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# HEALTH AND SAFETY IMPACTS OF CITRUS-BASED TERPENES IN PRINTED CIRCUIT BOARD CLEANING

Technical Report No. 6 1993

University of Massachusetts Lowell

# HEALTH AND SAFETY IMPACTS OF CITRUS-BASED TERPENES IN PRINTED CIRCUIT BOARD CLEANING

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**The Toxics Use Reduction Institute Research Fellowship Program**

June 1993

The Toxics Use Reduction Institute
University of Massachusetts Lowell



The Toxics Use Reduction Institute is a multi-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to governments to promote the reduction in the use of toxic chemicals or the generation of toxic chemical byproducts in industry and commerce. Further information can be obtained by writing the Toxics Use Reduction Institute, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854.

# PREFACE

In 1991 the Toxics Use Reduction Institute established the Research Fellows Program at the University of Massachusetts Lowell (UML). The Research Fellows Program funds toxics use reduction research projects performed by a graduate student and their advisor. The goals of the Research Fellows Program are:

- to develop technologies, materials, processes, and methods for implementing toxics use reduction techniques.
- to develop an understanding of toxics use reduction among UML graduate students and faculty,
- to facilitate the integration of the concept of toxics use reduction into UML research projects,
- to provide UML faculty with "incubator" funding for toxics use reduction related research, and
- to act as a liaison between Massachusetts industries UML faculty.

The types of projects funded through the Research Fellows Program are technology, methods, and policy research projects. Each final project report is published by the Institute. The opinions and conclusions expressed in this Research Fellow report are those of the authors and not necessarily those of the Toxics Use Reduction Institute.

**EXECUTIVE SUMMARY**

The threat posed by ozone depleting chemicals to the environment is well known. These chemicals slowly, but progressively deplete the earth's stratopheric ozone layer. Local and international regulation has been enacted to freeze, reduce, and eliminate ozone depleting chemicals from use in consumer goods as well as manufacturing processes. In response, one manufacturing sector, printed circuit board manufacturers, have performed investigations of possible alternative chemistries to alleviate their contribution to this problem. Investigations have included cleaning performance testing, health and safety issues, and environmental issues.

This report examines the health and safety impacts of d-Limonene as used in the printed circuit board cleaning operation. It focuses on animal and human toxicological studies and equipment safety features to conclude the impacts to the people involved in the printed circuit board cleaning operation. Data was obtained through data base searches and from manufacturers of d-Limonene, printed circuit board (PCB) defluxer manufacturers and PCB cleaning equipment manufacturers.

The primary health and safety concerns with the use of d-Limonene in the PCB cleaning operation are combustibility and toxicity. d-Limonene has introduced a fire hazard into the PCB cleaning operation due to its low flashpoint. This risk is made manageable through proper equipment safeguarding. d-Limonene also raises concern about toxicity to humans. Toxicological studies performed on animals and humans indicate that human toxicity may be low to moderate. Dermal exposure and inhalation in the occupational setting are concerns which can be minimized through the use of personal protective equipment and proper exposure safeguarding.

In summary, the achievable benefits of using d-Limonene as an alternative cleaning chemistry would be compromised if risk was shifted from one concern to another. But, in reality d-Limonenes use as a safe alternative to ozone depleters is supported by evidence of relatively low toxicity, and adequate safety procedures and features relevant to the cleaning operation.

**ABSTRACT**

A semi-aqueous terpene based cleaning formulation is rapidly finding acceptance as an alternative to ozone depleting solvents in the printed circuit board (PCB) cleaning operation. The formulation contains d-Limonene and a surfactant material. PCB manufacturers are qualifying this alternative based on extensive cleaning performance and material compatibility testing. Health and safety, and environmental issues are also being considered. This paper is a compilation of current information concerning the health and safety impacts of the primary constituent, d-Limonene, as used in the PCB cleaning operation. The purpose of this paper is to furnish readers with as much relevant information as possible about the health and safety concerns associated with d-Limonene.

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## INTRODUCTION

With ozone depleting solvents being phased out of manufacture and use, the USEPA Chlorinated Solvents Coordination Committee and the Office of Air and Radiation have identified terpene compounds as potential substitutes for ozone depleting solvents.[1] Consequently, solvent manufacturers are formulating the next series of printed circuit board defluxers which are designed to be more environmentally safe than the previous ones. Based on its natural abundance and commercial potential, d-Limonene has been selected as the primary constituent of an electronic PCB defluxer formulation.

One of the first questions to be asked when considering an alternative cleaning chemistry is, "Does it clean as well as the ozone depleting solvent that it is replacing?." Manufacturing qualification testing has identified many alternatives which perform as well or better than the solvents they are expected to replace. Nevertheless, many of these alternative chemistries have concerns with health and safety, and xvironmental issues. Printed circuit board manufacturers are realizing the potential dilemma of eliminating an atmospheric problem for some other health, safety, and/or environmental concern. This report compiles recent information from a variety of sources in an attempt to alleviate misconceptions in the use of this alternative solvent.

