

Investigation Into Environmentally Friendly Alternative Cleaning Processes for Hybrid Microcircuits to Replace Vapor Degreasing With 1,1,1 Trichloroethane

Federal Manufacturing & Technologies

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**INVESTIGATION INTO ENVIRONMENTALLY FRIENDLY
ALTERNATIVE CLEANING PROCESSES FOR HYBRID
MICROCIRCUITS TO REPLACE VAPOR DEGREASING
WITH 1,1,1 TRICHLOROETHANE**

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Published February 1997

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Contents

<i>Section</i>	<i>Page</i>
Abstract	1
Summary	1
Discussion	3
Scope and Purpose	3
Activity	3
Introduction.....	3
Background on Cleaning Chemistry	6
Experimentation	7
Results	8
Accomplishments	14
Recommendations	15
Appendices	
A. Summary of Results Obtained by Material Engineering for the Cleaning Ability of Various Solvents on Solder Flux Residue.....	16
B. Memorandums Discussing the Method of Incorporating the d-Limonene Cleaning Process	18

Illustrations

<i>Figure</i>	<i>Page</i>
1 Spacing Between Substrate and Surface Mount Devices	5
2 Sapphire Hybrid Spray-Cleaned at 80 psig for 20 Minutes Using d-Limonene	9
3 Sapphire Hybrid Cleaned by Microdrop Aqueous Saponification Process	11
4 Backside of LCCs Removed From Networks After Aqueous Saponification Cleaning.....	11

Tables

<i>Number</i>	<i>Page</i>
1 Average Meseran Residual Rosin and Omega Meter Results for Various Flux Removal Solvents on Drag-Soldered PWBs Using Kester 1544 Solder Flux.....	8
2 Visual Results for Various Cleaning and Assembly Methods	9
3 Meseran Measurements Made Under Surface Mount Components for Hybrids Cleaned With Three Different Solvents.....	11
4 Residual Rosin and Omega meter Testing Results for Hybrids	13
5 Compatibility Results for Various Components and Materials Exposed to Solutions for Five Days.....	14
A-1 Omega meter 600 SMD Test Results for Removal of Kester 197 Flux.....	17
A-2 Meseran and Visual Results of the Removal of Kester 197 Flux From Copper Panels	17
A-3 Measure of Residual Kester 197 Flux on Copper Panels Using Auger Spectroscopy	17

Abstract

Two cleaning processes, one aqueous and one nonaqueous, were investigated as potential replacements for the vapor degreasing process using 1,1,1 trichloroethane (TCA) for hybrid microcircuit assemblies. The aqueous process was based upon saponification chemistry. A 10% solution of either Kester 5768 or Armakleen 2001, heated to 140°F, was sprayed on the hybrid at 450 psig and a flow rate of 5 gpm through a specially designed nozzle which created microdroplets. The nonaqueous process was based upon dissolution chemistry and used d-limonene as the solvent in an immersion and spray process. The d-limonene solvent was followed by an isopropyl alcohol spray rinse to remove the excess d-limonene. The aqueous microdroplet process was found to be successful only for solder reflow profiles that did not exceed 210°C. Furthermore, removal of component marking was a problem and the spray pressure had to be reduced to 130 psig to eliminate damage to capacitor end caps. The d-limonene cleaning was found to be successful for solder reflow temperature up to 250°C when using a four-step cleaning process. The four steps included refluxing the hybrid at 80°C, followed by soaking the hybrid in d-limonene which is heated to 80°C, followed by spray cleaning at 80 psig with room temperature d-limonene, followed by spray cleaning at 80 psig with room temperature IPA was developed to remove residual flux from the hybrid microcircuits. This process was the most robust and most closely matched the cleaning ability of TCA.

Summary

Trichloroethylene (TCE) and 1,1,1 trichloroethane (TCA) have long been used as flux removal solvents for hybrid microcircuit assembly. These solvents were excellent cleaners, but the potential health risk associated with TCE and the o-zone-depleting nature of TCA have forced industry to look for less toxic, more environmentally friendly replacements. At AlliedSignal Federal Manufacturing & Technologies (FM&T), the materials engineering department ran many studies looking at the flux removal capability of several aqueous and nonaqueous solvents. All studies were run on coupons and looked at the solvency of Kester 135 flux in each of the solutions. From these data several candidates emerged as potential replacements for TCA in flux removal processes, with d-limonene appearing to be the best substitute.

For this project two cleaning processes, one aqueous and one nonaqueous, were investigated for the removal of residual flux from surface mount hybrid microcircuits. The aqueous process tested Kester 5768 and Armakleen 2001 in a heated high pressure spray cleaning application. The nonaqueous process tested d-limonene in three different cleaning processes: spray cleaning, centrifugal cleaning, and immersion cleaning (heated and unheated). All d-limonene cleaning processes were followed by an IPA spray rinse to remove residual d-limonene.

Two assembly methods were used during the evaluation. The first was soldering to reflowed solder bumps using flux as a tacking agent to hold the components in place. This left gross amounts of flux beneath each component, increasing the difficulty of flux removal. The second was placing components directly into solder paste and adding no additional flux. This minimized the amount of flux on the board and trapped beneath the components. However,

placing components in paste led to the problem of solder balls trapped under components with low standoff heights. The solder ball issue limited the number of components that could be placed in paste. Both thick film (TKN) and thin film (TFN) surface mount hybrids were assembled. On TKNs, 63/37 Sn/Pb solder was used and on TFNs, 50/50 Pb/In solder was used. The Pb/In solder presented an additional challenge because the peak reflow temperature reached 250°C, which increased the difficulty of removing residual flux because of rosin polymerization.

