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LLNL and TRW Extend Benchmark Environmental Stress Testing for Two Alternative Printed Board Cleaners

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ABSTRACT

TRW Corporation and LLNL jointly conducted a testing program to evaluate the effectiveness of non-CFC defluxing chemistries on printed boards designed for high-reliability military and aerospace applications. TRW assessed existing data for alternative chemistries, selected candidates for further testing, implemented the cleaning processes, and performed ionic conductivity testing on the spent solvents. LLNL designed and fabricated special circuit boards with interdigitated comb patterns to allow insulation resistance (IR) measurements under selected soldered components. LLNL designed the test and measurement setup and conducted accelerated environmental stress testing of flux residues for 28 days following cleaning. Statistical analyses of the IR measurements were correlated with visual observations and spectroscopic (FTIR) measurements.

Performance of the alternative chemistries was compared with that of a standard CFC cleaning agent also included in the test program. The program was designed to follow the same environmental stress and electrical measurement requirements as the IPC/DOD/EPA Ad Hoc Solvent Working Group's benchmark 7-day test plan, but with certain minor modifications and extension to 28 days.

Both alternative chemistries outperformed the CFC cleaner with respect to ionic conductivity measurements and to insulation resistance measurements recorded during the first 7 days of testing, but produced specimens that had greater observed quantities of residual flux. It was determined that neither ionic conductivity nor IR are good universal indicators of cleanliness, and that because of the encapsulating effect of solder flux resin on component land patterns, IR measurements were initially marginally better with more flux present. Effects of elevated temperature and humidity were thereby delayed, and became evident only during the extended (28-day) testing. The alternative chemistries did not work as effectively as the CFCs under surface-mounted components with minimal standoff height. Suitability of cleaners is therefore dependent on particular requirements, applications, or acceptance test methods.

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Introduction

The U.S. Government has agreed to adhere to the international agreement on the reduction and elimination of the production of ozone-depleting chemicals (ODC), known as the Montreal Protocol. Established in 1987, this United Nations environmental program originally called for a 50% reduction in the production of chlorofluorocarbons (CFC) by 1995, and a complete ban on CFC production by the year 2000. The Montreal protocol was revised at an international conference held in Copenhagen in November 1992. Based on 1986 production levels, the accelerated phase-out agreement called for reaching a 50% level by 1993, a 25% level at the beginning of 1995, and zero production by the end of 1995.

In 1993, TRW Corporation's Electronics Technology Division in Redondo Beach, California conducted testing of alternative cleaners for the removal of rosin-based solder fluxes from printed board assemblies (PBA). Their effort was based on benchmark testing previously performed by the Institute of Printed Circuits (IPC) / Department of Defense (DOD) / Environmental Protection Agency (EPA) Ad Hoc Solvents Working Group, which comprised a large number of representatives from industry, the military services, and government agencies.

TRW's Selection of Semi-Aqueous Chemistries to be Tested

TRW's purpose in conducting their tests was to select an alternative defluxing chemistry and the equipment to effectively use that chemistry to deflux PBAs specifically designed for spacecraft applications. They made a selection from already-proven chemistries, with the intention to retain the use of RMA flux and existing soldering processes in the manufacture of PBAs.

TRW assessed existing test data; health and safety considerations; environmental issues; and the reactivity of the solvents with PBAs, conformal coatings, and electronic components in both batch and in-line defluxing systems. Based on these assessments, they selected two candidate alternate chemistries for more extensive testing and evaluation: Dupont's Axarel 32 (a proprietary hydrocarbon) and Petroferm's Bioact EC-7R (a terpene-based solvent). TRW then developed a teaming relationship for a joint testing effort with the Waste Minimization Project and the Electronic Manufacturing Group at Lawrence Livermore National Laboratory (LLNL).

The TRW/LLNL Joint Testing Program

At the "Weapons Complex Alternative Cleaning Workshop" held in Phoenix, Arizona in December 1992, Michael Meltzer, LLNL's Waste Minimization Project Leader, made a presentation on some of LLNL's efforts to test and evaluate alternatives to ODCs. After the presentation, H.E. Arauco from TRW initiated a discussion about conducting a joint testing program with LLNL. Personnel from TRW and LLNL subsequently held a series of meetings, which resulted in the test program described in this article. In this program, resources and expertise were shared: TRW's manufacturing capabilities and cleanliness testing methods, and LLNL's non-destructive/non-intrusive surface analytical capabilities.

The basic purpose of the test program was two-fold:

- To obtain correlation to the Ad Hoc Solvents Working Group's Phase II benchmark test results both for the alternative cleaners selected for evaluation by TRW, and for baseline CFC cleaning using Freon 113.
- To obtain additional data to gain insight into the effectiveness of the alternative cleaners on various cleanliness parameters, and to determine their suitability for high-reliability military and aerospace applications.

LLNL Involvement

LLNL designed and fabricated special circuit boards that had conductors arranged into fine “comb patterns”. Figure 1 shows a representative land pattern with interdigitated comb patterns. These comb patterns allowed insulation resistance (IR) to be measured under selected soldered components. The boards were populated with electronic components of the type commonly used on TRW’s production circuit boards. TRW also used these LLNL-supplied boards for their third (final) round of cleaning tests and evaluations.

