

Aqueous and Semi-Aqueous Cleaning Processes

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AT&T's efforts to eliminate environmentally unsound manufacturing processes have included development of alternative fluxing and cleaning operations for use during printed-circuit board assembly. Innovations have been necessary because of health and stratospheric ozone depletion concerns. For wave-soldered through-hole assembly, elimination of solvent cleaning processes has been facilitated by detergent underbrush cleaning. Waste disposal problems associated with the detergent have been alleviated by "semi-aqueous" underbrush cleaning that uses an emulsion of water and a naturally-derived terpene hydrocarbon solvent. Improved surface insulation resistance of aggressive water soluble fluxes has allowed aqueous cleaning for products compatible with total immersion. Low solids, no-clean fluxes that leave minimal residue have eliminated the cleaning step for many products. For surface mount applications, where underbrush cleaning is not applicable, spray cleaning with terpene followed by water rinse has proven effective. Safety concerns about spray flammability and low flash temperature have been resolved, and excellent cleaning results have been obtained with a production machine running at AT&T's Merrimack Valley facility.

Introduction

This paper describes the evolution within AT&T of the cleaning processes used during printed-circuit board assembly. These processes have advanced from the use of environmentally hazardous halogenated solvents to aqueous and, more recently, semi-aqueous processes that are both economical and environmentally sound.

Two primary types of technology are used in the electronics industry for connecting components to printed-circuit boards. Most are assembled by wave-soldering component leads into plated-through-holes (PTHs) in the printed-circuit board. The newer surface mount technology (SMT) uses reflow soldering of component leads or terminations placed in "solder paste" on surface features of the printed-circuit board. Both technologies use a flux that promotes solder wetting by chemically reducing surface oxides and decreasing surface tension. In wave soldering, the flux is applied before the soldering

operation. In reflow soldering, it is contained in the solder paste. The cleaning or "defluxing" (i.e., flux removal) process required after assembly depends on the flux used.

Non-corrosive rosin (NCR) flux typically has been used to assemble telecommunications products. This flux provides acceptable reliability even if it is not totally removed after soldering. Defluxing of assemblies soldered with NCR flux usually is done to facilitate testing or to meet customer aesthetics requirements.

AT&T's efforts to eliminate the environmentally unsound solvent defluxing processes have included considerable work with aqueous cleaning. This work began when an underbrush detergent cleaning process was developed for wave solder assembly with rosin flux. A semi-aqueous process—terpene underbrush cleaning—subsequently was developed. Other advances involved water soluble flux (WSF) and low solids flux (LSF). Semi-aqueous cleaning has evolved into

a spray immersion process for surface-mount printed-circuit boards. Each of these developments will be discussed in more detail.

Through-Hole Assembly and Cleaning Technology

The technology associated with through-hole assembly previously was solvent underbrush cleaning. Aqueous underbrush cleaning, using detergents, eliminated the chlorinated solvents and offered improved worker safety. Increased use of detergent cleaning and the resulting spent detergent waste disposal problems led to the development of semi-aqueous underbrush cleaning, based on a naturally-derived, biodegradable terpene solvent. A comparison of costs for the various underbrush cleaning processes is shown in Figure 1. Advances also were made in the formulation of an improved water soluble flux. This allowed cleaning with water alone for components that are water immiscible. In many cases the cleaning operation has been eliminated entirely by using low solids flux.

Solvent Underbrush Cleaning. Wave soldered assemblies are transported over rotating brushes that are partially immersed in a chlorinated solvent such as trichloroethylene or perchloroethylene. Carbon absorber recovery units minimize ventilation losses of chlorinated solvent. Even with appropriately sized and efficiently operating recovery equipment, chlorinated solvent from a 25 gallon cleaning system is consumed at a rate of about 0.25 gallons per hour. At first, chlorinated solvents were used because they cleaned effectively, and were inexpensive and easy to use. When these solvents were recognized as potential carcinogens, alternative materials were investigated.