Cleaning of surface mount hybrids was proven to be dependent upon the cleaning process, the solder reflow temperature, the part geometry, the component density, the component standoff height, and the operator's assembly techniques. No singular d-limonene process (meaning spray, immersion, or centrifugal only) could successfully remove residual solder flux from surface mount hybrids. Only when hybrids were refluxed at 80°C, followed by soaking in heated d-limonene, followed by spraying with d-limonene, and finally spraying with isopropyl alcohol was flux successfully removed from the entire hybrid (including under LCCs). The aqueous high pressure spray cleaning process using a saponifier successfully removed the solder flux from under the LCCs when 63-37 Sn-Pb solder was used. However, problems arose with the removal of ink marking on components and damage to end caps of the capacitors. Reducing the spray pressure to 130 psig resolved the capacitor end cap problems, but ink marking was still being removed. Aqueous saponification with DI water rinse could not remove even minimal amounts of residual flux when the reflow temperature for 50/50 Pb/In solder was used. That same residue could be removed by the four-step d-limonene/IPA process mentioned above. Placing components directly into solder paste to minimize flux usage could not be used for every component because of solder ball formation during reflow. The solder balls would get trapped under the low profile components and could short adjacent pins.

Based upon the results of the cleaning experiments, it is recommended that the assembly department incorporate the four-step d-limonene cleaning process for hybrid manufacturing. The four steps include

- 1) heated reflux of hybrids at 80°C,
- 2) ten-minute soak in d-limonene heated to 80°C,
- 3) spray clean with room temperature d-limonene for one minute at 80 psig, and
- 4) spray clean with room temperature IPA for one minute at 80 psig.

This process is the most robust and least operator dependent. Aqueous saponification cleaning could be incorporated on hybrids or PWAs provided the reflow temperature remains below 210°C, component marking can be protected, and spray pressures are maintained at 130 psig. Refluxing hybrids heated to 80°C prior to cleaning will also improve the aqueous process.

Discussion

Scope and Purpose

The purpose of this investigation was to develop environmentally conscious cleaning processes for the removal of flux residue from surface mount hybrid microcircuits. The new processes were to meet or exceed the current environmental regulations and maintain the reliability and manufacturability of the product to current levels.

Activity

Introduction

Trichloroethylene (TCE) and 1,1,1 trichloroethane (TCA) have long been used as flux removal solvents for hybrid microcircuit assembly. These solvents were excellent cleaners, but the potential health risk associated with TCE and the o-zone-depleting nature of TCA have forced industry to look for less toxic, more environmentally friendly replacements. Switching to an environmentally friendly cleaning process is no different than any other process modification. The key to a smooth conversion is through an analysis of existing cleaning process, questioning the key areas of concerns related to cleaning, and demonstrating that the alternative process meets the requirements of the concerns.

In selecting a cleaning process the key questions which must be answered are the following:

1. Is cleaning necessary?
2. What contaminants are being removed (organic, inorganic salts, particulate)?
3. Can the range of contaminants be reduced?
4. Can the amount be reduced?
5. What materials are being cleaned?
6. What are the part geometry and assembly method?
7. Is there a cleaning standard? (How clean is clean?)
8. Are the materials compatible with the cleaning solution?
9. How does cleaning affect other production processes?
10. What is the environmental impact of new cleaning process?
11. What is the health and safety impact for the operator?
12. What is the economic impact of the new process?

In this investigation the first seven questions were used to determine what cleaning processes to investigate, and the remaining five questions would be answered after the investigation was completed.

Is cleaning necessary?

Although it has been argued that leaving rosin flux behind poses no threat to the hybrid microcircuit, the fear is that trapped ionic contaminants may be present in the residual flux; and upon exposure to humid air, water will attach to the circuit and a conductive path will form on the surface of the network. Therefore, it is important to remove all contamination from the board surface, so that no conductive paths can form.

What contaminants are being removed?

For surface mount hybrid assembly, the purpose in cleaning is to remove residual rosin flux left after soldering. The typical residues which exist after soldering include

- unmodified, oxidized, and polymerized rosin,
- mono- and dicarboxylic acids,
- metallic halides and abietates,
- metallic mono- and dicarboxylates,
- hydrochloric acid (RA and RMA fluxes only),
- quaternary ammonium halides (for RA and RMA fluxes only).

Can the range or amount be reduced?

The range of contaminants has already been minimized to improve cleaning. Currently, only RMA and pure rosin fluxes are being used in soldering processes in the assembly department (Radar Hybrid Microcircuit). Furthermore, all soldering processes have been optimized for the desired solder reflow profiles for the given components and substrates. The quantity of flux being used is an issue. Steps have been taken to minimize the use of solder flux, such as adding a nitrogen cover gas to the solder belt and using premixed solder paste and flux. This has helped to reduce the quantity used.

What materials are being cleaned?

The materials being cleaned include gold, gold-plated kovar, aluminum oxide (ceramic), fired thick film gold paste, ceramic capacitors, thick film resistors, tinned Cu/P edge clips, Sn/Pb solder, Pb/In solder, green cover glass, tantalum nitride, and titanium palladium thin film resistors.

What are the part geometry and assembly method?

