US Army Corps
of Engineers
Construction Engineering
Research Laboratory

USACERL Technical Manuscript N-91/12
May 1991

The Economic and Environmental Benefits of Product Substitution for Organic Solvents

by
Sarah C.K. O'Connor

U.S. Army installations require solvents for effective maintenance and equipment refurbishing operations. Because solvents are used frequently in the Army, spent solvent generation has become a significant environmental and economic concern. Of increasing concern are toxic air emissions, threshold limit values, and increasing restriction on land disposal. Coupled with these environmental issues is the rising cost of both waste disposal and new solvent purchase. These concerns have prompted the Army to investigate waste minimization to protect human health and the environment as the Army accomplishes its strategic responsibilities.

This manuscript evaluates the environmental and economic benefits of substituting aqueous terpene-based cleaners for petroleum-based Stoddard solvent, currently used in parts cleaning. With characteristics such as low volatility, biodegradability, and reduction of land disposal, terpene cleaners have become the favored substitution alternative.

This research showed that implementing terpene cleaner substitution for Stoddard solvent requires a site-specific study of each installation. Each installation must evaluate the terpene cleaners' compatibility with current treatment processes, its effect on cleaning equipment and parts, and cost of implementation. Cost may include additional floor space and equipment for rinsing and drying cleaned parts, cleaning enhancement equipment or chemicals, and disposal of residual sludge and accumulated rinsewater.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	May 1991	Final

4. TITLE AND SUBTITLE

The Economic and Environmental Benefits of Product Substitution for Organic Solvents

5. FUNDING NUMBERS

PE 4A162720
PR A896
WU TQ1

6. AUTHOR(S)

Sarah C.K. O'Connor

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

U.S. Army Construction Engineering Research Laboratory (USACERL)
PO Box 4005
Champaign, IL 61824-4005

8. PERFORMING ORGANIZATION REPORT NUMBER

USACERL TM N-91/12

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

USAEHSC
ATTN: CEHSC-FU-S
Bldg. 358
Fort Belvoir, VA 22060-5516

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Copies are available from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

U.S. Army installations require solvents for effective maintenance and equipment refurbishing operations. Because solvents are used frequently in the Army, spent solvent generation has become a significant environmental and economic concern. Of increasing concern are toxic air emissions, threshold limit values, and increasing restriction on land disposal. Coupled with these environmental issues is the rising cost of both waste disposal and new solvent purchase. These concerns have prompted the Army to investigate waste minimization to protect human health and the environment as the Army accomplishes its strategic responsibilities.

This manuscript evaluates the environmental and economic benefits of substituting aqueous terpene-based cleaners for petroleum-based Stoddard solvent, currently used in parts cleaning. With characteristics such as low volatility, biodegradability, and reduction of land disposal, terpene cleaners have become the favored substitution alternative.

This research showed that implementing terpene cleaner substitution for Stoddard solvent requires a site-specific study of each installation. Each installation must evaluate the terpene cleaners' compatibility with current treatment processes, its effect on cleaning equipment and parts, and cost of implementation. Cost may include additional floor space and equipment for rinsing and drying cleaned parts, cleaning enhancement equipment or chemicals, and disposal of residual sludge and accumulated rinsewater.

14. SUBJECT TERMS

organic solvents substitutes
economic analysis environmental impact

15. NUMBER OF PAGES

148

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	SAR

FOREWORD

This research was funded by the U.S. Army Engineering and Housing Support Center (USAEHSC) under Project 4A162720A896, "Base Facility Environmental Quality," Work Unit TQ1, "Technology for Waste Solvent/Oil Recycling."

This manuscript was submitted in partial fulfillment of the requirements for the degree of Master of Science in Environmental Engineering in Civil Engineering in the Graduate College of the University of Illinois at Urbana-Champaign. The advisor for the thesis was Dr. Roger A. Minear.

Technical guidance and support were provided by Mr. Bernard Donahue and the U.S. Army Construction Engineering Research Laboratory Environmental Division (USACERL-EN). Dr. Edward W. Novak is Acting Chief of USACERL-EN.

COL Everett R. Thomas is Commander and Director of USACERL, and Dr. L.R. Shaffer is Technical Director.

Contents

Contents

Tables

Tables (Cont'd)

Figures

Figures (Cont'd)

Chapter 1

Introduction

The U.S. Army requires large quantities of solvents for effective maintenance and equipment refurbishing operations on its installations throughout the continental United States and overseas. Because solvents are used so frequently in the Army, spent solvent generation has become a significant environmental and economic concern.

Nonhalogenated Stoddard solvent, most frequently used in the cold cleaning of metal parts at Army installations, accumulates oxidized metals, grease, and oil until it is no longer satisfactory for its designated use. Any spent solvent which is not recyclable is classified as "hazardous waste" due to its toxicity, flammability, or as a result of being listed as such by the U.S. Environmental Protection Agency (EPA), and is subject to proper disposal management. The EPA listing is in accordance with the Resource Conservation and Recovery Act (RCRA) as amended in 1984. Under these environmental regulations, the spent Stoddard solvent can no longer be disposed by "standard practices" used in the past.

By amending RCRA, Congress established hazardous waste reduction as a national priority. The amendments, known as the Hazardous and Solid Waste Amendments of 1984 (HSWA), impose substantial new legal responsibilities on waste generators, treaters, and disposers. HSWA mitigates against land-based disposal by requiring that hazardous waste generators voluntarily institute in-house waste minimization programs, that generators meet predisposal treatment standards for certain hazardous wastes, and that new landfills and other wastes disposal facilities must be equipped with additional technological controls prior to receiving wastes.

Since the early 1980's, the U.S. Army Construction Engineering Research Laboratory (USACERL) has been investigating the use of solvents on Army installations and evaluating proper methods for the management and ultimate disposal. Over the past 10 years the Army has been in the process of reducing solvent related wastes by techniques such as substitution of less toxic solvents whenever applicable, waste solvent minimization, waste solvent reuse/recycling, and waste solvent disposal. The Army's motivation to adopt waste

minimization techniques is driven by installation-wide environmental and economic concerns. In carrying out this objective, the Army has decided to make proper waste management one of its overall goals.

Meanwhile, new regulations and restrictions involving solvent usage, phased in between 1986 and 1990, have had a significant impact on industrial production and material management practices. Laws currently restrict--and will eventually eliminate--land disposal, escalating off-site treatment and disposal costs 5 to 10 times. These restrictions prohibit land disposal of untreated and concentrated spent solvents. It is further estimated that in a few years commercial land disposal will only be available to hazardous waste residues from treatment processes. Furthermore, generators will be financially liable under the so called cradle-to-grave liabilities enacted under RCRA. In addition to regulations established under RCRA, the replacement of the Stoddard solvents at Army installations is desirable to long term effects under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), enacted in 1980.

Threshold limit values (TLVs) for human exposure have been lowered and are likely to be lowered even further in the future. Solvents that release volatile organic compounds (VOCs) contributing to the deformation of ozone layer in the atmosphere, creating smog and toxic air emissions, are becoming restricted. Coupled with these environmental issues is the rising cost of both new solvents and waste disposal. Furthermore, it has been acknowledged that much of the waste generated by solvents is or will be considered hazardous as stricter regulations are developed and enforced in the future. These concerns have prompted the Army to seek safe and cost-effective methods of managing waste solvents.

The Army's goal is to achieve "zero hazardous waste discharge" technologies, which is defined as those that do not require manifesting and shipping of unnecessary hazardous waste off-site for treatment and disposal. The U.S. Air Force (USAF) is also committed to the elimination of hazardous chemicals and toxic air emissions from all USAF facilities. The Army's effort to achieve the "zero discharge" goal is ultimately driven by the desire to protect human health and the environment as the Army accomplishes its strategic responsibilities.

Objective

The objective of this thesis is to develop a methodology for evaluating an alternative solvent to be used in the cold cleaning degreasing operations of metal parts. Stoddard solvent

will be compared against the class of terpene solvents specified for industrial cleaning operations. The methodology for selecting and evaluating the alternative solvent considers cleaning efficiency, environmental factors and overall costs.

Chapter 2

Justification

2.1 Background

The 1984 RCRA amendment included a national policy statement that, "whenever feasible the generation of hazardous wastes is to be reduced or eliminated." A 1986 congressional study further stated, "those who have implemented waste reduction effectively, generally see it as a way to improve profitability and competitiveness."[14*] A state of California study concludes that: "Waste reduction, as opposed to waste management, is the financially and environmentally preferred strategy. At the very least, source reduction and on-site treatment reduce the generator's risk and expense of transportation." Associated liability issues and new disposal laws have led private industries and governmental facilities, such as the U.S. Army, to consider near-term eliminations of land disposal and long-term zero hazardous waste discharge.[14]

Wastes are classified as hazardous under RCRA in two ways. First, a waste can contain a specific constituent listed as hazardous under RCRA regulation. Second, the residue is considered to be hazardous if it exhibits one of the four characteristics defined under RCRA. These characteristics are toxicity, ignitability, corrositivity, and reactivity.[14] Key land disposal regulations under RCRA legislation and the corresponding Army processes and waste streams affected are listed in Table 2.1. Many firms and agencies assume that all forms of land disposal will be prohibited after 1990.[14]

Recognizing the liabilities of improper disposal and the advantages of waste minimization, the Army has set out to achieve the Department of Defense's goal of a 50 percent reduction in hazardous waste generation by 1992, based on the baseline generation of 1985. In achieving this goal, the Army has set up various waste minimization programs throughout its installations.

---

*References are listed numerically beginning on p 132.

REGULATION	EFFECTIVE DATE	AFFECTED ARMY PROCESS
Land Disposal Restriction (Solvents, Sludges)	Nov.8,1986	Degreasing
Land Disposal Restriction (California List)	July 8,1987	Degreasing, All Surface Finishing
Land Disposal and Deep Well Injection Restriction "First-Third" (1/3 of Listed Wastes) "Second-Third" (2/3 of Listed Wastes)	 Aug. 8, 1988 Aug. 8, 1989	 All
Land Disposal and Deep Well Injection Restrictions Remaining Listed and Characteristic Wastes All "Third-Third" Wastes	May 8, 1990	All

Table 2.1 - Summary of Key Land Disposal Regulations[14]

2.2 Waste Minimization

The process for reducing the net outflow of hazardous solids, liquids, and gaseous effluents from a given source or generating process is called "Waste Minimization." In its October 1986 report to Congress, EPA broadly defined waste minimization as: "the reduction to the extent feasible of hazardous waste that is generated or subsequently treated, stored or disposed of."[14] In reference to solvent usage, minimization more specifically involves the reduction of air emissions and the contamination of surface water, groundwater, and land by means of source reduction, recycling processes, and treatment leading to complete destruction. However, the transferring of pollutants from one medium (e.g., water) to another (e.g., air) and vice versa, by treatment processes is not waste minimization.

Minimization includes any reduction in total volume or quantity of hazardous wastes generated, in the toxicity of hazardous waste produced, or both, as long as it is consistent with the national goal of minimizing present and future threats to the environment. The main goal of any waste minimization program, therefore, must be to reduce the total volume or quantity and/or to reduce the toxicity of liquid/solid waste and air emissions generated. The Army has found that waste minimization of spent solvents can be achieved through various techniques.[10]

1. Source reduction - the reduction or elimination of the spent solvent generation at the source, usually within the processes. It also implies any action taken to reduce the amount of waste leaving a process.

2. Recycling/Reclaiming - the use or reuse of the spent solvents as an effective substitution for a commercial product, or as an ingredient for feed stock in a process. Recycling implies reclamation of useful constituent fractions from within a spent solvent or removal of contaminants allowing it to be reused.

3. Treatment - the elimination of hazardous characteristics of the spent solvent making it nonhazardous to human health and the environment. Treatment includes the destruction or degradation of the spent solvent to reduce the volume and or toxicity without generating resulting hazardous by products (e.g., air emissions).

A number of Army installations have initiated programs for recycling and reclaiming spent Stoddard solvent. These programs have been instituted either on-site with distilling processes or through the use of a private contractor in a closed-loop recycling program.[10] The reclaimed material has been proven to be of suitable quality and is effective for reuse in cleaning operations under Army Specifications.[47] This method of waste management is effective; however, the ultimate goal in any waste minimization program is reduce the spent solvent at the source.

Additionally, due to the new restrictive regulations, increasing treatment/disposal expenses, and increasing liability costs, conscientious agencies like the Army are forced to critically examine source reduction of pollution as opposed to end-of-pipe treatment methods such as recycling/reclaiming and waste treatment. Although waste minimization programs are strictly voluntary at present, legal responsibilities for generators could change in the near future. The Army is aware that EPA mandatory reduction regulations may be set in the near future; therefore, they have set out to attack solvent waste at the source.

2.3 Source Reduction

Source reduction is the ideal technique for minimizing wastes.[10] When dealing with solvent wastes, source reduction can have many benefits such as reducing requirements for storage, treatment, transportation, and ultimate residue disposal, and, therefore, a reduction in associated liabilities.

Source reduction of solvents in Army installations, can be achieved through several avenues.[12]

1. Product/Material Substitution - the substitution of a less hazardous or non-hazardous solvent

2. Material Control - improving handling procedures to ensure that solvents do not become hazardous wastes due to expired shelf life, are not allowed to evaporate, and are not released into surface/groundwater

3. Waste Management - proper containment, improved storage facilities, segregation of wastes types, and improvements in the transport and disposal of wastes

4. Process Changes - changes in the process that will minimize chemicals which produce wastes or changes which lead to safer hazardous chemical uses.

Because source reduction is, in effect, a waste avoidance technique that utilizes in-house practices to reduce waste generation, there is very little, if any, liability risk is associated with this option (assuming proper management and no leaks or spills within the facility). Coupled with potentially huge economic savings for an agency, the reduced liability aspect of source reduction makes it an attractive compliance option. The possibilities and probability of using any one of the techniques for source reduction depends to a great extent on the degree of cleanliness required and on the type of surface or combination of surfaces to be cleaned.[31] Many products cannot be manufactured without producing some hazardous waste; therefore, source reduction techniques usually have to be combined with another compliance option such as recycling or treatment.

The U.S. Army is currently considering material substitution of terpene cleaners to achieve source reduction of the Stoddard solvent used in cold cleaning of metal parts.

2.4 Material Substitution

The proposal to investigate a material substitute was launched in recognition of the large amounts of spent solvent generated from metal parts cleaning. The ultimate goal in the material substitution investigation is to identify a less hazardous solvent that would lessen the environmental impact and associated wastes.

Terpene cleaners, naturally derived and aqueous-based, have been proposed as the substitution for Stoddard solvent. Characteristics such as natural components, bio-degradability, low volatility, and reduction of land disposal have made the terpene cleaners a favorable alternative.

Chapter 3

Literature Search

3.1 Stoddard Solvent

To evaluate the material substitution of terpene cleaners, a review of the processes and applications in which the Stoddard solvent is currently used at Army installations will be outlined. By developing an understanding of the use of Stoddard solvent, the alternative cleaners can be assessed as to their position in the existing processes and facilities at the different installations.

3.1.1 Stoddard Solvent Usage

Stoddard solvent, known as PD-680 by Army installations, is also identified variously by different agencies as: dry cleaning solvent, Varsol (Exxon), turpentine substitute, white spirits, mineral spirits, and petroleum solvent. It has been widely used as a diluent in paints, coatings, and waxes as a dry cleaning agent; and as a herbicide. It has been most commonly used, however, as a degreaser and cleaner in mechanical maintenance shops.[7]

Stoddard solvent is the most frequently used solvent in equipment and metal parts cleaning at Army installations. Cleaning agents such as Stoddard solvent play a very important function in equipment maintenance and refurbishing.[10] Installations use Stoddard solvent to perform various functions, such as to:[20]

1. restore or maintain the operating efficiency of equipment (e.g., to restore adequate heat transfer rate and low pressure drop in heat exchangers),
2. avoid or limit product contamination,
3. minimize corrosion and extend equipment life,
4. allow for inspection and repair of equipment, and
5. improve exterior appearances.

3.1.2 Special Cleaning Procedures

Stoddard is generally used in cold cleaning processes. Cold cleaning is the major nonvapor, surface preparation process, designed to remove grease, oil, carbon, and other soil from parts. Typical techniques in which Stoddard solvent is employed in the Army installations are described below:[10,12,30]

1. Wash Station - in this operation, solvent generally is circulated by pump and the part washed continuously with a stream of liquid. Dissolved material accumulates in the solvent, and solids are often removed with screens or filters.

2. Spray Booth - solvent is aspirated from a container, mixed with air, and impacts the part to be cleaned. The sprayed solvent is collected and recirculated. Soluble materials accumulate and solids are removed as noted above. Organic vapors generally are carried out as exhaust and may or may not be collected and recycled.

3. Dip Tanks - a large container of solvent is used for immersion of the parts. Mixers may be added to accelerate cleaning. As above, soluble and insoluble materials accumulate. Some solids may settle out.

4. Hand/Bucket Cleaning - this is the simplest operation, commonly used by small operators. Brushes or rags are often used to remove tough dirt.

In all of the above processes, the Stoddard solvent continuously degrades in quality because of accumulation of soluble and insoluble material. The amounts of various soluble and insoluble contaminants allowed to accumulate before changing the solvent are a function of process requirements.[10]

3.1.3 Generating Sources

Stoddard solvent is use in a number of different areas throughout an Army installation. The largest amount of spent Stoddard solvent is generated at active troop installations. The three main areas that use Stoddard solvent at active troop installations are the Motor Pool and Vehicle Maintenance Facilities (MPVMF), the Aviation Maintenance Facilities (AMF), and the Small Arms and Maintenance Facilities (SAMF), and the general cleaning areas. A description of each facility and its use of Stoddard solvent is as follows. For a summary of Stoddard solvent usage at Army installation see Table 3.1.

USER ACTIVITY	PRIMARY USE OF SOLVENTS
Aviation Maintenance	Degreasing, Cleaning
Entomology Shop	Mixing Agent
Fire Department	Practice Fires
Laundry Facilities	Cleaning
Motor Pools	Degreasing, Corrosion Control
Munitions & Ordnance Maintenance	Degreasing, Cleaning
Paint Shops	Paint Thinners, Cleaners
Photographic Plants	Processing
POL Yard	Degreasing, Cleaning
Troop Units	Degreasing, Cleaning, Corrosion Control
Vehicle Rebuilding-Depot Level	Degreasing, Cleaning, Corrosion Control
Vehicle Rebuilding-Installation	Degreasing, Cleaning, Corrosion Control
Vehicle Maintenance	Degreasing, Cleaning, Corrosion Control

Table 3.1 - Common Stoddard Solvent Usage at Army Installation

1. Motor Pool and Vehicle Maintenance Facilities (MPVMF) - Army installations have a variety of MPVMF for tactical and nontactical vehicles. Nontactical vehicle motor pools are used to service and maintain all the administrative vehicles (e.g., cars, vans, and trucks, etc.), engineering maintenance vehicles (e.g., trucks bulldozer, forklifts, etc.) and grounds maintenance vehicles (e.g., tractors, mowers, etc.) on the installation. The maintenance of tactical vehicles is performed at various troop and tactical vehicle motor pools. Tactical vehicles can be divided into track-laying vehicles (self-propelled howitzer, guns, mortars, armored personnel carriers, recovery vehicles, etc.) and wheeled vehicles (cargo trucks, ambulances truck tractors, wreckers, etc.).[10]

Typically, Stoddard solvent is used in these facilities in repair operations, including grease removal, engine parts and equipment cleaning, and solution replacement. The equipment commonly used to apply Stoddard solvent for cleaning and degreasing are: solvent sinks (parts cleaning), hot tanks (for engine and radiator cleaning), and spray equipment.[10]

2. Aviation Maintenance Facilities (AMF) - AMF are involved in maintaining different sizes of helicopters and airplanes. Various levels of services are performed on the aircraft at each of the AMFs. The services involving the use of Stoddard solvent include, periodic maintenance (e.g., fluids change, tune-up, etc.), engine repair, brake servicing, and unique repair required for different aircraft.[10]

The equipment commonly used at the AMF to apply Stoddard solvent is very similar to that used in the MPVMF (i.e., solvent sinks, hot tanks, and spray equipment).