Aqueous Underbrush Cleaning. During the late 1970s, aqueous detergent mixtures began to replace chlorinated solvents in the underbrushing process. These monoethanolamine detergent systems saponify rosin (i.e., turn it into a soap), allowing it to be removed with an aqueous rinse. Though the aqueous detergents are less hazardous to employees than chlorinated solvents, they present other problems.

For underbrush cleaning, 5 to 10 percent detergent concentrations are used. A typical underbrushing facility generates more than 800 gallons of spent detergent effluent per week, and disposal is not easy. With a pH of approximately 11, the effluent has to be neutralized. Also, the detergents have high biochemical oxygen

Panel 1. Acronyms Used in This Paper

BOD	biochemical oxygen demand
CFC	chlorofluorocarbon
DI	deionized
IPA	isopropyl alcohol
LEL	lower explosive limit
LSF	low solids flux
MeOH	methanol
NFPA	National Fire Protection Association
PTH	plated-through-hole
SIR	surface insulation resistance
SMT	surface mount technology
WSF	water soluble flux

demand (BOD) and are complexing agents for heavy metals, making metal separation difficult. Thus, disposal involves storing the neutralized effluent in tanks, and periodically transporting it to a large municipal activated sludge plant for treatment. Disposal costs initially were low (about 10 cents per gallon), but with increasing demand on municipal sewage plants the cost increased to about one dollar per gallon by 1985.

Semi-Aqueous Terpene Underbrush Cleaning. As an alternative to aqueous detergent defluxing, a semi-aqueous terpene hydrocarbon material, known as BIOACT® EC-7™, was developed by Petroferm Inc.¹ according to AT&T specifications. This terpene hydrocarbon solvent is derived from natural sources, and is biodegradable, non-toxic, and non-corrosive. Special non-ionic surfactants are added to allow it to form an emulsion with water so the assembly can be rinsed.

AT&T has used EC-7 underbrush cleaning of wave soldered printed-circuit board assemblies for over five years. The EC-7 product concentration used for underbrush cleaning is typically 35 to 50 percent, and the rosin loading capability of the material is extremely large (EC-7 compound holds roughly its own weight in rosin). Biodegradability allows easy waste management.²

Aqueous Total Immersion Spray Cleaning. Water soluble fluxes are very aggressive and provide excellent soldering. However, to ensure product reliability, the aggressive WSF must be removed thoroughly from assemblies using total immersion spray cleaning. WSF residues can be removed effectively with water alone.³ However, the assemblies and components must be compatible with immersion in water. An adequate flow of

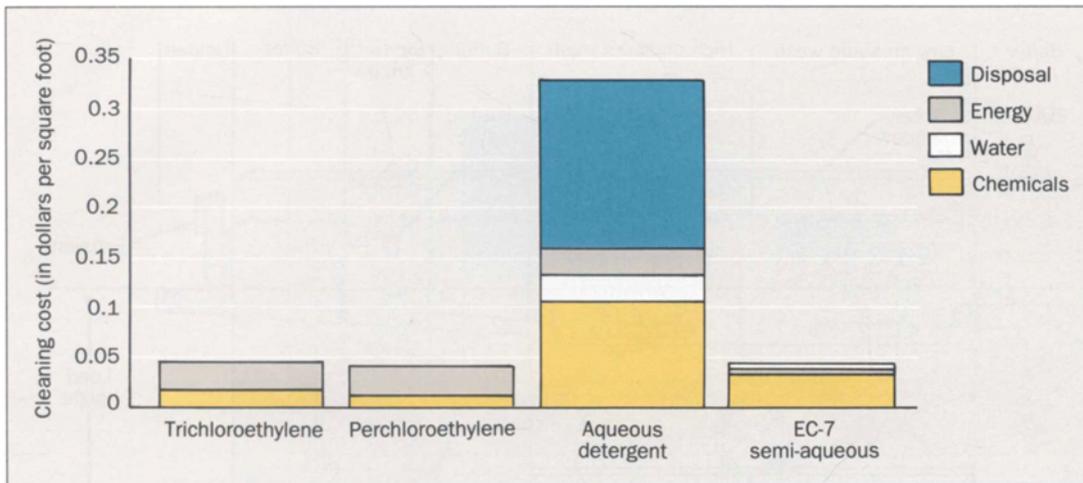


Figure 1. A comparison of the costs for various underbrush cleaning processes, including trichloroethylene, perchloroethylene, aqueous detergents, and semi-aqueous EC-7 compound.

heated deionized (DI) water is required (typically 3 to 6 gallons per minute at 60 to about 71° C). The energy consumption for these systems is large.

