N94-30400

NON-AQUEOUS CLEANING SOLVENT SUBSTITUTION

2462
p. 9

Gerald J. Meier, Senior Engineer
AlliedSignal Inc.
Kansas City Division*
P.O. Box 419159 D/343 MY40
Kansas City, Missouri 64141-6195

ABSTRACT

A variety of environmental, safety, and health concerns exist over use of chlorinated and fluorinated cleaning solvents. Sandia National Laboratories, Lawrence Livermore National Laboratories, and the Kansas City Division of AlliedSignal have combined efforts to focus on finding alternative cleaning solvents and processes which are effective, environmentally safe, and compliant with local, state, and federal regulations. An alternative solvent has been identified, qualified, and implemented into production of complex electronic assemblies, where aqueous and semi-aqueous cleaning processes are not allowed. Extensive compatibility studies were performed with components, piece-parts, and materials. Electrical testing and accelerated aging were used to screen for detrimental, long-term effects. A terpene, *d*-limonene, has been selected as the solvent of choice, and has been found to be compatible with the components and materials tested. A brief history of the overall project will be presented, along with representative cleaning efficiency results, compatibility results, and residual solvent data. The electronics industry is constantly searching for proven methods and environmentally-safe materials to use in manufacturing processes. The information in this presentation will provide another option to consider on future projects for applications requiring high levels of quality, reliability, and cleanliness from non-aqueous cleaning processes.

INTRODUCTION

For many years, complex electronic assemblies have been successfully cleaned with trichloroethylene (TCE), rinsed with isopropyl alcohol (IPA), and dried with trichlorotrifluoroethane (FREON). Spray cleaning by hand and vacuum baking have been used in production at the Kansas City Division for over twenty years, and are the preferred methods for cleaning and drying electronic assemblies. This cleaning process has been extremely effective in removing the intentional surface contaminants (solder fluxes and mold releases) and any unintentional contaminants (silicones, greases, lotions, and oils) from electronic assemblies prior to encapsulation.

* Operated for the U.S. Department of Energy under contract number DE-ACO4-76-DP00613.

However, a variety of environmental, safety, and health concerns exist over use of these chlorinated and fluorinated solvents. Sandia National Laboratories, Lawrence Livermore National Laboratories, and the Kansas City Division of AlliedSignal combined efforts to find alternative cleaning solvents and processes which are effective, environmentally safe, and compliant with local, state, and federal regulations. Work was performed to identify, qualify, and implement the alternatives to the chlorinated and fluorinated cleaning solvents. Several aqueous, semi-aqueous, and non-aqueous cleaning solvents and processes were evaluated. *d*-Limonene, a terpene, has been selected as the solvent of choice to replace TCE and FREON in electronic assembly cleaning.

STATEMENT OF THE PROBLEM

In January 1989, the future availability of halogenated cleaning solvents was in jeopardy. There was growing concern over the environmental impacts of FREON usage and an increased awareness of TCE toxicity. New development programs were reluctant to select baseline cleaning processes because of the uncertainty of halogenated solvents.

Non-Aqueous Requirements

Systems Engineers are concerned with the material compatibility problems caused over time by water (i.e. corrosion). As a result, system requirements prohibited the use of water in processes where organic materials are present, to limit the amount of water absorbed by the organic materials and control the overall water content of a final assembly. Since most of the mechanical parts and assemblies that require solvent cleaning are inorganic, aqueous and semi-aqueous cleaning solvents and processes could be used as replacements for TCE and FREON. However, most electrical parts and assemblies contain organic materials that absorb water (which sometimes can not be easily removed), and new non-aqueous cleaning solvents and processes had to be found. The majority of the work performed on this project went into identifying and evaluating suitable non-aqueous cleaning processes for use on the electrical parts and assemblies.

Eliminating CFC and CHC Usage

The search for alternative cleaning solvents and processes began at the Kansas City Division, and was primarily driven by draft requirements to reduce and eliminate use of chlorofluorocarbons (CFC's) and chlorinated hydrocarbons (CHC's) in traditional cleaning processes. Since then, increasing numbers of regulations have been issued by federal, state, and local regulatory agencies to ban, or to place more stringent controls on the production, use, and disposal of these halogenated solvents. In addition, company policy also dictated that usage of CFC and CHC materials at the Kansas City Division be eliminated.

CLEANING EVALUATIONS

A new development project, consisting of a final unit with twelve subassemblies, was selected as the pilot project to evaluate new cleaning solvents and processes. The subassemblies were primarily printed wiring boards containing resistors, capacitors, diodes, transformers, and hybrid micro-circuits; special design components bonded together with epoxy adhesives and electrically connected with wires or flat cables; and multi-pin connectors in wiring harnesses. These modules were assembled in a stainless steel housing to become the final unit.

