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Designed to Eliminate the Use of
Ozone-Depleting Chemicals*

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**EVALUATION OF NO-CLEAN SOLDER PROCESS
DESIGNED TO ELIMINATE THE USE OF
OZONE-DEPLETING CHEMICALS**

by

M. T. Paffett, J. D. Farr, Y. C. Rogers, and W. B. Hutchinson

ABSTRACT

This paper summarizes the LANL contributions to a joint Motorola/SNLA/LANL cooperative research and development agreement study on the reliability of an alternative solder process that is intended to reduce or eliminate the use of ozone-depleting chemicals in the manufacture of printed wire boards (PWBs). This process is termed self-cleaning because of the nature of the thermal chemistry associated with the adipic and formic acid components used in place of traditional solder rosin fluxes. Traditional rosin fluxes used in military electronic hardware applications are cleaned (by requirement) using chlorofluorohydrocarbons. The LANL contribution centers around analytical determination of PWB cleanliness after soldering using the self-cleaning method. Results of these analytical determinations involving primarily surface analysis of boards following temperature, temperature and humidity, and long-term storage testing are described with representative data. It is concluded that the self-cleaning process leaves behind levels of solid residue that are visually and analytically observable using most of these surface analysis techniques. The materials compatibility of electronic components soldered using the self-cleaning soldering process is more fully described in the project report issued by SNLA that encompasses the complete project with statistical lifetime and accelerated aging studies. Analytical surface specificity and suggestions for further work are also given.

INTRODUCTION

Alleviating the environmental destruction of the earth's protective ozone layer is one of today's largest pressing scientific and societal concerns. Solvent emissions that result from cleaning electronic parts such as printed wiring boards (PWB) are primary contributors to this destruction. Environmental legislation and international cooperative efforts, such as the Montreal Protocol, are striving to eliminate all ozone depleting chemical (ODC) usage by 2000. The electronics manufacturing industry has responded to this challenge by developing new self-cleaning soldering processes and by using alternative cleaning agents, which eliminate the need for subsequent PWB cleaning using chlorofluorohydrocarbons. However, military hardware applications demand unusually stringent cleanliness and reliability of manufactured electronic components. The new processes and alternative soldering processes and cleaning methods have not been approved for military application.

The program is a joint effort undertaken by Motorola Inc., Sandia National Laboratory and Los Alamos National Laboratory. 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. The objective was to evaluate the new self-cleaning soldering process and to prove that hardware produced by the process is acceptable for military applications. The breakdown of tasks under the CRADA is as follows: Motorola supplied the self-cleaning soldering hardware, PWB test bed manufacturing and some of the environmental testing; SNLA provided most of the environmental testing and statistical analysis of the component electronic reliability data; and LANL provided the analytical determinations of surface cleanliness and materials compatibility. The data from these tests will be used to support approvals of the process for military hardware applications.

The experimental approach and testing methods employed by LANL personnel are described herein. A detailed listing and discussion of the SNLA and Motorola portions of this program are not described in this report; these details can be found in the complete project result document.¹ This document is organized into the following sections: (a) background descriptions of the known procedural and chemical details of the self-cleaning soldering process, (b) analytical results of each aspect of the surface cleanliness program preceded by a brief description of the analytical method and information gained, (c) summary of the results obtained, and (d) suggestions regarding future work.

BACKGROUND ON THE SELF-CLEANING SOLDER PROCESS

Several self-cleaning soldering processes that have been developed over the past few years.²⁻⁴ The specific process utilized in this study deploys an ultrasonic spray of dilute adipic acid board-preparation solution over the advancing PWB coupled with a formic acid vapor in a nitrogen cover blanket extending into the soldering zone. This board preparation precedes the soldering process, and thermal heat from the soldering process may largely degrade these chemical components into innocuous by-products.