## GENERAL SOLVENT INFORMATION

### Source Background

Classified as cyclic and acyclic hydrocarbons, terpenes generally encompass a series of isoprene oligomers and may include derivatives such as alcohol, aldehydes, esters, and other nonvolatile, high-boiling components that can not be detected by gas chromatography.[2 cited in 8] Produced mainly from citrus fruits and coniferous plants, terpenes are among natures most common substances and d-Limonene (CAS #5989-27-5) is the most widely distributed terpene. Variations of this terpene include the racemic form dl-limonene (CAS #138-86-3) and l-limonene (CAS #5989-54-8).[3]

d-Limonene, the major component of orange (p-mentha-1,8-diene; Figure 1) is a monoterpene hydrocarbon with molecular formula $C_{10}H_{16}$ and is widely distributed in nature. It forms the main constituent of the terpene fraction of citrus essential oils, can be found in many plants and spices[4] (eg. pine trees, caraway, dill, bergamot etc.) and has even been isolated in marine plants (algae).[5]

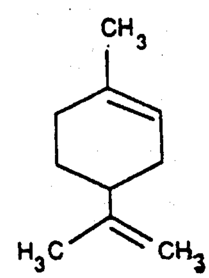


**Figure 1.** d-Limonene, the major component of orange oil.

The orange industry provides the main feedstock for the electronics defluxer formulation.[6] d-Limonene obtained from orange oil within orange flavedo (rind), is present at concentrations of at least 96%.[7] The location of orange oil is detailed in Figure 2.

Recovery of d-Limonene is accomplished by extraction in either of two methods. The Brown Oil Extractor recovers oil before juice extraction whereas the FMC In Line Extractor recovers oil from the

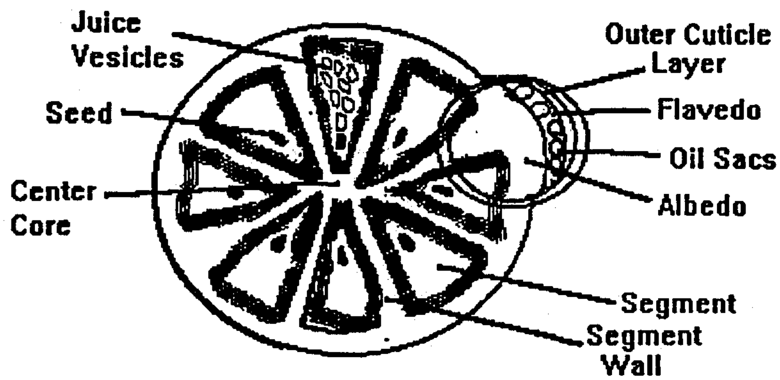


**Figure 2.** Schematic cross section of an orange, showing the location of oil sacs within the flavedo. (Food Technology)

fruit during the juice extraction process.[8] A process flow diagram is shown in Figure 3. Additional processing by alkali treatment and steam distillation is performed for other applications of d-Limonene.[9]

### Applications of d-Limonene

Great quantities of d-Limonene are used in a variety of consumer and industrial products. d-Limonene movement for the first half of July 1992 was 132,292 pounds for one manufacturer.[10] d-Limonene is used primarily as a starting raw material in the synthesis of polyterpene resins. It is also used to produce growth retardants, immitation citrus and essential oils, and synthetic sweeteners. Because of its sweet citrus taste and odor, it is used as a flavor and fragrance additive in perfumes, soap and detergent, creams and lotions, and in a variety of foodstuffs at levels regulated by the Food and Drug Administration. Its use in consumer and household cleaning products (ie. CitraSolve, PineSol, Orange Mexo, etc.) led to the development of industrial cleaning products and an electronics defluxer, thereby becoming an alternative to chlorinated hydrocarbon solvents.

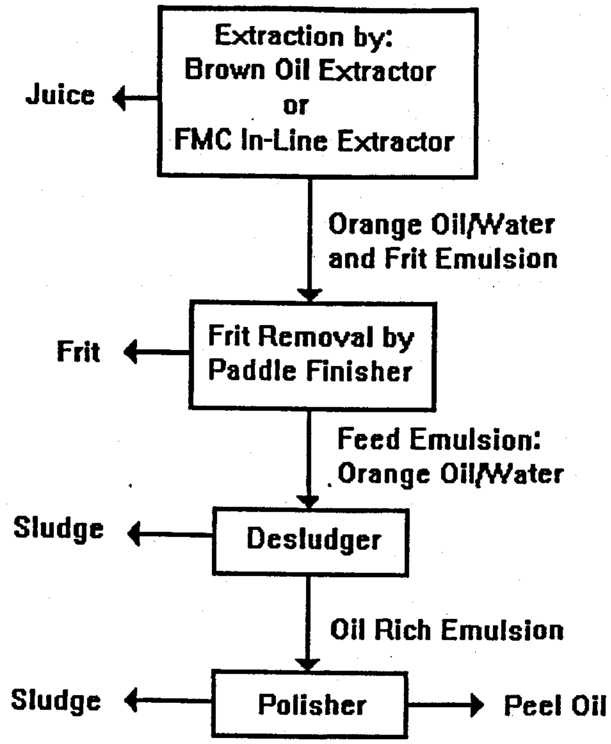


**Figure 3.** Orange peel oil recovery process schematic.

The identification of terpene compounds and its use in household cleaners provided the impetus for electronics industry involvement in the development of an alternative terpene-based electronics defluxer. A U.S. patent issued to Hayes et al[11] in 1987, describes a rosin flux cleaner consisting of a terpene material and emulsifying surfactants. In 1988, AT&T and Petroferm Inc., determined d-Limonene as having the most commercial potential as an electronics defluxer. Petroferm then announced the formulation of the semi-aqueous terpene-based cleaner BIOACT EC-7(TM), consisting of d-Limonene and a surfactant material, that could serve as an alternative electronics defluxer.[12] This product was reformulated into BIOACT EC-7R(TM) which has the advantage of being recyclable.[13] Dependent on the type of contamination and level of cleanliness desired, recycled d-Limonene can be used as a solvent or blended as a fuel additive for incineration. (The manufacturer, distributor, recycler and contacts are listed in appendix A.)

