanliness of the boards after wave soldering. The most significant effects influencing cleanliness and visual defects are reported in the order of their listing:

<u>Cleanliness influence</u>:

Single factor effects:

- Time on solder pot (high level)
- Preheat (high level)
- Flux conveyor speed (high level)

Two factor interaction effects:

- Flux conveyor speed and preheat (both at high level)
- Preheat and time on solder pot (both at high level).

Visual defects influence:

Single factor effects:

- Formic acid presence (high level)
- Wave angle (high level)

Two factor interaction effects:

- Formic acid (low) and solder temp (high)
- Wave angle (high) and formic acid (either level)
- Preheat (low) and solder temp (high)
- Preheat (low) and formic acid (low)

The flux conveyor speed, preheat temperature and time in the solder pot were selected as the variable parameters for the reliability evaluation test hardware on the basis of the screening experiment. The remaining parameters were fixed at their respective high levels. A lower adipic acid percentage, lower formic acid flow rates, alternate wave angles or solder pot temperatures should not adversely impact board cleanliness. The selected combination of variable and fixed parameters were thought to best define an overall process window that would produce reliable hardware. The statistical analysis of the screening experiment data suggested that a wider range of the selected variable parameters levels should be used. The new levels of the varied parameters are shown in the following table.

Table 3. Reliability Evaluation Experiment Soldering Parameters

Factors	Levels	
	Low	High
Flux conveyor speed	0.7	1.4 meter/min.
Preheat temperature	85	130 deg C
Time in solder pot	1.0	4 sec.

A 2^3 factorial experiment was designed, utilizing the three varied soldering parameters, this yielded an eight cell experiment. An additional set of boards was soldered using the traditional rosin flux process, followed by a solvent cleaning operation. The performance of the self-cleaning process boards was compared to the rosin flux boards throughout all tests. Sample boards from both processes had their ionic cleanliness measured on a Model 500 Ionograph.

An attempt to measure free adipic and formic acid residues on the boards was made using the IPC Honeywell Procedure 355 for HPLC analysis for conventional solder residue component determinations (e.g., abietic acid, neoabietic acids, Pb and Sn salts of these acids). Although this procedure works well for conventional solder fluxes, the uncomplexed formic and adipic acids are only sparingly soluble in the acetonitrile solvent used for elution. Regardless of this limitation, modifications to the IPC Honeywell 355 procedure were developed that allowed an analytical detection limit of ≅40 μg cm^{-2} for adipic acid to be achieved. An ASTM procedure for hydrocarbon greases and oils was followed for determinations of residual contaminates on an identical set of boards. This procedure entailed washing the solder side of the board with 113 Freon and monitoring the absorbance of the CH stretch region in a long (0.5-2.0 mm) path length liquid IR cell.

A suite of pre and post-mortem surface analytical techniques have also been utilized to examine the state of initial surface cleanliness and corrosion products following long term storage. These methods have included optical microscopy, electron microprobe analysis (EMPA), scanning Auger microscopy (SAM), imaging secondary ion mass spectroscopy (SIMS), and small area Fourier transform infrared spectroscopy (FTIR).

The effects of corrosion on the soldered PWB's and solder joint electrical and mechanical integrity were evaluated by subjecting boards to temperature-humidity and temperature cycle testing. The temperature-humidity testing followed the specification MIL-STD-331B, Table C1-2. The temperature cycling experiment was a custom designed test with a low temperature of -54 deg C, and a high temperature of +71 deg C. The boards were subjected to over 40 cycles, with 2 hour dwell times at temperature extremes, and a 2 hour ramp rate between extremes.

The corrosion evaluation included visual inspection, followed by surface analysis of any noted residues. The PWB's had the electrical resistance measured through five different solder joints per board. The resistance was measured by probing the joint using a four point Kelvin measurement technique. Two probes were placed on the bottom of the joint, and two on the lead on the top side of the joint, and the measured resistance was recorded. Mechanical joint strength was measured by pulling on select component leads and special pull test pins until failure.

Electrical and mechanical parameters were measured before and after environmental conditioning, and on control sample boards.