Solvents and Processes Evaluated

Seven different cleaning solvents and processes (two aqueous, three terpenes, a hydrocarbon, and an alcohol) were evaluated. They are listed below:

1) An aqueous mixture of ethanol amines (5% solution in deionized water), rinsed with deionized water and then isopropyl alcohol.
2) An aqueous solvent based on n,n-dimethylacetamide, rinsed with deionized water and then isopropyl alcohol.
3) A terpene (*d*-limonene) with emulsifiers, rinsed with deionized water and then isopropyl alcohol.
4) A terpene (*d*-limonene) with phase separation agents, rinsed with isopropyl alcohol only.
5) *d*-Limonene (Food Grade--97% pure), rinsed with isopropyl alcohol only.
6) A hydrocarbon solvent based on octadecyl acetate, rinsed with isopropyl alcohol only.
7) Isopropyl alcohol (solvent and rinse).

Musts and Wants

Four "must" requirements were defined for the solvents:

- not compromise quality or reliability,
- not require a design change,
- be acceptable to the Environmental, Safety, and Health Departments, and
- have cleaning comparable to TCE.

Only after meeting these four must requirements would the new solvents be judged against other requirements, including:

- compatibility,
- corrosion-resistance,
- cleaning effectiveness,
- environmental, safety, and health conformance,
- manufacturing efficiency, and
- low implementation and operating costs.

Solvent Screening

A solvent evaluation matrix was defined to screen each solvent. The matrix contained four general categories:

1) Cleaning Evaluations, consisting of solvent cleaning, ionic contamination testing, organic contamination testing, AES/XPS surface analysis, and process development;

2) Solvent Analysis, consisting of composition, removal, and residuals;

3) Material Compatibility, consisting of screening tests, individual evaluations, and physical properties; and

4) Hardware Evaluations, consisting of accelerated aging and electrical performance testing.

There were three categories of contaminants that each replacement solvent had to remove from various substrates. The categories were: solder flux, mold release, and general contaminants consisting of resins, curing agents, cover coats, waxes, greases, oils, lubricants, plasticizers, and other contaminants found in a typical manufacturing environment. Other solvent evaluation methods used to screen the candidate cleaners were adhesion strength testing, high voltage testing, corrosion testing, and thermal characteristics testing.

Cleaning Results

For solder flux and mold release removal, the hydrocarbon solvent and the three terpenes were comparable to TCE. For removing the general contaminants, only the hydrocarbon solvent and the terpene containing emulsifiers were comparable to TCE for all of the general contaminants. *d*-Limonene and the terpene containing phase separation agents were able to remove most of the general contaminants, but more time and solvent were necessary. Generally speaking, *d*-limonene was not quite as effective as the terpene containing phase separation agents, which was not quite as effective as the terpene containing emulsifiers. Table 1 highlights the cleaning results for the general contaminants that were the most difficult to remove.

Test results from adhesion strength testing, high voltage testing, and corrosion testing agreed with the solvent cleaning results mentioned above: the hydrocarbon solvent and the terpene containing emulsifiers are comparable to TCE; *d*-limonene was not as effective as the terpene containing phase separation agent, which was not as effective as the terpene containing emulsifiers. However, *d*-limonene had the best thermal characteristics of the three terpenes.

FREON was used primarily as the drying agent in the TCE cleaning process, and was not used for removing contaminants from the assemblies. Adequate drying was being obtained from the existing nitrogen drying and vacuum baking processes, and the FREON drying process was simply halted.

Solvent and Rank		Epoxy Resin	Curing Agent	Acrylic Cover Coat	Mold Release
1)	Baseline (TCE)	Clean 15 sec	Clean 30 sec	Clean 15 sec	Clean 60 sec
2)	Terpene With Emulsifiers	Clean 15 sec	Clean 90 sec	Clean **4 min**	Clean **2 min**
3)	Hydrocarbon Solvent	Clean 15 sec	Clean **3 min**	Clean **2.5 min**	Clean **4 min**
4)	Terpene With Separation Agent	Clean 45 sec	Clean **4 min**	******Gross* **4 min**	Clean **4 min**
5)	*d*-Limonene (97% Pure)	**Dirty** 1 min	**Dirty 4 min**	******Gross* **4 min**	**Dirty 4 min**

* Note: Although the coupons were still grossly contaminated, there was no concern. This acrylic material was used as a cover coat for ink marking, and there was no desire to remove it. In actual practice, it was discovered that both solvents easily remove normal amounts of the acrylic cover coat.

Table 1: General Contaminant Removal From Aluminum Coupons (grossly contaminated and allowed to air cure for 3 days).