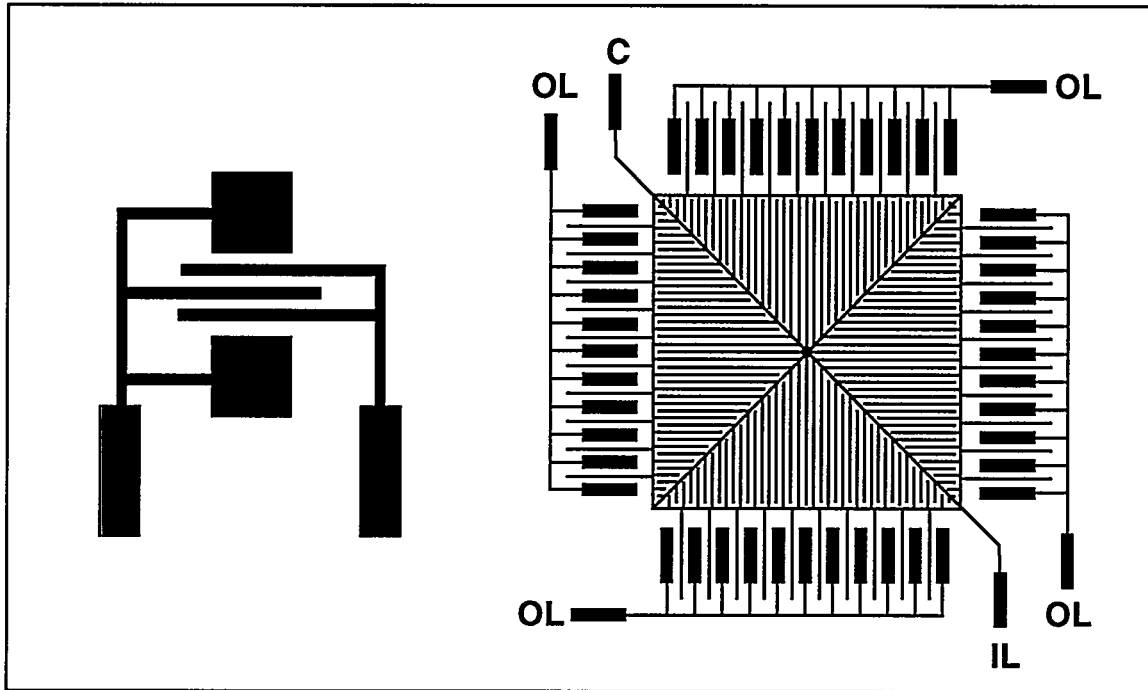


Figure 1. Interdigitated Comb Patterns for IR Measurement

LLNL performed environmental stress testing of the flux residues (after cleaning) while monitoring changes in IR. This data was used to determine the efficiency of the cleaning chemistry, assess long-term stability, and identify any corrosion problems associated with having RMA flux trapped under surface mount device (SMD) components.

Ionic Conductivity Testing

TRW tested the cleaned boards according to the requirements of MIL-STD-2000A. This specification requires removal of all visible flux residues. It also requires daily process control verification testing of sample boards for ionic contamination, and establishes the acceptance levels. MIL-STD-2000A specifies cleaning with a solution of 75% isopropyl alcohol (IPA)/25% deionized water (DI H₂O) in an approved ionometer test machine. Method of testing is not specified, so TRW chose the newer dynamic method, wherein a PBA is placed in a test chamber and sprayed while immersed in the IPA/DI H₂O solution. The test machine then pumps the solution out of the test cells through deionizing columns and the conductive ion content is measured and recorded.

Environmental Stress Testing

LLNL performed accelerated environmental stress testing by placing PBAs in a chamber at 85 °C/85% RH—first for 7 days, then for an extended period of 28 days. Corrosion was

thereby stimulated under the larger components to reveal any IR changes, such as might occur under normal conditions after a longer period of time.

Individual PBA test specimens were wired to test connectors and mounted in a holder as a subassembly. Up to ten of these subassemblies were then mounted in each racking tray and placed in the environmental stress chamber for testing, as shown in Figure 2.