EXPERIMENT 3 – SURFACE INSULATION RESISTANCE EVALUATION:

The IPC B-24 printed wiring board was used as the test vehicle for surface insulation resistance (SIR) testing. This board was selected over the IPC B-36 board, which has a surface mounted IC thereon. The B-36 was not used because soldering of the IC on the board could introduce another contaminant, even if the board was cleaned after soldering of the part. Figure 3 shows a soldered IPC B-24 board. The unsoldered board is bare copper, except for the gold plated connector fingers

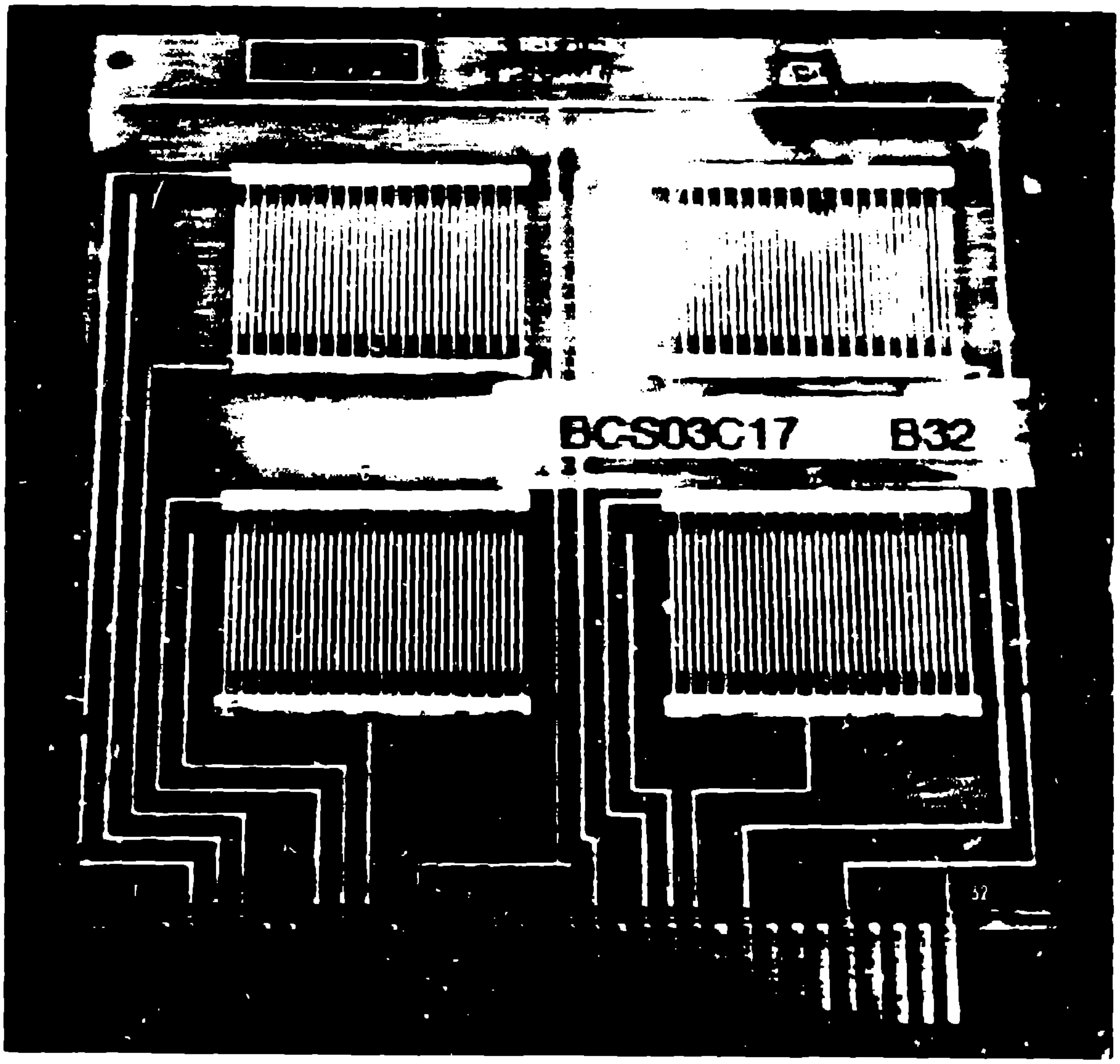


FIGURE 3. IPC B-24 PWB Used For Surface Insulation Resistance Testing

Approximately one-half of the IPC boards were pre-cleaned before soldering, in an effort to remove potential supplier contaminants. The boards were soldered at the same time as the Motorola test boards, with as-received condition and pre-cleaned boards being soldered in each of the eight cells. Similarly, a group of as-received and pre-cleaned boards were soldered with the rosin flux process, followed by a solvent cleaning. In addition, unsoldered PWB's, in the as-received condition were supplied for SIR testing. These boards had PWB supplier contaminants only

IPC test method 2.6.3.3. defines two different test conditions for SIR testing: 85 deg C, 85% RH; and 50 deg C, 90% RH. The standard test period is 7 days, with measurements at 4 and 7 days being evaluated. Both test conditions were used, with electrical measurements of the board's pattern A being taken at time = 0, 1, 4, 7, 14, and 21 days. Measurements were also taken at time 0 outside of the chamber, and after completion of the testing.