## MATERIAL REGULATIONS AND SAFETY DATA

### Status, Regulations, and Recommendations

As a flavoring substance, the US FDA lists d-Limonene as "generally recognized as safe" (GRAS).[14] Although d-Limonene is not listed as a hazardous or toxic substance by any of the EPA federal statutes,[15] it is listed on the TSCA chemical inventory and TSCA test submissions database (TSCATS).[17] No recommendations on use levels have been generated by OSHA, ACGIH, NIOSH, or NFPA,[18,19] although the manufacturer of the electronics defluxer suggests a Permissible Exposure Level/Threshold Limit Value (PEL/TLV) of 400ppm. A more realistic PEL/TLV is suggested by at 100ppm which coincides with of the PEL of $C_{10}H_{16}$ turpentines listed in the NIOSH/OSHA Pocket Guide to Chemical Hazards.[16,20]

### Material Reactivity and Safety Data

Information on product composition, physical data and fire hazard data are listed in Tables 1, 2, and 3.d-Limonene is stable under normal conditions of storage although cold storage in closed vessels is suggested to reduce the potential oxidation of d-Limonene.[21] It is incompatible with strong mineral acids, strong oxidizers and will react violently with (iodine pentafluoride+tetrafluoroethylene.[22] In the presence of dry hydrogen chloride or hydrogen bromide, it will form monohalides; with aqueous hydrogen chloride or hydrogen bromide, it will form dihalide.[23]

| Ingredients | % Composition | CAS # |
|---|---|---|
| Terpene Hydrocarbon (d-Limonene) | 90% - 98% | 5989-27-5 |
| Surfactant * (aliphatic ester) | 2% - 10% | Proprietary |

* used to improve emulsification properties of product

**Table 1.** Electronic PCB defluxer composition (Petroferm)

| | |
|---|---|
| Appearance | Clear, free flowing liquid |
| Odor | Slight citrus odor |
| Boiling Point | 340-372 degF (@ 760mm Hg) |
| Vapor Pressure | 1.6mm Hg (@ 70 degF) |
| Vapor Density | 4.7 |
| Specific Gravity | 0.84 (water = 1 @ 77 degF) |
| Solubility in Water | Insoluble |
| % Volatile by Weight | 100 approximately |
| Evaporation Rate | Less than 1 (BUAC = 1) |
| Ph (5% solution) | 5-7 |
| VOC d-Limonene | 7.0 pounds/gallon |

**Table 2.** Physical Data (Petroferm)

| | |
|---|---|
| Flash Point | 117 degF (COC)<br>145 degF (TOC) |
| Flammable Limits | LEL - 0.7, UEL - 6.0<br>(% by vol. in air) |
| Extinguishing Media | Dry chemical, foam, carbon dioxide |
| Fire Fighting Procedures | Use NIOSH approved SCBA |

**Table 3.** Fire hazard data. (Petroferm)

## APPLICATION IN PCB CLEANING OPERATION

### Background

Because of the high demand and variety of uses for printed circuit boards (PCBs), electronics manufacturers have become a vanguard for the qualification of alternative cleaning chemistries for defluxing PCBs. Printed circuit boards are used in a variety of assemblies to manufacture products ranging from consumer electronics (eg. toys, home appliances) to military hardware. Due to the variety of applications, various levels of cleanliness apply. PCBs not used in critical applications (eg. military applications, computers, etc.) wouldn't require a high level of cleanliness because of higher component tolerances. Alternatively, PCB components with critical component tolerances would be affected by leftover contamination in areas of circuit performance and degradation.

The soldering operation is the predominant source of contaminants. Soldering provides for the mechanical attachment as well as electrical continuity of electronic components to the printed circuit board (PCB). Flux aids the PCB soldering process by removing oxidation from the surface receiving solder and also wets the surfaces of the metals to be joined. Solvent cleaners are used to remove rosin flux residues as well as contamination produced by handling and other sources shown in Table 4. The flux residues include ionic contamination such as flux activators and nonionic rosin residue. A primary reason terpenes remove soldering related contaminants so well is that solder rosin contains abietic acid, which is a derivative of terpenes, thereby creating a natural affinity with terpene-based solvents.[24]

| Contamination Type | Origin |
|---|---|
| Organics | Fluxes, solder masks, tape, fingerprints |
| Inorganic soluble | PCB processing, flux residues |
| Organic metal | Flux residues, white residues |
| Soluble inorganic | Flux residues, white residues, acids, water |
| Particulate matter | Airborne matter, debris |