3. Small Arms Maintenance Facilities (SAMF) - Stoddard solvent is used at the SAMF in various operations such as equipment and vehicle repair, metal cleaning, metal finishing, and surface preparation cleaning. It is used to clean or degrease parts prior to repair, rebuilding, or finishing. Stoddard solvent is generally used in cold cleaning operations with techniques such as dip tanks and buckets. In metalworking operations small quantities of the solvent are used for cleaning and for the cutting and threading of metallic pipes and other surfaces.[10]

4. General Cleaning Areas - Each work area has its own 10 to 12 gallon degreasing tank filled with Stoddard solvent. Each unit is designed with a small electric pump and a safety lid that closes in the event of a fire and to prevent solvent loss due to evaporation. Parts to be cleaned are placed inside the tank and washed using a jet of solvent provided by the pump. When clean, the parts are removed and allowed to dry.[12]

3.1.4 Chemical Characteristics

Stoddard solvent is generally a mixture of straight and branched-chain paraffins, napthenes, and aromatic hydrocarbons. It is a rapid drying aromatic and medium boiling aliphatic solvent consisting primarily of C_9-C_{12}, hydrocarbons. It is a clear and colorless liquid with a mild kerosene-like odor.[7] Insoluble in water, Stoddard solvent is a combustible liquid, miscible with most common organic solvents such as benzene, absolute alcohol, ether, chloroform, carbon tetrachloride, and carbon disulfide.[38]

Stoddard solvent is available in two forms. These are defined by U.S. Army specifications as:

Type I - "Regular Stoddard Solvent" is intended as a comparatively safe dry cleaning solvent. Flash point is 105 °F.

Type II - "High Flash Point Solvent" is intended to be used where a solvent with a higher flash point is desired. Flash point is 140 °F.

Type II is always recommended for parts cleaning use over Type I in the Army installations for safety and regulatory reasons due to its higher flash point.[47]

The government has set up specifications for producing Stoddard solvent to which all manufacturers must adhere when selling their products to the U.S. Army. Government specifications stipulate that the Stoddard hydrocarbon solvent shall be a virgin grade or recycled solvent derived from the petroleum distillates fraction in the reclaiming and re-refining processes, or a mixture of these fractions.[47]

The Stoddard solvent produced by Unocal Chemical, 140 Solvent 66/3, meets the government specifications physically and chemically for parts cleaning operations. This chemical, like that of many other manufacturers, is generally treated to reduce aromatics and olefins and meets the definition of nonphotochemically reactive as defined by the South Coast Air Quality Management District and the Bay Area Air Quality Management District. The typical physical properties of Stoddard solvent are listed in Table 3.2.

3.1.5 Toxicity

Stoddard solvent has not been identified as a carcinogen by the National Toxicity Program (NTP) or Occupational Safety and Health Administration (OSHA), although reports have associated repeated and prolonged occupational overexposure to solvents with permanent brain and nervous system damage (sometimes referred to as painters' syndrome). However, among the millions of industrial and domestic workers exposed to Stoddard solvent, minimal evidence of serious health effects, apart from its defatting and irritating action on the eyes and skin, have been reported.

It is reported that intentional misuse of Stoddard solvent by deliberate ingestion and inhalation may be harmful to the nose and throat or, in some instances, fatal. Aspiration of the Stoddard liquid has been shown to result in diffuse chemical irritation of the lungs culminating in edema. Only a few milliliters in such an instance may be fatal.[7]

Boiling Point	367-405 °F
Vapor Density (Air = 1)	5.2
Evaporation Rate	.21
% Volatile	100
% Solubility in H_2O	<0.1
Vapor Pressure (mmHg)	<1.0
Specific Gravity (60°F/60°F)	0.772
Molecular Weight	128.25 C_9H_20
Flash Point	>140 °F
Approx. Bulk Density (lb/gal @ 60°F)	6.43
Appearance	Clear liquid
Odor	Kerosene-like

Table 3.2 - Physical Data of Stoddard Solvent

Current values for limits on Stoddard solvent have been developed. The permissible exposure limits in air are set by Federal Standard at 500 ppm for a 30 minute inhalation period. The maximum human TLV assigned to Stoddard solvent is 200 ppm; however, 100 ppm is usually practiced among chemical vendors. Lethal dosage (LD_{50}) by ingestion is estimated at 0.5 to 5 g/kg.[38,21]

3.1.6 Reactivity

Stoddard is stable under normal conditions of storage and handling. However, because it is a combustible liquid, all possible sources of ignition should be avoided. This product is incompatible with strong acids or bases, oxidizing agents, and selected amines, so contact with these materials should be avoided.[38] Combustion of this material may yield carbon monoxide and/or carbon dioxide.[46]

3.1.7 Hazardous Considerations

Although this chemical is not listed as highly hazardous, caution should be used at all times when handling. The material, as indicated previously, causes mild eye and skin irritation, irritation of the nose and throat, and signs of nervous system depression at incidences of prolonged and repeated use. To avoid hazardous health impacts, protective equipment such as goggles, gloves, respirator, and appropriate clothing must be worn. Additionally, proper ventilation or exhaust systems are required to maintain airborne concentrations below the established exposure limits.

The precautions and handling procedures that should be known before using this chemical are defined and discussed in Appendix B. They include:

1. hazardous intake precautions
2. special protection information
3. spills and leaks procedures
4. handling and storage precautions
5. fire and explosive hazard data.

3.1.8 Recycling/Reclaiming

Stoddard solvents are recyclable, since they are not consumed in the cleaning processes, but they become contaminated by other substances. The solvents are ready for recycling when the contaminant level exceeds certain criteria limits.[12] These limits vary widely upon the particular processes.

The Stoddard solvent can be recycled onsite using distillation stills. In this process the solvent is boiled and the vapors are condensed and collected in a separate container. Substances with higher boiling points than the solvent (e.g., oil, metal, residues, etc.) remain in the still bottom and are then disposed of.[10]

The solvent can also be recycled/reclaimed through a contractor off-site. This is a popular option currently in practice at many installations. The contractor recycles and replaces the spent solvent on a periodic basis, generally once a month.[10]

3.1.9 Disposal Methods

The portion of the solvent that accumulates on the bottom of the cold cleaning tank and distillation still is not recyclable or reclaimable. Army installations currently dispose of

it through incineration, fuel substitution, surface disposal, or sale. A description of each method follows:

- Incineration - Incineration is an attractive disposal method for wastes that contain a variety of hydrocarbon products that cannot be reclaimed. Segregation of these wastes from metal and water contaminants is essential so that emissions from the incinerator satisfy EPA and state regulations.

- Fuel Substitution - Installations can burn spent or waste solvents in boilers and other firing equipment. This option is preferable to incineration because the fuel energy of the waste solvent is used beneficially. However, the wastes have to be segregated so no halogenated hydrocarbons contaminate the waste streams.

No noticeable increase in burner maintenance cost or adverse air pollution effects has been shown with the blending of waste solvents with regular fuel. The advantages over combustion are that liquid wastes are disposed of profitably and safely, resulting in conservation of solvent resources.

- Surface Disposal - Sanitary landfilling has been selectively used for disposal of Stoddard waste, usually in combination with other landfill wastes. Use of this mechanism for disposal of solvent waste is still experimental.

- Sale - This option is profitable as well as an environmentally acceptable disposition practice, provided the buyers use appropriate reprocessing methods. Used solvent material offered for sale must be segregated at the point of generation and labeled properly. It is reported that Stoddard solvent wastes have been sold at some Army installations for $0.04/gal.[12]

3.2 Terpene Cleaners

The use of terpene in cleaning applications has been practiced for many years. Terpene Cleaners have long been recognized as highly effective for a variety of organic compounds, including grease and oil. As far back as the 1930's, the U.S. Department of

Agriculture (USDA) sponsored work on terpenes as industrial cleaning compounds.[23] However, there has been little interest in their use as industrial cleaners since that time, probably due to the lower costs and faster evaporation characteristics of halogenated solvents and petroleum distillates like Stoddard solvent. In the past decade, as a result of the increased awareness of health and environmental dangers inherent in the widespread use of halogenated and nonhalogenated solvents, a substantial reawakening of interests in terpene cleaners has occurred. In recent years, terpene cleaners have been the subject of considerable attention as safe, environmentally acceptable cleaning products for use in a variety of heavy-duty applications.[22]

Terpene-containing cleaners have been investigated as potential maintenance solvents in the aerospace industry. For example, General Dynamics at Fort Worth, TX (GD/FW) has evaluated a number of terpene cleaners as the material substitute for "Safety Solvent" (a Stoddard derivative) currently used in their maintenance operation.[18] Additionally, terpene cleaners have provided a practical replacement for chlorinated and freon solvents used for a variety of electronic industry cleaning jobs such as circuit board degreasing.[22] Furthermore, terpene cleaners have made their way as industrial cleaning solvents, as suggested in a number of patents, such as U.S. Patent 4,511,488 in which the inventor describes the use of a terpene hydrocarbon formulation for removing soils from a variety of surfaces.[23] Further examples include U.S. Patents 4,640,719 and 4,740,247, which describe the use of terpene to remove tape residue, solder flux residue, and other contaminants from printed wiring assemblies.[23]

3.2.1 Terpene Cleaners Usage

Uses for terpene cleaners have been growing substantially in recent years. Terpene cleaners have proven capable of dissolving heavy petrpleum greases and residues. For example, they have been used to clean difficult-to-remove materials such as Cosmoline.[17] There are also several nonsolvent uses which have formed the basis for a stable demand for these products. These uses include resi rance precursors and intermediates, and flavor compounds.[23]

Terpene cleaners are generally considered aqueous cleaners, which are broadly defined as cleaning solutions made up of water plus chemical additives, namely surfactant, builders, corrosion inhibitors and antioxidants, and emulsion systems.

3.2.2 Special Cleaning Procedures

The typical cleaning procedure involved in using the terpene cleaners begins with a spray or immersion in a terpene concentrate followed by a water rinse. Terpene cleaners are only slightly volatile, having very high boiling points. Because of their low volatility, it is desirable to remove cleaning compounds via a water rinse at the end of the cleaning process. With terpene cleaners, after a water rinse and drying, no residue remains.

Terpene cleaners work at low temperatures, so it is not necessary to heat terpene cleaning baths; room temperature is ideal for them. Terpene cleaners are not suitable for vapor degreasing processes, due to their low flash points and therefore high combustibility.

Terpene cleaners are to be diluted with water for various soil removal situations. The dilution rates suggested by one manufacturer are listed in Table 3.3.

When using terpene-based cleaners, polymeric materials that may contact the solvent should be first checked for compatibility. Additionally, the manufacturer warns that prolonged immersion may attack certain aluminum alloys and other soft metals.[28]

3.2.3 Chemical Characteristics

Terpene compounds are widely distributed in nature and occur in virtually all living plants; however, wood and citrus products are the principal sources of terpene. Some of the terpene compounds are used as extracted, but most are obtained from natural oil refining processes.

SOIL	WATER DILUTION	IMMERSION TIME
Grease & Carbon		
Light	1:4 - 1:20	- 30 minutes
Moderate	1:2 - 1:10	- 2 to 4 hours
Heavy	1:1 - 1:2	- Overnight or longer
Solidified Grease	1:1 - 1:2	- 1 to 4 hours, depending on severity of soil. Some agitation may be necessary.
Gelled Oils	1:1 - 1:5	- 30 to 90 minutes. Mild agitation will reduce tank time.

Table 3.3 - Suggested Terpene Cleaning Dilutions[28]

Terpenes are cycloalkenes, generally with the formula $C_{10}H_{16}$.[18] They are generally regarded as derivatives of isoprene (2-methyl-1,3-butadiene), in which the isoprene units are arranged in a head-to-tail fashion, although there are some exceptions to this. These compounds are classified according to the number of isoprene units in their carbon skeletons with a single (mono) terpene unit being regarded as two isoprene units.[23,24]

Examples of some representative terpene molecular structures such as camphene, d-limonene, α- and β-pinene, α-terpineol, are provided in Figure 3.1.[23] The most promising candidates for metal surface cleaning are based predominantly on the d-limonene isomer, such as that found in the most commercial cleaning products.

Terpene cleaners formulated for heavy-duty degreasing and cleaning are made up of natural hydrocarbons (nonpetroleum), carbon removers, and surfactants. Typical components include d-limonene, alkyl sulfonate, diethylene glycol monobutyl ether, alkylaryl polyether, ethanolamine, EDTA-type chelate, butylate hydroxytoluene, water, and oxygenated aliphatic hydrocarbon.[27,28] These cleaners are suggested by manufacturers to serve as an effective replacement for caustic, phenolic, cresylic, chlorinated, and most specifically, Stoddard solvents.[28]

Terpene cleaners are generally clear, light yellow liquids with a citrus-like odor similar to that of oranges. These cleaners are not water soluble, but incorporation of surfactants that form their cleaning composition renders them emulsifiable and therefore water rinsable. The typical physical properties of terpene cleaners are listed in Table 3.4.

3.2.4 Toxicity

As a class, the terpenes are listed as low in mammalian toxicity. Many are listed as GRAS (Generally Recognized As Safe) in the Code of Federal Regulations and are used as food additives in flavoring.[22] However, recent studies have shown the terpene isomer d-limonene, common in heavy duty degreasing and cleaning products, to be of concern. Studies conducted by the NTP show that d-limonene is a carcinogenic material. The NTP panel agrees that d-limonene showed clear evidence of cancer in male rats at 300-600mg/kg, but no evidence of cancer in female rats or either gender of mice tested. The 2 year study of d-limonene indicated that the kidney is the primary target organ for chemically related lesions of cancer.[36]

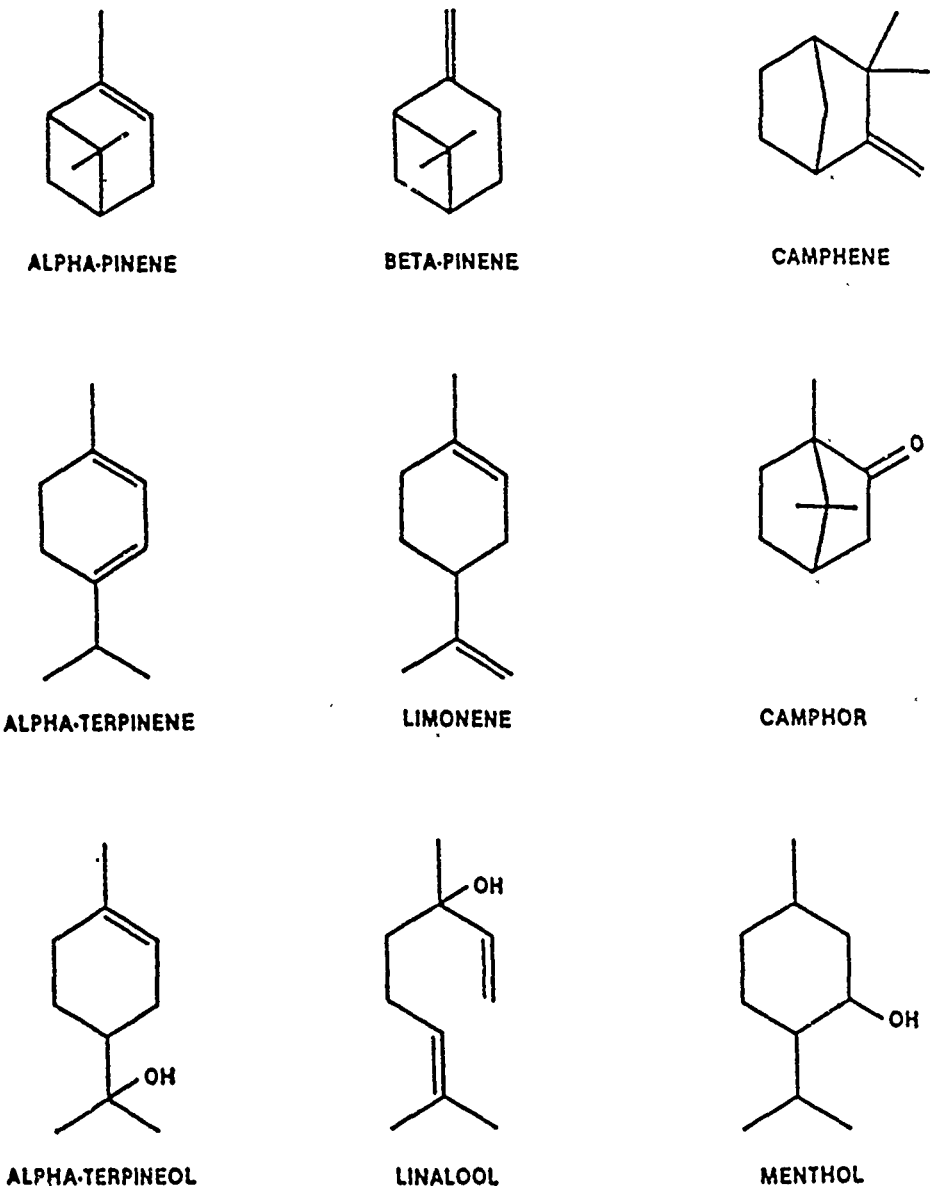

Figure 3.1 - Molecular Structures of Selected Terpenes[23]

Commercial grades of d-limonene can cause dermatitis due to contamination with other terpene and related materials. Therefore, it is important that the degreaser be formulated with high grade or medical grade d-limonene of 99 percent minimum purity. The d-limonene causes pulmonary irritation and central nervous system depression in high concentrations. In the case of accidental ingestion, the d-limonene compound may cause episodes of vomiting. The probable lethal dose in humans is estimated between one pint and one quart of the d-limonene material.