For any rosin flux removal techniques, the quality of cleaning can vary enormously with part geometry and assembly method for a given flux chemistry. The part geometry can be broken down to include component density, component size, component standoff height, and solvent flow restrictions under surface mount components due to solder joints. For hybrids built in two assembly departments (Radar Hybrid Microcircuit and Surface Mount HMC Assembly), the standoff height ranges from 0.001 inch (1 mil) to 0.003 inch (3 mil). Figure 1 shows the 3-mil clearance that a 20-pin LCC has when soldered to a ceramic network. Two assembly methods were used during evaluation. The first was soldering to reflowed solder bumps using flux as a tacking agent to hold components on the solder bumps. This left gross amounts of flux beneath each component, increasing the difficulty of flux removal. The second was placing components directly into solder paste and adding no additional flux. This minimized the amount of flux on the board but created a solder ball problem for low profile surface mount components. Both thick film (TKN) and thin film (TFN) surface mount hybrids were assembled. On TKNs, 63/37 Sn/Pb solder was used and on TFNs, 50/50 Pb/In solder was used. The Pb/In solder presents a second challenge in that the peak reflow temperature reaches 250°C. The higher peak temperature increases the difficulty in removing residual solder flux because of the polymerization of the rosin.

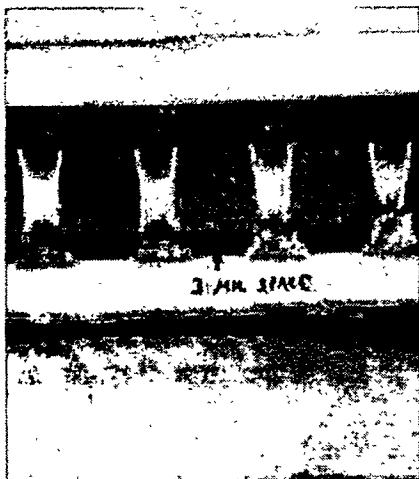


Figure 1. Spacing Between Substrate and Surface Mount Devices

Is there a cleaning standard?

A cleaning standard has been developed in industry for omega meter testing and is described in the following paragraph. AlliedSignal developed its own cleaning standard known as meseran testing. Its description follows the omega meter discussion. Several testing methods were used in this investigation including meseran testing, omega meter testing, residual rosin testing, Auger analysis, and visual inspection at 30X under normal and ultraviolet (UV) lighting. Results of the tests were compared to cleaning results using TCA to determine the ability of the processes and solvents. A brief description of each test method follows.

Omega meter testing - This is an indirect test method which measures the amount of ionic contamination removed from a test panel (or printed wiring assembly [PWA]), using a heated solution of 75% IPA and 25% DI water. The test panel is submerged in the solution for 10 minutes during which time the solution's resistivity is measured. The change in the resistivity is converted to $\mu\text{g NaCl}/\text{in}^2$ equivalents. The board or test panel is considered clean if the total equivalence of sodium chloride is less than $10 \mu\text{g NaCl}/\text{in}^2$. The concern of this test is that not all of the ionic contamination on the test panel is removed from the board.

Meseran testing - This test procedure uses an evaporative rate analysis technique to detect organic contamination. A carbon-14 tagged radioactive chemical is deposited on the test board surface, and a Geiger counter measures the rate of evaporation for a given time period. A clean surface yields a low meseran number, indicating a quick evaporation of the tagged solvent. As a general rule based on experience, a count of 200 or higher indicates a contaminated surface and counts less than 100 indicate a clean surface. The concern with this test is that surface roughness affects the evaporation rate of the solvent which can lead to wide variation of results among tested PWAs.

Auger electron and X-ray photoelectron spectroscopy - This is a direct test method that measures the surface elemental composition of the top 50 angstroms of the test panel. This is not necessarily a quantitative test but instead qualitative. Auger electron spectroscopy is accomplished by exciting the sample with a 3 to 20 keV electron beam and measuring the kinetic energy of the Auger electrons which are emitted from the sample surface. The technique for chemical analysis of surfaces can be visualized as a two-step process. First, a high energy photon, generated by an electron beam, ejects an electron from a core orbital (1s) of an atom. Second, an electron falls from a higher energy orbital to fill the vacancy, thereby releasing sufficient energy to eject a second photoelectron from one of the higher energy orbitals. The ejected photoelectron has a measurable characteristic energy which relates to the element from which was ejected.

Residual rosin testing - This is an indirect test method which measures the amount of abieatic acid remaining on the test coupon. The test board is soaked in a heated solution of 98.9% IPA, 1% phosphoric acid, and 0.1% water solution for 1 hour. A sample of the solution is then placed in a UV analyzer which is set at 242 nm. Absorbion reading at this wavelength coincides with the amount of abieatic acid in solution, which gives an indication of the residual rosin on the board surface in $\mu\text{g}/\text{in}^2$. Again, the concern is that not all contamination is removed from the board during analysis.

Background on Cleaning Chemistry

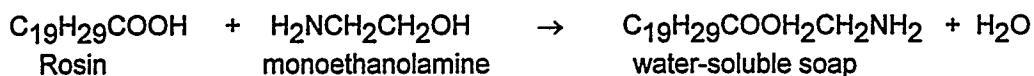
Two types of cleaning processes were evaluated in this study. Dissolution chemistry using d-limonene and isopropyl alcohol was tested as well as saponification chemistry in an aqueous solution. A brief description of each follows.

Dissolution Chemistry

Intermolecular forces are of primary importance in explaining the solubility of a substance. Dissolution of a solid in a liquid is like melting a solid. The orderly crystal structure of the solid is destroyed, and the result is the formation of a more disorderly arrangement of the molecules in solution. In the process of dissolving, the molecules or ions must be separated from each other, and energy must be supplied for both changes. The energy required to overcome lattice energies and intermolecular or interionic attractions comes from the formation of new attractive forces between the solute and the solvent. The addition of heat to the solution will improve solubility of the solute. The heat adds the required energy to break the intermolecular bonds and dissolve the solute. The simple rule for dissolution chemistry is "like dissolves like." Rosin fluxes are typically 97% abieatic and pimaric acids of the diterpene carboxylic type. D-limonene, being in the terpene family, is chemically similar to flux, and therefore is a good solvent for flux. However, d-limonene may not remove all the thermal breakdown components of flux after soldering. Following the d-limonene with IPA will improve cleaning by dissolving a wider range of contaminants, including ionic residues left by activators used in RMA and RA fluxes. For dissolution chemistry (d-limonene), the process parameters which must be optimized are time, mild heating, and mechanical agitation.