CLEANING SOLVENT SELECTION

The hydrocarbon solvent and the terpene containing emulsifiers were chosen for further evaluation. However, the terpene containing emulsifiers was used with only an isopropyl alcohol rinse, to make its cleaning process similar to the hydrocarbon solvent's, and to avoid anticipated compatibility problems from cleaning with water. Both solvents were eventually eliminated, though, because solvent residue from either solvent could not be removed from the actual assemblies with the isopropyl alcohol rinse. Next the terpene containing phase separation agents was evaluated. It did not require any deionized water rinse, which eliminated the compatibility concerns from using water. However, the terpene containing phase separation agents was eliminated. Once again, the isopropyl alcohol rinse could not remove the residual solvent.

Selection of *d*-Limonene

During the cleaning evaluation of the terpene containing phase separation agents, two extreme formulations were detected. While most of the formulations contained 90% *d*-limonene, one formulation contained nearly 100% *d*-limonene. The key discovery was not finding the two extreme formulations but in the observed cleaning results. There were no differences in the cleaning efficiencies of the two extreme formulations. The presence of the additives (which remained on the assemblies after the cleaning process) did not affect the cleaning ability of the *d*-limonene. When this fact was determined, the terpene containing phase separation agents was replaced with food grade *d*-limonene (97% pure). The existing cleaning processes had little difficulty removing the residual *d*-limonene, and since the additives were no longer present, the amount of residual solvent remaining in each assembly was substantially decreased.

COMPATIBILITY EVALUATIONS

Compatibility studies involving accelerated aging, functional testing, solvent absorption, and residual solvent removal were performed on all of the components, piece-parts, and materials in the assemblies. The materials were divided into two categories: organic and inorganic. The inorganic materials compatibility testing consisted of corrosion studies on copper and solder dipped copper. The organic materials were further divided into adhesives, encapsulation foams, and a general category consisting of polyurethanes, acrylics, polycarbonates, silicones, polyolefins, epoxies, solder masks, cables, inks, and others.

Material Compatibility

No adverse affects were observed in the inorganic material corrosion studies or in the organic material encapsulation foam studies. As for the remaining organic materials, only one known material was determined to be completely incompatible with *d*-limonene: polystyrene. Other organic materials that are known to absorb *d*-limonene are: polyurethane elastomers, polyolefin sleevings, some nylon tie wraps, acrylics, silicones, and rubbers (EPDM). Note that these conclusions were based upon worst-case *d*-limonene exposure testing--soaking and/or saturated vapor. Vacuum baking processes are effective in minimizing actual amounts of absorbed solvent in these materials. All other organic materials, and all of the components and piece-parts tested were judged to be compatible with *d*-limonene. Table 2 contains selected information on material compatibility with TCE and with terpenes containing at least 90% *d*-limonene.

	90+% Terpene	TCE
POLYURETHANES		
Polyurethane EN-7	15%	33%
Polyurethane EN-8	15%	30%
L-100/Cyanocure	5%	16%
Polyurethane Sleeving	30%	N/A
ACRYLICS		
Lacquer Covercoat	5%	22%
POLYCARBONATES		
Polycarbonate	<1%	4%
SILICONES		
Sylgard 184/GMB	5%	7%
Cellular Silicone	200%	126%
Red Silicone	40%	40%
747U (white)	20%	22%
Floro- (blue)	3%	7%
POLYOLEFINS		
Sleeving (as received)	25%	14%
Sleeving (shrunk)	20%	16%
Sleeving (white)	15%	3%
Sleeving (black)	15%	6%
POLYSTYRENE		
Not Compatible With Either Solvent		

	90+% Terpene	TCE
OTHERS		
Scothcast 8	<1%	3%
Syntactic Polysulfide	<1%	6%
Diallyl phthalate (DAP)	<.1%	<.1%
Polytherimide	<1%	<1%
Polyethyleneterephthalate	<1%	N/A
Polyetheretherketone	<1%	<1%
Polyphenylene sulfide	<1%	<1%
Phenolic (cotton)	<1%	<.1%
Teflon rod	<.1%	<.1%
Nylon rod	1%	<.1%
Polymethylpentene	<1%	1%
Polyvinylidene fluoride	<.1%	<.1%
Mylar (PET)	.2%	<.5%
Kapton/Pyralux/Kapton	↓ data per in^2 ↓	
(14 mil)	<1mg	40mg
Kapton/Pyralux/	15mg	8mg
Kapton (6 mil)	<1mg	0.3mg
Polyimide/glass	<1mg	<1mg
Parylene	.1mg	1.5mg
CABLES		
ETFE wire (black)	.4 mg	2 mg
ETFE wire (white)	5 mg	8 mg
ETFE wire (white)	2 mg	3 mg
Coax cable (white)	25 mg	33 mg
Coax cable (white)	10 mg	15 mg