Other hazardous ingredients common in terpene cleaners are ethanolamine and diethylene glycol monobutyl ether. Ethanolamine is of concern due to its low TLV of 3 ppm as listed by OSHA. Diethylene glycol monobutyl ether is a form of antifreeze and, although it makes up only 3 percent of cleaner, it must still be recognized as a hazard.[27]

Boiling Point	212-220°F
Vapor Density (Air = 1)	Not determined
Evaporation Rate	0.08 - 0.10
% Volatile	70 - 80
% Solubility in H_2O (% by wt. @ 68°F)	Forms emulsions
Vapor Pressure (mmHg @ 68°F)	Not determined
Specific Gravity (H_2O = 1 @ 75°F)	0.94 - 0.98
Flash Point	117 - 125°F
Approx. Bulk Density (lb/gal)	Not determined
pH (10% in Solution)	9.8-10.2
Appearance	Clear liquid, light yellow
Odor	Citrus

Table 3.4 - Physical Data of Terpene Cleaners

3.2.5 Reactivity

Terpene cleaners are stable under normal conditions of storage and handling. However, in concentrated form, this material is very combustible due to a generally low flash point of around 120 °F; therefore, all sources of ignition should be avoided. This product is said to be incompatible with strong acids; however, no hazardous decomposition products are known at this time.[27]

Additionally, conditions contributing to polymerization and metal corrositivity of the terpene cleaners are under question at this time.

3.2.6 Hazardous Considerations

Although terpene cleaners are not highly hazardous, strict caution should be taken at all times when handling them, especially when the chemical is in concentrated form. This material, as indicated previously, can cause mild skin and eye irritation at high concentration and prolonged use. Additionally, it can be corrosive to the nose, throat, and esophagus on contact and can cause dizziness, drowsiness, and irritation to the mucous membrane. Because of these health hazards, certain precautions should be taken before using this chemical.

To avoid hazardous health risks, protective equipment such as goggles, gloves, respirator, and appropriate clothing must be worn as needed. Additionally, proper ventilation is required to maintain airborne concentrations below the established exposure limits.

The precautions and handling procedures that should be known before using this chemical are defined and outlined in Appendix B and listed below.

1. hazardous intake precautions
2. special protection information
3. spills and leaks procedures
4. handling and storage precautions
5. fire and explosive hazard data.

3.2.7 Recycling/Reclaiming

Terpene cleaners, once contaminated, do not physically separate as a solvent and therefore cannot be recycled, either by conventional methods or ultrafiltration. Terpene cleaners are expected to destroy current ultrafilter adhesives and support materials due to their corrosiveness.[14] Alternative recycling process are being researched at this time.

3.2.8 Disposal Methods

Most chemical manufacturers suggest terpene cleaners be disposed of in the storm sewer or receiving water, after used emulsions have been allowed to separate and the top layer of oil has been skimmed.

Running the rinse water through an oil/water separator is the typically suggested treatment process in using the terpene cleaners. The oily contaminants within the terpene solutions, when left in an oil/water separator or holding pond after cleaning, will rise to the surface. Permitted to stand overnight, oil, greases, and carbonaceous particles should rise to the top of the tank, so that residues can be easily skimmed. The accumulation of soil remaining at the bottom of the tank is said to be biodegradable, and therefore easily disposed of in accordance with local, state, and Federal EPA regulations.

3.3 Case Studies

A number of studies have been conducted during the past few years to evaluate the credibility of new, commercially available terpene cleaners. The following organizations have evaluated terpene cleaners for use in industrial maintenance cleaning:

1. General Dynamics
2. Air Force Engineering and Services Center (AFESC)
3. Kelly AFB
4. U.S. Army - Aberdeen Proving Grounds
5. Fort Hood Army Base
6. NTP.

The evaluations of the terpene cleaners completed in each study are summarized in Table 3.5. A brief summary of the studies conducted by each of these agencies. A more indepth discussion of the criteria, findings, and elements surrounding each study can be found in Appendix B.

3.3.1 General Dynamics[18]

In 1987, GD/FW evaluated terpene cleaners. The comments and results of this study are summarized in Table 3.6.

EVALUATIONS	GD/FW	AFESC	KELLY AFB	FT HOOD ARMY	ABERDEEN ARMY	NTP
Biodegradability	X	X	X	X	X	X
Cleaning Efficiencies	X	X	X			
Cleaning Enhancements	X	X	X			
Ultrasonics	X	X	X			
Mixers	X	X	X			
Combustibility	X	X	X			
Corrositivity - Metals	X	X	X			
Corrositivity - Plastics	X		X			
Dilution Rates	X		X			
Disposal Methods	X		X	X	X	X
Drying Requirements	X	X	X			
Operating Temperatures	X	X	X			
Ozone Depletion	X	X	X			
Rinsing Requirements	X	X	X		X	
Solution Life Expectancy		X				
Solubility	X	X	X			
Toxicity Testing				X	X	X
Full Scale Demonstration /Implementation	X	presently working on	X	X		
Economics	X	X	X			

Table 3.5 - Evaluations Performed on Terpene Cleaners

GENERAL DYNAMICS STUDY OF TERPENE CLEANERS	
EVALUATIONS	COMMENTS AND RESULTS
Biodegradable	Cleaners will degrade in time, depending on dilution rate, formulation, contaminants, and appropriate treatment facilities.
Clean Efficiently	Cleaners found to be only accepted for a narrow line of cleaning at nonproduction plant areas. Currently used to clean cosmoline, a tar-like soil from floors and maintenance equipment.
Cleaning Enhancements	Cleaners required enhancements to achieve effective cleaning efficiencies.
Ultrasonics	Not applicable, heats up solvent to combustible level and becomes, expensive as tanks become large.
Mixers	Work satisfactorily, however become expensive when used in large tanks.
Combustibility	Cleaners are highly combustible, flash point averages 120 °F. Avoid all sources of heat and ignition, strict temperature control is required.
Corrositivity - Metals	Cleaners were found to be corrosive to common metal on parts and cleaning equipment.
Corrositivity - Plastics	Rapid and severe crazing to plastics and acrylics on parts and equipment was witnessed.
Dilution Rates (% Citrius Terpene in water)	Light cleaning: 10-20 Moderate cleaning: 20-30 Heavy cleaning: 100 Garage cleaning: No
Drying Requirements	Evaporation rate similar to that of water, dryers are therefore required in cleaning procedures.
Operating Temperatures	Strict temperature control is required to maintain safe operating conditions.
Ozone Depletion	Cleaners are the most photochemically reactive substances known.
Rinsing Requirements	All parts cleaned require a clear water rinse. Poor rinsing efficiencies witnessed.
Solubility	Good, however cleaner tends to polymerize in aqueous solutions
Full Scale Demonstration/ Implementation	Problems with using cleaners include cleaning rag fires, maintaining safe operational temperatures, obtaining cleaning efficiencies, and factory worker complaints of irritation to skin and eyes.

Table 3.6 - Study of Terpene Cleaners by General Dynamics at Fort Worth, TX[18]

Following extensive evaluation, the selected terpene cleaners were found to be suitable for maintenance cleaning of nonproduction parts in selected factory areas. At present, terpene cleaners are used only as a bridging material that has allowed elimination of perchloroethylene and methylene chloride use, found in Safety Solvent (a Stoddard solvent derivative), from production plants. General Dynamics has strong concerns over the use of terpene cleaners in large applications, industries, or installations due to many unfavorable characteristics and multiple unknown possibilities acknowledged in their evaluations.[18]

3.3.2 Air Force Engineering and Services Center Study[39,40]

Hundreds of terpene cleaners were evaluated as potential substitutes for halogenated (i.e., chlorinated) and nonhalogenated (i.e., Stoddard) solvents used in the USAF in the program titled, "Substitution of Cleaners with Biodegradable Solvents." This program was conducted by the AFESC at Tyndall AFB, FL. The study was begun in 1987, shortly after the General Dynamics study was started.

The USAF study was initiated because of concerns resulting from solvents used in both cold cleaning and vapor degreasing cleaning processes. The purpose of the study was to identify biodegradable solvents for removing wax, grease, and oil, and to develop procedures for and implement their use. The study involved three phases:

Phase I - Solvent Selection and Performance Evaluation

Phase II - Extended Performance Testing

Phase III - Full-Scale Demonstration/Implementation of Solvents into Industrial Processes at the Air Force Logistics Center.

Phases I and II have been completed, comments and results concluded at this time have been summarized in Table 3.7. Phase III was begun in the late spring of 1990, it is expected that evaluation will be completed in the spring of 1991.

3.3.3 Kelly AFB Study[43]

Kelly AFB, TX, conducted a site specific study on the use of terpene cleaners in 1988, just one year after the AFESC study began. The study was initiated in the process of identifying less hazardous alternatives to solvents and cleaners currently used on service equipment at the base. The terpene cleaners were evaluated to substitute for solvents used in

AFESC STUDY OF TERPENE CLEANERS	
EVALUATIONS	**COMMENTS AND RESULTS**
Biodegradable	Degradation of cleaners is dependent on dilution, formulation, and a bioacclimated treatment facilities.
Clean Efficiently	Cleaners proved to clean satisfactorily, after cleaning enhancements were employed.
Cleaning Enhancements	Enhancements are required to achieve effective cleaning.
Ultrasonics	Works good for inner surfaces, notches and crevices inherent to parts; however, cost increases significantly when ultrasonic tanks become large.
Mixers	Works satisfactorily; however is expensive in large tanks and may create volatile organic compound (VOC) emission problems.
Combustibility	Cleaners are very combustible; flash points average 120° F. Cleaners must be used in diluted form to avoid ignition.
Corrositivity - Metals	Cleaners are corrosive to common metal parts and cleaning equipment.
Drying Requirements	Evaporation rate of cleaners is similar to water. Dryers are required to avoid flash corrosion and to perform maintenance procedures.
Operating Temperatures	Strict temperature control is required to maintain safe operating conditions.
Ozone Depletion	Cleaners are not nearly as volatile as baseline solvents (i.e., Stoddard and trichloroethane)
Rinsing Requirements	Rinsing is required to achieve cleaning efficiencies and to avoid flash corrosion.
Solution Life Expectancy	Dependent on cleaners' formulation and cleaning application.
Solubility	Solubility of cleaners is satisfactory compared to that of baseline solvents.
Full Scale Demonstration /Implementation	Implementation of selected cleaners is currently in progress.

Table 3.7 - AFESC Study of Terpene Cleaners[39,40]

cold cleaning processes and treatment schemes currently available on base. A summary of the comments and results obtained from this study can be found in Table 3.8.

Selected terpene cleaners have been approved for limited use at Kelly AFB. Cleaning guidelines have been developed for the use of terpene cleaners on jet exterior washing and parts cleaning, cleaning exterior surfaces of T37/38 aircraft, and for aircraft exterior spray-on, wipe-off cleaning. Reference Appendix B for examples of the guidelines developed. The selected terpene cleaners have been approved at Kelly AFB for limited use on the following:

1. external and parts washing of TF39 engines
2. external washing of TF34 engines
3. external and parts washing of T56 engines
4. exterior wash of C-5 aircraft
5. exterior wash of OV-10 aircraft
6. exterior wash of A/T-37 aircraft
7. exterior wash of T-38 aircraft
8. parts washing of GTEs (Depot Level)
9. cleaning of Noise Suppressor Facilities
10. cleaning of Support Equipment, TO 35-1-12.

Ongoing projects associated with the terpene based cleaners at Kelly AFB are:

1. writing a specification; Cleaning Compound, Aerospace Equipment
2. testing for electrical/electronic equipment cleaning
3. testing for engine gas path cleaning
4. testing for bearing cleaning
5. testing for toxicity (conducted for the EPA).

3.3.4 U.S. Army Water Study - Aberdeen Proving Grounds[30]

Because of the widespread use of the terpene solvents, the Army requested that a water study be conducted on a terpene based product, Citrikleen, manufactured by Penetone Corporation. An environmental assessment was performed on the product. The assessment was requested by the Environmental Management Division at the U.S. Army Aberdeen Proving Ground Support Activity, MD.

KELLY AFB STUDY OF TERPENE CLEANERS	
EVALUATION	**COMMENTS AND RESULTS**
Biodegradable	Decomposition of the cleaners in effluent treatment facilities varies on the method, bacteria, dilution and product used.
Clean Efficiently	Cleaning procedures are similar to those of alkaline soaps. Accepted for use in cold dip tanks, sprayers, foamers and brush-on applications.
Cleaning Enhancements	Brushing and pressure spray may be required to achieve efficient cleaning of different shaped parts.
Ultrasonics Cleaning	Cleaners are not to be used in heated ultrasonic tanks because of temperature requirements and probable emission of nauseous odors.
Combustibility	Flash point of cleaners average around 120 °F in concentrated form. When cleaners are used in diluted forms, flash points increased accordingly.
Corrositivity - Plastics	Deterioration of rubber and neoprene may result if immersed in cleaner for extended periods. Do not use cleaner on acrylics or plastics.
Corrositivity - Metals	For cleaned parts that will not be immediately coated with primer, it is necessary to apply a corrosion prevention compound or light lubrication oil to the cleaned part to prevent flash rusting and corrosion. Do not leave any metal exposed in the cleaner beyond recommended time limits. Do not use on indium, lead, aluminum or other soft metals.
Dilution Rates (terpene cleaner : water)	Exterior Cleaning - 1:4 to 1:10 Parts Cleaning - light to medium 1:5, heavy 1:2 Cleaner is not recommended to be used in concentrated form, undiluted cleaners can stress craze acrylics and corrode metal.
Disposal Methods	Pretreatment is required through an oil/water separator after tank has been skimmed. Rinse water should only be disposed of in a satisfactorily operating effluent treatment facility.
Drying Requirements	Do not allow cleaner to dry on equipment or parts. Evaporation rate of cleaner is similar to that of water, therefore, a dryer may be required in certain maintenance procedures.
Operating Temperatures	Cleaner is not to be heated over 115 °F.

Table 3.8 - Kelly AFB Study of Terpene Cleaners[43]

KELLY AFB STUDY OF TERPENE CLEANERS (cont.)	
EVALUATION	**COMMENTS AND RESULTS**
Ozone Depletion	Air sample testing for in-application use show concentration levels within exposure limits of 8.0 mg/m^3.
Rinsing Requirements	All parts or surfaces cleaned require a clear water rinse to remove all remaining residue.
Solubility	Cleaners tested compared satisfactorily to solubility traits of baseline solvents (i.e., Stoddard solvent and trichloroethane).
Toxicity	Cleaners tested generally have a low TLV, 3 ppm.
Full Scale Demonstration/ Implementation	Solvents are currently used to clean jet engine exteriors, for washing and parts cleaning, for cleaning exterior surfaces of T37/38 aircraft, and for aircraft exterior spray-on, wipe-off cleaning. Cleaners have been approved for cleaning procedures on a limited basis.

Table 3.8 (cont) - Kelly AFB Study of Terpene Cleaners[43]

U.S. ARMY WATER STUDY - ABERDEEN PROVING GROUNDS	
EVALUATIONS	**COMMENTS AND RESULTS**
Biodegradable	Cleaners will degrade with appropriate time alloted and in an appropriate bioacclimated treatment facility.
Disposal Methods	Cleaners cannot be pretreated completely in a gravity-type, oil/water separator due to emulsified oil formation. Cleaners will inhibit biological treatment system at concentration greater than 100 mg/L as COD, therefore no more than 40 gallons/ million gallons of sewage flow should be discharged to sanitary treatment plant.
Rinsing Requirements	Rinse water should be collected and transported to treatment plant to allow treatment personnel to conduct a bleed-in operation into treatment facility. This procedure will help to ensure conformance with the recommended rate of discharge.
Toxicity	At high concentrations the cleaners will have an adverse effect on aquatic organisms and stream life. Special precautions must be taken to control effluent discharges to receiving waters.

Table 3.9 - U.S. Army Water Study of Terpene Cleaner at Aberdeen Proving Grounds[30]

The methodology used for this consultation included a preliminary toxicity screening, a simplified treatability study and a review of the manufacturer's brochure. The preliminary toxicity screening performed was a simple static biotoxicity test in which several concentrations of the cleaner were evaluated in test beakers.

A summary of the comments and results obtained from this evaluation can be found in Table 3.9; a more detailed discussion can be found in Appendix B.

3.3.5 Fort Hood U.S. Army Study[48]

Fort Hood, TX, initiated a study of the terpene cleaners following a commercial product cleaning demonstration performed on base.

The cleaning demonstration was conducted at the vehicle washracks. Effluent water samples were retrieved from the washracks following the cleaning demonstration. The samples were sent to a laboratory for testing.

A summary of the comments and results from this study of terpene cleaners can be found in Table 3.10. Appendix B gives a detailed discussion and description of this study.

The conclusion arrived at following this study was that use of terpene cleaners will result in permit violations, regulated under the National Pollution Discharge Emission Standards (NPDES). Such violations can lead to the assessment of fines at the cost of $25,000 per day of violation. Additionally, adverse effects on aquatic life are also to be expected if cleaners are used installation-wide. Terpene cleaners are currently banned from Fort Hood for use in cleaning operations.

Steam cleaning without the use of chemicals is the recommended method for degreasing. The steam alone will, in most instances, do a reasonably good degreasing job. Generally, a degreasing job takes just as much "elbow grease," with or without chemicals.

3.3.6 National Toxicity Program Study[36]

A study of the terpene cleaners was conducted by the NTP because of concern that several of these new cleaners contain the chemical d-limonene. Studies conducted show that there is no evidence to suggest that the d-limonene compound is mutagenic or teratogenic; however, signs of carcinogenicity have been witnessed. Terpene formulas containing d-limonene were suggested for NTP testing because of the increasingly widespread exposure in industrial cleaners.

In a 2-year study conducted by the NTP, evaluations of industrial solvents and food additives showed clear evidence of cancer in male rats but no evidence of cancer in female rats or in either gender of mice tested. This study confirmed the kidney as the primary target organ for chemically-related lesions.

A summary of the comments and results obtained from this study are listed in Table 3.11. Appendix B provides a more detailed discussion of the findings from this study.

FORT HOOD STUDY OF TERPENE CLEANERS	
EVALUATIONS	COMMENTS AND RESULTS
Biodegradable	With time, cleaner is biodegradable, however treatment is required prior to discharge to avoid NPDES permit violations by exceeding standards for oil, grease, and COD.
Disposal Methods	Close supervision must be kept over effluent to avoid permit violations by exceeding standards for oil, grease, and COD.
Toxicity	Cleaner showed to adversely effect aquatic life downstream of outfall (i.e., fish kills). Adverse effects to biological growth are expected to occur at treatment facilities.
Full Scale Demonstration/ Implementation	Cleaners are banned from Fort Hood until further notice or testing.

Table 3.10 - Fort Hood Study of Terpene Cleaners[48]

NATIONAL TOXICITY PROGRAM STUDY OF TERPENE CLEANERS	
EVALUATIONS	COMMENTS AND RESULTS
Biodegradability	Dependent on the dilution, degree of contamination, and soluble components' concentration.
Disposal Methods	Close supervision must be kept over effluent to avoid health hazards. Samples should be taken periodically to determine hazardous waste characteristics as defined by applicable federal and state regulations.
Toxicity	A two year study of cleaners showed evidence of cancer in male rats. The kidney was confirmed as the primary target organ for chemically-related lesions. Cleaners were not found to be mutagenic.

Table 3.11 - NTP Study of Terpene Cleaners[36]

Chapter 4

Experimental Design

4.1 Background

The Army rigorously controls solvent use in all its industrial cleaning activities so military standards and specifications are not compromised. Several factors determine if a solvent is acceptable for each particular military application. Performance (ability to meet job standards and specifications), availability, costs, toxicity, and environmental and health safety are typical factors evaluated for each solvent to be implemented in cleaning processes at Army installation.