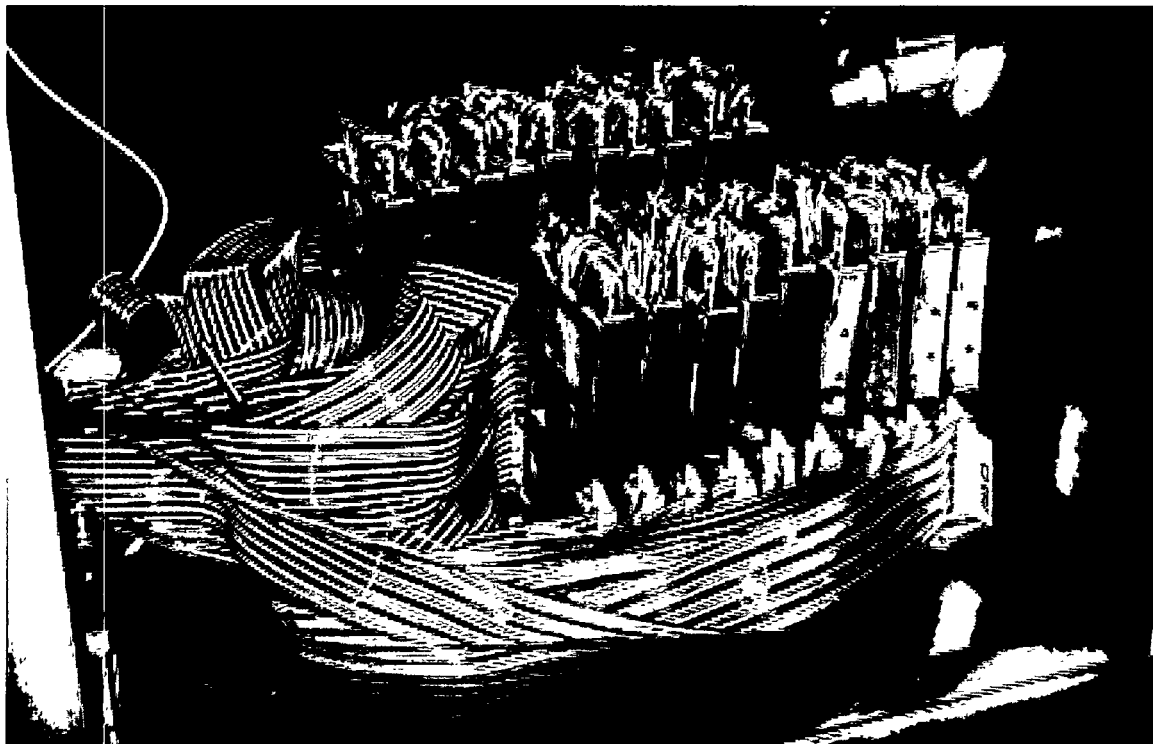


Figure 2. Environmental Stress Testing Setup

Testing Performed by TRW

Preparation of Test Article PBAs

TRW populated test article PBAs of various designs with dummy components, including the specially designed boards supplied by LLNL. The dummy components were both hand-soldered with brush-on RMA flux (Kester 197) and vapor-phase-soldered using solder paste applied onto the lands through a metal screen. Components included plated-through-hole devices, chip-capacitors, and small- and medium-sized "flat-packs". TRW used both gull-winged and J-leaded SMDs (the majority of TRW's recent production circuit boards have had a high percentage of SMDs).

Initial Semi-Aqueous (SA) Cleaning Test

Initial test-article PBAs were SA-defluxed at Electronic Control Devices (ECD) in Milwaukee, OR, and returned to TRW and LLNL for analysis. TRW measured the residual flux by spectrophotometry. RMA fluxes fluoresce visibly in ultraviolet (UV) light, and neither the Axarel or Bioact cleaners do, thus providing a quick and simple method for visual inspection. The UV/visible spectrophotometry yielded spectra for the residue consistent with pre-recorded spectra for the soldering fluxes, and gave reasonable measures of total residual flux left after the SA cleaning and ionic conductivity testing. Table 1 details

quantitative results for measured ionic conductivity (average on two PBAs) and for mass of residual Kester 197 flux (on each of four PBAs).

Table 1. TRW Cleaning Test 1 Results

Defluxing Chemistry	Average Ionic Conductivity, $\mu\text{g}/\text{in}^2$ (ROSE test)	Total Residual Flux, μg
Axarel 32	7.15	12-13
Bioact EC-7R	7.88	10-11
CFC-113	10.5	(not measured)

The 2 μg measured difference in flux residue is very small, especially considering that the PBAs in the initial test were not identical. The slightly better results obtained for ionic conductivity by Axarel in this test do not necessarily provide an accurate indication of Axarel 32's cleaning ability, since it was not heated to its optimum cleaning temperature in the 130 to 170 °F operating range. This was because the cleaning machine used by ECD did not have a heater installed. The Axarel was used at a temperature between 105 and 109 °F, whereas the Bioact solvent was used at 85 to 89 °F (within its normal range). The total residual flux data were also biased in favor of Bioact for the same reason.

Second SA Cleaning Test

TRW performed the second test on complex higher-level assemblies typical of the kind of production boards they expect to process with the alternative chemistries. The first type consisted of a Milstar power converter slice, the second a two-board RF slice, and the third a three-board digital slice. Three of the power converter slice assemblies were tested. These were very complex and had some hidden or mechanically shielded areas, presenting a "worst-case" exposure to potential water or solvent attack and water entrapment problems.

In this test, the Axarel 32 was also heated to about 138 °F to check how it would perform at a more effective defluxing temperature—one within its recommended operating range. Defluxing was conducted for 15 minutes, followed by three DI H₂O rinses prior to the ionic conductivity measurement made with the Omegameter model 600SMD ionometer (a model specifically designed for use with surface mount devices). The ionometer implements the so called "ROSE" (resistivity of solvent extract) test specified in IPC-TM-650, method 2.3.25. Table 2 gives ionic conductivity measurements for each assembly type, before and after defluxing with Axarel 32.

Table 2. TRW Cleaning Test 2 Results

Assembly	Ionic Conductivity—Before Defluxing, $\mu\text{g}/\text{in}^2$ (ROSE test)	Ionic Conductivity—After Defluxing, $\mu\text{g}/\text{in}^2$
Milstar Power Slice	65.8 (avg.)	9.9
RF Slice	14.4	3.0
Digital Slice	(not measured)	(not measured)

TRW electrically retested the three power converter assemblies to compare their post-cleaning performance with the pre-cleaning baseline performance measured earlier. No change was found for the power converter assemblies or the three-board digital slice assembly. However, the two-board RF slice assembly exhibited some degradation of grounding with respect to the chassis. (The impedance measured from the coaxial output connector to the frame holding the printed boards was higher than it should have been.) The cause for this could not be determined with certainty. Several conductive-epoxy grounded components were installed on the boards, so TRW suspected solvent attack on the 56-C type conductive epoxy and possible leaching of the conductive material away from grounding connections. However, subsequent examination determined that the machine screws holding the RF boards in their slice assembly had not been properly torqued, and that was more likely to have caused the poor grounding. It was noted in this test that Axarel 32 softened conformal coatings and black paint on the boards, removed some marking inks, and attacked pressure-sensitive tapes and labels.