Adipic acid ($C_6O_4H_{10}$) is a white, crystalline dicarboxylic acid that is dissolved in anhydrous isopropyl alcohol for use as a flux. The typical concentration for use as a board-preparation material ranges from 1% to 3%. 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 physical and chemical properties of adipic acid have been evaluated to characterize the effects of the material after wave soldering.⁵ Most of the adipic acid is consumed by thermal decomposition during the soldering process. At the end of the process, only a small percentage of the original material remains on the PWB. The adipic acid reduces the tin and lead oxides on the surface of the

solder during the preheat stage, just as normal rosin fluxes do. During preheat 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 the PWB by thermal heat transfer 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 gas 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 heat supplied in the soldering process thermally decomposes formic acid into CO_2 and H_2O . An additional benefit of the inert atmosphere is the reduction of dross on or in the solder pot.

The analytical portions of the testing focus on confirming the presence (or nonexistence) of specific residues of adipic and formic acid and on assessing the role that they play in the long term stability of the PWB's components. From a logistic point of view, the analytical methodology proceeded initially with nondestructive techniques followed by methodologies requiring smaller physical samples and destructive sample preparation. Specifically the testing proceeded with high-performance liquid chromatography (HPLC) techniques, followed by infrared spectroscopic (IR) and optical micrographic examinations. None of these techniques required modification of the test PWBs. The next set of analytical determinations consisted of electron microprobe analysis, secondary ion mass spectroscopy (SIMS- both quadruple and time-of-flight mass selection), and occasionally scanning Auger electron spectroscopy (AES). Because of the vacuum requirements inherent to these techniques, PWB sample preparation required destructive sectioning.

ANALYTICAL RESULTS

Motorola Test Board - Surface Analysis

The Motorola test board (MTB) is a nonfunctional test board that was surveyed for free and complexed chemical residues using several techniques. These techniques included HPLC analysis for conventional solder flux residues and free adipic acid, a 1,1,2 - trichlorotrifluoroethane board rinse followed by an infrared examination of the C-H region of the eluant for total hydrocarbon and grease determination, small-area ($10^2 - 10^4 \text{ mm}^2$) optical microscopy and FTIR examination of deposits atop solder pads, and time-of-flight mass spectroscopic (TOFMS) examinations of solder residues on conventional and self-cleaned soldered portions of these PWBs. The purpose of these examinations was to assess whether process contamination leads to any degradation or observable differences in performance parameters between test cells in the long-term testing of the International Printed Circuit (IPC) B-24 and FMU-139 boards.

It might be expected that the self-cleaning solder process might result in incomplete removal of adipic and formic acids. Furthermore, salts of lead and tin with adipic and formic acid might be present along with partially degraded adipic and formic acid by-products. These analytical determinations were pursued to assess the level of surface contamination and the chemical nature of the material left after the self-cleaning. In addition, these examinations verified that solder rosin flux was effectively removed (as expected) from the control set of conventional soldered boards that were solvent-cleaned according to conventional military specifications.

The HPLC analysis procedure was closely based on the IPC Honeywell 355 method⁸ for determination of conventional solder residue components (for example, abietic and neoabietic acids). Although this procedure works well for conventional solder fluxes, the uncomplexed formic and adipic acids are only slightly soluble in the acetonitrile elution solvent. Regardless of this limitation, the modified procedure could effectively determine free (uncomplexed) adipic acid concentrations $\leq 40 \text{ mg cm}^{-2}$. Eighteen boards were examined before environmental testing, and free adipic acid levels were below detection limits for all boards.

Total hydrocarbon and grease contamination levels were determined following an ASTM method that entailed washing the solder side of the MTB PWBs with 1,1,2 - trichlorotrofluoroethane and monitoring the absorbance of the C-H stretch region in a 0.5- to 2.0-mm-path-length liquid IR cell. Only two of the nine boards examined exhibited any detectable hydrocarbon contamination, and these levels were below 2mg cm^{-2} .