Additional boards were conformal coated and subjected to SIR testing at 65 deg C, 90% RH for 14 days, with measurements at time = 0, 8 hrs, 1, 2, 4, 7, and 14 days. These additional environmental test conditions are defined by MIL-I-46058C, as referenced in Appendix A to MIL-STD-2000A.

RESULTS AND DISCUSSION

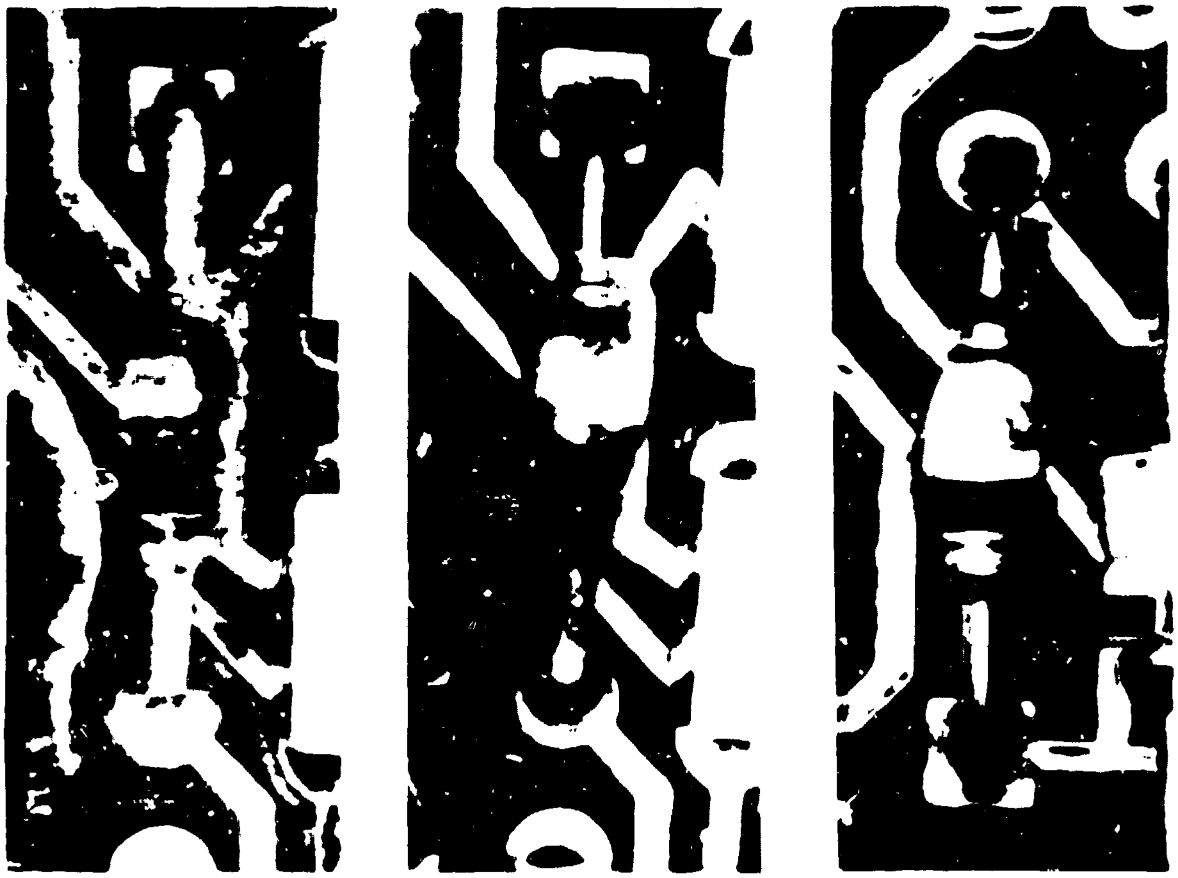
The results through early December 1991 have shown that the new self-cleaning soldering process is capable of producing reliable hardware, with visual solder quality equivalent to that achieved with existing soldering systems. Each of the three experiments supported these conclusions with very few anomalies noted.

LONG-TERM STORAGE TEST RESULTS

The long term storage testing compared hardware soldered with the existing rosin flux/solvent cleaning process to the new self-cleaning soldering process over a simulated 20 years of storage. Three different combinations of soldering parameters were used for the new process, in an effort to demonstrate that acceptable hardware reliability could be obtained when processed over a wide range of soldering conditions. Cell 1 PWB's had a solder visual quality similar to that experienced in production, and an average ionic cleanliness of 3 9 micrograms per square inch, as measured on an ionograph. Cell 2 PWB's had an average cleanliness of 3.7 micrograms per square inch and marginal solder quality. Cell 3 was deliberately soldered with conditions known to produce higher ionic contamination levels, and averaged 27 micrograms per square inch. This level is in excess on the MIL-STD-2000A ionograph machine acceptance limit.