Third (Final) SA Cleaning Test

Six identical boards supplied by LLNL were cleaned for the final test—three by Axarel 32 and three by Bioact EC-7R. Both solvents were used within their respective normal operating temperature ranges (Axarel at 146 °F; Bioact at approximately 85 °F).

After defluxing, ionic conductivity was measured, and UV/visible spectrophotometry readings were taken to determine the residual flux. Table 3 presents these measurements in average values calculated for each set of three boards (each solvent).

Table 3. TRW Cleaning Test 3 Results

Defluxing Chemistry	Average Ionic Conductivity, $\mu\text{g}/\text{in}^2$	Average Non-Volatile Residue, Extraction, mg
Axarel 32	2.37	2.6
Bioact EC-7R	2.43	3.6

Axarel outperformed Bioact, demonstrating slightly lower levels of ionic conductivity, residual flux, and non-volatile residue. These results were taken to be an accurate indication of the relative performance suggested earlier by the results of the initial test.

Testing Performed by LLNL

Design of the Test Program

LLNL designed its test program to follow the same environmental stress testing and measurement requirements as the IPC/DOD/EPA Ad Hoc Solvents Working Group's 7-day test plan. LLNL added a second phase, extending the testing to a total of 28 days in order to more fully characterize the effectiveness of alternative cleaners when subjected to more lengthy or more severe environmental stress.

The Ad Hoc Solvents Working Group's tests ramped the temperature and relative humidity to 85 °C/85% in 30 minutes. LLNL's test system required 6 hours to ramp up to the same environmental conditions, but the specimens were subjected to a full seven days (Phase I) at the elevated temperature and humidity, combined with electrical voltage stresses. LLNL made periodic IR measurements during the environmental stress sequence, which was used to accelerate aging processes. The test results are not really suitable for reliability modeling,

since there were a limited number of test specimens. Two specimens were cleaned with CFC-113, eight were cleaned with Axarel 32, and nine were cleaned with Bioact EC-7R.

Phase I Testing

Phase I testing began with a 2 hour "conditioning" step that subjected test specimens to a standardized environment of 25 °C/50% RH prior to the initial (reference) IR test measurements made at that temperature and humidity. Following this, the environment was ramped up as described in the previous paragraph, while a current-limited, 50 Vdc reverse bias voltage was applied to each of the specimens' IR test patterns. IR testing was performed after 24, 96, and 168 hours of environmental stress. The bias voltage was removed for a cumulative total of about four hours during these tests, but otherwise remained on continuously during the seven day period. After the final IR tests on day 7, the temperature and humidity were ramped down (in four hours), and final conditioning IR measurements were performed after another two-hour period at 25 °C/50% RH. At the end of Phase I testing, LLNL removed some of the specimens from the environmental chamber for surface analysis and tests, while the remaining specimens underwent phase II testing.

Phase II Testing

Phase II testing extended the 7-day environmental stress sequence for an additional 21 days (28 days total), with minor variations. The concluding IR conditioning step for phase I was used as the initial conditioning step for phase II. LLNL made IR measurements during the initial and final conditioning steps at the standardized environment, and after 8, 14, 21 and 28 days (cumulative) at the elevated temperature and humidity. The same bias voltage, temperature and humidity settings, and ramp-up and ramp-down times were used as in phase I. At the end of the 28 days, the phase II specimens were also removed from the environmental chamber for surface analysis and tests.

Insulation Resistance (IR) Measurement

The military specification requirement for printed board IR has been 0.5 GΩ or greater for decades. Industry requirements for IR have three different levels for different classes of product. Class 3 for high-reliability electronic products also establishes 0.5 GΩ as the minimum IR. Therefore LLNL and TRW chose 0.5 GΩ as the minimum acceptable IR for PBAs in the alternative cleaner test program.

LLNL reduced its test voltage and the time for insulation resistance measurements from the classical military values of 500 Vdc and 60 seconds, respectively. At 500 Vdc, the electrical gradient between conductive patterns was too severe for the 127 μm conductor spacing featured on the test article PBAs. LLNL performed the measurements using 100 Vdc, the same value used by the IPC/DOD/EPA Ad Hoc Solvents Working Group.

Although the solvents working group used a 60 second measurement time, LLNL was concerned that the 13 hours of total test time required to implement 60-second measurements could reduce the effectiveness of the 50 Vdc reverse bias voltage (removed manually for each measurement, then reapplied). To determine if the times could be shortened, LLNL recorded a series of 30 IR measurements with 10 second durations, and another series with times ranging from 10 to 60 seconds (in one second increments). Analysis of the resulting test data indicated that measured resistances were relatively stable after 10 seconds and did not differ significantly from the values recorded at 60 seconds.