**Table 4.** Types of contamination found on printed circuit boards (Surface Mount Technology, McGraw-Hill)

Typical manufacturing qualification tests include two IPC - approved cleanliness test methods, ionic contamination and surface insulation resistance (SIR) and are benchmarked against an existing CFC-113/methanol/nitromethane solvent reference value.[25] Other testing includes: thermal cycling and humidity aging, long term SIR, material compatibility, and fungus resistance.[26] Extensive testing is a requirment for printed circuit board manufacturers but more so for military contractors as they must bear the burden of proof for PCB cleanliness to meet rigid military specifications.[27] As qualification test results prove the credibility of d-Limonene for use as a PCB defluxer,[28-31] its industrial use should necessitate the evaluation of health, safety and environmental issues relevant to the PCB cleaning operation.

## HEALTH AND SAFETY ISSUES

### Background

The information reviewed suggests that the primary health and safety issues with d-Limonene in electronics cleaning are dermal toxicity and fire hazard. Toxicological issues are reported in Toxicology of d-Limonene and Exposures sections, and flammability issues are discussed in the Equipment/Process Safety section.

### Solvent Safety Concerns

A significant concern when using a terpene-based solvent is combustibility and possibly flammability. Matta stated that the formulation of a cleaning product based on d-Limonene is a problem due to safety concerns with low flashpoint.[32] Marino et al stated concerns about low flashpoint after solvent samples taken from the batch system sump generated a low flashpoint of 104 deg F (TCC),[33] and later, a flashpoint of 97 deg F (TCC) was reported although concerns with test reproducability and sample contamination were not resolved.[34]

The terpene defluxer under consideration has a flashpoint of 117 deg F, and per OSHA regulations[35] is considered a combustible Class II liquid. At temperatures below the flash point, a fire is not possible except under conditions where a mist may occur and an ignition source is present. Fire prevention methods based on principles such as exclusion of ignition sources, exclusion of air (oxygen), ventilation to prevent accumulation of vapor, and use of an inert atmosphere[36] are necessary equipment process design parameters for safe use of terpenes in printed circuit board cleaning equipment.

### Process/Equipment Safety

There are two process modes for cleaning PCBs: enclosed-conveyorized and batch. The enclosed-conveyorized mode transports parts automatically and continuously whereas the batch mode requires an operator to transport fixed lot quantities. Both can be generally thought of as 3-step procedures with intermediate solvent/residue removal and water removal steps. Two approaches treated in this report for enclosed-conveyorized equipment are: Spray under immersion and direct spray. The systems are fully enclosed and consist of solvent wash, water rinse, and drying sections. As for the batch system, a popular "dishwasher", "dishdryer" approach is covered. Schematics of each mode are shown in Figs. 4 and 5.

The cleaning systems used in each process mode have extensive safety features designed into them due to combustibility concerns with d-Limonene. Typically, mechanical, electrical, and logic systems are constructed to comply with the National Electrical Code, the National Fire Protection Association Codes and Standards, the Joint Industrial Council and OSHA regulations.[37,38] The safety features in each system are described in the following sections.

**Enclosed-**
**Conveyorized:** Solvent wash consisting of direct spray or spray under immersion
---- Air knife excess solvent and residue
Water rinse

Quinn, M.M., T.J. Smith, T. Schneider, H.A. Feldman, E.A. Eisen, **M.J. Ellenbecker**, D.H. Wegman, G. M. March, and R.A. Stone, "A Method to Adjust Fibrous Aerosol Monitoring Data to Biologically-Based Indices of Exposure," submitted to Annals Occ. Hyg., 1996.

Quinn, M.M., T.J. Smith, E.A. Eisen, T. Schneider, D.H. Wegman, **M.J. Ellenbecker**, H.A. Feldman, G. M. Marsh, R.A. Stone, "Determinants of Airborne Fiber Size in the MMVF Production Industry," submitted to Annals Occ. Hyg., 1996.

**Ellenbecker, M.**, "Engineering Controls as an Intervention to Reduce Worker Exposure," American Journal of Industrial Medicine, 1996

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**LeBlanc C.**, "Surface Cleaning Lab Seeks Better, Cleaner Ways to Spruce Up Surfaces," Today's Chemist at Work (American Chemical Society), May 1997.

Quinn, M.M., T.J. Smith, **M.J. Ellenbecker**, DH. Wegman, E.A. Eisen, " A model to Predict Deposition of Man Made Vitreous Fibers in the Human Tracheobronchial Region," accepted by Annals Occ. Hyg., 1997.

Lee, B.K. and and **M.J. Ellenbecker**, "Analyses of Medical Waste and the Resulting Emisions of Dioxins and Furans," submitted to J. Air and Waste Mgmnt. Assoc., 1996.