Saponification Chemistry

Aqueous saponification cleaning technology has been in use since the 1960s. Simply put, saponification is the chemical conversion of rosin flux to a water-soluble soap using an alkaline amine. When rosin flux is combined with monoethanolamine, it forms a soluble soap as shown in the chemical equation below.



The reaction requires the addition of heat to push it to completion. The solution must be heated to between 140°F and 160°F for optimum results. Once the rosin acids are converted to water-soluble soaps, a DI water rinse will remove the contamination.

Quaternary ammonium halides are activators used in flux to improve the solderability. The two most commonly used are dimethyl- and diethylammonium chloride. Theoretically, at soldering temperature, they decompose to HCl gas and dimethyl or diethyl amine gas. In practice, the decomposition will be only partial and residues of the unmodified activator and the two reaction gases will be found trapped in the rosin. These are all water soluble, and the alkalinity associated with saponifiers will neutralize any HCl, rendering it harmless. The metallic chlorides and organometallic salts that can form during soldering (often referred to as white residue) are insoluble in chlorinated solvents, have limited solubility in water, and are typically removable with water using complexing agents. Process parameters for saponification include time, mechanical agitation, temperature, and solution concentration.

Experimentation

Materials Engineering ran many studies looking at the flux removal capability of several aqueous and nonaqueous solvents. All studies were run on copper and aluminum panels and looked at the solvency ability of each solution when used in a spray cleaning or ultrasonic immersion cleaning process. The cleaning ability of each solvent was assessed by meseran testing, visual inspection under long wave UV light, and some omega meter testing. From these data several candidates emerged as potential replacements for TCA in flux removal processes, with d-limonene appearing to be the best substitute. A sample of the data collected by Materials Engineering is included in Appendix A.

The first effort of this investigation was to verify Materials Engineering's results on drag soldered printed wiring board assemblies and IR belt soldered ceramic substrates. Omega meter testing, meseran testing, and residual rosin testing were run for each cleaning solution. Auger surface analysis was run on networks cleaned in TCA and a 5% solution of Kester 5768 in DI water. Concurrently, based on the Materials Engineering's results of the original study mentioned above, d-limonene was being tested on scrap production surface mount parts using three different cleaning processes, spray cleaning, centrifugal cleaning, and immersion cleaning, all followed by IPA spray rinse. Aqueous saponification in a high pressure spray process was also tested on scrap production surface mount hybrids.

Initially, the primary method for determining the cleaning ability of each process used on the scrap production parts was visual inspection of parts under 30X magnification. Any evidence of residual flux indicated insufficient cleaning by the process. To ease the verification of cleaning beneath components, hybrids were assembled on sapphire substrates. Using sapphire allowed the visual examination under components without destructively removing the component. Ultimately omega meter testing and residual rosin testing were done on TKN and TFN hybrids which were belt soldered using 63/37 Sn/Pb solder on TKNs and 50/50 Pb/In solder on TFNs. In this study the efficacy of TCA, d-limonene followed by IPA, and aqueous saponification with DI water rinse was tested and compared. Meseran testing was also run on the TKN hybrids assembled by solder bump method and cleaned by d-limonene/IPA spray cleaning, TCA vapor degreasing, and microdrop aqueous saponification cleaning. The meseran measurements were taken from underneath surface mounted LCCs which had been mechanically removed.

Finally, a short-term compatibility study was run for each material or component that would be exposed to the cleaning solution. The study included a five-day soak of the material in the solution. Changes in mass, coloration, and volume were measured.

Results

Phase I

The results of the initial screening tests run on printed wiring boards can be seen in Table 1.

Table 1. Average Meseran Residual Rosin and Omega Meter Results for Various Flux Removal Solvents on Drag-Soldered PWBs Using Kester 1544 Solder Flux

Solvent	Meseran No.	Residual Rosin ($\mu\text{g}/\text{in}^2$)	Ionic Residue ($\mu\text{g}/\text{in}^2$)
Alpha 2110	812	1232	9.1
Aquanox 101	873	921	9.4
Aquanox SSA	848	1157	5.5
Axarel 38	327	587	nt
Bioact EC Ultra	638	849	nt
Detergent 8	1020	973	8.3
Ethyl Lactate	1121	1064	nt
Exxate 600	604	112	nt
Flux Off II	305	221	nt
Ionox FC	792	1348	nt
Kester Biokleen 5768	824	1058	4.2
D-limonene	377	68	nt
Loncoterger 255	923	1255	13.1
Prozone SL9	1031	509	nt
Re-Entry KNI 2000	645	144	nt
THFA	995	914	nt
TCE	67	26	22.3
Vi Chem 600A	930	315	11.0

The initial screening indicated that d-limonene was the closest match to TCE, followed by Flux Off II, Exxate 600, and Re-Entry KNI 2000. From these results, d-limonene was tested on scrap production hybrids. Three processes were investigated, aspirated spray cleaning at 80 psig, centrifugal cleaning, and room temperature immersion cleaning. Hybrids built on sapphire substrates were visually examined for flux residue after cleaning. The hybrid assembly technique used was to apply solder flux to reflowed solder bumps on the network to hold the LCC in place during soldering. This technique traps large amounts of flux under the LCCs. A photograph of a d-limonene spray cleaned hybrid assembled on a sapphire network showing gross contamination remaining can be seen in Figure 2. The visual results for each cleaning processes and assembly method are listed in Table 2.