Therefore, when addressing the merits of various solvents as possible substitutes, the product's capacity and effectiveness must be weighed equally against workers' safety and prevention of pollution. New regulations from the Occupational Safety and Health Administration (OSHA), and such as the Toxic Substance Control Act (TSCA) and the RCRA have emphasized the importance of evaluating toxicity and safety aspects of hazardous materials and waste. Personnel responsible for user safety have looked to substituting less hazardous solvents whenever possible.

To systematically review the substitution of terpene cleaners in Army installations, a decision logic diagram (Figure 4.1) devised by USACERL was used. This diagram has assisted facilities and user activity personnel, safety officers, and industrial hygienists to systematically review solvents used in their installations. The successful and widely recognized solvent-to-solvent substitutions shown in Table 4.1 have been performed at Army installations using similar decision diagrams.

In addition to the decision diagram, the following characteristics of terpene cleaners are evaluated and compared to those of the Stoddard solvents.

1. chemical and physical characteristics
2. toxicity
3. biodegradability
4. cleaning efficiency

5. reactivity
6. corrositivity
7. recycling/reclaiming
8. disposal methods
9. economics.

The experimental design of this thesis consists of a literature search, telephone contacts, site visits, case studies, and computer modeled economic analysis.

START			
(1) Modify process/application to eliminate use of Solvent A?	Yes	Investigate alternatives	Where MIL SPECS do not clearly indicate substitutes, consider using such alternatives as: abrasives, detergent/water solutions, steam
No			
(2) Consider substituting Solvent B for Solvent A			
(3) TLV of Solvent B is less than TLV of Solvent A?	No	Do not use Solvent B	Considerations include suspected carcinogens, vapor toxicity, liquid toxicity.
Yes			
(4) Nat'l Fire Protection Assoc. Flammability rating of Solvent B is lower than Solvent A?	No	Do not use Solvent B	Must consider reactivities of Solvent B with other process chemicals. Is flash point below 140 °F (60 °C)?
Yes			
(5) More personal protection required to use Solvent B than Solvent A?	Yes	Do not use Solvent B	Is special ventilation needed; flame sources; safety can; grounding; respirator; goggles; face shield; coveralls?
No			
(6) Is Solvent B better than Solvent A in meeting job specs? (Performance/Use Criterion)	Yes	DECISION COMPLETE USE SOLVENT B	Production efficiency; cost; ease of disposal; maintain job quality.
No			
(7) Do not use Solvent B. Select Solvent C and recheck criteria.			

Figure 4.1 - Solvent Substitution Decision Diagram

SOLVENT	TO BE REPLACED BY
Methanol	Isopropanol
Methyl Ethyl Ketone (MEK)	Acetone Ethyl Acetate Aliphatic Naphtha
Toluene	Stoddard Solvent Acetone TCA
TCE	TCA Methylene Chloride
Xylene	Stoddard Solvent TCA

Table 4.1 - Solvent-to-Solvent Substitutions

4.2 Literature Search

An extensive search of the literature on solvent use, management, and disposal within both government and private industries was performed on both Stoddard solvent and terpene cleaners.

Applicable Army regulations, manuals, publications, and current studies were reviewed as were Federal laws and regulations on hazardous material storage, use, treatment, and disposal.

4.3 Telephone Contacts

Phone contacts were made with Army installations that:

1. conducted cleaning demonstrations of the terpene cleaners
2. currently use terpene cleaners in cleaning process
3. have shown interest in using terpene solvents.

A list of the military agencies that have been introduced to one specific terpene cleaner, Citrikleen manufactured by Penetone Corporation, can be found in Appendix C. This list was obtained from the Penetone Corporation, and was only used to represent the military agencies

that have received, or have come in contact with Citrikleen at some time. This list was used mainly as a tool to contact installations.

A list of telephone contacts concerning solvent use for both Stoddard solvent and terpene cleaners also can be found in Appendix C.

4.4 Site Visits

Two Army installations were visited to obtain information on current Army methods of solvent procurement, use, and disposal and to identify actual or potential problems with solvent use and management. The installations visited were Fort Carson in Colorado Springs, CO and Fort Lewis in Tacoma, WA.

Key personnel were interviewed concerning details of the procurement, use, disposal, and toxic effects of Stoddard solvent at each installation. An observation of several typical installation activities that required use of Stoddard solvent included degreasing operations using cold solvent on aircraft, tank, and locomotive maintenance; motor vehicle maintenance; heavy and light equipment maintenance; and small and heavy arms maintenance.

To obtain additional information, appropriate personnel in the following offices were interviewed.

1. Depot Operation, Defense Supply Agency
2. Waste Disposal Engineering Division, U.S. Army Environmental Hygiene Agency
3. Director of Industrial Operations
4. Department of Engineering and Housing
5. Director of Industrial Waste Water Treatment Plant.

Some of the major observations noted during the site visits are detailed in Appendix D.

4.5 Case Studies

A number of studies have been conducted on terpene cleaners over the past few years. Studies managed by the following agencies evaluated the substitution of commercial terpene cleaners designed for industrial cleaning.

1. General Dynamics
2. AFESC
3. Kelly AFB
4. U.S. Army - Aberdeen Proving Grounds

5. Fort Hood
6. NTP.

These studies evaluated the acceptability of the terpene cleaners as a possible alternative to currently used solvents. Terpene cleaner characteristics such as solubility, biodegradability, cleaning efficiency, corrositivity, toxicity, disposal methods, and cleaning procedures were tested. For a detailed discussion of each study's comments and results, consult Appendix B.

4.6 Economic Analysis

An economic comparison was performed to compare the cleaning process using Stoddard solvent purchased through an off-site, closed loop recycling contract (i.e., Safety Kleen), with the terpene cleaner, Citrikleen, at three different dilution rates. The dilution rates used for comparison were recommended by the manufacturer of Citrikleen for cleaning and degreasing heavy (concentrate), medium (1:3) and light (1:5), Army installation soiling problems.

It has already been demonstrated through a study conducted by USACERL in 1989,[10] that favorable economic return can be provided by recycling and reusing spent Stoddard solvent compared to off-site disposal through waste minimization and reduced raw material dependency. Implementation of a solvent recycle program through either an off-site, closed-loop recycler such as Safety Kleen, or through the purchase of distillation equipment for use on-site, reduces the quantity of solvent related wastes requiring disposal as well as the liability associated with hazardous waste disposal. The flexibility of implementing a specific recycling program is dependent on the type or volume of spent solvent generated. Due to the apparent popularity and flexibility of Safety Kleen contracts at Army installations, this technique of spent solvent management was used as the basis to evaluate and compare the Stoddard solvent economics to terpene cleaners.

With the aid of a computer model, all costs are summed to obtain life cycle cost over the assumed economic lifetime for each option. Comparisons of Net Present Value (NPV) of the total life cycle cost provide the basis for selecting the favorable waste minimization technique.

4.6.1 Computer Model

The economic analysis was performed using a computer model developed by USACERL. The computer model is called CERL Economic Analysis for Minimizing Hazardous Wastes (CEAMHW). The model was developed to assist installation managers in performing economic analysis of various alternatives for selecting, recycling, or disposing of used solvents.

The model provides a procedure for determining the life-cycle costs of proposed alternatives which can then be compared with the cost of current operating practices. Installation managers can use results of the economic analyses to help choose cost saving alternative solvents or to help obtain funding for specific waste minimization projects. The program flow is described in the following section.

4.6.2 Program Flow of CEAMHW

The program flow describes the typical order of the program for examining a problem and determining its most economical solution using CEAMHW. The steps are defined and described below. The generalized program flow chart is presented in Figure 4.2.

1. Choose a Waste Stream - If the problem is not a member of one of the listed waste streams, then the general model should be used.

2. Assumptions Window - Before any costs are entered or calculated, the default option should be selected to verify known values of items such as specific equipment costs, discount rates, or adjustment percentages. Since these values are used to calculate suggested costs later in the program, accurate default values will result in more accurate defaulted costs.

3. Choose a File - After the defaults have been viewed, a work file must be opened. Previously entered files will be listed along with a New Problem option. One of these files must be selected.

4. Define Problem - After a file has been chosen, a new menu will appear that includes. Problem Information, Comparisons, and the three waste minimization techniques, solvent substitution, recycle/reclaim, or treatment. Choose the Problem Information option first, and enter the appropriate information.

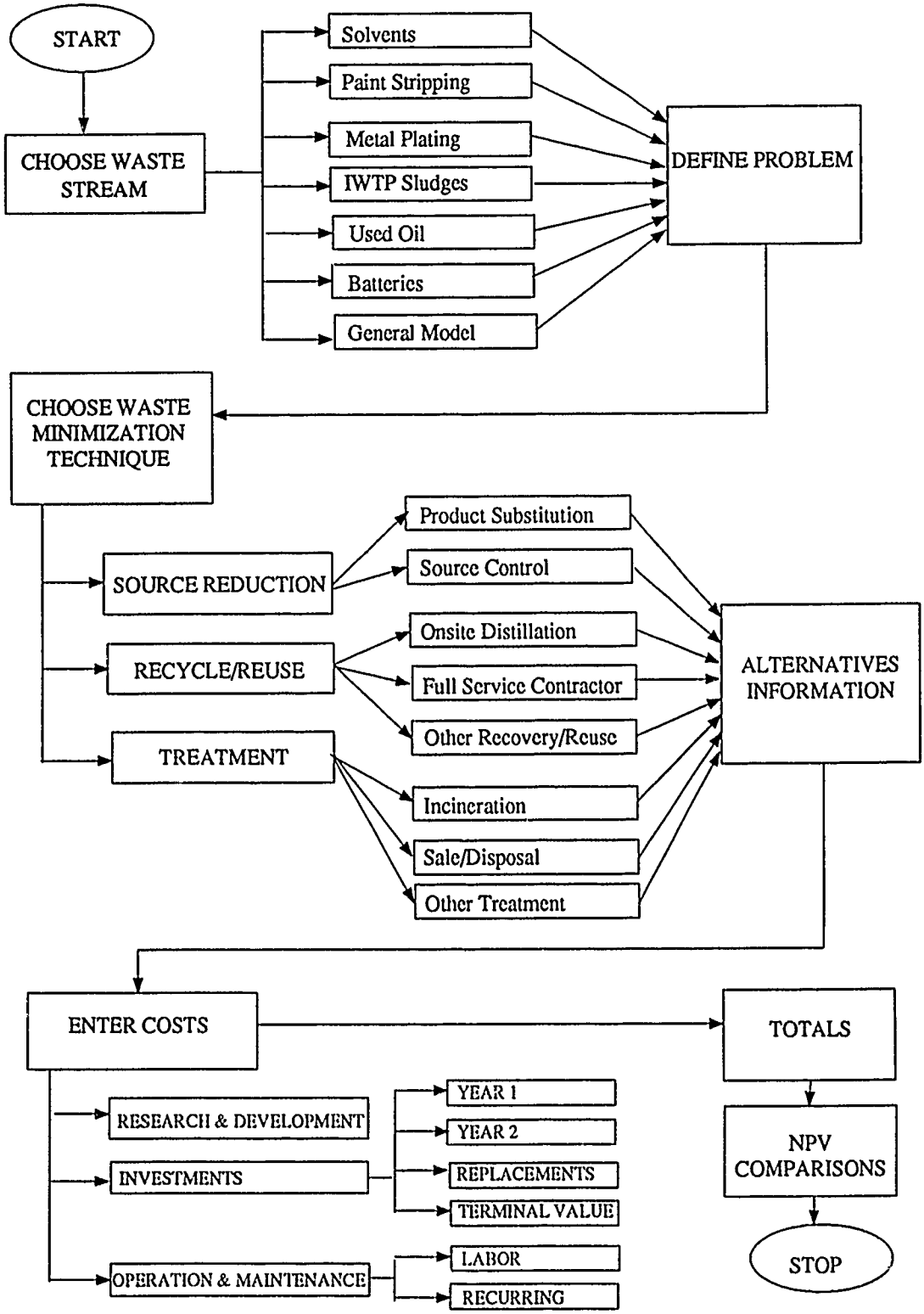

Figure 4.2 - Generalized CEAMWH Program Flow Chart

Information Screens:

The set of information screens ask specific questions about a problem or alternative and are unique to each waste stream and alternative. An example of a question on the informational screen is the number of gallons of waste produced per year and whether or not the waste is hazardous.

5. Input Alternatives - After the problem has been defined, choose a waste minimization technique and a specific alternative to consider. The first thing to do in each alternative is enter the alternative-specific information. There are usually two pages of information and both should be completed before any other information about the alternative is entered.

6. Enter Costs - First enter any nonrecurring costs. If there are research and development (R&D) costs, enter the yearly totals. If there are investment costs, enter the yearly investment costs, major replacement costs, and a terminal value. Then, enter the operations and maintenance (O&M) costs. A brief discussion of each of these cost subjects are as follows:

Research and Development Cost:

Depending in the number of R&D years specified in the Alternative Information screen, this screen allows you to input the total R&D costs for each year. The costs are not separated into categories as in other screens, they are total yearly costs.

Investment Cost Screens:

The investment costs are those costs incurred before operation. Included are costs for items such as major equipment, shipping, permits, and start-up. Inside the investment menu selection, the costs are divided into yearly investment costs, replacement costs, and a terminal value. It is assumed that the maximum number of years needed for investment is two. Therefore, two screens are provided for entering the investment costs for each year. These screens operate in the same manner as the cost screens.

Operations and Maintenance Costs Screens:

In the Operations and Maintenance menu option, there are two cost screens: Labor Calculations and Annual Recurring Costs. The Labor Calculations screen is a worksheet that aids in calculating the labor costs for an alternative. The values calculated here appear in the Annual Recurring Cost Screen in the labor field. If the total labor cost for the alternative is known, then these costs can be entered directly into the Annual Recurring Cost screen and there is no need to use the labor calculation screen.

The Annual Recurring Costs screen displays costs incurred during each year of operation, including the total labor cost that was calculated on the previous screen. Common entries for annual recurring costs include electricity, labor, equipment, and transportation expenses.

7. Totals - After all of the costs have been entered, the total screen can display the alternative's costs by year. This display will include yearly present values for the alternative for each year of its project life.

8. Comparison - After at least two alternatives have been entered, comparisons can be made to determine which alternative is more economically feasible.

The program flow chart used to evaluate the economics of Stoddard solvent and the terpene cleaner (Citrikleen) are shown in Figures 4.3 and 4.4, respectively.

4.6.3 Assumptions

The description and explanation of the assumptions chosen for the economic analysis are as follows.

- **Economic Life**

In accordance with the Department of Defense (DOD) criteria that all purchased equipment must have at least a 10 year life expectancy, an "economic life" of 10 years and a midyear discounting rate of 10 percent were selected for all options.[8]

However, if a shorter economic life is desired for equipment to be used, make sure it is documented. This may be necessary in some instances where corrosive