Waste management techniques, using exchange resins and filters to remove ionic and organic material, are available to minimize rinse water effluent. These water re-use techniques also reduce significantly the energy needed to heat fresh incoming DI water.

WSF Improvements. One problem with WSF assembly has been absorption of the water-soluble vehicles of the flux (typically polyglycol surfactants) in the printed-circuit board matrix during soldering. Although these materials are non-corrosive, they can reduce the surface insulation resistance (SIR) between conductors by increasing the hydrophilic (i.e., water attracting) nature of the printed-circuit board material. The decrease in SIR has prompted concerns that the electrical isolation properties of the printed-circuit board may be affected adversely. A recent AT&T development⁴ has eliminated this problem by altering the chemistry of the WSF vehicle. Mixing traditional hydrophilic glycol vehicles and a small amount of hydrophobic (i.e., water repelling) surfactants, the SIR of the WSF processed assembly has been improved by up to three orders of magnitude. This effect is a direct result of the hydrophobic surfactant being preferentially absorbed into the printed-circuit board matrix in place of the hydrophilic glycol.

No-Clean Assembly. Cleaning is a non-value-added operation, and the most cost effective approach is to not clean at all. Because flux is required in soldering, a no-clean assembly process is possible only if the flux

residues are minimal and do not cause testing problems or compromise product reliability. One class of low residue fluxes is known as low solids flux. These have far lower solids concentrations than the rosin fluxes historically used for soldering, which have been composed of 30 to 40 percent rosin solids in isopropyl alcohol (IPA). Low solids fluxes, however, typically have less than 5 percent solids. They often consist of organic acid activators (rather than rosin), along with other additives, dissolved in IPA. The flux residues remaining after soldering are minimal.

LSF, mainly because it eliminates the need for cleaning solvents and equipment, is gaining wide acceptance in the electronics industry for wave solder assembly. To avoid degrading product reliability, the amount of LSF applied to an assembly must be controlled.⁵

Surface Mount Assembly and Cleaning Technology

In SMT assembly operations, infrared or hot air heating is used to reflow solder paste. Efforts to formulate an effective water soluble paste that meets AT&T requirements have not been completely successful, and LSF technology still is being developed. Consequently, surface mount devices are assembled using rosin-based solder paste.

Underbrush cleaning techniques for SMT assemblies are ineffective due to the close spacing between and beneath components. SMT assemblies typically are cleaned by spraying them with an azeotrope of chlorofluorocarbon (CFC) 113 and methanol (MeOH). However, the relationship between CFCs and stratospheric ozone depletion,