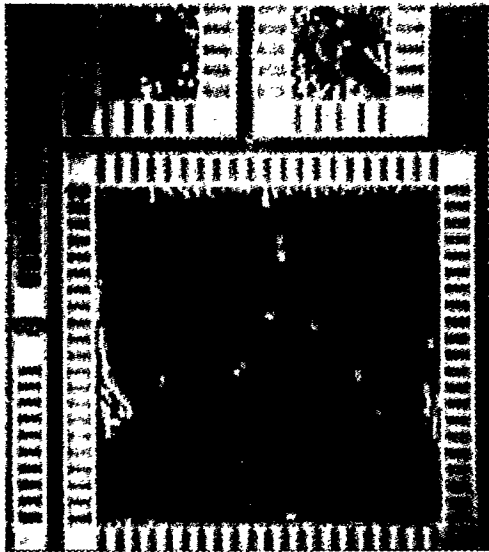


Figure 2. Sapphire Hybrid Spray-Cleaned at 80 psig for 20 Minutes Using d-Limonene

Table 2. Visual Results for Various Cleaning and Assembly Methods

Cleaning Method	Assembly Method	Network Type	Visual Results
d-limonene spray	Attach to solder bumps	TKN	Flux remained under components
d-limonene spray	Attach in solder paste	TKN	All flux removed
d-limonene spray	Attach in solder paste	TFN	All flux removed
Aqueous saponification	Attach to solder bumps	TKN	All flux removed
Aqueous saponification	Attach in solder paste	TKN	All flux removed
Aqueous saponification	Attach in solder paste	TFN	Residual flux rosin remains
d-limonene immersion	Attach to solder bumps	TKN	Flux remained under components
d-limonene centrifugal	Attach to solder bumps	TKN	Flux remained under components

Results of meseran testing used to compare d-limonene spray cleaning to vapor degreasing in trichloroethane and spray cleaning with an aqueous saponifier (Kester 5768) are given in Table 3. The area under the surface mounted LCC was examined during the testing.

Table 3. Meseran Measurement Made Under Surface Mount Components for Hybrids Cleaned With Three Different Solvents

Solvent	Meseran No. (LCC 1)	Meseran No. (LCC 2)
TCA	225	325
D-limonene	700	725
Kester 5768	400	50

The preliminary results indicated that although d-limonene appeared to be the best solvent, it would not sufficiently clean under the components of the surface mount hybrids by spray cleaning, centrifugal cleaning, or room temperature immersion cleaning.

The next step was to investigate the aqueous saponification process using Biokleen 5768. A special spray nozzle was designed that forms microdroplets when operated at 450 psig and a flow rate of 5 gpm. D-limonene could not be used in this process because of its combustibility. When tested on hybrids built on sapphire, the high pressure, aqueous saponification process removed all the residual solder flux from beneath the LCCs as seen in Figure 3. When tested on production hybrids, the LCCs were mechanically removed from the substrates after cleaning and visually examined. Figure 4 shows the results of spray cleaning for various amounts of time. The visual examination revealed that high pressure spray cleaning with an aqueous saponifier successfully cleaned surface mount hybrids which had been soldered with 63/37 Sn/Pb solder and Kester 197 flux after spraying for 10 minutes minimum.

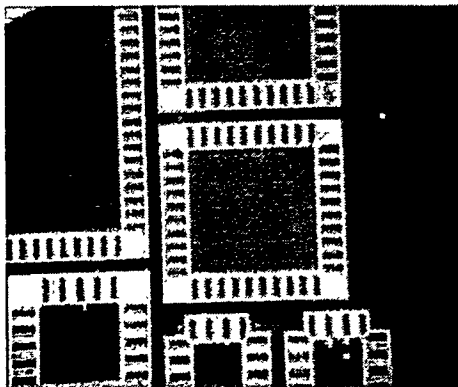


Figure 3. Sapphire Hybrid Cleaned by Microdrop Aqueous Saponification Process

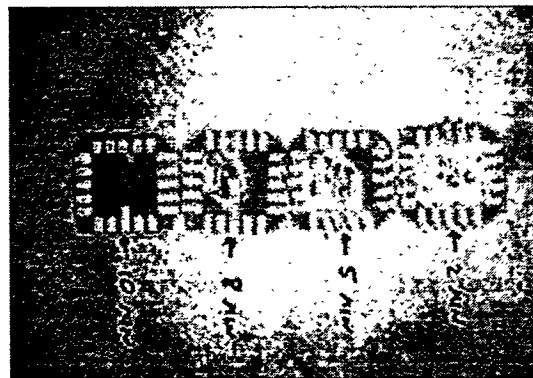


Figure 4. Backside of LCCs Removed From Networks After Aqueous Saponification Cleaning

Phase II

With the success of the aqueous saponification on the sapphire substrates and scrap production parts, the process was implemented in the assembly department on development build. Running the microdrop process on a daily basis revealed the shortcomings of the process which are listed below:

1. Damaged end caps of the ceramic capacitors due to the high pressure, high flowrate spray.
2. Removal of many of the component's marking.
3. Inability to remove flux residue from thin film networks solder with 50-50 Pb/In solder.

None of these problems could be eliminated with further characterization studies of the microdrop process. For these reasons, the process was eliminated, and d-limonene cleaning was reinvestigated for the common radar. The implementation of the d-limonene cleaning was coordinated with the design lab. Appendix B contains a brief history of the discussions and studies run during the implementation process.