For its actual IR testing, LLNL used a total measurement time of 15 seconds. Each measurement consisted of a 15-second application of the 100 Vdc test voltage to one of the IR test patterns on a PBA while current was monitored. A series of five IR samples (data points) were recorded on one-second intervals in each IR measurement, after the test voltage had been applied for 10 seconds. Values measured for each of the samples were

analyzed for range and slope to verify that the test data was asymptotic to the average of the five samples. All-in-all, 6000 data points were recorded for the 7-day testing sequence (Phase I), and another 3000 data points were recorded for the additional 21 days (Phase II). The recorded test data was edited to correct obvious errors (due to shorts caused by assembly operations or to transients caused by electromagnetic coupling to the cabling of the test and measurement system) that would otherwise skew results.

Visual Observations

Neither of the alternative cleaners produced boards that looked as clean as the CFC-cleaned specimens. Bioact EC-7R outperformed Axarel 32 in this respect, but it should be remembered that the Axarel-cleaned samples were processed at a below-optimum temperature for that solvent. Examination of residual flux and other materials revealed a wide variation in cleaning effectiveness. Nearly all of the PBAs had flux residues remaining on both base material and conductive patterns.

After components were removed from the test specimens, remaining surface contamination residues were identified, primarily under smaller components and under those with lower standoff mounting heights such as surface-mounted chip components. Some of the specimens exhibited a "shadowing" condition, a very thin white or light gray film that ran along the edges of or bridged between conductive patterns on the surface of the board, and in some cases coated large areas between conductive patterns. Variations observed in color density and location of the shadowing effect indicate that it resulted from the combination of residual surface contamination, elevated humidity, and the electric fields generated on the specimens by the bias voltage applied during the environmental stress sequence.

LLNL personnel performing the visual inspections made subjective evaluations (there was a consensus) of all of the specimens regarding the amount of residual flux observed. It appeared that the source for most of the residual flux was liquid solder flux applied during manual soldering operations. Liquid flux flows under components, filling the gap between the components (especially those with low mounting height) and the board surface. The flux tends to stay trapped there, making its removal more difficult during cleaning operations. This problem may have been accentuated by the high-density interdigitated comb patterns used under the components on the test article PBAs.

CFC-Cleaned Specimens

In general, the two CFC-cleaned specimens looked cleaner than those processed by either alternative cleaner. Most areas of the PBAs had little or no residual flux under the components (Figure 3). Some areas had minimal solder flux residues bridging the test patterns, while a few had massive residual solder flux.



Figure 3. CFC-Cleaned Test Specimen with Little or No Flux Residue

Axarel 32-Cleaned Specimens

The eight specimens cleaned with Axarel 32 appeared to have the greatest amounts of residual solder flux under the components. Many of the IR test patterns were clean, while others had small amounts of flux residue. Some of the IR test patterns had significant amounts of solder flux residues bridging the conductors, yet had very good IR test values (Figure 4a). Still other patterns had massive amounts of residual flux and exhibited a much greater spread in IR test values (Figure 4b). Some lands had large areas of thick flux residues bridging the IR test patterns. Shadowing was also found in or around many of the patterns.

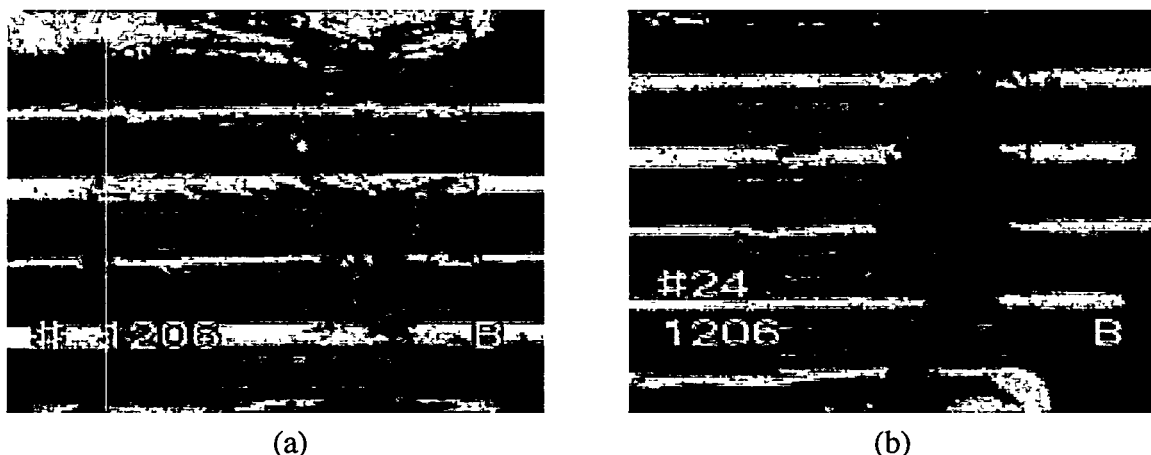


Figure 4. IR Test Patterns with Large Amounts of Solder Flux Residue

Bioact EC-7R-Cleaned Specimens

The nine Bioact EC-7R-cleaned test specimens ranked below the CFC-cleaned specimens but above the Axarel 32-cleaned specimens in visual cleanliness. However, they had a greater incidence of shadowing than specimens processed by the other cleaners. Figure 5a shows light shadowing over relatively large areas, with some increase in shadowing in areas of greater electrical stress. Several conductive patterns had a yellow tint caused by long, porous, film-like organic deposits (residual flux). These occurred more frequently in the leaded component land patterns (Figure 5b).