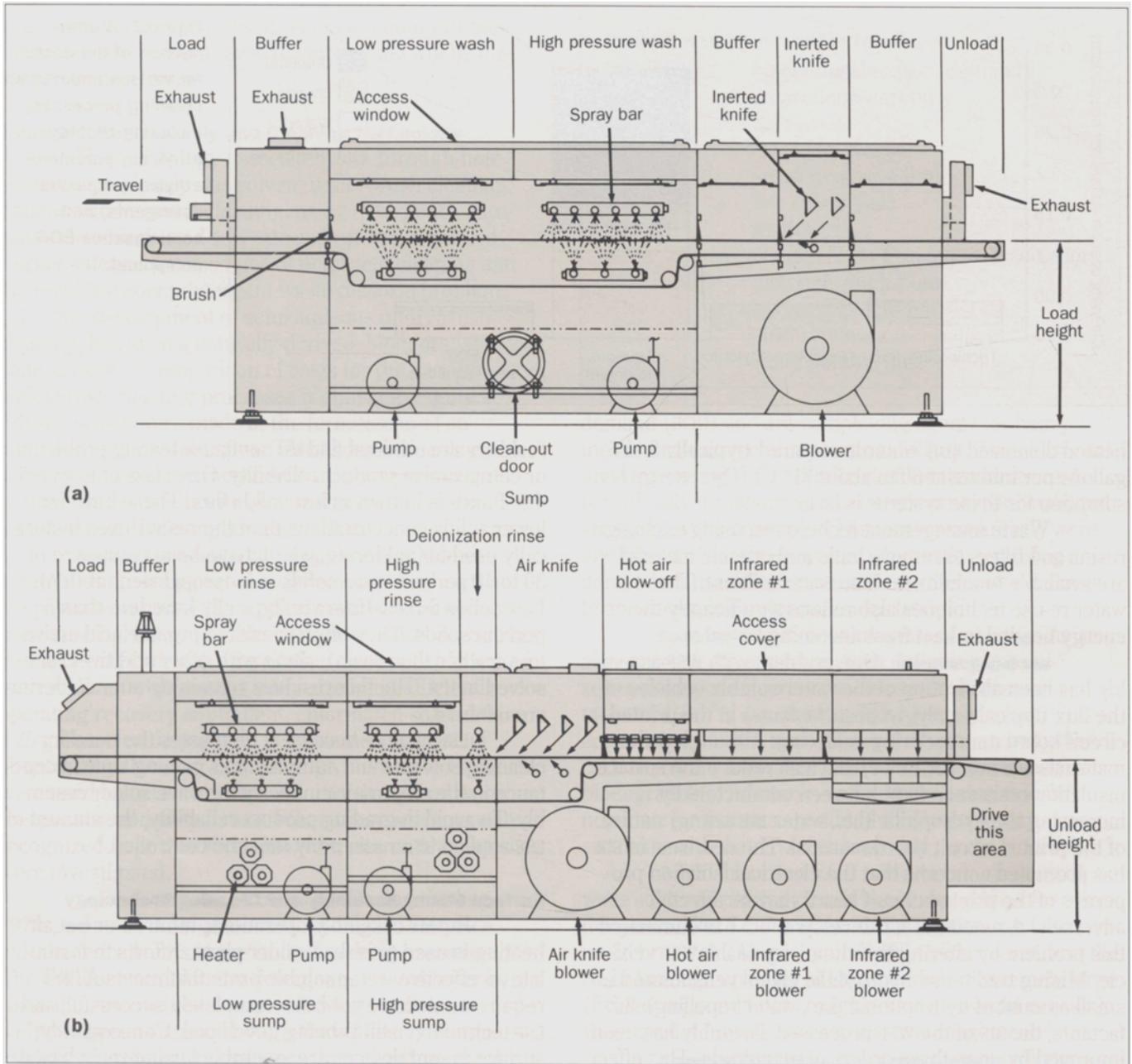


Figure 2. A schematic diagram of the EC-7 terpene spray facility in service at AT&T's Merrimack Valley manufacturing location, consisting of two in-line conveyORIZED spray modules. The wash module (Figure 2A) sprays concentrated EC-7 product from a 110 gallon room temperature recirculating sump. The rinse module (Figure 2B) sprays DI water from a 110 gallon recirculating sump.

and the excise tax imposed on CFCs in January 1990, are forcing companies to seek alternative cleaning materials.

Terpene Spray Cleaning. Successful spray cleaning trials with the EC-7 compound were conducted during the summer of 1987.⁶ Specifications for a production semi-aqueous spray cleaning machine were developed, and the Detrex Company was chosen to build AT&T's