Despite the inconclusive results that relied on removing potential contaminants from the PWBs, optical microscopy and small-area FTIR examination clearly indicated that nonmetallic residues were present on the MTBs. In Fig. 1, a representative IR spectrum is shown along with an optical micrograph from a small area of a MTB processed using the self-cleaning method. In general, the conventional rosin-flux soldered/solvent cleaned boards possess bright, clean solder joints, as is expected using a well-refined technology. The boards soldered using the self-cleaning process exhibited some white deposits around the edges of the solder lug bases and occasionally in the center of depressed, solder-filled printed via holes. These deposits are evident in the optical micrograph accompanying the IR spectrum. Although a detailed discussion of all the data sets obtained is beyond the scope of this report, several distinct IR features are worthy of mention. Most of the deposits examined exhibited a broad, featureless vibrational band from 3000 to 3600 cm^{-1} identified with the O-H stretch of adsorbed water, sharper bands in the 2900 to 3000 cm^{-1} region consistent with C-H stretches, and a strong band at $1620 \pm 20\text{ cm}^{-1}$ assigned to a C=O stretch. All of these spectral features are consistent with the presence of surface functionalities that arose from partial decomposition of carboxylic acids in the self-cleaning process (for example, formic and adipic acids). Small-area FTIR examination of the conventional rosin flux/solvent-cleaned boards revealed no measurable organic residue. IR spectra recorded from residues on the self-cleaned boards were noticeably different from reference spectra derived from free adipic and formic acid. This observation coupled with the inability to remove these crystalline deposits with the 1,1,2-trichlorotrofluoroethane wash procedure suggest that the deposits arise from partial thermal degradation product(s) of the adipic and/or formic acid vapor as the board moves from the self-cleaning process stream. The question remains as to the most appropriate global (for example, board wide or per cm^{-2}) analytical measure of this hydrocarbon residue that would represent a meaningful measure of processing quality.

More specific confirmatory information regarding the chemical makeup of the residues left behind after self-clean solder operations was obtained following time-of-flight mass analysis (TOFMS) of selected MTBs. The specific MTBs analyzed included boards numbered MNS01C26 (self-cleaned solder process abbreviated MNS) and MNR01C16 (traditional solder/flux/chlorofluorohydrocarbon [CFC]-cleaned board abbreviated MNR). Each of these boards had FTIR spectra recorded from each of the solder pad regions examined by TOFMS. On the MNS board the presence of carboxylate residues left behind as a result of the self-cleaned solder process was clearly identified in the IR data. Both positive and negative ion spectra were recorded up to mass 600. Positive ion spectra from solder pads on the MNR and MNS boards contained prominent Sn^+ , Pb^+ , and low-mass hydrocarbon peaks. The C^+ peak at mass 12.00 was more intense in spectra from board MNR, whereas the adventitious hydrocarbon peaks (masses C_xH_{2x}) were more intense from board MNS. Polydimethylsiloxane (PDMS) was present on solder pad regions on both MNS and MNR boards, although at higher intensity on the MNS board. PDMS is used as a mold-release agent in plastic and presumably PWB manufacturing processes. The implication of higher PDMS concentration on the MNS board is presumably a consequence of the CFC cleaning step that removes some (if not most) of this agent. The negative ion spectra of both of these samples contained prominent F^- peak identifiers with the peak more intense on the MNS board. Various fluorocarbon mass identifiers and Br^- were observed in spectra from solder pads regions on both the MNR and MNS boards. Generally, peaks above 200 were more intense from the MNR board. Parent peaks for adipate ion were not observed from the MNS solder pad regions. However, carboxylate fragmentation mass ions (C_2HO^- [$m/e = 41.00$], CHO_2^- [$m/e = 45.00$], $\text{C}_2\text{H}_2\text{O}_2^-$ [$m/e = 58.01$], $\text{C}_3\text{H}_3\text{O}_2^-$ [$m/e =$

Fig. 1a. Photomicrograph of Motorola test board at 4x magnification. Highlighted region expanded 40x below and is representative of IR data shown in Fig. 1c.

Fig. 1b. Photomicrograph of region highlighted in Fig. 1a.

Fig. 1c. Infrared spectrum from photomicrograph shown in Fig. 1b.