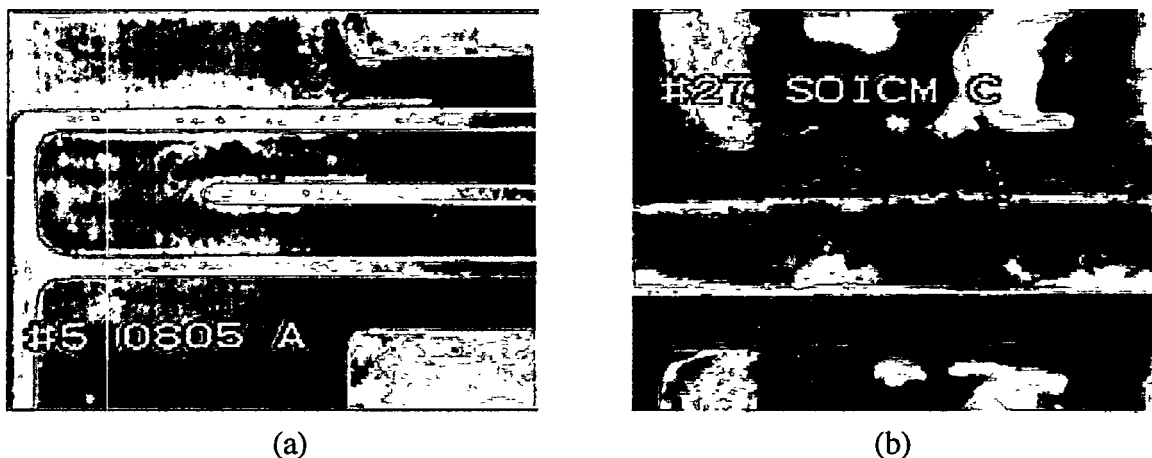


Figure 5. Shadowing and Organic Deposits

Electrical Test Results

Summary Comparisons

Electrical test results for the 7-day and 28-day testing were mixed. Figure 6 is a semi-logarithmic graph that plots the geometric mean of all IR measurements taken for each type of cleaner vs. time. The graph also includes the specified requirement as a reference line. The alternative cleaners had better IR test results for the 7-day period. However, the one CFC-cleaned specimen subjected to the 28-day period yielded IR measurements about an order of magnitude better than the nine specimens processed with alternative cleaners. This highlighted concerns about the statistical validity of the CFC test data. Individual analysis of the two CFC-cleaned specimens used in the 7-day environmental stress period lead to speculation that the one that continued on through the 28-day period was a "golden" or exceptional PBA.

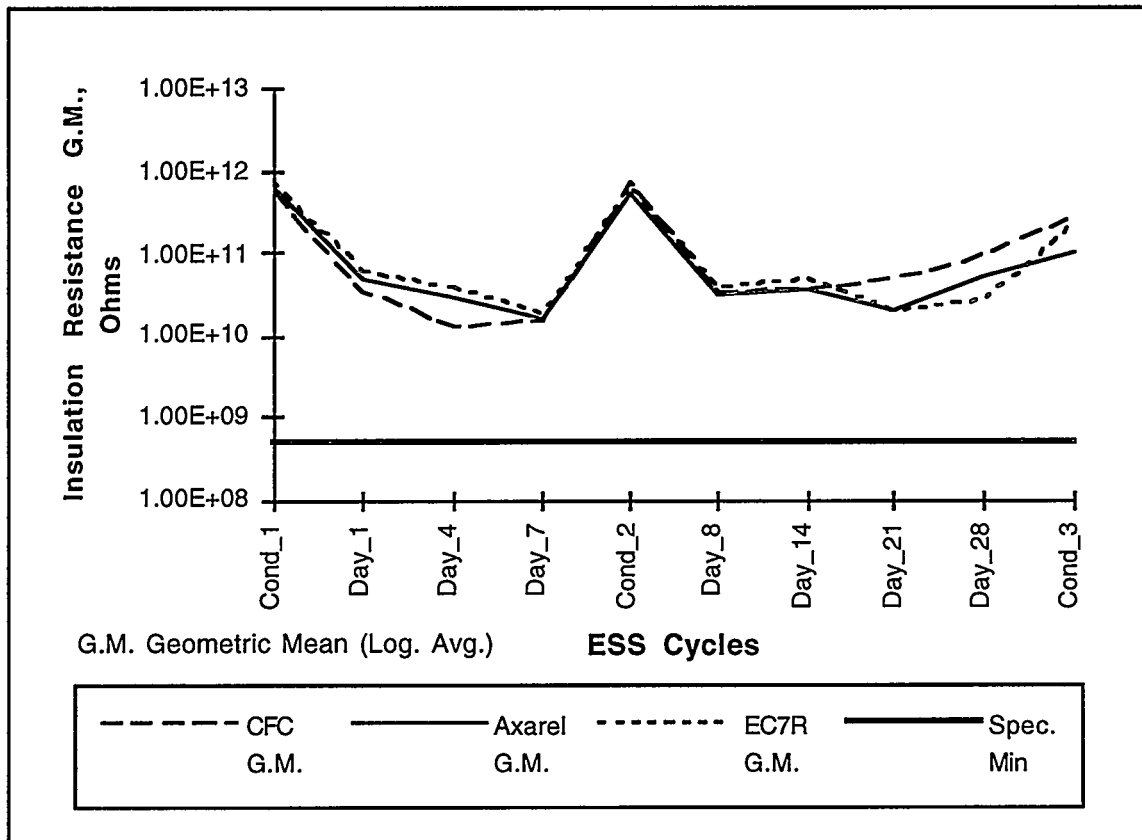


Figure 6. Geometric Mean of IR Data, Differentiated by Cleaner Type

Analysis of the IR measurements made under smaller components and larger components yielded plots similar to those shown in Figure 6. The shape of neither the 7-day nor the 28-day plot indicates any significant differentiation by component size. As expected, actual average IR values were somewhat higher under the smaller components, due to the differences in size of the IR test patterns.