Ten PWB's from each cell, and 10 rosin flux soldered boards, were functionally tested periodically during the long term storage testing. All 40 boards passed a production line electrical function acceptance test after t= 0, 1, 10 and 13.3 years (note: the product was designed for a 10-year shelf life). However after 20 years of simulated storage (2522 hours), three units had electrical performance anomalies.

The units with electrical anomalies were visually examined and found to exhibit physical damage to a particular type of ceramic body diode, and localized residue on the board. The remaining boards were examined, and a few were found to exhibit similar visual anomalies, despite being fully electrically functional. Figure 4A shows a damaged diode on a board from cell 1, which failed the electrical function test in one mode. Figure 4B shows similar damage to the same diode on a board soldered with rosin flux, followed by a solvent cleaning process. Figure 4C shows an undamaged diode of the same type. The diode damage phenomena appeared to be independent of the soldering conditions.



A B C

FIGURE 4. Eroded Diode Phenomena Was Also Observed On Rosin Flux soldered Boards A) Self Cleaning Soldering Process; B) Rosin Flux/Solvent Cleaned Process; C) Undamaged Diode

The residue on the board shown in Figure 4A appears to have run down the right side of the board. It appears that water dripped on the board when it was suspended vertically in the environmental chamber. A subsequent examination of the chamber revealed that water condensed on the sides and inside ceiling, and water was dripping down one side. The chamber was disassembled and found to have a bad float in its steam generator. It is suspected that the float failed sometime between 13.3 and 20 simulated years. If so, this would increase the chamber humidity and could cause water to drip along the edge of some of the boards. These conditions would dramatically change the environmental stress on the test samples.

The damaged diodes and residues are being subjected to a post test analysis to verify the suspected cause of the failures. This analysis will not be completed until early 1992, and therefore is not discussed in this paper.

Two extra boards from each cell, and two rosin flux soldered boards were conformal coated and subjected to 14 days of 65 C and 90% RH conditioning. No visual damage to the suspect diodes was noted, and no visible residues were observed.

RELIABILITY EVALUATION TESTING RESULTS

The Motorola test boards (MTB's) were soldered under eight different soldering parameter conditions. None of these boards exhibited any significant problems during subsequent evaluation testing. Figure 5 shows the average results from ionograph testing of five boards per cell, along with five rosin flux soldered boards. An average of 24.5 μg/in^2 for cell 1 boards exceeds the MIL-STD-2000A ionograph machine acceptance limit of 20 micrograms/in^2.

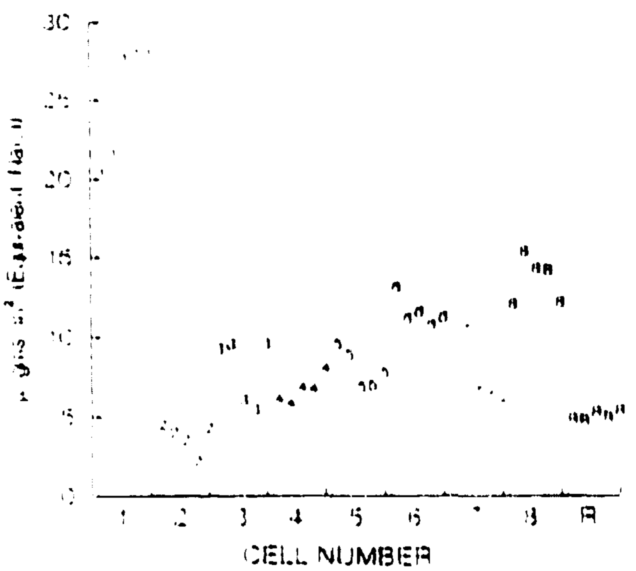


FIGURE 5. Ionic Cleanliness Was Function of Machine Soldering Parameters

Additional ionograph testing was performed by the Navy's EMPF facility in Indianapolis. They used an Ionograph Model 500 SM which employs a heated solution, and therefore should remove more contaminants. Table 4 compares their average results, per cell, to those ionographed at Motorola.