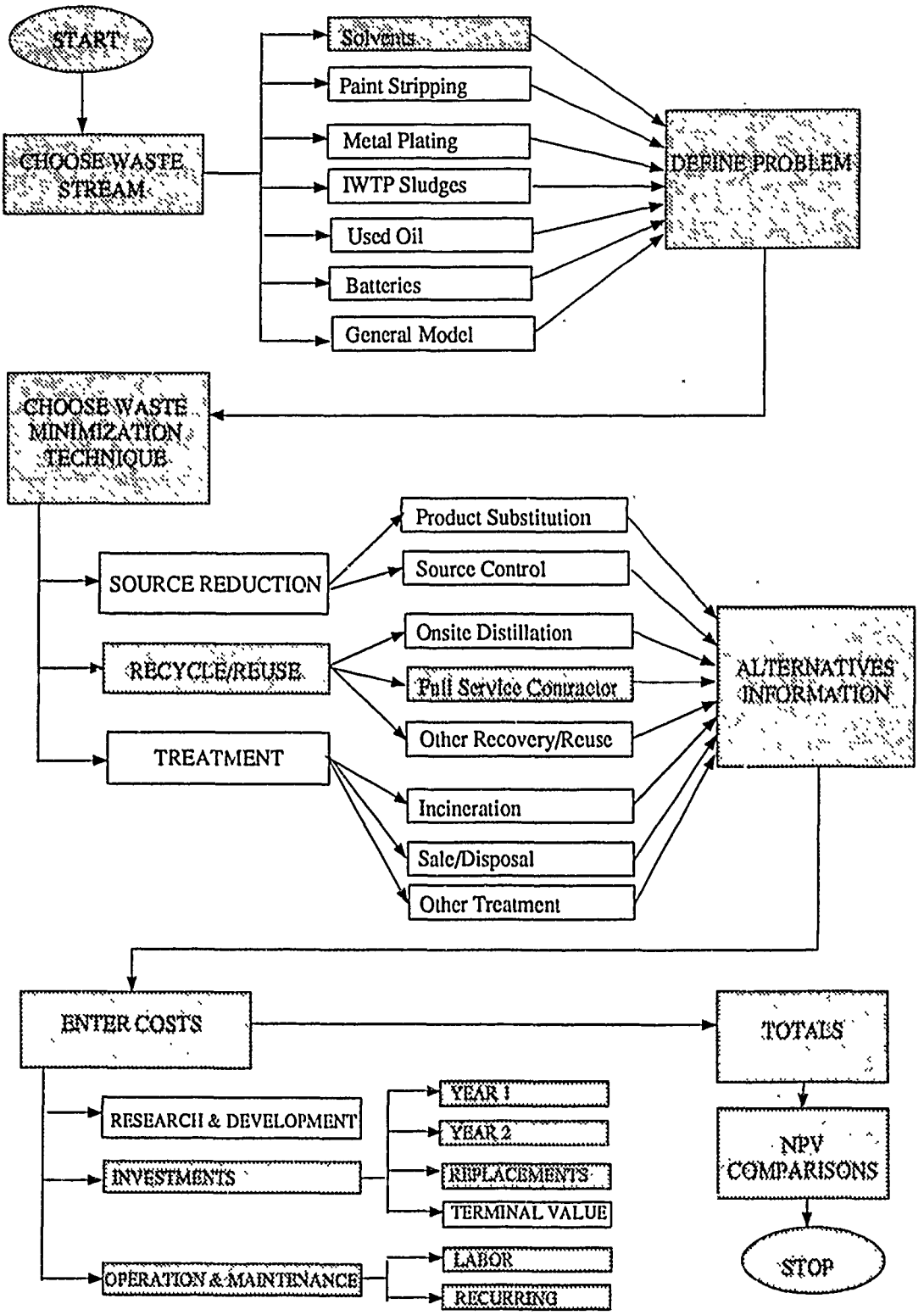

Figure 4.3 - Program Flow Chart for Stoddard Solvent Economic Evaluation

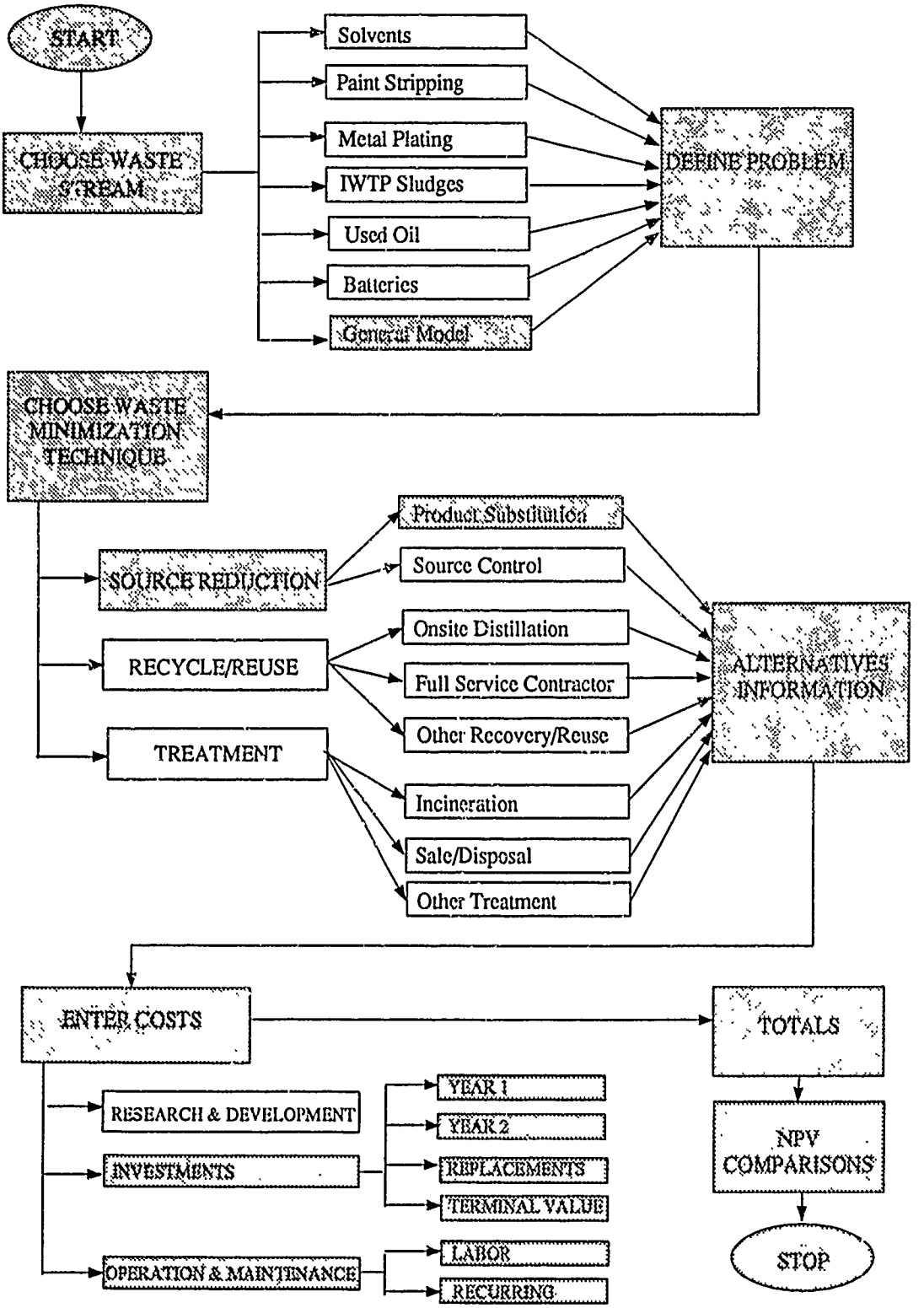

Figure 4.4 - Program Flow Chart for Terpene Cleaner Economic Evaluation

wastes severely shorten equipment lifespan, which could be the case when using terpene cleaners.

- **Research and Development**

Under R&D are all expenditures necessary to implement the alternatives and test laboratory or bench scale operations prior to initial start up but subsequent to the decision point to proceed with the alternative. In other words R&D does not include any sunken cost.

For this analysis, it is assumed that the number of years of R&D required is zero for all options. It is assumed that existing technology will be implemented.

- **Nonrecurring Costs**

The basic definition of nonrecurring costs states that such costs are incurred on a one-time basis. Due to investment costs in facilities occuring over a single year of funding as opposed to in increments, a 1 year time schedule was selected for all options.

Circumstances may arise where such one-time costs as plant rearrangement and retooling, relocation, and purchase and installation of new equipment may be spread over more than 1 year, although rarely over more than 2 years. The time value of money dictates that equipment purchased in subsequent years be treated separately in determining the net present value of the alternative. If nonrecurring costs are expected to be spread over more than 1 year, cost incurred for each year must be broken down.

- **Recurring Cost**

Due to the prior assumption that no R&D efforts or nonrecurring (investment) costs are expected to be incurred for only 1 year, recurring (operating) costs would be expected to first occur in year 2. The year in which the alternative begins operation is assumed to be the year immediately following the occurrence of any investment costs.

- Labor

To estimate the amount of labor required to operated each alternative, the number of workdays in a year is assumed to be 260 (5 workdays/week x 52 weeks/yr = 260). Provisions for holiday and leave are automatically taken into account by the model in determining overhead.

Labor rate values used are $11.00/hour for laborers, $16.00/hour for management and supervisory personnel.

Adjustments for leave, such as sick leave, annual leave, and holiday, are prescribed as 18 percent of the total man hours. The prescribed rate for fringe benefits in the military is 36.2 percent of adjusted base labor costs.

- Escalation Rates

An annual escalation rate of 4 percent was applied to raw materials and replacement materials, maintenance and repair, other materials and supplies, utilities, sampling and testing, and liability.

Escalation rates of 7 percent and 6 percent were used for recurring disposal and contractual costs, respectively.

- Property Acquisition

Property acquisition cost associated with the acquisition of real estate or easements are assumed to be zero as the Army already owns the land and facilities to be improved or expanded.

- Logistics and Procurement

Included here are the initial costs of local procurement, accounting, legal fees, medical, police, fire, and any other services included in the acquisition of equipment and its installation. The default value in the model for local procurement and logistics costs for acquiring and installing equipment has been estimated for all options at 7 percent of installed equipment costs.

- **Contingencies**

Allowances for contingencies to meet unexpected installation cost, engineering, etc., are estimated at 10 percent of total installed equipment costs for all options.

- **Stoddard Solvent Assumptions**

Assumptions applied in the calculations for the Stoddard solvent use under a Safety Kleen contract are:

1. Raw materials/replacement materials is an estimated price for Safety Kleen services. Determined by taking the average price per gallon for Safety Kleen services for a solvent similar in makeup to PD-680, Type II, and multiplying by the installation's solvent usage/initial need (in gallons per year).

2. There are no maintenance and repair costs associated with full service contracting.

3. Liability costs associated with Full-service contracting differs from liability cost typically associated with hazardous waste management. The full-service contractor is assumed to bear the burden of liability costs for landfill of sludges, etc., associated with the solvent that he removes. Nevertheless, there still exists the potential for on-site spills, cleanups, and legal claims. For this reason, liability cost involved with full service contracting are estimated at $0.01 per gallon for the total amount of solvent usage indicated.

4. Direct disposal cost associated with this alternative will be zero as all wastes are handled by a full service contractor.

5. No additional equipment or operating cost, other than the cost of using the Safety Kleen solvent, are anticipated.

6. Ideally, cold cleaning vats would be tested on a regular basis to insure solvent purity. If the solvent proved to be spent, it would be replaced. Under a full-service contract, however, solvent will be removed at regular intervals, regardless of its cleaning power, and replaced with new solvent. Sampling and testing are unnecessary; therefore, costs will be zero.

7. As no handling of used solvent is expected to occur under this alternative (all handling of spent solvent is performed by the full-service contractor), the value for transportation and warehousing/storage of hazardous wastes is zero.

8. The costs for procurement and logistics, including annual preparation and review of bid schedules and contract preparation and supervision is estimated at 3.0 percent of the total contract costs.

9. Twenty percent of the solvent is assumed lost due to open lids (evaporation) and other bad operating practices such as carry-off and spillage.

10. Volume of the still bottom is assumed to be 10 percent of the waste volume.

11. Contractor is assumed to change solvent 12 times in a year.

12. A one time installation charge of $40.00 is associated with each 30 gallon capacity washer unit and is considered an investment cost.

13. Labor time for parts cleaning and degreasing is estimated at 2.0 hours per day, per individual, per shift.

14. Contractor is responsible for collecting and distributing solvent, no onpost personnel labor is required.

- **Terpene Cleaner Assumptions**

Assumptions applied to economic calculation in the use of Citrikleen are:

1. The price of Citrikleen on military order is estimated at $11.00/gallon.

2. The estimated costs of maintenance and repair for regular repair to buildings, equipment, etc., is 5 percent of the total equipment costs. This will include parts and filters replaced in the normal operation of the alternative. As a guideline, anywhere from 2 to 10 percent of the initial purchase price for the technology is suggested by the model, therefore an average percentage was employed.

3. The wastes generated after the cleaning are considered to be hazardous for the concentrate Citrikleen option and for the 3:1 dilution option. The 5:1 dilution is considered to be nonhazardous.

4. Investment costs are estimated at $1700 for existing tank modification, which includes such items as pumps and tank top skimmer.

5. Site preparation and installation, including engineering and supervision, is assumed to be 15 percent of the total equipment costs.

6. Liability costs are assumed to be $0.01 per gallon of waste generated.

7. No cost is assumed for the construction of new storage tanks or storage facilities to hold hazardous materials/hazardous wastes, assuming that preexisting facilities on installation are satisfactory.

8. Site preparation costs are approximated at 15 percent of the total equipment costs. The site preparation costs include both new construction costs and construction costs related to demolition and rehabilitation.

9. Disposal cost for nonhazardous wastes in landfills is assumed to be $0.024 per gallon. Restricted liquids, not landfillable, are estimated at $5.30 per gallon.

10. Laboratory analysis costs, sampling, and testing are estimated as 3 percent of the direct labor costs.

11. Onsite transport/storage of hazardous wastes/materials is estimated at $0.33 per gallon. Onsite transport/storage of nonhazardous wastes is estimated at $0.008 per gallon.

12. The default value of 1.6 percent of the total of all previous recurring costs including labor costs is used for the ongoing cost of logistics and procurement. This category includes the ongoing costs of local procurement (e.g., for acquiring replacement material or chemicals), administrative costs associated with the warehousing/storage and subsequent distribution of products, accounting services and any legal or medical fees, and the charges for services such as security, fire, and any other services which arise as a consequence of the alternative's operation

13. Wastewater treatment costs and sewer fees are not included in this analysis due to unknown amounts of rinsewater containing Citrikleen generated per year.

Chapter 5

Results

5.1 Background

A comparison to evaluate the viable substitution of terpene cleaners for Stoddard solvent in parts cleaning operations at Army installations is presented here. Although, each terpene based cleaner differs slightly in formulation amongst the many commercial manufacturers, a generalized comparison of the key issues concerning the use of these cleaners has been addressed. The environmental and economic impacts of material substitution have been evaluated. The informational support used to develop this comparison was obtained from literature searches, site visits, case studies, and an economic evaluation. The comparison is summarized in Table 5.1.

5.2 Chemical Characteristics

Stoddard solvent is a nonhalogenated, petroleum-based solvent. As indicated in the literature review, it is generally a mixture of straight and branched chain paraffins, napthenes, and aromatic and aliphatic hydrocarbons (C_9-C_{12}).[35] The aliphatic hydrocarbons help to reduce the boiling point and make the solvent only slightly water soluble. The chain paraffins assist in the cutting of oils from metal parts.[31]

Terpenes are generally known as aqueous cleaners, which are broadly defined as cleaning solutions made up of water plus other chemical additives, namely surfactants, builders, corrosion inhibitors and antioxidants, and emulsion systems.[37] Terpene cleaners formulated for degreasing and cleaning of metal surfaces are based predominantly on the d-limonene terpene isomer which is extracted from natural products, primarily citrus and wood products.[22] Commercial terpene cleaners also tend to contain components such as ethanolamine, diethylene glycol monobutyl ether, and oxygenated aliphatic hydrocarbons.

	STODDARD SOLVENT	TERPENE CLEANER
SOLVENT TYPE	PETROLEUM BASED	AQUEOUS BASED
BOILING POINT	367-405 °F	212 - 220 °F
VAPOR DENSITY (air=1)	5.2	NOT DETERMINED
EVAPORATION RATE	0.21	0.08 - 0.10
% VOLATILE	100	70 - 80
% SOLUBILITY IN H_2O	<0.1	FORMS EMULSIONS
VAPOR PRESSURE (mmHg)	<1 0	NOT DETERMINED
SPECIFIC GRAVITY	0.772 (60 °F/60 °F)	0.94 - 0.98 (75 °F/75 °F)
FLASH POINT	>140 °F	117 - 125 °F
pH	NOT APPLICABLE	9.8 - 10.2 (in 10% solution)
APPEARANCE	COLORLESS/CLEAR	LIGHT YELLOW/CLEAR
ODOR	KEROSENE-LIKE	CITRUS
TLV (ppm) - FEDERAL STANDARDS	100	3
VOLATILE ORGANIC COMPOUNDS	795 g/L Not recognized as an ozone depleting substance.	500 g/L Not recognized as an ozone depleting substance. (Averages 50% of the cleaner,depends on the percentage of terpene-based material and ethanolamine contained in the product. In a 2:1 dilution VOC content is approx. 166 g/L)
HAZARDOUS CHEMICAL COMPOUNDS SUBJECT TO REPORTING (UNDER SARA REGULATION)	NONE	D-LIMONENE= 50% ETHANOLAMINE= 10 - 15% DI&MONO BUTYLETHER= 2-3%

Table 5.1 - Summary Comparison Table

	STODDARD SOLVENT	TERPENE CLEANERS
HEALTH HAZARDOUS	EYE, SKIN, THROAT, AND NOSE IRRITATION	EYE, SKIN, AND NOSE IRRITATION CORROSIVE TO THROAT
TOXICITY	DEFATTING OF SKIN NERVOUS SYSTEM DEPRESSION PERMANENT BRAIN DAMAGE	DEFATTING OF SKIN NERVOUS SYSTEM DAMAGE POSSIBLE CARCINOGEN
BIODEGRADABLE	NO	PARTIALLY,IN APPROPRIATE TREATMENT SYSTEM
RECYCLABLE	YES	NO
REACTIVITY	-STABLE UNDER NORMAL CONDITIONS -AVOID STRONG ACIDS, BASES, AND SELECTED AMINES -AVOID ALL SOURCES OF IGNITION	STABLE UNDER NORMAL CONDITIONS AVOID STRONG ACIDS AND ALL SOURCES OF IGNITION HIGHLY PHOTOREACTIVE SUBSTANCE
FIRE HAZARDOUS RANKING	SLIGHT-MODERATE	MODERATE-HIGH (concentrated formula)
CORROSITIVITY	SAFE FOR ALL METALS AND PLASTICS	CORROSIVE TO SELECTED METALS AND PLASTICS
CLEANING PROCESS	SOLVENT ONLY CLEANING PROCESS	CLEANER AT SPECIFIED DILUTION RATE RINSING REQUIRED ENHANCEMENT METHODS REQUIRED APPLY CORROSION PROTECTION ALLOTTED DRYING TIME
DISPOSAL	INCINERATION, BLENDING, SALE, FUEL SUBSTITUTION	RINSE WATERS - WASTE WATER TREATMENT OIL&GREASE SKIMMING - SEPARATION,RECLAMATION CLEANING TANK BOTTOMS- TREAT AS HAZARDOUS WASTE CONTAMINATED WITH METALS, PLASTICS, OILS, AND GREASE
COST ($/GALLON)	1.50 - 3.00	11.00 - 13.00

Table 5.1 - Summary Comparison Table (cont.)

5.3 Physical Characteristics

- Boiling Point

The boiling point of the Stoddard solvents greatly exceeds that of the terpene cleaners. Unlike the Stoddard solvent, the low boiling point of the terpene cleaners makes them unsuited for heated cleaning processes because of nauseous and harmful vapor transfer to the atmosphere.[23]

- Flash Point

Stoddard solvent is listed as a combustible liquid, however its flash point (>140 °F) is in the acceptable range as regulated by EPA (>100 °F).

The flash point of the concentrated terpene cleaners varies around 120 °F, and is a much more critical combustible liquid than the Stoddard solvent. Extra caution must be taken in handling and storage as well as in the workplace, for even the slightest spark has the ability to ignite the cleaner in its concentrated form. However, when the cleaner is diluted with water, the resulting emulsion can provide a flash point comparable to or higher than 140 °F.

- Evaporation Rate

Stoddard solvent evaporates on contact. It is a relatively high volatile solvent, however, its rapid drying characteristic, owed to its aromaticity, helps to reduce volatility adsorption into the environment. This high evaporation rate is a very beneficial characteristic in equipment cleaning because very little process drying time is required.

Terpene cleaners have an evaporation rate comparable to that of water. The cleaners generally have a lower volatile percentage than the Stoddard solvent, however there is only a slight difference. Only a 10 to 15 percent nonvolatile residue is found to be common in most terpene formulations.[18] The slower evaporation rate is a beneficial characteristic, because it reduces the probability of mobility and adsorption of volatiles. However, use of the cleaner can poses danger to the environment through the accumulation of contaminated rinsed waters, and to

working personnel put in contact with remaining residues.[18] Additionally, the low evaporation rates characteristic of terpene cleaners result in longer drying times. Additional equipment, such as dryers, to obtain cleaning efficiencies and production quality may be required.

- Solubility

The Stoddard solvents are only slightly soluble in water whereas the terpene cleaners generally tend to form emulsions with water and soils. The terpene cleaners usually are not water soluble, however incorporation of surfactants renders them emulsifiable and therefore water rinsible.[28] The emulsions that form must be evaluated as to their effects on treatment processes and downstream aquatic life.

The U.S. Army Water Study conducted at the Aberdeen Proving Grounds[30] found the terpene cleaners to be effective oil solvents, comparable to Stoddard solvent. The cleaners remove soil from the part by solubilizing the soil. In contrast, the Stoddard solvents remove soil by breaking down the adhesion of the soil to the part, which allows the soil to be removed mechanically through an oil water separator.

It is expected that more emulsified oil (chemical emulsion) will enter the sanitary sewer with the cleaner use. Concerns are generated because the emulsified oil cannot be removed in a gravity-type oil/water separator, and oil in concentration greater than 100 mg/L has been known to inhibit the biological treatment system.

- pH

The terpene cleaners operate at relatively high pH levels, therefore special care must be exercised when it is used. Skin contact can lead to burns or irritation and personnel must be cautioned accordingly. Aluminum or galvanized surfaces can be etched and painted surfaces can be softened and even stripped.[31] In such cases, it may not be possible to replace solvents. The use of such aggressive cleaners should be determined on a case-by-case basis.

5.4 Toxicity

The Stoddard solvent is identified as a hazard due to its defatting and irritating action on the skin. Minimal evidence of serious health effects has been reported aside from

permanent brain and nervous system damage as an effect of repeated and prolonged occupational overexposure. Additionally, aspirations of the liquid results in diffused chemical irritation of the lungs resulting in edema; a few milliliters may be fatal in these incidents.[25]

The recommended current time-weighted TLV for Stoddard solvent is set at 100 ppm. This limit was calculated from data on the toxicities of its major ingredients, and was designed primarily to prevent the irritative and narcotic effects of the vapors.[35]

Studies conducted on the Stoddard solvent show minimal evidence of toxicity. Carpenter et al. found that inhalation of 1400 ppm and substantial air saturation at 25 °C caused death in 1 of 15 rats in 8 hours.[4] Dogs (beagle) and cats had spasms and died at this concentration. There were no significant effects in dogs that inhaled 330 ppm, 190 ppm and 84 ppm, 6 hours daily, 5 days/week for 13 weeks. However, rats exposed to 330 ppm for this period showed slight kidney damage.