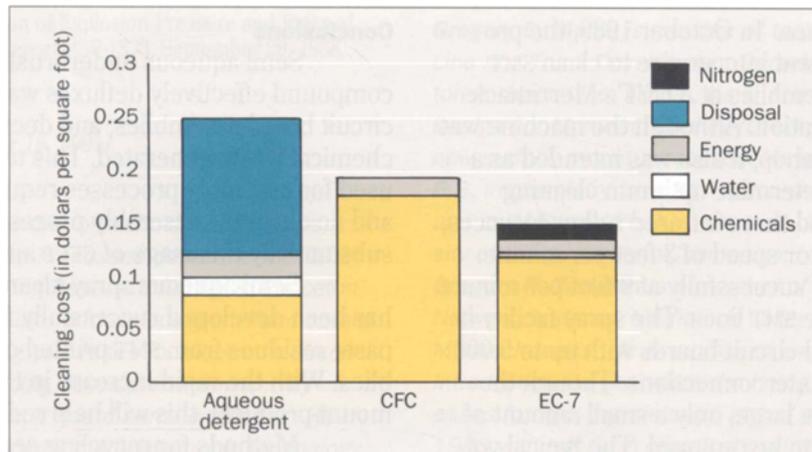


Figure 3. A comparison of semi-aqueous costs to CFC spray cleaning costs.

first system. During construction of the production machine, a portable spray facility was constructed so that material compatibility and process studies could continue. The EC-7 terpene product was found superior to the CFC-113/MeOH material for removing reflowed solder paste residues.⁷

The production spray machine consists of two in-line conveyerized spray modules. A schematic diagram of the system appears in Figure 2. Each module has low pressure and high pressure spray sections [30 and 90 pounds per square inch (psi)] followed by an "air knife" to remove excess liquid from the printed-circuit board surface. The wash module (Figure 2a) sprays 100 percent concentrated EC-7 compound at room temperature. This is recirculated from a 110 gallon sump. The rinse module (Figure 2b) sprays DI water, also recirculated from a 110 gallon sump. Before exiting the rinse module, assemblies are sprayed with a final rinse of fresh DI water. The final rinse water cascades forward into the recirculated sump at a flow rate of approximately 0.75 gallons per minute. The rinse module is equipped with air knives to remove most of the rinse water, followed by infrared heaters for final drying.

Safety and Flammability Issues. Although the EC-7 product has positive attributes, it has a closed-cup flash point of approximately 47° C. Therefore, precautions must be taken in handling and using the liquid. Most of these, including requirements for design of the cleaning machine, are set forth in the standards of the National Fire Protection Association (NFPA).

Evaluations⁸ were made of the hazards associated with the EC-7 compound, concurrently with design and fabrication of the production facility. An independent

testing laboratory's evaluation⁹ proved that a flammable atmosphere is created by the impact of the EC-7 spray against a printed-circuit board, because the "bounce-back" spray creates an ignitable mist. The evaluation recommended an explosion protection system for the EC-7 spray wash module. Calculations showed that explosion venting or containment is impractical because of the rapid pressure rise and high maximum pressure measured for the terpene product.¹⁰ Either of these options also would place restrictions on both the design and installation of the machine. An explosion suppression system was considered undesirable in a factory environment because of the possibility of false activation.

Explosion prevention was judged preferable to suppression, venting, or containment. A system was installed to inert the EC-7 compound's spray chamber using nitrogen, and to monitor the oxygen concentration continuously. If this increases above 8 percent, the machine is shut off automatically.

Because of heat being supplied by the entering printed-circuit boards and pumping of the liquid, a cooling system was included to limit the EC-7 compound's sump temperature to 25° C. This limits the vapor concentration inside the machine to 25 percent of the lower explosive limit (LEL). The temperature of recirculating air used in the wash module air knife also is controlled.

The EC-7 product's spray module was designed with vestibules and convective barriers on each end to minimize nitrogen consumption and contain the compound's strong citrus odor. Exhaust is provided at the exit and entry end of the machine to capture any vapors or aerosol that might escape, but the wash chamber itself is not vented.

Operating Experience. In October 1989, the production spray machine went into service to clean SMT printed-circuit board assemblies at AT&T's Merrimack Valley manufacturing location. Although the machine was installed in a production shop, it also was intended as a development facility to determine optimum cleaning parameters. The shop had three infrared reflow furnaces, each running at a conveyor speed of 3 feet per minute. The machine is operated successfully at 9 feet per minute, thus supporting the three SMT lines. The spray facility is used to clean SMT printed-circuit boards with up to 5,000 surface mount reflowed interconnections. Though the interconnection density is large, only a small amount of solder paste residue has to be removed. The typical volume of solder paste applied per interconnection is less than 0.001 cubic inches, and the paste is only 11 percent flux by weight. Because of the large rosin loading capacity of EC-7 compound, approximately a year would be required for the 110 gallon charge to saturate with flux.