71.01], were readily observed from all the solder pad regions on board MNS. Intensities of these carboxylate ion fragments were much lower (or nonexistent) from the MNR board solder pad regions. Representative spectra from both positive and negative ion mass ranges are shown in Figs. 2 and 3 for the MNS board solder pad region and Figs. 4 and 5 for the MNR board solder pad region. Accompanying tables are given beneath each figure that display mass spectral assignments. Fig. 6 is a photomicrograph of the representative, identical solder pad region from both boards. In summary, carboxylate decomposition products were readily observed at solder bond pad regions from the self-cleaned-process PWB but not on the traditional solder/flux/CFC-cleaned PWB solder bond pads.

Comb Pattern Board - Surface Analysis

A set of six IPC B-24 surface-insulation resistance (SIR) PWBs were examined following temperature-humidity testing to determine the chemical residues and to assess whether these residues reflect differences between SIR test cell results. The SIR boards examined were those that displayed lowered resistance values during and at the end of the temperature-humidity environmental testing program. The analytical procedure began with photomicroscopy followed by electron microprobe analysis (EMPA), SIMS, and scanning AES of selected target areas of the less desirable SIR PWBs. Only a representative case will be discussed but in general the six less desirable SIR boards all had regions of similar surface corrosion and contamination.

In Fig. 7, a photomicrograph of a portion of the SIR board is shown along with SIMS elemental maps of elemental contaminants of one of the corrosion deposits. The elemental image maps clearly show the inhomogeneous presence of lead and tin. Copper and potassium are evident as well as a number of common impurities (sodium and calcium not shown) that are typically found following water evaporation. Of note is the increase in the lead ion yield over a specific region of the solder runner and a decrease in the tin ion yield in the same region. The SIR PWBs that displayed these corrosion deposits always had some level of copper underneath or mixed in with a rather thick (many micrometers deep) mixed lead and tin oxide layer. Frequently the lead and tin oxide regions were found between the comb runners with the lead in greater chemical abundance than found in the source solder. Remnant moisture from ambient air or residual from the humidity chamber testing would lead to noticeably lower resistance values or even a potential electrical short. Assuming that the SIR boards did not possess any observable gross initial defects, the source of the deposits is most likely the process water contamination level at the end of the test and the environmental chamber surfaces with which it came into contact during testing.

Visual examination of the six affected SIR PWBs clearly indicated that section A of the IPC B-24 board had the highest density of corrosion defects. The fact that this portion of the test board was typically run with an applied potential suggests that the predominant mode of corrosion deposits was driven by an electrochemical process. Unfortunately, the self-cleaned solder process and conventional rosin flux/solvent-cleaned SIR boards were simultaneously run in the environmental test chamber. It is thus impossible to assess whether the observed corrosion deposits were influenced by adipic and formic acid residues being picked up and transported in the humidity water. In fact, one of the rosin flux/solvent-cleaned SIR boards displayed a prominent corrosion short of chemical composition similar to that shown in Fig. 7 for a self-cleaned soldered board.

Functional Test Board-Surface Analysis

A set of four FMU-139 boards were examined for chemical residues following environmental temperature and humidity testing at the Motorola plant. This set of boards was selected on the basis of the poor visual appearance and in some cases poor electrical performance following environmental testing. In all cases the suspect portion of the board was centered around a particular diode type. Other boards clearly displayed evidence of water dripping down one side of the PWB. Figure 8 shows a photomicrograph of the region of the PWB with the suspect diode. Note the obvious

Fig. 2. TOF mass spectrum, positive ions 0-300 m/z, MNS board.