The original problem with d-limonene cleaning was the inability to remove residual flux from under the surface mount components. The original technique used to attach the components was to use flux as a tacking agent for the components on previously reflowed solder bumps. This technique trapped large quantities of flux under the components. To reduce the amount of flux used during soldering, components with standoff heights greater than five mils were placed in solder paste, and no additional flux was added. This helped to reduce the quantity of flux residue and aided the cleaning process. However, LCCs and surface mount capacitors were still attached to reflowed solder bumps and were held in place with flux. These components could not be placed in paste because solder balls would get trapped under components during solder reflow. Some of these solder balls were large enough to short adjacent pins. Also, rework processes still required copious amounts of flux which increased the difficulty of cleaning. To overcome the difficult cleaning, a four-step cleaning process was developed. The process included

1. dripping flux on a contaminated hybrid heated to 80°C,
2. soaking in d-limonene heated to 80°C for 10 minutes,
3. spraying with room temperature d-limonene for one minute at 80 psig, and
4. spraying with room temperature isopropyl alcohol for one minute at 80 psig.

The most important steps in the cleaning process were the heated refluxing and heated immersion soak. As new flux is dripped onto a heated hybrid (which has just been soldered), convection currents form within the added flux because of the temperature gradient through the liquid. These currents have a scrubbing effect, and with the additional heat energy they loosen and dislodge the flux residue, bringing it into solution with the new added flux. The tight spacing under the surface mount devices pulls the added flux under the components by capillary action. The added flux continues to form eddy currents under the components because of the temperature gradient and remove the baked-on flux under the devices. Following the refluxing with a heated d-limonene soak, the additional flux which now contains the baked-on flux residue is easily removed. The heated soak also pulls flux out from under the components because of the flux's concentration gradient. The last two spray cleaning steps of the process are to ensure that all flux and d-limonene are removed from the hybrid surface.

The cleaning ability of the new d-limonene process was compared to the cleaning ability of trichloroethane and Biokleen 5768 (aqueous saponifier) on actual production hybrids. The results of these tests can be seen in Table 4.

Table 4. Residual Rosin and Omega Meter Testing Results for Hybrids

HMC	Cleaning Method	Residual Rosin ($\mu\text{g}/\text{in}^2$)	Omega Meter ($\mu\text{g}/\text{in}^2$) FM&T	Omega Meter ($\mu\text{g}/\text{in}^2$) SNL/NM
TKN C	TCA	4	1	2.67
	TCA	14	0	
	TCA	16	0.9	
	d-limonene	13	7.8	5.81
	d-limonene	20	3.8	
	d-limonene	96	1.4	
	aqueous	0	5.5	0.9
TFN V	TCA	8	Omega meter failure at FM&T required testing to be done at SNL/NM	1.32
	TCA	11		
	TCA	6		
	d-limonene	65		1.32
	d-limonene	145		
	d-limonene	51		
	aqueous	666		1.06
TFN F	d-limonene	62		1.75
TFN T	d-limonene	82		3.5
TFN M	d-limonene	215		1.04

The data indicated that d-limonene closely matched the cleaning ability of TCA.

Compatibility Testing

Short-term compatibility testing of the hybrid microcircuits was run in d-limonene and Biokleen 5768. The short-term testing consisted of soaking each component and network in the solvent for up to five days. Table 5 shows the results of the testing.

To test the long-term compatibility of a radar to residual d-limonene, two complete radar channels were assembled and run through a one-year aging and temperature cycle study. The channels were electrically tested periodically during the aging, and at the conclusion of the study the radars were d-tested. No degradation of the electrical characteristics or mechanical integrity of the radar channel was found.

Table 5. Compatibility Results for Various Components and Materials Exposed to Solutions for Five Days

Material	d-limonene	Biokleen 5768
Aluminum	no reaction	etching of aluminum
Ceramic	no reaction	no reaction
Gold-plated kovar	no reaction	no reaction
TKN	no reaction	no reaction
TFN	no reaction	no reaction
Sn/Pb solder	no reaction	etching of Pb
Pb/In solder	no reaction	etching of Pb
Cu/P edge clips	no reaction	etching of Cu
LCC	no reaction	no reaction

Accomplishments

Cleaning of surface mount hybrids has proven to be dependent upon the cleaning process, the solder reflow temperature, the component density, the standoff height of components from the substrate surface, and the operator's assembly techniques. The quantity of flux remaining can affect the ability of the cleaning process by restricting flow under surface mount components. This is also true for densely populated substrates and for surface mount devices with low standoff height. A high reflow temperature such as occurs when reflowing Pb-In solder causes flux to polymerize and become unreactive. Before a solvent can remove solder flux residue, it must be delivered by a process that gets the solvent to the necessary areas and contains the energy required to break chemical bonds and take the residue into solution.

In the first study it was found that d-limonene cleaning by spray, immersion, and centrifugal cleaning all done at room temperature was unsuccessful at removing solder flux from under LCCs when excessive amounts of flux were used during soldering. Gross contamination remained on each part after cleaning for up to 20 minutes. On the other hand, aqueous saponification cleaning using the microdrop technology successfully removed the solder flux for the same situation. However, aqueous saponification damaged capacitor end caps, removed component marking, and could not remove even a minimal amount of residual flux when the reflow temperature for Pb/In solder was used. Because of the damage caused by the microdrop process and the inability of aqueous saponification to remove flux residue after Pb/In soldering, the process and the solvent were eliminated as a potential replacement for vapor degreasing in TCA.

D-limonene was shown to be a good solvent for rosin flux; however, the geometry of surface mount hybrids made flux removal very difficult with the available processes. Although the microdrop process increased the available energy for cleaning, it also caused mechanical damage to the hybrid. Also, d-limonene is a combustible material and can not be used in the microdrop machine. To overcome d-limonene's inability to remove residual flux at room temperature, a heated refluxing step and heated d-limonene soak were added to the cleaning process. The added flux and heat increased the available energy for dissolution of the flux residue. Heating d-limonene required the installation of an explosion-proof hood. Furthermore, an upper limit of 80°C was set for the d-limonene. The addition of heat greatly improved the cleaning process using d-limonene.