Table 4. Comparison of Motorola and EMPF Ionograph Readings

	ROSIN	1	2	3	4	5	6	7	8
MOTOROLA	5.12	24.45	3.7	8.02	6.78	8.04	11.60	7.7	13.64
EMPF	3.53	30.91	4.52	7.55	6.97	7.94	11.04	7.95	8.24

NOTES: Motorola used Ionograph Model 500
EMPF used Ionograph Model 500SM (heated solution)
Values are cell averages

Several MTB boards were set aside prior to environmental conditioning for analytical determinations for uncomplexed adipic and formic acid residues. All of the test boards examined showed that free adipic acid determinations were below detection limits (40 $\mu g/cm^2$) for HPLC testing. Additional boards were set aside for total residual hydrocarbon content. Free hydrocarbon contamination was barely detected (<2 $\mu g/cm^2$), on only 2 boards. It should be pointed out that the rosin flux soldered boards underwent a solvent cleaning after soldering, and that free formic and adipic acids are insoluble in the 113 Freon eluant used in this testing. Further tests using more appropriate elution solvents were in-process, in December 1991.

Figure 6 shows portions of the MTB boards that were soldered with rosin flux and with the self cleaning soldering process. Figure 6A shows a rosin flux soldered board at 7X, and Figure 6B the same board at 20X. Figures 6C and D show corresponding locations on a board soldered with the new process. The rosin flux soldered/solvent cleaned boards possess bright, clean solder joints, as expected using a well refined technology. The boards soldered with the new process exhibit some white deposits at the base of the solder joints, and in certain depressed regions of the PWB itself. Small area FTIR examination identified the presence of very low levels of adipic and formic acids in certain regions of a few boards. In other regions, the presence of very low levels of partially decomposed adipic and formic acids, and residues from the respective acids, have been spatially imaged using small area reflectance FTIR and SIMS.

FTIR analysis was also performed by the Electronics Packaging Technology Branch of the Product Assurance Division, at the Naval Weapons Center at China Lake California. They concluded that there appeared to be no significant residues, and that the little or no contamination is very encouraging.

Additional boards from each cell, and rosin flux soldered boards, were subjected to temperature-humidity or temperature cycling conditioning, in an effort to evaluate potential corrosion or internal solder joint integrity problems. A subsequent visual examination showed no copper corrosion, and limited amounts of residues as previously discussed. These boards were also subjected to electrical and mechanical testing.