Table I

Positive Ion Mass Assignments

Intensity [counts]	Mass [amu]	Norm.Int.	Formula
34125	11.9808	0.9439	C
9484	12.9950	0.2623	CH
10552	14.0076	0.2919	N
14561	15.0219	0.4027	CH3
1520	18.9979	0.0420	F
12922	22.9860	0.3574	Na
2983	23.9713	0.0825	C2
968	24.9873	0.0268	C2H
8683	26.0139	0.2402	C2H2
50216	27.0259	1.3889	C2H3
23705	27.9694	0.6557	Si
44857	29.0426	1.2407	C2H5
2298	30.0326	0.0636	CH4N
10692	31.0058	0.2957	HNO
1578	38.0171	0.0436	C3H2
29820	39.0155	0.8248	C2HN
5209	39.9991	0.1441	C2O
36154	41.0505	1.0000	C3H5
6862	42.0501	0.1898	C3H6
35006	43.0617	0.9682	C3H7
2340	44.0529	0.0647	C2H6N
7615	45.0490	0.2106	CH5N2
679	46.9938	0.0188	HNO2
992	50.0100	0.0274	C4H2
1228	51.0333	0.0340	C4H3
633	52.0392	0.0175	C4H4
4260	53.0501	0.1178	C4H5
1515	54.0566	0.0419	C4H6
15918	55.0704	0.4403	C4H7
3690	56.0802	0.1021	C4H8
21542	57.0932	0.5958	C4H9
3071	58.0880	0.0849	C4H10
4049	59.0731	0.1120	C3H9N
605	65.0645	0.0167	C5H5
2237	67.0844	0.0619	C5H7
766	68.0796	0.0212	C5H8
8458	68.9140	0.2339	Ga
5342	69.0845	0.1478	C5H9
6173	71.1190	0.1707	C5H11
735	72.1032	0.0203	C5H12
8781	73.0947	0.2429	C4H11N
792	74.0935	0.0219	C4H12N
725	75.0674	0.0201	C3H9NO
747	77.0683	0.0207	C2H9N2O
726	79.0836	0.0201	C6H7
1197	81.1032	0.0331	C6H9
1115	83.1168	0.0308	C6H11
720	85.1182	0.0199	C6H13
752	87.0888	0.0208	C4H11N2
696	91.1003	0.0193	C3H11N2O
581	95.1211	0.0161	C7H11
3036	115.8839	0.0840	116Sn
2644	116.8919	0.0731	117Sn
5669	117.8826	0.1568	118Sn
3415	118.8905	0.0945	119Sn
7060	119.8846	0.1953	Sn
2058	120.9098	0.0569	HSn
866	121.8779	0.0240	122Sn
1202	123.8849	0.0332	124Sn
1240	132.9928	0.0343	C7H03
1204	134.9277	0.0333	H3N118Sr
1287	136.9253	0.0356	CH3122Sn
2239	147.1787	0.0619	C7H19N2O
3486	205.9668	0.0964	206Pb
3734	206.9861	0.1033	207Pb
7291	207.9709	0.2017	Pb

Fig. 3a. TOF mass spectrum, negative ions 0-100 m/z, MNS board.

Fig. 3b. TOF mass spectrum, negative ions 20-100 m/z, MNS board.

Fig. 3c. TOF mass spectrum, negative ions 100-200 m/z, MNS board.

Fig. 3d. TOF mass spectrum, negative ions 200-300 m/z, MNS board. (See Table III for representative mass assignments for Figs. 3a-d.)

Fig. 4. TOF mass spectrum, positive ions m/z 0-300, MNR board.

Table II

Positive Ion Mass Assignments

Intensity [counts]	Mass [amu]	Norm.Int.	Formula
627	10.9984	0.2211	B
176437	11.9854	62.2133	C
24895	12.9996	8.7782	CH
13513	14.0112	4.7648	CH2
5982	15.0233	2.1093	CH3
2458	15.9632	0.8667	O
3387	18.9838	1.1943	H3O
3484	26.0130	1.2285	C2H2
7623	27.0260	2.6879	C2H3
17112	27.9566	6.0339	Si
5960	28.9986	2.1016	CHO
12090	30.9930	4.2630	CF
599	38.0109	0.2112	C3H2
3776	39.0222	1.3315	C3H3
2836	41.0403	1.0000	C3H5
757	42.0232	0.2669	C2H4N
2767	43.0262	0.9757	C2H3O
793	49.9974	0.2796	CF2
668	55.0534	0.2355	C4H7
130	55.8932	0.0458	Fe
405	57.0571	0.1428	C3H7N
33034	68.8704	11.6481	Ga
649	111.8670	0.2288	112Sn
1235	114.8694	0.4355	115Sn
8656	115.8626	3.0522	116Sn
6337	116.8727	2.2345	117Sn
14945	117.8663	5.2697	118Sn
7541	118.8778	2.6590	119Sn
21879	119.8659	7.7147	Sn
3780	120.8869	1.3329	HSn
2589	121.8663	0.9129	122Sn
3270	123.8689	1.1530	124Sn
766	133.9128	0.2701	H20116Sn
2224	134.9166	0.7842	H0118Sn
915	135.9095	0.3226	H20118Sn
2815	136.9130	0.9926	HOSn
2220	138.8908	0.7828	H0122Sn
1777	205.9599	0.6266	206Pb
1580	206.9653	0.5571	207Pb
3341	207.9510	1.1781	Pb
213	226.9214	0.0751	PbF