The short-term compatibility studies run with d-limonene showed it to be compatible with all materials. The saponifier solution reacted with the Sn/Pb and Pb/In solder, the Cu/P edge clips, and any aluminum handling fixtures. The etching is a surface reaction and does not impair the mechanical or electrical properties of the materials. Rinsing the hybrids for as little as 15 seconds will stop the reaction of saponifier with Cu, Pb, or Al. All other materials were compatible with the aqueous solution.

Recommendations

Based on the results of the experimentation, it is recommended that the assembly department use the four-step heated refluxing, heated immersion cleaning in d-limonene followed by spray rinsing with d-limonene, and last spray cleaning with isopropyl alcohol to remove excess solvent from the hybrids. This recommendation is based on the current soldering practices within the department and because both thin and thick film hybrids are assembled in the area. The aqueous saponification cleaning process using the microdrop technology is too aggressive and damages components during operation. Furthermore, residual flux could only be removed from thick film hybrids and printed wiring boards using 63/37 Sn/Pb solder when using the aqueous saponifier.

Appendix A

Summary of Results
Obtained by Material Engineering
for the Cleaning Ability of Various Solvents
on Solder Flux Residue

Table A-1. Omega Meter 600 SMD Test Results for Removal of Kester 197 Flux

Solvent	Contamination Level ($\mu\text{g NaCl/in}^2$)*
Act 100	0.73 ± 0.35
Kester 5769 (5% solution in DI water)	0
Exxate 1000	0.07 ± 0.06
Bioact EC-7	0
Bioact EC-7/Isopropyl Alcohol	0
Isopropyl Alcohol	1.47 ± 0.12
Trichloroethylene/Isopropyl Alcohol	0.13 ± 0.06

*9913000 Specification Acceptance Limit = $10 \mu\text{g NaCl/in}^2$

Table A-2. Meseran and Visual Results of the Removal of Kester 197 Flux From Copper Panels

Solvent	Spray Time (s)	Meseran No.	Visual Exam (UV)
TCE	60	0	Removed after 15 s spray
Exxate 1000	60	7	Removed after 45 s spray
Bioact EC-7	30	0	Removed after 45 s spray
Kester 5769	480	12	Slight remained after 15 minute spray
Act-100	120	0	Slight remained after 15 minute spray
IPA	600	197	Moderate remained after 15 minute spray

Table A-3. Measure of Residual Kester 197 Flux on Copper Panels Using Auger Spectroscopy (Atomic weight percent of contaminant on surface)

Solvent	Spray Time (s)	Contaminant on Bare Cu	Contaminant on Cu/solder Interface	Contaminant on Solder
TCE/IPA	30	4.03	1.8	0.25
Exxate 1000	30	5.78	2.17	0.26
Bioact EC-7	30	3.06	2.82	0.33
Kester 5769	300	3.43	2.49	0.35
Act 100	90	2.76	1.19	0.34
IPA	300	6.07	3.77	0.13

Appendix B

Memorandums Discussing the Method of Incorporating the d-Limonene Cleaning Process

Date: January 25, 1994
To: Distribution
From:
Subject: Minutes of HMC and PWA Cleaning meeting, January 25, 1994.

A meeting was held at KCD to discuss changing the cleaning process on HMC's from Aqueous cleaning to d-Limonene cleaning.

The purpose of the meeting was to determine if changing over to d-Limonene cleaning on HMC's was feasible and if so what needed to be done to insure its success.

The meeting began with short presentations explaining the present Aqueous cleaning process and a chronology of how the cleaning process was developed. It was stated that Aqueous cleaning of Thick Film HMC's proved to be much easier than Thin Film HMC's. This is due to the fact that the 50/50 lead/indium solder used on TFN's is reflowed at a higher temperature than the 63/37 tin/lead solder used on TKN's.

During the beginning of HMC build it was determined that aqueous cleaning was not adequate for flux removal. A quick evaluation of d-limonene spray cleaning on a sample of eight networks (four TFN and four TKN) gave very good visual indications that it cleaned better than aqueous saponification.

Since the biggest question was about the compatibility of TKN's and d-Limonene, was invited to discuss this issue. has been involved in evaluating d-Limonene and the fireset. stated that they had indeed evaluated TKN's cleaned in d-Limonene. They had also ran extensive testing and concluded that there was no problem. This testing had included a significant number of TKN's (>150).

Discussions during the day were very productive and yielded the following group consensus:

1. There are no apparent show stoppers or risks blocking the use of d-limonene on HMC's and PWA's.
2. It is OK to change over to d-Limonene cleaning on HMC's and PWA's if there are no component compatability problems and the following is completed prior to change over.
 - a. The d-Limonene process is to be further characterized to eliminate the d-Limonene/flux soaking. It is desirable to only soak in d-Limonene.
 - b. The two vacuum ovens to be used for vacuum baking are to be characterized and found to be capable of at least maintaining PWA's and HMC's at 70 deg. C. for 15 minutes minimum.
 - c. The sequencing of temperature cycling and vacuum bake shall be changed to perform vacuum bake prior to temperature cycling.
3. Concurrent with build using d-Limonene cleaning sample HMC's will be build per the following matrix.