Rector et al. exposed rats, guinea pigs, rabbits, dogs, and monkeys 8 hours/day, 5 days/week for 30 exposure days and also for 90 days continuously to vapor of Stoddard solvent. In an 8 hour exposure of 290 ppm there was minor congestion and emphysema in guinea pig's lungs only. The rat did not show any signs of kidney damage as that reported by Carpenter.[25]

Relatively few data are available on the actual concentrations of vapor exposure. However, Oberg, in a survey of 30 dry cleaning plants in Detroit, found an average exposure of 65 ppm with a TLV of 35 ppm, for Stoddard solvents with flash points of about 105 °F. The worst plant had an estimated average exposure of 135 to 200 ppm.[25]

As a class, the terpenes are currently listed as low in mammalian toxicity. Many are listed as GRAS (Generally Recognized As Safe) in the Code of Federal Regulations and are used in food additives, see Table 5.2.[22] However, recent studies have shown that the terpene isomer, d-limonene, common in heavy duty degreasing and cleaning products, to be of concern. This component makes up more than 50 percent of most metal cleaning terpene formulations. Studies conducted by NTP,[36] as summarized in Chapter 3, show that d-limonene is a possible carcinogen. The study of d-limonene by NTP, indicated that the kidney is the primary target organ for chemically-related lesion of cancer.[36] Recent testing on laboratory animals is raising health concerns similar to those of the halogenated chlorinated solvents. D-limonene is currently under EPA scrutiny regarding its suspected carcinogenic characteristics.

COMPOUND	FDA	FEMA	COUNCIL OF EUROPE
Camphene	Permitted	GRAS	Permitted Temporarily
Camphor	Permitted	GRAS	Permitted
Linalool	Permitted	GRAS	Permitted
Limonene	Permitted	GRAS	Limited
Menthol	Permitted	GRAS	Limited
α-Pinene	Permitted	GRAS	Permitted
β-Pinene	Permitted	GRAS	Permitted
α-Terpinene	Permitted	GRAS	Not Permitted
α-Terpineol	Permitted	GRAS	Permitted

Table 5.2 - Regulatory Status of Selected Terpenes[23]

Commercial grades of d-limonene terpene cleaners cause dermatitis because of contamination with other terpene isomers and related materials. Therefore, it is important that the cleaner be formulated with high grade or medical grade d-limonene of 99 percent minimum purity.[36]

The d-limonene terpene cleaners cause pulmonary irritation and central nervous system depression in high concentration, much like the Stoddard solvent. The probable lethal dose in humans is currently estimated between one pint and one quart of the d-limonene material.

Other components that make up the terpene cleaners are monobutyl ether, which is a form of antifreeze. Although this chemical only makes up a small percentage of the product (2 to 3 percent), it is hazardous to human health and the environment. Additionally, ethanolamine found in some of the commercially available terpene cleaners is listed as a hazardous compound by OSHA, owing to its low TLV of 3 ppm.

5.5 Biodegradability

The Stoddard solvents are not biodegradable while the terpene cleaners have been found to be biodegradable in varying degrees. Biodegradability is defined as the ability of microorganisms to oxidize the solvent of toxic compounds in solution. According to the General Dynamics study, the terpene cleaners were found to be nonbiodegradable at concentrations required to achieve cleaning efficiencies.[18] However, the study conducted at Kelly AFB concluded that the terpene cleaners were biodegradable in time, as long as they are treated in an appropriate treatment facility. Additionally, the time required to decompose the cleaners in effluent treatment facilities varies depending on the method, bacteria, dilution, and product used.[43]

In the AFESC study, the solvent that could be biologically degraded to meet the National Pollution Discharge Elimination Standards (NPDES) discharge limits by the activated sludge treatment system at Tinker AFB's Industrial Wastewater Treatment Plant (IWTP) were considered biodegradable.[40] At Tinker AFB, the retention time of the activated sludge system is 6 hours. Figure 5.1 illustrates comparison examples for the biodegradation of solvents in the biodegradability testing. To establish a basis for comparison, the biodegradability test of the solvents was run with phenol as the standard solvent. Examples of the results obtained from the evaluation of the terpene cleaner, Citrikleen, are shown in Figures 5.2 and 5.3. These figures indicated that this particular terpene cleaner was not biodegradable in the 6 hour retention time recommended by the AFESC study criteria. In contrast, the data obtained from the evaluation of the terpene cleaner, 3D Supreme, illustrates a terpene cleaner that is biodegradable under the 6 hour retention time specified (see Figures 5.4 and 5.5).

In a treatability study of a terpene cleaner, conducted by the U.S. Army at Aberdeen Proving Grounds,[30] Citrikleen was found to be biodegradable in an aerobic biological treatment system at standard temperature and pressure. However, at concentration greater than 100 mg/L as chemical oxygen demand (COD), it is expected to inhibit the microbial growth that could result in noncompliance with permit limits. It was also found that acclimation of the receiving treatment system with the terpene cleaner will increase the rate of its biodegradation.

Biodegradation of organic materials is a natural process that has been practiced on a broad range of substances. Bacteria and microorganisms can be found in nature to decompose most substances. Most organisms are ubiquitous, but for use in engineered

facilities for treatment and disposal of wastes such as solvents, the rates of decomposition of the specific wastes and how to maximize their rate of degradation in the desired environment must be defined.

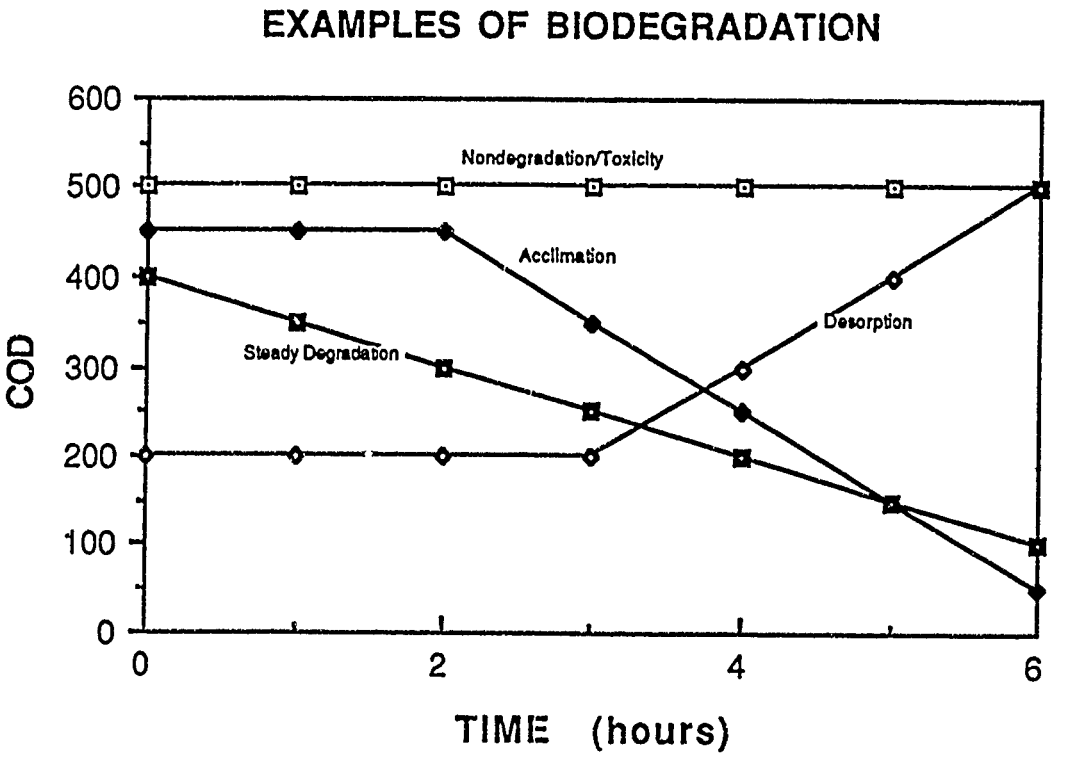

Figure 5.1 - Examples of Biodegradation in the Biodegradability Test[40]

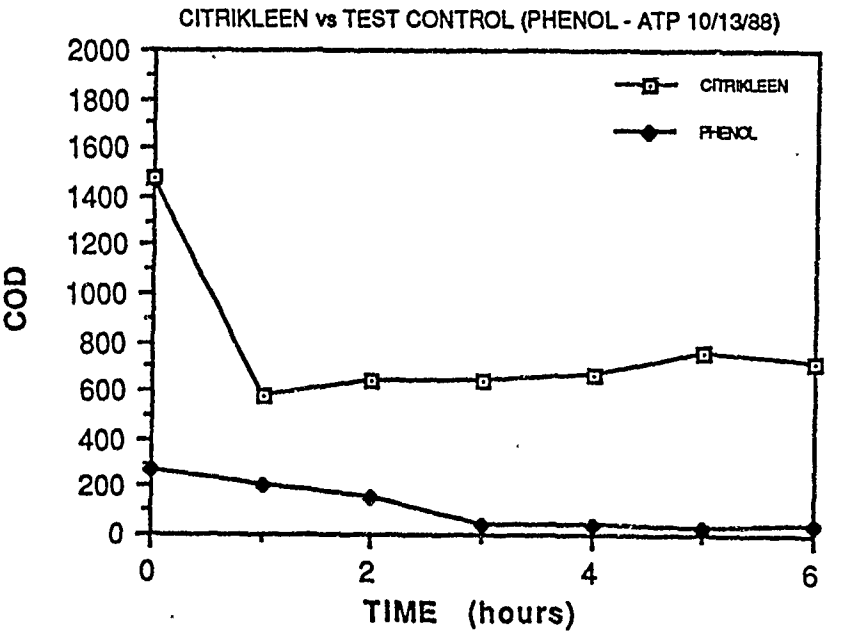

Figure 5.2 - Biodegradation Study of a Terpene Cleaner - Citrikleen, Penetone[40]

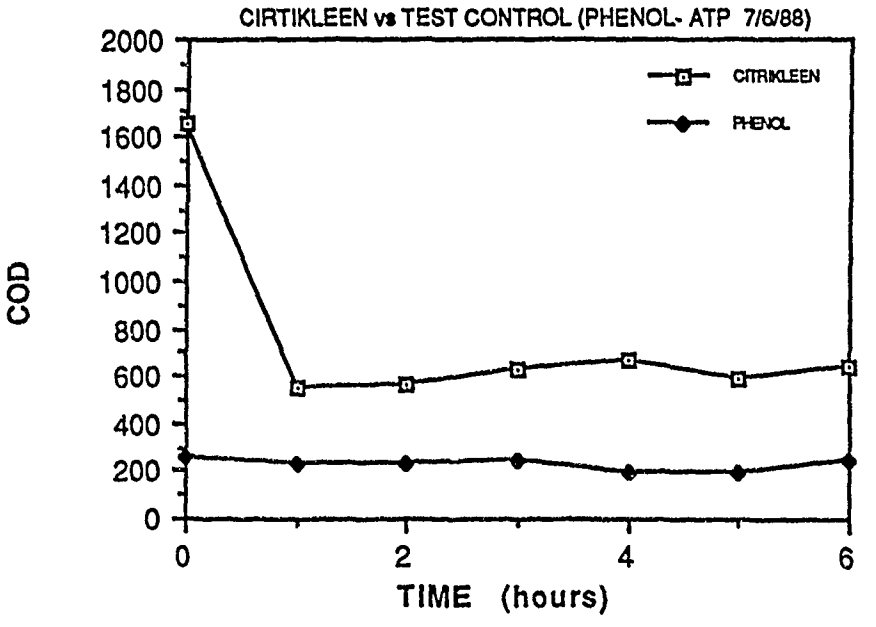

Figure 5.3 - Biodegradation Study of Terpene Cleaner - Citrikleen, Penetone[40]

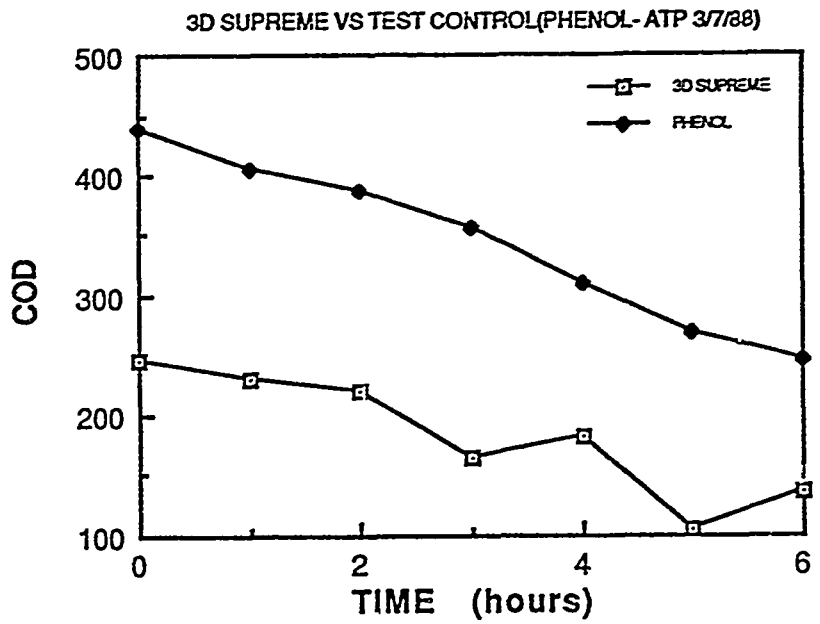

Figure 5.4 - Biodegradation Study of a Terpene Cleaner - 3D Supreme[40]

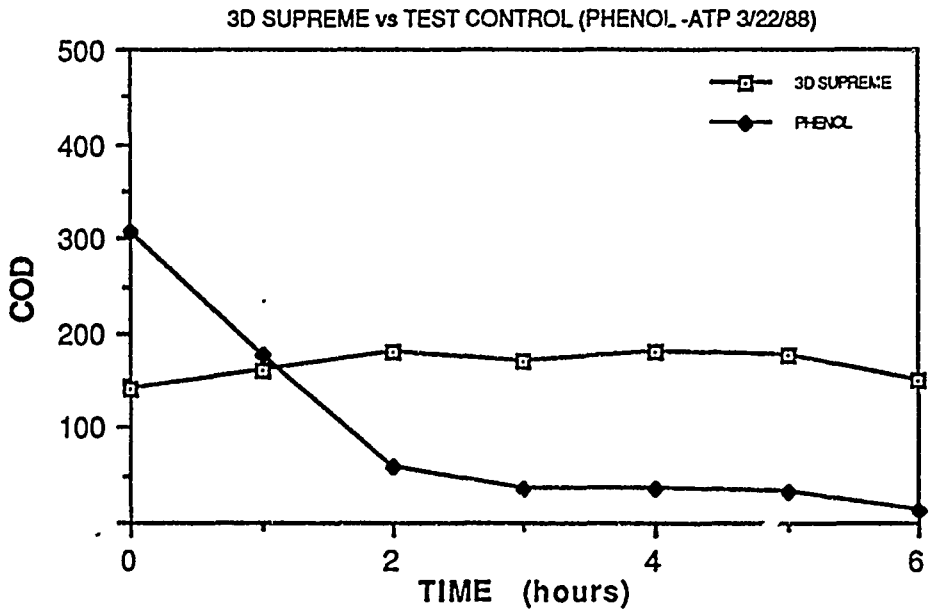

Figure 5.5 - Biodegradation Study of a Terpene Cleaner - 3D Supreme[40]

5.6 Cleaning Efficiency

- Cleaning Procedures

Stoddard solvent is to be used in straight form, dilution is not recommended with any substance. Cleaning processes such as spray-on or immersion in the solvent, will result in the removal of oil, grease, and soil. Stoddard is used in a solvent-only process, no other steps are required. The solvent is used until all cleaning efficiency has been depleted due to contamination.

Unlike the Stoddard solvents, the terpene based cleaners are water dilutable and in most instances require a clear water rinse. The cleaner surfaces must then be allowed to dry before handling. After cleaning bare metals, corrosion protection might be required to prevent flash corrosion. The cleaning procedures are similar to those for an alkaline soap.[43]

In the General Dynamics study of terpene cleaners, dilution rates were tested and evaluated for cleaning efficiencies (see Table 5.3).[18] Kelly AFB has determined dilution rates for terpene cleaner in its cleaning application also (see Table 5.4).[43] Is should be noted that dilutions of the cleaners decreased the available cleaning efficiency.

SOIL	% CITRUS TERPENE	RESULTS
Light	10-20	Superior Cleaning
Moderate	10-20	Adequate Cleaning
Heavy	100	Adequate with Spray/Brush
Garage	--	Failed to Clean

Table 5.3 - GD/FW Recommended Dilution Rates[18]

APPLICATION	DILUTION RATE (Cleaner:Water)	TIME LIMIT
Exterior Surface Liquid Foam	 1:4 - 1:10 1:9 - 1:15 with agitation	 10 minutes 20 minutes
Parts Cleaning Immersion	1:10 - 1:20 with agitation	1 hour
Part Cleaning Dip Tank	1:2 - 1:10	1 hour
Exterior Spot Cleaner (metal surfaces)	1:4	Spray on and wipe off

Table 5.4 - Kelly AFB Recommended Dilution Rates[43]

Rinsing was required to remove the residual soil from the parts, either with water or fresh solvent, depending on the application in the AFESC study.[40] In some cases, the residual solvent could be completely removed by drying within 30 minutes, but in other cases rinsing with water was required. Rinsing requirements obtained on selected solvent are listed in Table 5.5, and drying requirements in Table 5.6.

		IMMERSION		IMPACT	
SOLVENT	SOIL	CLEAN[a] (%)	TIME (MIN)	CLEAN[a] (%)	TIME (MIN)
Exxate	Wax Oil/Xylene	100 97.6	5 30	100 98.5	5 30
De-Solv-It	Wax Oil/Xylene	99.0 99.0	30 1	97.8 100	30 1
Supreme	Hydraulic Fluid Grease	100 83	1 5	100 73.0	5 10
Calla 301	Hydraulic Fluid Grease	100 40	5 10	100 95.0	1 10

[a]*Maximum cleaning efficiency*

Table 5.5 - Rinsing Requirements[40]

SOLVENT	CLEANING EFFICIENCY (%)	TIME (MIN)
Water	100	30
Exxate	92	30
De-Solv-It	83	30
Calla 301	94	10
Supreme	100	20

Table 5.6 - Drying Requirements[40]

Additionally, Figures 5.6 through 5.9 illustrate that rinsing of a terpene cleaner is required to achieve cleaning efficiency comparable to the Stoddard solvent (PD-680) in removing wax, oil/xylene, hydraulic fluid, and grease from parts. However, once rinsing is applied, comparable cleaning efficiencies can be achieved. These figures also illustrate that rinsing of Stoddard solvent is not required to achieve cleaning efficiencies. These data were obtained from the AFESC study.[40]

- **Enhancements**

To enhance cleaning and reduce operating temperatures, cleaning enhancement methods must be employed to achieve required cleaning efficiencies when implementing the terpene cleaners. The two methods of ultrasonic and mechanical agitation, were evaluated in the AFESC study to enhance soil removal by increasing the mass transfer and abrasive effects of the solvent, thus removing soil faster and at lower temperatures.[40] High operating temperatures will increase the operating expense of the replacement solvent and increase danger to operating personnel.