Sidel, V. W., B. Levy , **B. Johnson**, "Environmental Injustice: What Must Be Done?" Health & Environment Digest, Vol.9, No.10, 1996

**Johnson, B.**, "Toxics Use Reduction Networking Grants Program: A Community Education Program Designed to Educate Community Residents About Toxics Use Reduction and Pollution Prevention," Empowering the Disadvantaged, Social Justice in Public Health, American Public Health Association, Nov. 1996

---- Air knife excess water

Hot air / IR dry

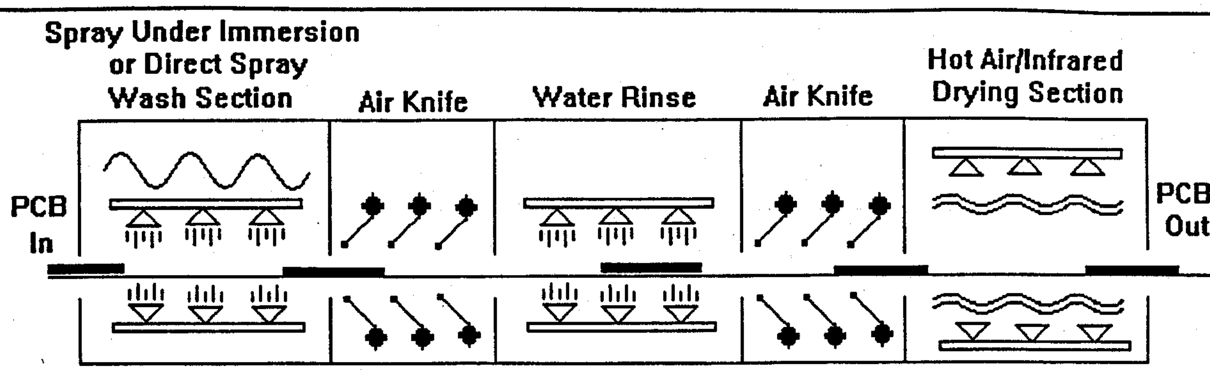


**Figure 4.** Enclosed-Conveyorized Cleaning Equipment Schematic (Detrex)

**Batch:** Solvent wash module in inert atmosphere

---- Residue and solvent drip-off

Water rinse module

---- Water drip-off

Oven dry module

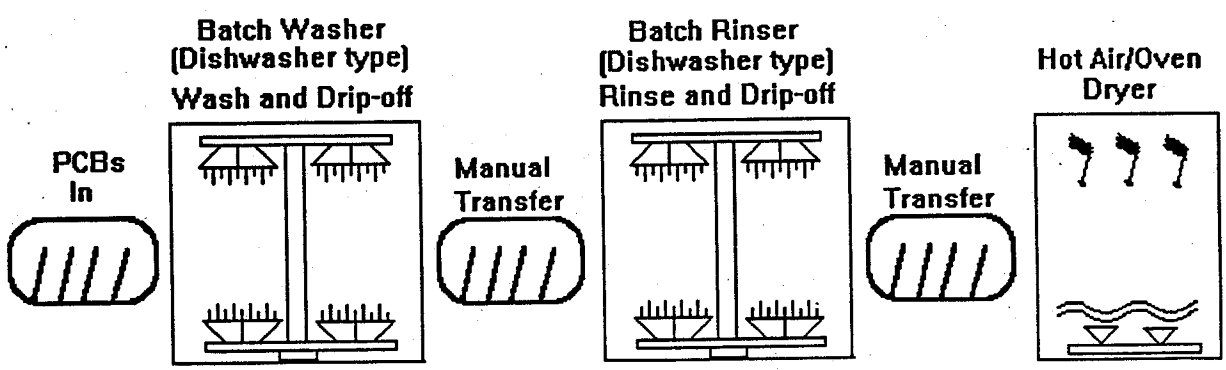


**Figure 5.** Batch Cleaning Equipment Schematic (Vitronics)

**Spray Under Immersion: Enclosed-Conveyorized Equipment**

PCBs enter the wash zone of by conveyor and descend into an agitated spray under immersion, bath of solvent. By spraying under immersion, atomization of solvents is eliminated. Heat inputs in the form of warm PCBs and pump friction are monitored by temperature control logic and kept within a safe operating range by a chilled water supply system. Control logic monitors solvent levels, rinsewater levels and specific gravity. If levels fall or rise beyond set points, the control system logic will signal an operator.

A CO2 fire suppression system protects the solvent wash section, the mechanical pump compartment and the associated ventilation exhaust stacks. Fire suppression control logic terminates equipment and exhaust operation and can be externally connected to a facilities main fire alarm system. Finally, electrostatic ignition is eliminated by equipment bonding and grounding.

**Direct Spray: Enclosed-Conveyorized Equipment**

Printed circuit boards are fed on a horizontal conveyor into the wash stage where upon it receives a high impingement spray of terpene solvent. This action causes misting of the solvent, presents a flammability hazard. This hazard is eliminated by designing all components in the spray area to meet NFPA Class 1, Division 1 specifications and, pumps and other associated electrical devices to meet NFPA Class 1, Division 2 specifications. Designing equipment to this specification eliminates equipment and electrical ignition sources.[39] Possible fire sources external to the machine are prevented from entering by an ignition source detector. The detector is mounted at the front of the equipments wash section and will shutdown the equipment to prevent ignition sources from entering the system. Additionally, redundant fire detection control circuitry, coupled with $CO_2$ fire suppression in the wash section protects the equipment from fire hazard. Factory Mutual Research performed fire testing on a direct spray system and the results prove that this form of fire detection/suppression is very effective.[40] (See Figure 6 for fire test summary performed by Factory Mutual Research.) Air scrubbers packed with filtering material that prevent mist and odor in the work environment may prevent a fire hazard. This situation is eliminated by a continuous flow of water against the filtering material which rinses solvent buildup to drain.