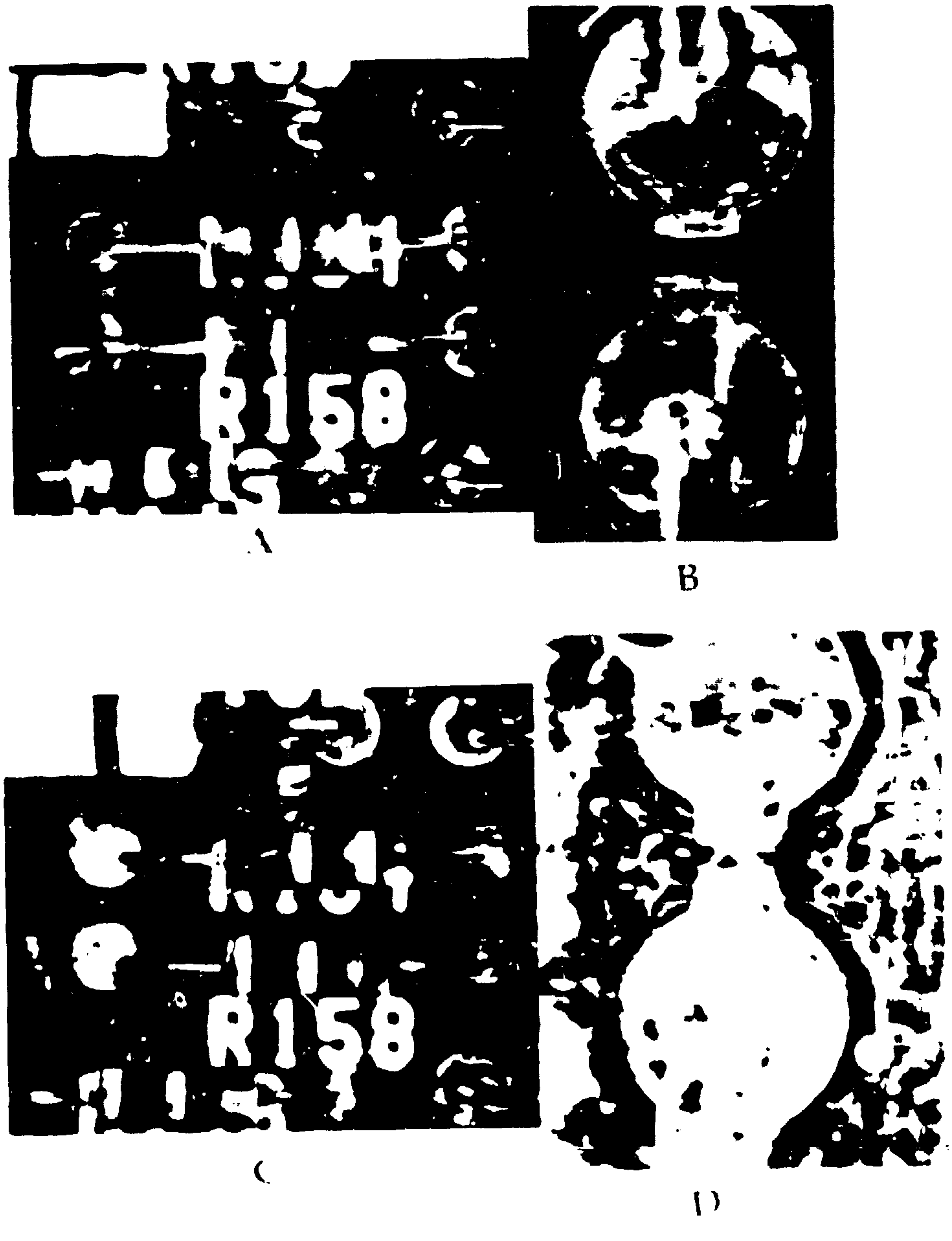


FIGURE 6. Small Amounts of Residues Were Noted on Some Boards

The electrical testing of internal solder joint resistances before and after environmental conditioning differed by less than 250 micro-ohms. There appeared to be no significant difference between boards soldered with the new adipic/formic acid process or the existing rosin flux process. Also, there appeared to be no significant differences between boards subjected to the temperature-humidity and those subjected to temperature cycle testing, or the control sample boards which had no conditioning.

The same boards were subjected to mechanical pull tests, which were designed to verify solder joint mechanical integrity. Component leads and specially designed pull test pins were pulled with all failures coming at greater than 40 pounds.

SURFACE INSULATION RESISTANCE TEST RESULTS

A total of 128 IPC B-24 boards were subjected to SIR testing, with only six boards having low SIR values after 4 and/or 7 days of testing. These boards and their respective test conditions are shown below. The average ionograph readings for MTB's, soldered under the same conditions, is provided as a reference.

Table 5. Select Parameters for Low SIR Value Boards

Cell No.	Pre-solder Status	Envir. condition	MTB cell ave. ionograph
cell 5	pre-cleaned	85 deg C, 85% RH	8.04
cell 8	as-received	85 deg C, 85% RH	13.64
cell 3	pre-cleaned	50 deg C, 90% RH	8.02
cell 8	pre-cleaned	50 deg C, 90% RH	13.64
rosin	pre-cleaned	50 deg C, 90% RH	5.12
cell 1	as-received	50 deg C, 90% RH	24.45

Overall, the SIR values look good, except for the few "bad apples" listed above. Figure 7 shows SIR values, by cell, for pre-cleaned boards, tested in a 50 deg C and 90%RH chamber, for measurements taken on day seven. Notice how the other boards in cells 3,5 and rosin are significantly higher than the their corresponding low readings. It appears the low board readings are independent of the soldering process or parameter levels. These low value boards are being subjected to post test analysis, which should be complete in early 1992. Despite a few low individual values, the average within any cell was in excess of the MIL-SPEC limit of 100 meg-ohms. Cell 1 had the lowest average, which was 105 meg-ohms.

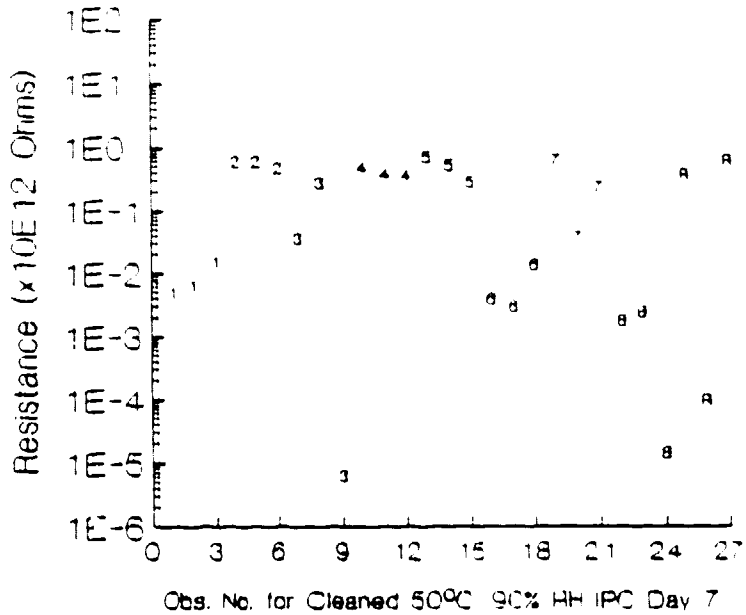


FIGURE 7. SIR Values Looked Good, Except for a Few Bad Apples

Figure 8 is a composite photo of the cell 1, low SIR value board. Figure 8A is an optical image of three of the fingers comprising the test comb pattern. The region outlined in Figure 8A was further examined using EMPA and SAM. The secondary electron image is shown with X-ray maps of Pb, Sn, and Br. Other elements were also analyzed, but were omitted for brevity. The data indicate that this portion of the board grew corrosion residue (10-50 microns thick), over the 21 days of the test (a factor of three over the required seven day test). This residue was determined to be primarily Pb and Sn oxides, intermixed with low levels (<2 wt. %) of Cl, S, and F. The residue is evident in nearly all of the SIR boards with low values.