Enhancements as simple as stirring, were found to improve cleaning efficiencies. Figure 5.10 indicates an increased cleaning efficiency of hydraulic fluid removal by stirring. Possible enhancement methods for a terpene cleaner include:

1. air agitation
2. mechanical agitation
3. ultrasonic agitation.

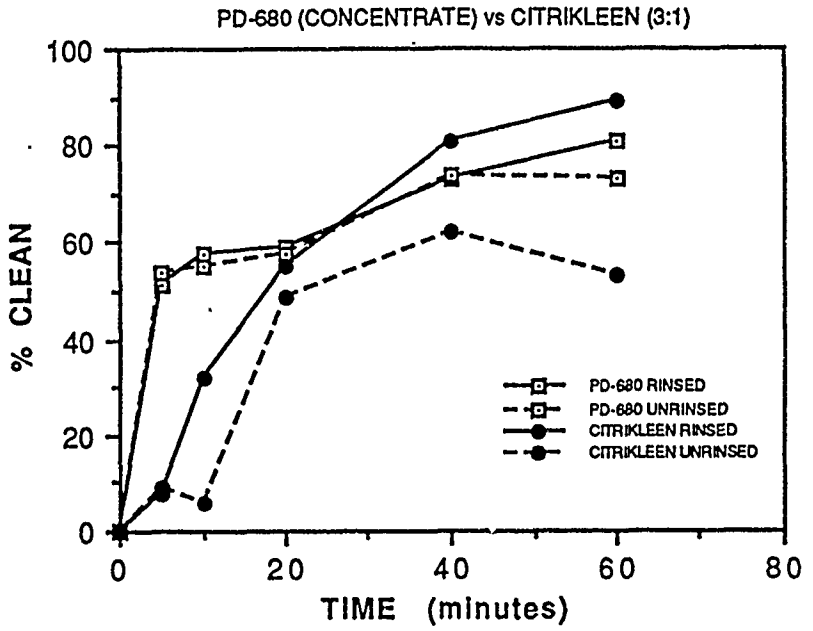

Figure 5.6 - A Comparison of Cleaning Efficiencies Reached With Rinsing - Wax Removal

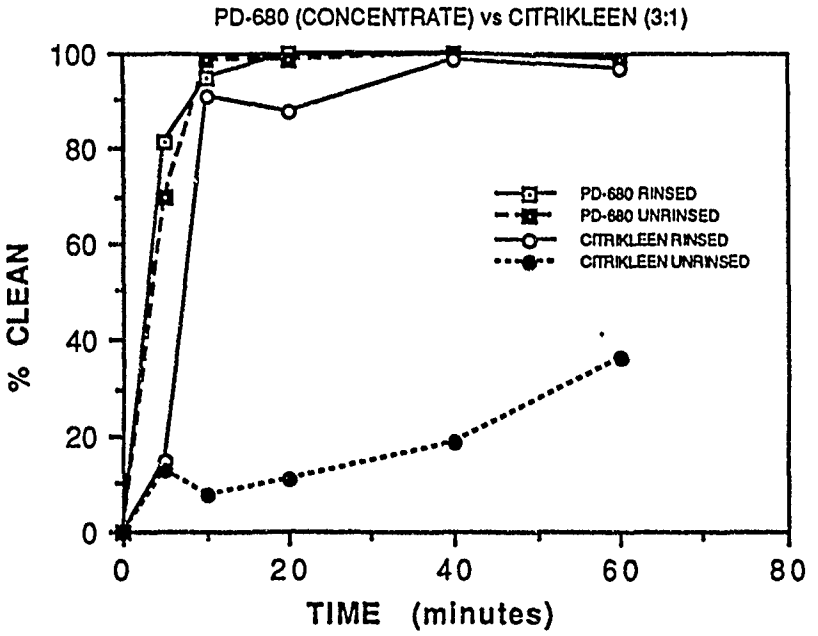

Figure 5.7 - A Comparison of Cleaning Efficiencies Reached With Rinsing - Oil/Xylene Removal

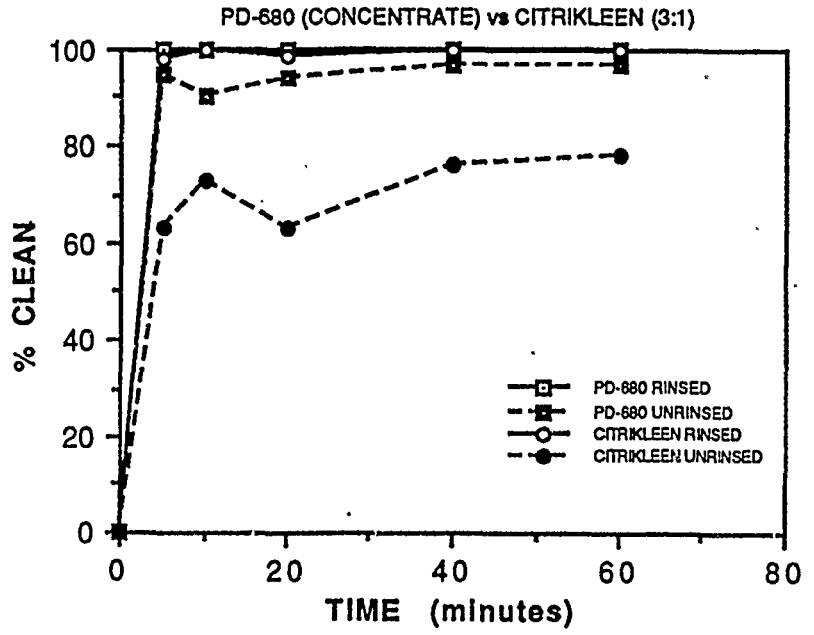

Figure 5.8 - A Comparison of Cleaning Efficiencies Reached With Rinsing - Hydraulic Fluid Removal[40]

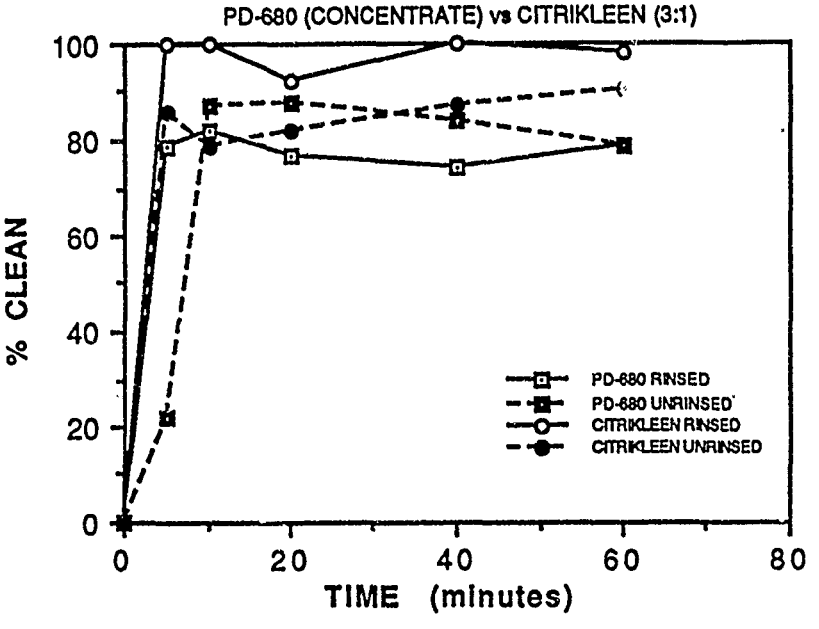

Figure 5.9 - A Comparison of Cleaning Efficiencies Reached With Rinsing - Grease Removal[40]

Ultrasonic enhancement was selected by the AFESC study because of the high currents created by the microstreaming cells and cavitation. Ultrasonic agitation is much like mechanical agitation in its effect, but is more intense and does not create the VOC emission problem associated with air agitation. At 120 °F and 300 watt ultrasonic agitation, cleaning efficiency without rinsing was approximately 75 percent. With rinsing, cleaning efficiency increased from 80 percent after 20 minutes to nearly 95 percent after 30 minutes (Figure 5.11). At 600 watt ultrasonic agitation, cleaning efficiency was 96 percent without rinsing and near 100 percent with rinsing after 20 minutes immersion at 120 °F (Figure 5.12).[40]

Although it was found that ultrasonic improved cleaning, operating, and maintenance costs are expected to escalate as cleaning tank sizes increase.

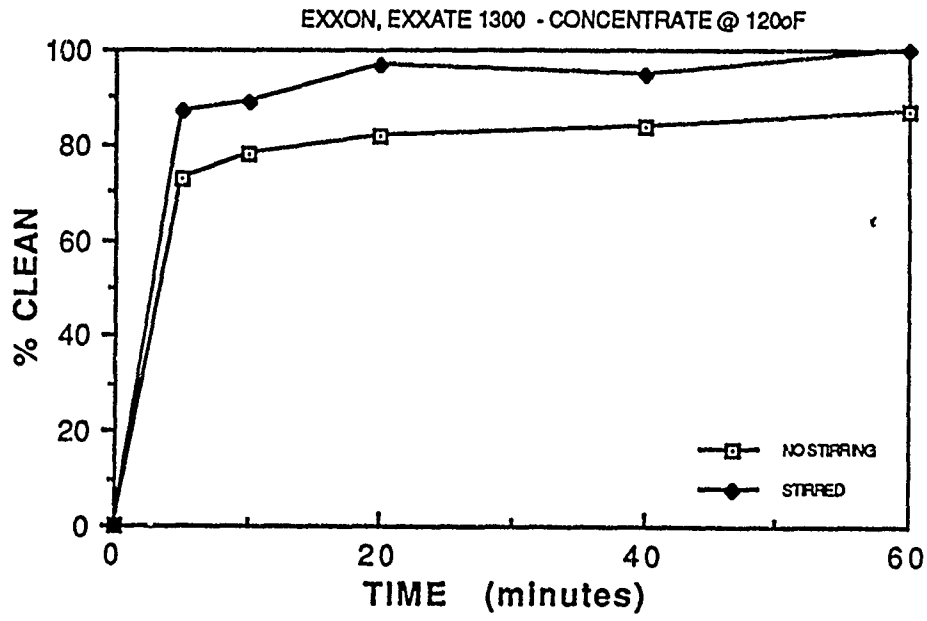

Figure 5.10 - Cleaning Enhancement With Stirring[40]

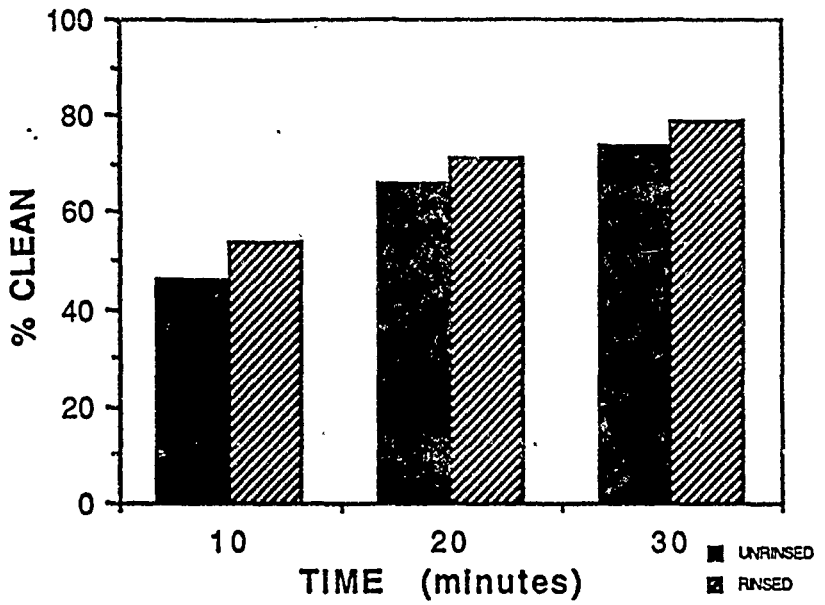

Figure 5.11 - Oil/Xylene Removal With Orange Sol De-Solv-It at 120 °F; Ultrasonic Agitation at 300 W[40]

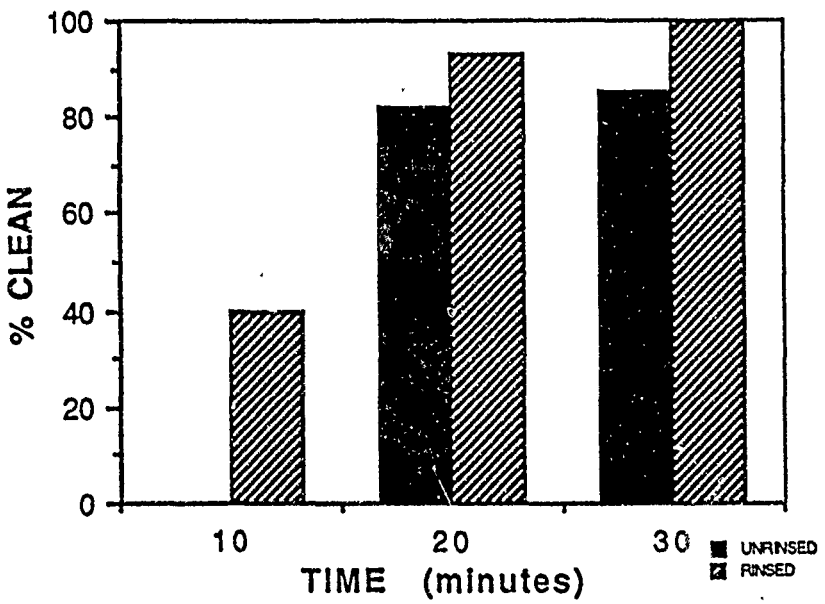

Figure 5.12 - Oil/Xylene Removal With Orange Sol De-Solv-It at 120 °F; Ultrasonic Agitation at 600 W[40]

5.7 Reactivity

Stoddard solvents and the terpene cleaners are stable under normal conditions of storage and handling; however, all possible sources of ignition should be avoided.

Stoddard solvent is incompatible with strong acids and bases, oxidizing agents and selected amines, while the terpene cleaners are generally incompatible with strong acids.

The terpene cleaners are also very photochemically reactive. A variety of terpenes are produced by nearly all living plants, therefore they are abundant components of the atmosphere over both rural and urban areas. Hundreds of millions of terpene isomers are released into the air each year by plants particularly coniferous forests.[23] Indeed, the abundance of terpenes in the air above large tracts of evergreen forests is one of the reasons that the air in those regions is frequently hazy due to the β-pinene terpene.

The d-limonene terpene, present in most metal surface cleaners, is listed in the highest reactivity class in the classification system that categorizes hydrocarbons. This classification system categorizes hydrocarbons on the basis of their reactivity with hydroxyl radicals compared to the reactivity of methane with hydroxyl radicals. This high photoreactivity classification indicates that the d-limonene based terpenes can contribute to smog formation and possible ozone depletion (see Table 5.7).

Reactivity Class	Reactivity Range	Approximate half-life in the atmosphere	Compounds in increasing order of reactivity
I	<10	>10 days	methane
II	10-100	24 hr - 10 days	CO, acetylene, ethane
III	100-1000	2.4 - 24 hr	benzene, propane, *n*-butane, iopentane, methyl ethyl ketone, 2-methylpentane, toluene, *n*-propylbenzene, isopropylbenzene, ethene, *n*-hexane, 3-methylpentane, ethylbenzene
IV	1,000-10,000	15 min - 2.4 hr	*p*-xylene, *p*-ethyltoulene, *o*-ethyltoulene, *o*-xylene, methyl isobutyl ketone, *m*-ethytoluene, *m*-xylene, 1,2,3-trimethylbenzene, propene, 1,2,4-trimethyl-benzene, 1,3,5-trimethylbenzene, *cis*-2-butene, β-pinene, 1,3-butadiene
V	>10,000	<15 min	2-methyl-2-butene, 2,4-dimethyl-2-butene, *d*-limonene

Table 5.7 - Relative Reactivities of Hydrocarbons[42]

5.8 Corrositivity

The Stoddard solvents have not been reported to be noticeably corrosive to equipment in cleaning processes or to parts that are cleaned. After cleaning with Stoddard solvent, a light film of oily residue remains to protect the part from corrosion during storage and in-plant maintenance.

Unlike the Stoddard solvents, the terpene cleaners do not leave a protective oil film on the cleaned parts. Kelly AFB recommends[43] that cleaned parts which will not be coated with primer immediately, receive a light application of a corrosion prevention compound (CPC) or light lubrication oil (VV-L-80). This procedure will prevent flash rusting and corrosion of the cleaned part. Corrosion is also highly probable, resulting from the required water rinses following cleaner application.

In the AFESC study,[40] extensive corrosion testing on terpene cleaners was conducted. An example of a terpene cleaners' corrosion of metal coupons is presented in Table 5.8. The coupons were exposed for 168 hours to the cleaner, at the temperature indicated as optimum from enhancement tests.

METAL	TEMPERATURE (°F)	AGITATION	CORROSION RATE (mils/year)	Maximum Depth (mm)
Aluminum	140	US[a], 600W	0.33	Heavy Oxidation
Magnesium	140	US, 600W	2.01	Light Oxidation
Steel	140	US, 600W	4.57	High Oxidation
Copper	140	US, 600W	0.41	Light Oxidation
Nickel	140	US, 600W	0.56	High Oxidation
Carbon Steel	140	US, 600W	3.07	High Oxidation

[a]*Ultrasonic Agitation*

Table 5.8 - Corrosion Testing Results of Orange Sol, De-Solv-It[40]

The terpene cleaners have also indicated abrasive action on plastic materials. The tests have found that the cleaners can cause softening, swelling, and sometimes severe crazing of plastic material on parts and equipment. All plastic materials should be tested before a

particular terpene cleaner is used, to avoid possible equipment damage. The effects of the terpene cleaner BIOACT, EC-7 on selected plastics are shown in Table 5.9.

PLASTICS	AMBIENT	140 °F
Conventional Polyethylene (low density)	F	N
Linear Polyethylene (high density)	G	F
Polypropylene	G	F
Polymethylpentene	F	F
Polyallomer	G	G
Teflon FEP (Fluorinated Ethylene Propylene)	E	E
Tefzel ETFE (Ethylene Tetrafluoroethylene)	E	E
Polycarbonate	F	F
Polyvinyl Chloride	F	N
Polysulfone	G	N
Polystyrene	N	N

Chemical Resistance Classification

E - Thirty days of constant exposure with no damage. Plastic may even tolerate chemical for years.
G - Little or no damage after thirty days of constant exposure to BIOACT, EC-7.
F - Some effect after seven days of constant exposure to BIOACT, EC-7. Solvent may cause softening, swelling and permeation losses.
N - Not recommended for continuous use. Immediate damage may occur, severe crazing, cracking and permeation losses.