	90+% Terpene	TCE
EPOXIES		
Epon 828/Versamid 140	2%	5%
FM123 (epoxy/glass)	1%	8%
Epon 826/U	<.1%	<.1%
Green Hysol	<.1%	<.1%
Red Epoxy/Z/Mica	<.1%	<.1%
Epoxy Glass Cloth	<.1%	<.1%
A2 (white)	<.1%	<.1%
Brown Epoxy Molding	<.1%	<.1%
Brown Epoxy/Z/Mica	<.1%	<.1%
GMB/CTBN/DEA	<.1%	<.1%
GMB/CTBN/U	<.1%	<.1%
INKS		
Stamp pad	OK	OK
Epoxy (blue)	OK	OK
Epoxy paints	OK	OK
Hysol DK17 conformal	OK	OK
coating on components	OK	OK
SOLDER MASK		
Dark Green (non-aqueous	OK	OK
Apple Green (aqueous)	OK	OK
COMPONENTS		
(Component Material Before & After Soaking)		
Epoxy Capacitors	OK	OK
Epoxy Resistors	OK	OK
Epoxy R&P Connectors	OK	OK
DAP Triax Connector	OK	OK

Note: This information is primarily comprised of weight gain data taken immediately following soak testing in solvent at 50°C (122°F, TCE soaked at ambient) for 15 minutes, rinsing with IPA, and blow drying with dry nitrogen. Data not presented in percentages (%'s) was considered functional, or "pass/fail" compatibility data only.

Table 2: Solvent Weight Gain in Samples of Selected Materials.

Hardware Compatibility

Ten complete sets of modules and five complete final units were built for the accelerated aging testing. The units were separated into three groups of five. Within each group, one set was cleaned with TCE and aged in a nitrogen environment, while four sets were cleaned with *d*-limonene and aged in a saturated *d*-limonene environment. Each unit completed 99 thermal cycles from -54 to 71°C (-65 to 160°F) and six months of isothermal aging at 71°C (160°F). After the accelerated aging testing was complete, all ten module sets and all five final units were judged to be compatible with *d*-limonene (no visual or electrical failures caused by *d*-limonene).

RESIDUAL SOLVENT ANALYSIS

A gas analysis technique was developed and optimized to quantitatively determine the amount of *d*-limonene remaining in a final unit. The *d*-limonene concentrations were measured as a function of time. Aging canisters containing units cleaned with *d*-limonene were evacuated through a liquid nitrogen cold trap. The trap was washed with methylene chloride, and the wash solution was analyzed using gas chromatography (flame ionization detection). Known quantities of *d*-limonene were used to characterize and optimize the process. After six generations of improvement, recovery efficiencies from 92% (for a 50 mg sample) to 99.5% (for a 2000 mg sample) were achieved. Earlier in the project, it was estimated that 1000 to 2000 mg would remain in the final unit after the subassemblies and the final unit were cleaned with *d*-limonene.

Results

Three *d*-limonene units were tested three repetitive times using this gas analysis process (one unencapsulated unit, one encapsulated unit, and one alternate encapsulated unit). Test results concluded that negligible amounts of *d*-limonene were detected in these assemblies. The results are tabulated in Table 3.

	Sample 1	Sample 2	Sample 3
Unencapsulated Unit:	1.26 mg	1.70 mg	1.08 mg
Encapsulated Unit:	2.75 mg	0.31 mg	< .01 mg
Alternate Encapsulated Unit:	< .01 mg	< .01 mg	< .01 mg

Table 3: Residual Solvent Remaining in a Final Unit

Given this actual data and the uncertainty at these detection levels, it was decided (with at least 92% confidence!) that less than 50 mg of solvent remained in the final units cleaned with *d*-limonene. These measured values were acceptable and quite pleasing, especially when 1000 to 2000 mg was expected!

CONCLUSIONS

Halogenated cleaning solvents used to clean complex electronic assemblies have been replaced with *d*-limonene, an environmentally safe, terpene cleaning solvent. This enhances the hazard elimination efforts at the Kansas City Division by following company policy to eliminate CFC and CHC usage, and complies with environmental regulations by eliminating the emission of CFC's (known ozone depleters) and the exposure to CHC's (suspect carcinogens).

All materials tested in this evaluation were judged to be compatible with *d*-limonene under routine, everyday operating conditions. Through accelerated aging testing, the long-term compatibility of the modules and final assemblies *d*-limonene was verified. Functional testing of complex electronic assemblies was completed. No electrical failures were caused by the use of *d*-limonene. New analytical techniques were developed and used to measure and quantify residual solvent levels in the assemblies. Only trace amounts were detected in each of three consecutive tests.