Factory Mutual Research was contracted to witness fire testing of the wash section of the enclosed-conveyorized direct spray terpene cleaning equipment. The purpose of the test was to determine what would happen when an ignition source was introduced into the spray section of the washer while operating under normal conditions.

...A pine board was soaked with a terpene-based electronics defluxer, ignited, and fed into the spray section of the equipment at two different conveyor speeds - 3 fpm and 4.5 fpm. Flashover of solvent occured , followed by fire system detection and total fire suppression within 6 seconds and 7 seconds, respectively. No visible flames occurred. At the conclusion of the test, the interior of the equipment was inspected and noted to be in working condition.

**Figure 6.** Fire Testing of Direct Spray Wash Equipment (Factory Mutual Research, provided by Vitronics Corp.)

**Batch Equipment**

A fixed-lot quantity of circuit boards are manually loaded into the batch wash module. The wash module cycle begins by purging the chamber with an inert gas, thus reducing the oxygen content and the flammability of the contents. A safety interlocked, pressurized nitrogen supply is used to dispense the solvent directly from the shipping container to the sump, thus eliminating the need for pumps while greatly reducing combustibility concerns and preventing spillage. The solvent sump is filled, the circuit boards are washed, and the chamber drains. If power loss were to occur or nitrogen pressure were to drop, solvent would simply flow back into the container. A control system monitors air flow, liquid level and solvent temperature, and shuts the system down if any exceed set levels. Electrostatic ignition is eliminated by equipment bonding and grounding the equipment. The quantity of boards are then manually transferred to the rinse module. After rinsing, batch drying of printed circuit boards is performed in a drying module or oven. Two types of oven drying modules are available: intrinsically safe ovens or ovens that meet NFPA 86 code requirements. The intrinsically safe oven air knife dries or evaporates flammable or combustible materials while presenting no ignition source in the oven. The second design would meet NFPA 86 code through certified engineering and design testing for the specific type of material to be vaporized in the oven.

## Discussion

The new risk with d-Limonenes use in the PCB cleaning operation is fire hazard where it was not before with ozone depleting solvents. But through proper equipment design and process control, the fire hazard is a manageable risk. Adequate equipment safety features have been designed into both enclosed-conveyorized and batch systems. Continued improvements of equipment design and a defluxer formulation with higher flashpoint would achieve maximum safety of this alternative.

**TOXICOLOGY of D-LIMONENE**

**Toxicity**

Ingestion of small quantities to d-Limonene should not pose a significant threat to human health although ingestion of large quantities may have deleterious effects.[41,42] In contrast, it is interesting to note that the average concentration of d-Limonene in orange juice is 100ppm.[43] Furthermore, d-Limonene has been granted the status of "generally recognized as safe" (GRAS) under the conditions of its origional use as a flavor ingredient.[44] As a flavoring ingredient, d-Limonene is used in foodstuffs at use levels noted in Figure 7.

| | |
|---|---|
| Non-Alcoholic Beverages | 31ppm |
| Chewing Gum | 2300ppm |
| Ice Cream | 68ppm |
| Candy | 49ppm |
| Baked Goods | 120ppm |
| Gelatins/Puddings | 48-400ppm |

Figure 7. Typical use levels of d-Limonene as a food additive (Fenarolis Handbook of Flavoring Ingredients)

Formulations consisting of d-Limonene have undergone testing for direct dissolution of gallstones in animals and humans.[45-47] Healthy male adults ingested d-Limonene in capsules at a single dose of 20g. No abnormalities were found in the subjects after functional examinations although all the subjects complained of diarrhea and tenesmus.[45] A probable lethal dose for humans would be the ingestion of 0.5-5 g/kg.[48] In addition, studies on human occupational exposure to the monoterpene alpha-pinene, determined that there was a significant exposure-response relationship for irritation to eyes, nose, and throat[49] and a certain degree of lung function impairment.[50]

**Absorption and Metabolism**

Studies characterizing absorption and metabolism suggest terpenes are to be absorbed through the skin, from the lungs and gastrointestinal tract.[51] Once in the system, humans and other species (Figure 8) metabolize d-Limonene. After metabolization, the hydroxy-substituted and carboxylic acid derivatives that are produced may be conjugated with glucuronic acid or excreted free in the urine. [51,52]