Fig. 5a. TOF mass spectrum, negative ions m/z 0-100, MNR board.

Fig. 5b. TOF mass spectrum, negative ions m/z 20-100, MNR board.

Fig. 5c. TOF mass spectrum, negative ions 40-100 m/z, MNR board.

Fig. 5d. TOF mass spectrum, negative ions 100-200 m/z, MNR board.

Fig. 5e. TOF mass spectrum, negative ions m/z 200-300, MNR board.

Fig. 6. Solder pad region from which data in Figs. 2-5 were taken.

Table III
Negative Ion Mass Assignments (specific to MNR board)

Intensity [counts]	Mass [amu]	Norm.Int.	Formula
69591	11.9979	0.3918	C
177605	13.0075	1.0000	CH
20256	14.0204	0.1141	CH2
1405	15.0116	0.0079	HN
437860	15.9897	2.4654	O
240240	17.0009	1.3527	HO
900	17.9944	0.0051	H2O
731825	18.9996	4.1205	F
16831	24.0015	0.0948	C2
34359	25.0135	0.1935	C2H
6425	26.0131	0.0362	C2H2
3231	30.9992	0.0182	CF
4613	31.9707	0.0260	O2
1267	32.9732	0.0071	HO2
4786	34.9639	0.0269	Cl
1263	36.0006	0.0071	C3
2256	36.9833	0.0127	37Cl
4558	37.9951	0.0257	F2
1267	39.0245	0.0071	C3H3
952	40.0029	0.0054	CN2
2431	41.0137	0.0137	CHN2
920	42.0127	0.0052	C2H2O
3315	43.0092	0.0187	CHNO
1162	45.0100	0.0065	HN2O
1432	47.9732	0.0081	SO
1344	49.0113	0.0076	C4H
748	50.9685	0.0042	O2F
664	58.0145	0.0037	CH2N2O
529	59.0248	0.0030	CH3N2O
951	59.9625	0.0054	CO3
769	61.9931	0.0043	NO3
2808	63.9705	0.0158	SO2
940	64.9997	0.0053	C4HO
579	66.9963	0.0033	H3O4
3182	68.9946	0.0179	C3HO2
540	71.0271	0.0030	C2H3N2O
652	73.0061	0.0037	C6H
726	77.9833	0.0041	NO4
8268	78.8854	0.0466	Br
2394	79.9692	0.0135	SO3
8803	80.8837	0.0496	81Br
2235	82.9698	0.0126	O4F
565	85.0201	0.0032	C3H3NO2
723	92.9945	0.0041	HN2O4
624	96.9828	0.0035	HO6
1100	118.9897	0.0062	C2HNO5
1251	168.9685	0.0070	CHN2O8
519	398.7514	0.0029	
135	418.7762	0.0008	O25F
3852	498.6580	0.0217	
329	525.6917	0.0019

Fig. 7a. Photomicrograph of SIR board at ~10x magnification.

Fig. 7b. SIMS positive ion maps of highlighted region in Fig. 7a.

Fig. 7c. SIMS ion maps (Na^+ , K^+ , Cl^- , O^-) of highlighted region in Fig. 7a.