Figure 9 shows the relationship between cell average ionograph readings and the cell average SIR values. These boards were soldered in the as-received condition, and were subjected to the 50 deg C, 90% RH testing condition. The SIR values were taken on day seven.

MIL-STD-2000A, Appendix A has a test method for qualifying alternate fluxes. Additional boards were conformal coated and subjected to the appropriate test conditions. There were no low SIR values in this group. Figure 10 shows the relationship between cell average SIR values and the temperature/humidity test conditions, on day four. The temperature of the test chamber appeared to have an impact on test values.

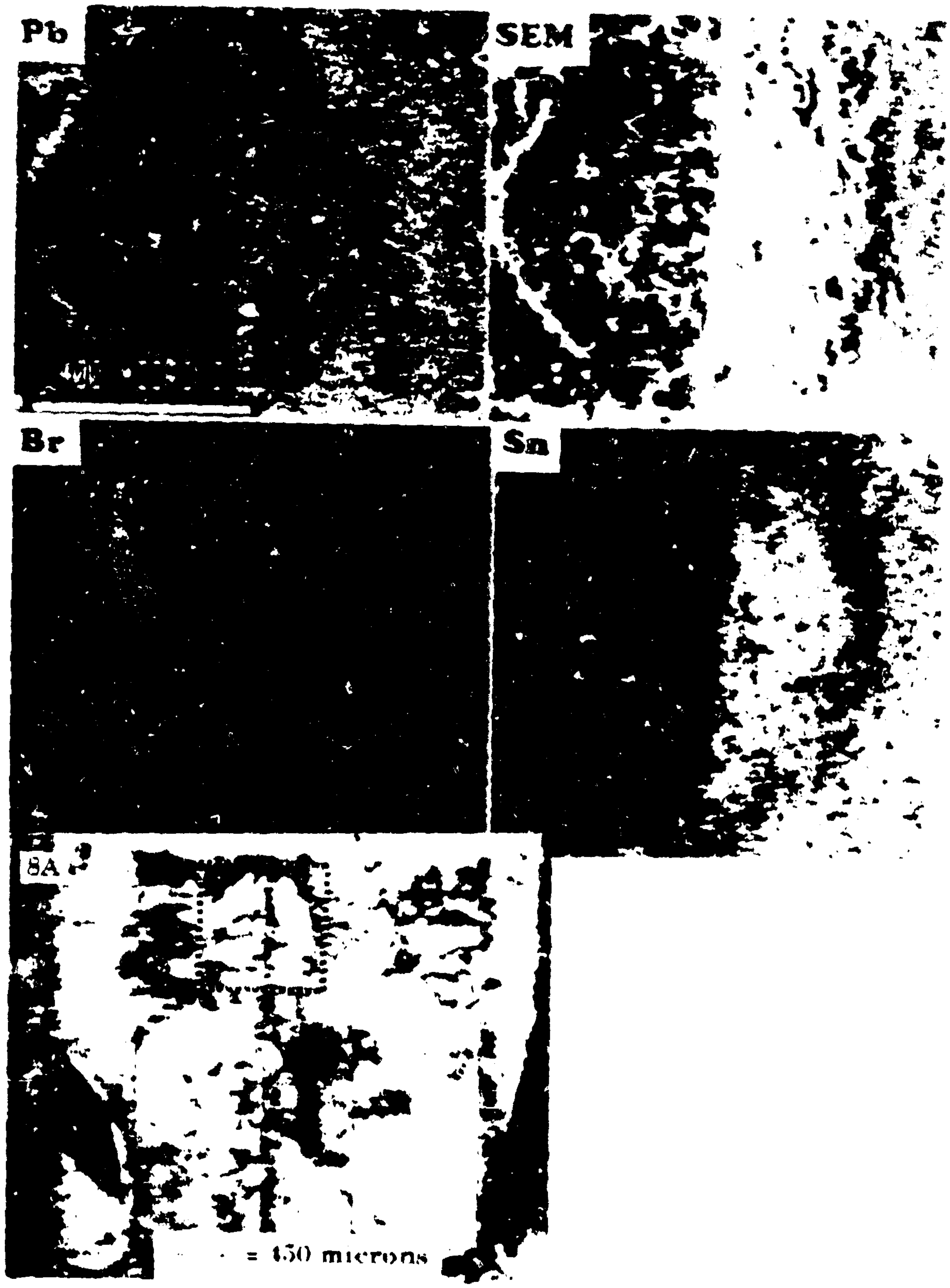


FIGURE 8. Primary Constituents of the Corrosion Spot Have Been Identified

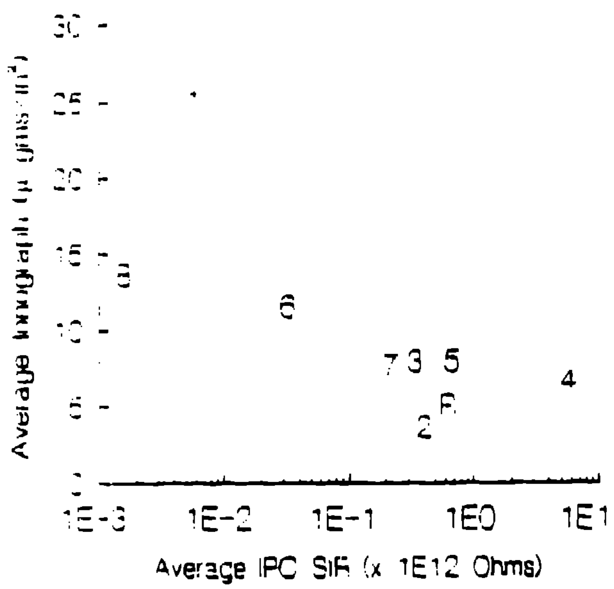


FIGURE 9. Higher Ionic Conductivity Tends to Reduce Surface Insulation Resistance

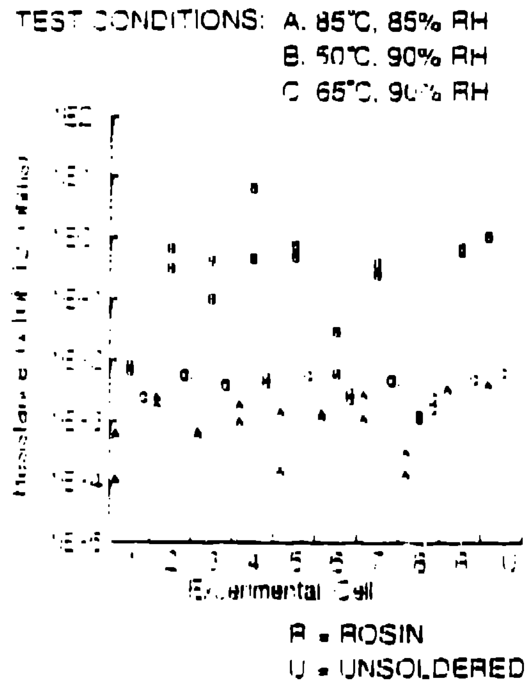


FIGURE 10. Test Temperatures Appear to Have a Larger Impact Upon Sir Values than Conformal Coating

CONCLUSIONS

The test results and analyses through early December 1991 indicate the self-cleaning soldering process will produce reliable hardware. The testing methodologies employed on this program proved sound, with testing parameters generally in excess of specification requirements. The response variables were measured in many ways beyond the usual ionograph and SIR testing. Long term storage, electrical, mechanical and surface analysis testing contributed to verifying the reliability of hardware soldered with the self-cleaning process.

Numerous conclusions were based upon this program's results, including:

1. Visual solder quality equivalent to the existing, optimized rosin flux soldering process could be achieved with the new self-cleaning soldering process. Additionally, the extra control features of the new process offer the potential of better results when the process is optimized.
2. The process produced reliable hardware over a wide range of process parameters. Boards with ionic cleanliness values in excess of the Military Specification limits still proved to be reliable.
3. Minimal residues were observed on hardware, and were judged to have no impact on hardware reliability.
4. Pre-cleaning of PWB's, prior to soldering, generally led to lower initial SIR values.
5. The new process will not degrade product shelf life.
6. The chemistry of the adipic acid solution is straight forward, consisting of a simple formulation of adipic acid and isopropyl alcohol. This provides a consistent material from lot-to-lot, with excellent reproducibility in properties. The advantage to the user is the elimination of dependency upon the addition of other activating agents typical of rosin fluxes.

In summary, this new self-cleaning soldering process appears capable of producing quality, reliable hardware, over a wide range of processing parameters. Adoption of this new process, which eliminates the need for supplemental cleaning, will have a positive impact on many current environmental problems, including depletion of the ozone layer.

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