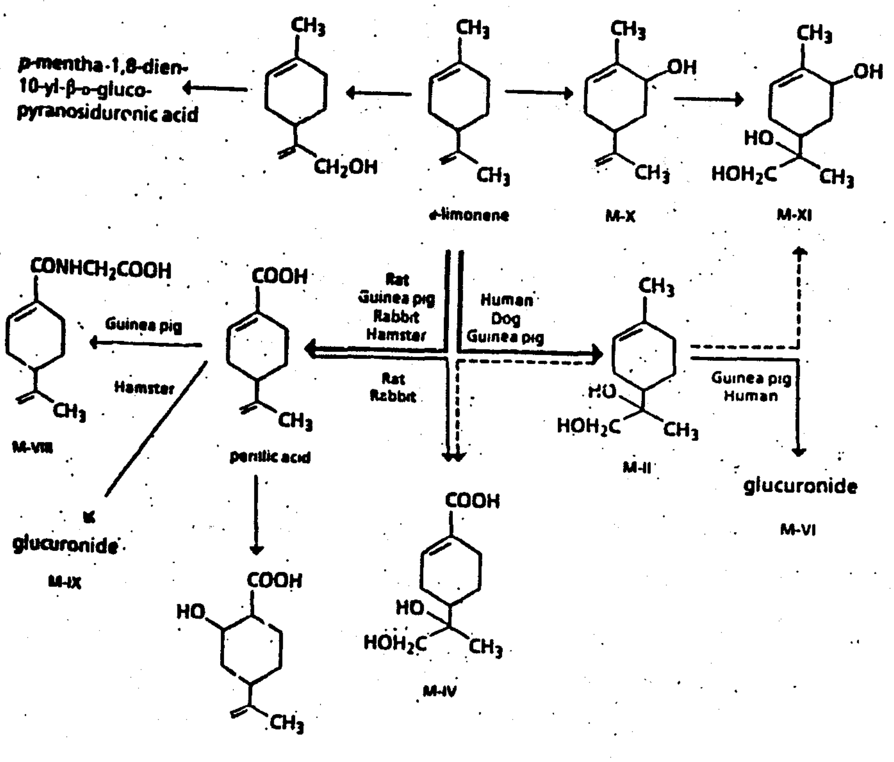


**Figure 8.** Possible metabolic pathways of d-Limonene (NTP-TR-347)

**Chronic and Sub-chronic Effects**

Chronic and sub-chronic tests have been performed which determine a pattern of histopathology predominant for the male rat. In the chronic oral feeding study, kidney toxicity was determined in male rats at the lowest dose tested.[43] The NTP long term study also reports general toxicity in mice. Reduction of body weights from 5%-15% in female mice and liver toxicity were noted in both high-dosed male and female mice. Still, determination of a NOAELs of 250/mg/kg/day for female mice and 500 mg/kg/day for male mice were determined.[51]

**Carcinogenic Effects**

The National Toxicology Program performed short and long term toxicologic and carcinogenic studies. Clear evidence of carcinogenic activity was determined in male F344/N rats whereas anticarcinogenic effects have been observed among female F344/N rats. No other carcinogenic activity has been observed. There was no evidence of carcinogenic activity in male or female B6C3F mice.

In short term tests (13 weeks), compound related nephropathy was observed only in the male rat at all dose levels and, deaths occurred at high dosage in each species and sex.[52] The long term test (2 years) confirmed the male F344/N rat kidney as the target for incidences of tubular cell hyperplasia, adenomas, and adenocarcinomas.[43] The pathogenesis of the nephropathy was determined to be a buildup of a sex-specific urinary protein called, alpha 2u-globulin induced by d-Limonene.[53,54] Also, similar experiments with NBR-NCI Black-Reiter rats confirm that this effect of d-Limonene may be specific to the male F344/N rat only and not other species.[54,55]

It has been suggested that the presence of alpha 2u-globulin is causal for the development of kidney disease in rats exposed to d-Limonene[54,55] This belief is due to the association of alpha 2u-globulin and a major metabolite of d-limonene, d-Limonene-1,2-oxide.[58] It is interesting to note that d-Limonene induced nephropathy in male F/344 rats may not be relevant to humans due to the fact that humans (and primates, dogs, and mice) do not produce alpha 2u-globulin.[Swenberg, cited 55] Although humans and other species share structurally similar urinary proteins to alpha 2u-globulin,[55] there is no evidence indicating toxicity to humans. In fact, Flamm et al assert that evidence supporting carcinogenic activity in rats is not relevant to humans and support the human safety of d-Limonene based on three points[56]:

> "...1) the male rat specificity of the nephrotoxicity and carcinogenicity; 2) the pivotal role that alpha 2u-globulin plays in the toxicity, as evidenced by the complete lack of toxicity in other species despite the presence of structurally similar proteins; and 3) the lack of genotoxicity of both d-Limonene and d-Limonene-1,2-oxide, supporting the concept of a nongenotoxic mechanism, namely sustained renal cell proliferation."

In addition, anticarcinogenic properties of d-Limonene have been reported. Elson et al[57] report that d-Limonene fed in dietary additions of 1% or 5%, was effective in reducing, preventing, and delaying the appearance of 7,12-dimethylbenz[a]anthracene (DMBA) induced rat mammary cancer. Further research corroborates these findings.[59,60] A plausible mechanism for the chemopreventive and chemotherapeutic activities of d-Limonene is suggested by Crowell et al.[61] The mechanism involves the selective inhibition of isoprenylation of a class of cellular proteins tested in vitro.