Table 1: TESTING MATRIX				
HMC	TCA CLEAN	AQUEOUS CLEAN	D-LIMONENE	TESTING
C	7	3	7	3 ea. Omega meter 3 ea. Residual Rosin 1 Charlie Cook
V	7	3	7	3 ea. Omega meter 3 ea. Residual Rosin 1 Charlie Cook
F	0	0	2	1 ea. Omega meter 1 ea. Residual Rosin
M	0	0	2	1 ea. Omega meter 1 ea. Residual Rosin
T	0	0	2	1 ea. Omega meter 1 ea. Residual Rosin

4. In addition, two V HMC's and two F-HMC's will be chosen from build. After normal electrical testing they will be aged a 160 deg. F. for 385 hours (unbiased) and retested. Two nonfunctional HMC's will also be subjected to this aging process and then tested for mechanical/chemical degradation.

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September 8, 1994

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On January 25, 1994, a meeting was held at AS-KCD to address a cleaning issue. At that time, an aqueous cleaner (Biokleen 5768) was successfully being used to clean RMA flux from thick film Hybrid Microcircuits (HMC's). When higher temperatures were required to build thin film HMC's, the aqueous cleaner was unable to remove the baked-on solder flux. As a result, d-limonene was recommended as a potential replacement for Biokleen 5768 for cleaning thin film HMC's. A cleaning matrix for qualifying d-limonene was established and included testing for ionic contamination.

Per your request, we have tested three thick film HMC's and seven thin film HMC's for ionic contamination. An Ionograph 500M was used to test the HMC's. The Ionograph measures the amount of ionic contamination extracted during a 15 minute test in a 75% isopropyl alcohol/25% de ionized water solution. The test gives an indication of how clean the HMC's are after processing. As a reference, Sandia soldering specification allows a maximum amount of ionic contamination per board of $10 \mu\text{g NaCl/in}^2$.

Prior to testing in the Ionograph, all HMC's were visually inspected. Several components on each of the three thick film HMC's were sheared off for purposes of inspecting the underside of the component and the surface of the board. All three thick film HMC's inspected were visually clean. The thin film HMC's were also visually inspected prior to testing with the Ionograph using 12X magnification. None of the components on the thin film HMC's were sheared off as they were for the thick film HMC's. The following visual observations were made on the thin film HMC's:

Visual Observations

HMC-F 199000 - solder spots on the gold conductor were noted in different places, i.e. it appeared that the solder was meant to fill the via holes. There were also solder spots on the conductor where there were no vias present. No physical defects were observed on the circuit or components. Minor scratches were observed on the gold conductor on both sides of the HMC.

HMC-T 409225 & 409285 - Some brown flux residue and brown spots were observed on HMC 409225 where the solder filled the via thru holes. Some brown flux residues were observed on HMC 409285 (not as much as 409225). Minor scratches were observed on the gold conductor on both sides of the HMC.

HMC-M 409184 - Brown flux residue was observed on the top and on the edges of the ceramic substrate and on the solder filled vias. Minor scratches were observed on the gold conductor on both sides of the HMC.

HMC-V 408409 - Brown flux residues were observed on the solder filled vias. Brown flux residue was observed at the solder interface between the ceramic substrate and the gold plated Kovar substrate. A large solder blob was observed on top of the IC. Small solder spots were observed on the bottom side where they probably shouldn't be. Minor scratches were observed on the gold conductor on both sides of the HMC. Several small solder balls observed within the solder joints of all capacitors.

HMC-V 408415 - Gross flux residue was observed at the solder interface between the ceramic substrate and the gold plated Kovar substrate; also flux residues were observed on the areas where the via holes were filled with solder. White "crusty" residue was observed on all component solder joints and many small solder balls were also observed within the component solder joints. Small amounts of scratches on the gold conductor were observed on both sides of the HMC.

HMC-V 408416 - Minute amounts of flux residue were observed. Several small solder balls were observed within the solder joints on the IC and the capacitors. Very little scratching on the conductor was observed on the topside. A large blob of what looks like solder paste was observed on the top of the IC.

Ionograph Results & Discussion

All thin and thick film HMC's tested were well below the maximum allowable ionic contamination limit of $10 \mu\text{g NaCl/in}^2$. Some of the HMC's had visible flux residues, yet ionics were barely detected by the Ionograph 500M. HMC-V 408415 in particular had gross amounts of flux residue visible to the naked eye, yet only measured $1.06 \mu\text{g NaCl/in}^2$ contamination. Normally, circuit boards are tested for ionics directly after being cleaned. In this case, the HMC's were not tested for months after they had been assembled. This allowed time for the baked on flux, particularly on the thin film HMC's to dry to completion thus rendering the flux insoluble in the 75% IPA/25% DIW solution. HMC-V 408415 was retested in the Ionograph for an additional 30 minutes to see if some of the flux could be dissolved over a longer period of time. Negligible results were obtained.

The following ionic contamination results were obtained with the Ionograph 500M:

Ionograph 500M Data

Thick Film HMC's/C

Cleaned With	Surface Area in^2	Total Equiv. $\mu\text{g NaCl}$	Total Cont. $\mu\text{g NaCl/in}^2$
Biokleen 5768	12.5	11.3	0.90
1,1,1 TCA	12.5	33.4	2.67
d-limonene/IPA	12.5	72.7	5.81

Thin Film HMC's

Cleaned With	Surface Area in ²	Total Equiv. μg NaCl	Total Cont. μg NaCl/in ²
d-limonene	7.5	13.1	1.75
d-limonene	12.9	13.4	1.04
d-limonene	7.6	26.8	3.50
Biokleen 5768	7.6	8.1	1.06
Biokleen 5768	7.6	10.1	1.32
Biokleen 5768	7.6	26.1	3.41

Repeat - 30 Minute Run

Biokleen 5768	7.6	1.1	0.14
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