Fig. 8. Photomicrograph of functional board. Highlighted region displays extreme corrosion of diode.

chemical residues in the immediate vicinity of the board. These deposits were characterized by EMPA, AES, and SIMS mapping (Figs. 9 and 10) and were found to consist of aluminosilicates with high levels of molybdenum oxide. The molybdenum oxide residue is unusual in that it has not been observed in previously analyzed PWBs retrieved from environmental test chambers. The source of this unusual contaminant was traced to the interior of the suspect diode. A microsection of the questionable diode type was analyzed using EMPA and SIMS from a board that under optical examination displayed initial corrosion attack. The corrosion pathway was traced to water and humidity penetration at the point where the solder cap, the covering ceramic, and the diode interior material (molybdenum metal) meet (Figs. 11 and 12). The ceramic coating appeared slightly porous and could, in principle, retain adipic and formic acid residues resulting from the self-cleaned solder process. In practice, only the diodes that clearly displayed water dripping on them had the prominent corrosion attacks. This diode type clearly was not meant to see this type of service. For conformal coated boards (boards coated with a water-resistant polyurethane coating) the corrosion displayed by this type of diode was not evident.

SUMMARY

The following conclusions are drawn about the use of adipic and formic acids as solder flux components in the self-cleaned solder process process:

1. Conventional military specification and IPC testing procedures show no difference between traditional rosin/flux soldering and the self-cleaned solder process. They do not possess sufficient sensitivity for extremely low contamination levels of adipic and formic acid residues.
2. Nondestructive spectroscopic examination coupled with small-area photomicroscopy can clearly identify solid deposits related to decomposition products of the adipic and formic acid components used in the self-cleaning process.
3. Scanning Auger electron microscopy, FTIR microscopy and TOFMS examination clearly identified these additional deposits as deriving from carboxylic acid decomposition by-products that were not readily soluble in CFC rinse solutions traditionally used in ASTM surface hydrocarbon/grease analysis.
4. Very good long term stability and reliability are indicated in the temperature and humidity testing despite the appearance of solid deposits arising from the decomposition of the adipic and formic acid components inherent in this solder process. See the complete project test result documentation for the specific details regarding this portion of the project. With the exception of one specific porous diode type, no serious solder corrosion problems were identified over the span of experiments and simulated aging encompassed by this project.

SUGGESTIONS AND FUTURE WORK

Despite the encouraging results obtained from the project, several analytical needs that might further enhance the implementation of the technology. Specifically, the need for an easy, rapid, quantitative, nondestructive analytical measure of adipic and formic residue is certainly warranted. Such a technique could, in principle, be developed based upon modification of current HPLC quantification techniques. Such modification would require further experimentation involving optimizing wash and elution solvents. Such testing would strongly complement ionographic testing (testing for ionic contaminants) but would be more specific for residue components of the self-cleaning process. Furthermore, with the push toward less costly and technologically superior alternative solder flux components that might degrade at lower thermal temperatures such a technique would help identify specific components in the solder flux. As an aid in identifying exact temperature regimes and

a.

b.

c. - Cu

d. - Zn.

Fig. 9a. SEMs of faulty diode showing corrosion deposit (a, 40x magnification; b, 100x magnification). Elemental x-ray maps corresponding to photomicrograph b.

a. - Mo

b. - Pb

c. - O

d. - Sn

Fig. 9b. Elemental x-ray maps corresponding to photomicrograph of Fig. 9a(b).

Fig. 10. SIMs elemental maps showing edge of affected diode type. Shadowing of diode by physical positions of ion gun and mass analyzer is very apparent over portions of figure.

Fig. 11. (a) Optical micrograph of diode that is metallographically mounted on PWB, (b) secondary electron image at 1500x of circles region of (a) (light area is P rich Cu region, note depletion in outer edge).

Fig. 12. Composite EMPA x-ray maps of the SEM in Figure 4.3b: (a) Cu, (b) Mo, (c) P, and (d) Ag.

surface chemistry pertinent to the solder flux degradation mechanism(s), physical chemistry experiments on the detailed interactions of adipic and formic acid at tin and lead oxide surfaces are envisioned as part of our fundamental surface science research efforts.

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