## Mutagenic Effects

No mutagenic properties have been found in tests with d-Limonene. Determinations were based on several types of bacterial and mammalian-cell tests performed in several studies.[43,62]

## Reproductive and Developmental Effects

Limited test results indicate that high oral doses of d-Limonene produce maternal effects on the rat, specific developmental abnormalities in mice and rats, and causes growth statistics and physical effects to newborn mice, rats, and rabbits. The relevance of these findings may be questionable if applied to humans due to the fact that these effects occured at very high dose levels.[17]

## Dermal Effects

d-Limonene is reported as a dermal sensitizer and irritant.[48] A USEPA report cites studies which test for dermal sensitization and irritation. The authors report that undiluted d-limonene is a moderate skin irritant to humans and animals but that any sensitization reaction may be due to contaminants of some terpene preparations.[51] In contrast, Falk et al, performed an experiment in which the hand of a male human was exposed to d-Limonene (98%) by immersion. Subjective responses to the exposure included painful itching and burning a few minutes after submission, continued burning after 10 minutes, and in 100 minutes swelling subsided. An allergic reaction in the form of a purpuric eruption, occurred six hours after exposure and lasted several weeks.[63] Another investigation examined the sensitizing potential of d-Limonene (97% pure) on guineapigs and determined that the allergenic activity of d-Limonene may increase with air exposure and that oxidation products may determine allergenicity.[21]

## OCCUPATIONAL EXPOSURES

There are no generally accepted occupational exposure limit guidelines for terpenes[19] although a PEL of 100ppm has been referenced for $C_{10}H_{16}$ turpentines.[16,20] At a conference of local PCB manufacturers it was learned that employees have voiced subjective complaints of citrus odors at airborne levels as low as a few ppm. In response, an odor threshold of 10ppm was propose.[64]

Occupational exposure to d-Limonene could occur through dermal absorption and inhalation. Exposure by inhalation and dermal absorption is minimal at enclosed-conveyorized equipment due to minimal operator interaction during this fully-enclosed, automated operation. In contrast, exposures at batch equipment may be higher due to increased operator interaction. This interaction is in the form of manual transfer of PCB's from the wash module to rinse module and routine maintenance.

Inhalation of d-Limonene vapors could occur when opening the batch washer door upon completion of the batch wash cycle. Also, errant vapors from maintenance or spill cleanup activities, and in general, odors from normally operating cleaning equipment are concerns.

Personnel and room air sampling has been performed using sampling pumps and activated charcoal methodology to better understand the concentrations to which the employee is exposed. Generally, terpene concentration levels around the enclosed-conveyorized spray under immersion equipment were at 1ppm, whereas levels relevant to the batch equipment were slightly higher at 5ppm.[27] Ventilation stack monitoring was performed at the enclosed-conveyorized spray under immersion line equipment. The sampling yielded typical terpene concentrations at 250-300ppm for solvent tank entrance and exit stacks and a concentration of 1-2ppm for the airknife stack.[27]

Control methods such as equipment ventilation, material handling procedures, and personal protective equipment (PPE) may be determinants of occupational exposures. To decrease inhalation exposure at the batch operation, operators are instructed to open the washer door minimaly for a few minutes to let the washer equipment lip exhaust capture the waft of terpene mist released upon opening the batch washer.[20] A time dwell should be allowed after the batch wash cycle for the racks of PCBs to adequately drip-dry before movement to the rinse equipment. The use of personal protective equipment is recommended during batch operations, routine maintenance activities, and emergency spill cleanup. Dermal absorption can be minimized by the use of PPE. Solvent resistant gloves and aprons made out of heavy-weight vinyl or nitrile rubber have been recommended for use[26], especially during the repetitive transfer of PCB's from the batch wash module to the rinse module. During routine maintenance or emergency spill cleanup, organic respirator protection (NIOSH/MSHA approval TC-23C-859 or equivalent) is recommended by the electronics defluxer manufacturer.[33]

**Discussion**

d-Limonene should not pose a significant threat to human health. Although it induced kidney toxicity, reproductive and developmental effects, and dermal effects in animals, the prediction of toxicity in humans based on these results is uncertain. The difficulty lies in extrapolating animal test criteria to humans.

Relevant to an occupational setting and based on the limited quantity of studies performed on human subjects, d-Limonene may be moderately toxic through dermal exposure and cause skin sensitization/irritation. It may also be an irritant to the eyes, nose, and throat.

In addition, it should be noted that occupational exposure is not to pure compound used in laboratory research,but to the commercial formulation of the product. There are no toxicological studies performed on the printed circuit board defluxer formulation which might prove interactive effective different that what has been learned based on the individual effects of the substances. strategies for studying the toxicology of mixtures in order to characterize more authentically the impacts to hearth and safety in the PCB cleaning operation should be considered.

# APPENDIX A: d-Limonene Background Information

**APPENDIX A**

The d-Limonene based electronics defluxer BioAct EC-7R™ is manufactured, distributed, and recycled by the following companies:

**Manufacturer:** Petroferm Inc.
5400 First Coast Highway
Fernandina Beach, FL 32034
(904)261-8286

**Contact:** Michael E. Hayes, Ph.D.
Director - Electronic and Specialty Chemicals

**Distributor:** Alpha Metals Inc.
600 Route 440
Jersey City, NJ 07304
(201)434-6778

**Contact:** Andy Hoover
Product Manager - Specialty Fluids

**Recycler:** Laidlaw Environmental Services
221 Sutton Street
N. Andover, MA 01845
(508)683-1002

**Contact:** Paul Deveau

There are approximately 22 suppliers of d-Limonene (CAS #5989-27-5), of which, 5 are bulk suppliers and 3 are high purity suppliers. Consult ChemSource USA for suppliers and contacts.

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