Since the difference in test data between the smaller and larger components was less than an order of magnitude, but the average difference in the number of squares in conductive patterns between the small and large components was greater than 2-1/2 orders (about 700 times), the IR test results are not presented using the traditional $\Omega/\text{sq.}$ method. The test

data, though incomplete, suggests that IR does not have a linear relationship to number-of-squares, but may instead have a logarithmic relationship.

Figure 7 gives a combined (all specimens) summary of all IR test data, by median and quartile values. Note the good consistency in the data, with the exception of the minimum IR plot. The relatively narrow range of values between the maximum IR and the first quartile indicates the cleaning processes were reasonably well controlled for producing consistent IR measurements. The wide range of five orders of magnitude between maximum and minimum, though, could be a concern for the design of some critical electronic or electrical equipment. The differences in the range of IR data between the median and the first quartile, and between the first quartile and the minimum, indicates that only a few low IR measurements were responsible for the minimum IR values.

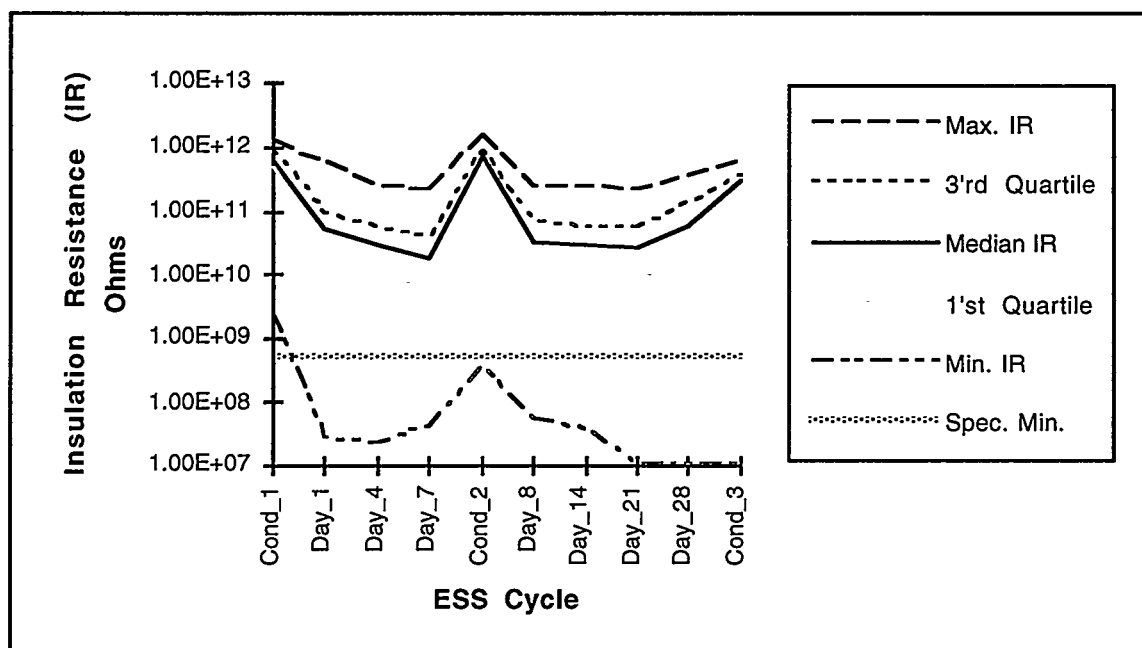


Figure 7. Summary of All IR Test Results, Median and Quartile Data

Individual Cleaners

Analysis of IR test data for the CFC-cleaned specimens indicates that for the two PBAs tested, IR remained relatively constant after the first day of environmental stress. For the Axarel 32 specimens, IR test data indicated a continuous reduction in IR up to the 14th day, at which time the values stabilized. The IR profile of the Bioact EC-7R-cleaned specimens has the same shape as for the Axarel 32 specimens, except for lower values measured during the first 7 days.

Interpretations and Conclusions

Both alternative cleaners produced better electrical IR test results than the baseline CFC cleaner. However, as a result of this test program, LLNL determined that IR was not a good general indicator of cleanliness. Visual examination after environmental stress and IR testing revealed that although several of the IR test patterns had varying amounts of residual flux under components, this had minimal effect on IR, since the flux was not sufficiently conductive to be measurable. In some cases, the measured IR was even marginally better with more residual flux present, because the solder flux resin encapsulated the IR test conductive patterns in the component land patterns, acting as a conformal coating or potting

would. The effect of elevated temperature and humidity were thereby delayed. This is also what will happen with no-clean fluxes. The electronics industry will need to establish requirements for IR cleanliness, and perhaps another set of requirements and acceptance test methods for assemblies that need high adhesion to its surfaces, such as for conformal coating.