The production facility also has been used to clean misregistered, stencil-printed solder paste from printed-circuit boards. The amount of solder paste removed has made it necessary to clean the facility and replace the EC-7 product charge a few times a year. Even so, semi-aqueous cleaning has minimized effluent waste and has been cost effective.

Terpene Qualification

Material qualification studies have been done on the EC-7 compound, and comparisons have been made to standard detergents. The product passes all standard tests: copper mirror, silver chromate, and pH. SIR evaluations have been made using interdigitated metallic conductors arranged in comb patterns on printed-circuit boards. These first were subjected to the EC-7 cleaning process, then exposed to elevated temperature and humidity (35° C at 90 percent relative humidity) for several days.

Because the surfactants used in the EC-7 compound are non-ionic, rinsing efficiency does not increase with higher rinse water temperature. This has been confirmed by SIR measurements, both for underbrush cleaning with dilute EC-7 compound and spray cleaning with concentrated material. Elimination of hot water for rinsing provides a considerable cost savings. Figure 3 shows a comparison of semi-aqueous, CFC, and detergent spray cleaning costs.

Conclusions

Semi-aqueous underbrush cleaning with EC-7 compound effectively defluxes wave soldered printed-circuit board assemblies, and decreases the amount of chemical waste generated. This technology still is being used for assembly processes requiring rosin flux. WSF and no-clean LSF assembly processes also are decreasing substantially the usage of CFCs and chlorinated solvents.

Semi-aqueous spray cleaning using EC-7 terpene has been developed successfully for removal of solder paste residues from SMT printed-circuit board assemblies. With the rapid increase in the number of surface mount products, this will help reduce CFC emissions.

Methods for recycling semi-aqueous solvents as well as recycling and reusing rinse water currently are being developed as the next step in the continuing evolution of assembly and cleaning technology.

Acknowledgments

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References

1. Michael E. Hayes, Craig C. Hood, Ronald E. Miller, and Robert Sharpe, U.S. Patent 4,640,719, February 3, 1987 (assigned to Petroleum Fermentations N.V.).
2. Stan Bernstein and James Green, "Effluent Pretreatment and Disposal When Cleaning Soldered PWAs With BIOACT EC-7 and Water," *Alpha Metals Application/Procedures Bulletin S/M-331*, February 1990.
3. George M. Wenger, Leslie A. Guth, and David A. Dickinson, "Advances In Cleaning Of Surface Mount Assemblies," *Circuit World*, Vol. 16, No. 3, March 10, 1990, pp 36-46.
4. Courtney V. Dodd and Gregory C. Munie, U.S. Patent 5,009,724, April 23, 1991 (assigned to AT&T).
5. Leslie A. Guth, "To Clean or Not To Clean?" *Circuits Manufacturing*, Vol. 29, No. 2, February 1989, pp. 59-63.
6. George M. Wenger and Gregory C. Munie, "Defluxing Using Terpene Hydrocarbon Solvents," IPC Technical Paper No. 678, April 1987.
7. Michael E. Hayes, "High Performance Cleaning With Terpene/Surfactant Mixtures," *Defeating The Ozone Problem—Alternative Cleaning of Surface Mount & PCB Assemblies*, Technical Symposium, National Physical Laboratory, Teddington, Middlesex, England, November 2, 1989.
8. George M. Wenger and David A. Dickinson, "Terpene Cleaning Applications and Technology," *Technical Proceeding of NEPCON East*, June 1989, pp. 812 - 824.
9. Hercules, Inc., "Preliminary Hazard Analysis of Printed Circuit Board Cleaning Process," Report AO8163-520-03-001, HERC 88-36, April 27, 1988.

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10. Fenwal, Inc., "Determination of Explosion Pressure and Rates of Pressure Rise For EC-7," Report PSR-1333, September 29, 1988.

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