Resistivity of Solvent Extract (ROSE)

The resistivity of solvent extract (ROSE) measurement from IPC-TM-650 method 2.3.25 is the national standard test method for determining PBA cleanliness. LLNL used a modified version of this method on one CFC-cleaned specimen, and on four specimens each cleaned with Axarel 32 and with Bioact EC-7R. The results are given in Table 4. All test specimens passed the MIL-STD-2000 cleanliness requirement.

Table 4. LLNL Measured Ionic Conductivity - ROSE Test

Ionic Conductivity, $\mu\text{g}/\text{in}^2$			
MIL-STD-2000	CFC-cleaned	Axarel 32-cleaned	Bioact EC-7R-cleaned
<10	5.5	3.7 (avg.)	2.5 (avg.)

Reflective Fourier Transform Infrared (Reflective-FTIR) Spectroscopy

LLNL performed reflective-FTIR spectroscopy on approximately one-half of the PBAs that were subjected to environmental stress testing. The following four steps were undertaken to identify residual surface contaminants on the test specimens' conductive patterns.

- Visually inspected PBAs to locate and identify obvious and significant conditions after specimens were removed from the environmental chamber.
- Removed all components from PBAs.
- Visually inspected specimens, correlating observations with corresponding IR test data obtained.
- Subjected residual surface contaminants located by visual inspection to reflective-FTIR surface analysis to identify composition.

This procedure was successful in identifying nearly all of the residual contaminants located by inspection personnel. A summary of the reflective-FTIR data and related observations is presented in Table 5.

Table 5. Reflective-FTIR Summary of Results

Cleaner Type	Description of Results
CFC	<p>Located several conditions visually for identification by FTIR. Most visual and FTIR identifications were in agreement.</p> <p>One residual contaminant visually identified as flux residue had an FTIR signature that was not an exact characteristic match for the chemicals that were reported to have been used for assembly. The residual material had the FTIR characteristics of a "modified flux".</p> <p>Identified a yellowish film on some of the conductor patterns as a hydrocarbon named carbonyl.</p>
Axarel 32	<p>Confirmed most residual contaminants to be flux residues.</p> <p>In several locations, globs and film-like streaks that were originally thought to be flux residues were identified by FTIR to be nylon.</p> <p>Other contaminating materials identified by FTIR were: hydrocarbons (carbonyl) and polyol.</p>
Bioact EC-7R	<p>Most residual contaminants were confirmed to be flux residues, but a significant number also contained nylon.</p> <p>Other contaminating materials identified by FTIR were: unidentified hydrocarbons; carbonyl; epoxy; hydroxyl; some materials with multiple -OH, C-H, and carbonyl molecular structures; and various combinations thereof.</p>

Comments: The presence of the FTIR-identified "modified flux" on the CFC-cleaned test specimen could have been caused by inadvertent use of a different flux during assembly of that particular PBA, or of one with a trace contamination. The rosin may also have chemically reacted or polymerized from heat or some other factor. The source of the nylon residue was from the adhesive of a temporary staking tape used to hold jumper wires in place during soldering. It was not removed by the alternative cleaners. Nylon was not found on the CFC-cleaned test specimen, but it is possible that no nylon was fused to that particular specimen's board surface. TRW has indicated plans to eliminate use of the nylon staking tape from their assembly procedures.

Final Conclusions and Recommendations

The joint TRW/LLNL testing program did obtain correlation to the benchmark testing previously performed by the IPC/DOD/EPA Ad Hoc Solvents Working Group. In general, results were mixed. Both alternative cleaners exhibited better performance than traditional CFC cleaners with respect to electrical insulation resistance measurements. They also produced lower levels of residual ionic contamination in the solvent extract measurements. From the visual examinations, however, LLNL determined that the alternative cleaners did not clean as effectively as the CFCs under surface-mounted components that had minimal standoff height from the PBA surface. Suitability of the cleaners is therefore dependent on particular requirements or acceptance test methods. None produced truly clean PBAs, and none can be considered effective for all requirements and situations. The test program did confirm that both alternative cleaners perform as good or better than the baseline CFC cleaner tested, according to established ROSE and insulation resistance measurement

methods. TRW and LLNL identified areas of concern that may not have been addressed by other alternative cleaner test programs. For example, the alternative cleaners outperformed the CFC cleaner in IR testing for the seven-day (Phase I) specimens, whereas the CFC cleaner fared better with the 28-day (Phase II) specimens. However, based on average data from the test results, there is not a major difference in the IR performance between the cleaners tested. It is apparent that all relevant cleanliness requirements must be specified, including visual, chemical, electrical, biological, and others. In addition, requirements for processes, equipment, procedures, and quality control all need to be considered and documented. Based on the results of this alternative cleaner testing program, we conclude that more testing is needed to establish a baseline of current cleaning processes for future requirements and comparisons.

Bibliography of Related Publications, Specifications, and Standards

Compatibility of Materials with Six Chlorofluorocarbon Alternative Cleaning Solvents, Honeywell Military Avionics Division, Honeywell, Inc., Minneapolis, MN

IPC-RB-276, *Qualification and Performance Specification for Printed Boards*, Institute for Interconnecting and Packaging Electronic Circuits, Lincolnwood, IL

IPC-TR-580, October 1989, *Cleaning and Cleanliness Test Program Phase I Results*, Institute for Interconnecting and Packaging Electronic Circuits, Lincolnwood, IL

MIL-STD-2000, *Standard Requirements for Soldering Electrical and Electronic Assemblies*, U. S. Department of Defense

MIL-P-55110, *Printed Wiring Boards*, U. S. Department of Defense

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