Table 5.9 - Terpene Cleaners' Effect on Selected Plastics[42]

5.9 Recycling/Reclaiming

Stoddard is completely recyclable because the solvent is not consumed in the cleaning process, but is only contaminated by other substances. Stoddard solvent is recycled when cleaning efficiency is judged no longer satisfactory for intended use by operations personnel. Stoddard solvent in typical maintenance service and under normal operating conditions is

spent every 4 weeks. Typical properties of used and virgin (or recycled) Stoddard solvent are given in Table 5.10.[33]

In contrast, the terpene solvents are not recyclable by conventional systems or ultrafiltration. The terpene cleaners do not physically separate from contaminants after use in cleaning but form emulsions with water and contaminants. It is reported through testing at General Dynamics[18] that the terpene cleaners will destroy an ultrafilters' adhesive and support materials. Presently, there is no recycling process available for the terpene cleaners.

TEST	TEST METHOD	USED SOLVENT	RECLAIMED SOLVENT
FLASH POINT, (°F)	ASTM-D-56	<100 - 120	102 - 110
DISTILLATION, (°F)	ASTM-D-86		
INITIAL BOILING POINT		150 - 330	315 - 330
10%		150 - 340	320 - 340
20%		170 - 340	
30%		300 - 345	
50%		325 - 350	325 - 350
70%		340 - 370	
90%		400 - 600	330 - 365
FINAL BOILING POINT		ABOVE 500	350 - 400
RESIDUE		30% VOL (max)	2 - 5% VOL
CHLORINE CONTENT		<0.1	<0.1
% WATER, OIL, AND SEDIMENT	ASTM-D-95	2 - 20	<0.1
APPEARANCE	VISUAL	BROWN/BLACK	CLEAR/WHITE

Table 5.10 - Properties of Used and Recycled Stoddard Solvent Type I[33]

5.10 Disposal

As previously indicated Stoddard solvent is primarily all recyclable, except for the residue remaining as distillation bottoms. The remaining residues are mainly oils and grease, and can often be blended with waste oil for disposal. Other methods for disposed include incineration, fuel substitution, surface disposal, or sale. Each of these methods use for disposal at Army installations is discussed in Chapter 3, Literature Search.

Cold cleaning tanks of terpene cleaners must be allowed to sit overnight undisturbed, to allow oil, grease, and carbonaceous particles to rise and separate from soils. These contaminants must then be removed by skimming and should be containerized for further treatment as hazardous wastes. The sediment that accumulated on the bottom of the tank must also be removed and treated in accordance with local, state, and Federal EPA regulations before disposal.[28]

According to manufacturers, rinse waters containing terpene cleaners can be safely disposed in storm sewers, water ways, and other outlets.[28] However, primary treatment in an oil/water separator or holding pond is recommended to remove remaining residue, especially if large concentrations of the cleaners are used. An oil/water separator removes the oil and grease that separates from the soils and rises to the surface. In a holding pond rinsed water should sit for at least 24 hours and then must be skimmed.[18]

The U.S. Army Water Study at Aberdeen Proving Grounds[30] found terpene cleaners containing extremely high biochemical oxygen demand (BOD) and COD wastes will cause an upset of the biological treatment system through inhibition of the microbial growth rate and consequently violation of permit limits for COD and BOD. Therefore, it was recommended that the discharge of wastewater from a terpene cleaner to a sanitary sewer should not exceed 40 gallons (concentrate) per million gallons sewage flow. Results of the testing on terpene cleaners also indicated that direct discharge to a receiving stream without treatment will have an adverse impact on aquatic organisms.[30]

Results received from laboratory testing of effluent containing terpene cleaner from the washracks at Fort Hood indicate NPDES permit violation, see Table 5.11. The evaluation indicates that permit limits for oil, grease, and COD have been exceeded.[48]

	TSS[a] (mg/L)	OIL & GREASE (mg/L)	COD[b] (mg/L)
GRAB SAMPLE	98	121.9	1725.3
NPDES STANDARDS	30	15	200

[a]*Total Suspended Solids*
[b]*Chemical Oxygen Demand*

Table 5.11 - Test Results of Effluent Sample Containing Terpene Cleaner, Citrikleen[48]

Applicable disposal guidelines for various waste categories pertaining to both Stoddard solvent and terpene cleaners is shown in Table 5.12.

5.11 Economic Analysis

The economic analysis comparing Stoddard solvent purchased through a contractor with the use of a terpene cleaner at varying dilutions suggested by the manufacturer was completed using the assumptions discussed in Chapter 4, Experimental Design.

With the aid of the CEAMHW computer model all costs were summed to obtain cost over the assumed economic lifetime of 10 years for each option. Comparisons were made of the Net Present Value (NPV) of the total life cycle costs versus the annual generation rate in gallons per year for each of the alternatives.

It can be concluded from Figure 5.13, that the Stoddard solvent purchased through the contractor is the most favorable alternative. Figure 5.13, shows that even at the lowest dilution of five parts water to one part terpene cleaner, the Stoddard solvent is still the favorable alternative.

An additional economic analysis was made to compare the dilution of seven parts water to one part terpene cleaner to the concentrated Stoddard solvent. This comparison indicated that such a dilution is needed to be cost comparable Stoddard solvent (see Figure 5.14).

This analysis illustrates that the cost of achieving cleaning efficiency using terpene cleaners will be considerably higher than the costs of cleaning with Stoddard solvent. Heavy soil and different cleaning methods require high concentration to achieve efficient cleaning and, therefore, result in an even greater cost penalty when using the terpene cleaners.

	RECLAMATION		TREATMENT							DISPOSAL		
Waste Type	Solvents	Oils	Neutra-lization	Oxida-tion	Dewater-ing	Devolatili-zation	Physical Blending	Fuel Supplement	Incinera-tion	Waste Water Treatment	Treatment Facilities	Secure Landfills
Soluble Oils		X					X	X				
Insoluble Oils		X					X	X				
Nonhalogenated Solvents	X					X	X	X	X			
Oily Residue							X	X				
Alkali Cleaners			X		X					X		
Aqueous Neutral Solution			X		X					X		
Aqueous Solution Containing Soluble Organics			X		X					X		
Reactive Solids				X					X			
Contaminated Floor Sweepings									X			X
Solvent Laden Rags						X			X			X
Metallic Sludges					X							X

Table 5.12 - Off-Site Disposal Guidelines[33]

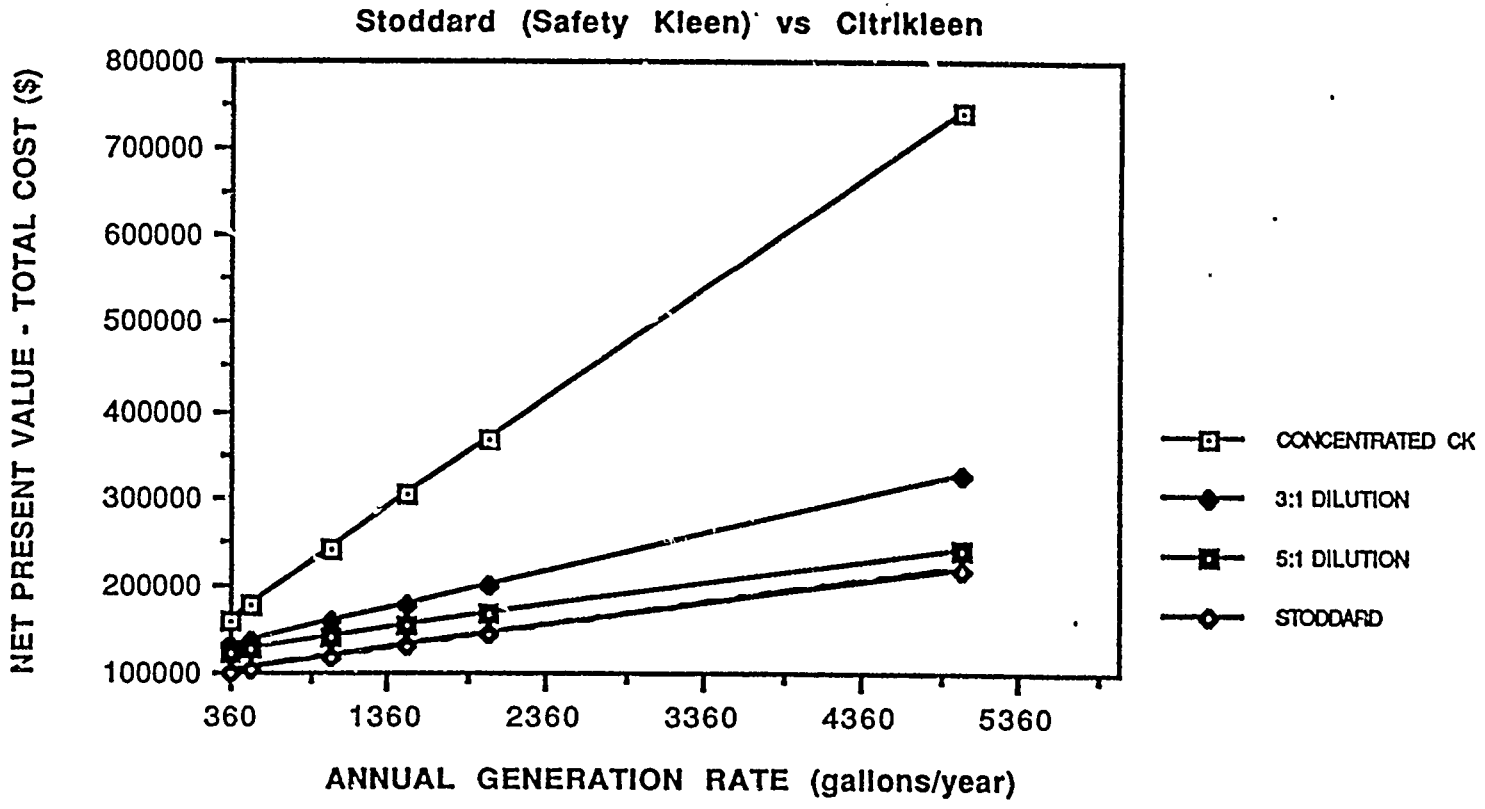

Figure 5.13 - Economic Comparison of Stoddard Solvent to Terpene Cleaner

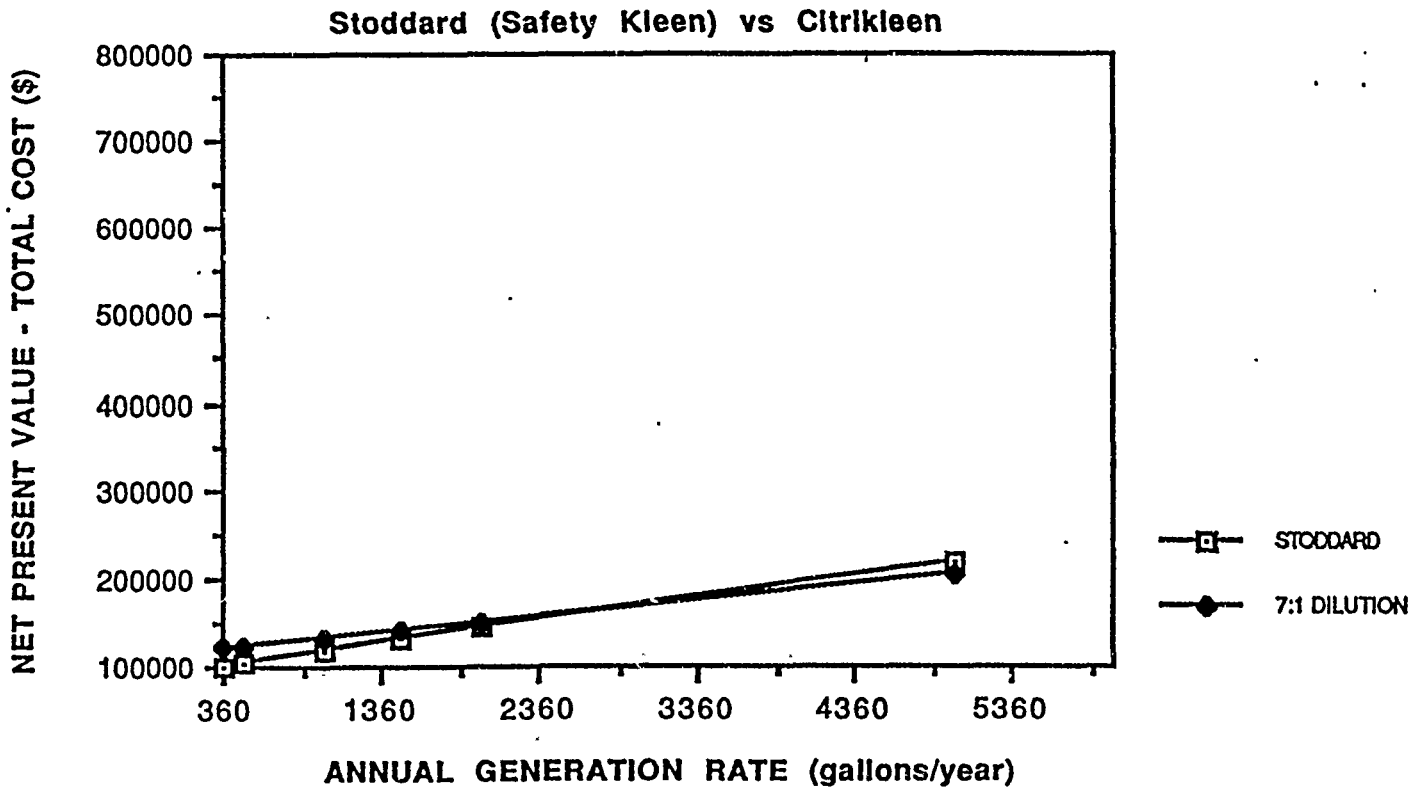

Figure 5.14 - Economic Comparison of Stoddard Solvent to Terpene Cleaner

Chapter 6

Discussion

Although the terpene cleaners have been found to be very effective agents in the metal cleaning processes at high concentration, there are other factors that need to be considered before implementation at all Army installations. A few strong concerns with the use of terpenes include:

1. The hazardous chemical components such as d-limonene and enthalomine present in most heavy duty cleaners.
2. The corrositivity of the cleaners towards elastomers and metals.
3. The effect on the wastewater treatment plant and other downstream process.
4. The high combustibility of the cleaners at high concentrations.
5. The high photochemical-reactivity of the cleaners and their potential contribution to smog in the atmosphere.
6. Cleaning efficiency at diluted concentrations.

There are additional factors such as process time and temperature limitations. Enhancement equipment, available plant floor space, and budgetary constraints should also be considered before implementing terpene cleaners.

In order to evaluate the terpene cleaners to be used in the Army, tests should be run on their cleaning efficiency, biodegradability, corrositivity, and toxicity. These tests should be used to evaluate the terpene cleaners taking into account all site specific factors. Factors to be included in the evaluation at a particular installation may include,

1. Typical soil generated
2. Existing treatment facilities
3. Existing equipment materials
4. Typical parts to be cleaned

By conducting such testing, evaluations can then be made as to the dilutions needed to achieve cleaning efficiency desired for heavy, moderate, and light soil along with avoiding an upset in the existing treatment facility, NPDES permit violations, and equipment damage.

An evaluation of the potenetial for implementing terpene cleaners at a given Army installation can be made by following these few steps.

1. Characterization of the Processes and Soils

A survey of operations and materials used in the installation should be conducted to identify, characterize, and test each soil with the terpene cleaner. This is necessary due to the wide range of soils, from light hydrocarbon oils to heavy asphaltic tars, and the varying amounts of soil placed on the metal surfaces. Generating data in this manner will provide a cleaner-time-temperature concentration data matrix for each soil and each installation area. Data such as these can be very helpful in implementing cleaning systems and in optimizing operating conditions.

2. Define Cleaning Efficiency

Soil can be categorized as organic, inorganic, and ionic. The degree of cleanliness necessary for metal cleaning is generally much less stringent, in terms of measurable residues, than with critical components of electronics. The focus in metal cleaning is usually on the organic residues, whereas all three soils are of concern in the aerospace industry. In most cases, quantifying the "residue threshold," that is the amount of soil that would make a surface unacceptable, is not realistically possible. Most of the tests indicative of real world situations and operational cleaner performances are quantitative.

3. Bench Testing of Terpene Cleaners

During initial testing, a control using the existing solvent process should be employed to ensure that the soil simulation and cleaning are representative. Initial tests should be conducted using the manufacturer's suggested concentrations and temperatures while varying immersion time within acceptable limits. The concentrations and temperature should then be

varied independently to identify optimum cleaning conditions for each soil. The initial should be done in beakers.

The terpene cleaners should then be tested in larger tanks, such as 2 to 3 gallons in volume, with enhancements such as spray mechanical agitation and air sparging capability. Variables to address for wash and rinse operations include immersion versus spray, mechanical agitation versus sparging.

4. Terpene and Process Integrity Testing

The ultimate measure of cleanliness is to evaluate a series of test specimens in the selected cleaner at the desired time, temperature, and concentration; then process the specimens through all subsequent surface treatments. A series of process integrity tests can then be conducted on the specimens to ensure that acceptable cleaning has been achieved and that no cleaner or rinsewater residues have been left on the part.

Concern with corrosion and oxidation is greatest with aluminum alloys, primarily those containing zinc and lithium, and with mild steels. Corrosion effects should be tested, as surfaces are affected when exposed to cleaner residues left on parts.

5. Pilot Testing

The factory pilot test, using a simulated process unit, should then be conducted on representative parts and scrap. The tests should be conducted over several months to address "real world" soils and parts configurations and to fine tune operating parameters and equipment requirements. The system design should define all operating tank conditions (temperature, concentration, time, spray, agitation, and parts orientation) and include testing of separation technologies which will minimize the amount of cleaner waste being generated.

Wastes stream quantities and properties should be characterized to identify a resource recovery technique or, if necessary, a disposal option which complies with all local, state, and Federal regulations.

6. Designing the Full-Scale Process

The full-scale design should rely on existing rack capacity to the maximum extent possible while maintaining enough of the existing degreasing capacity to ensure a smooth transition. Additional floor space will be necessary to accommodate rinsing and possible drying equipment for complex parts (tubes, honeycomb). The floor space issue is the most troublesome when attempting to minimize affect on existing operations, since two tanks (wash and rinse) and possibly a dryer will be substituted for each degreaser when implementing the terpene cleaners. In-process filtration and free oil removal are necessary, as well as some form of rinsewater treatment/recycle and makeup. Special gantrys, racks, and conveyors may be necessary with certain parts configurations in immersion systems. These issues must be addressed in the initial facility design.

Chapter 7

Conclusions

Based on . . terpene cleaner studies, literature review, and economic analysis, the following conclusions are made regarding the heavy duty commercial cleaners containing the d-limonene isomer, as represented by Citrikleen.

1. Although presented as biodegradable, the time required to decompose the cleaners in waste treatment facilities varies based on the method, bacteria, dilution, and the product used. Because each installation has unique conformance criteria for disposal of materials, a thorough site-specific evaluation is recommended.

2. Flash points of the concentrated cleaners vary around 120 °F, so the cleaners are not to be heated. Due to their low flash points, the terpene cleaners are not to be used in vapor degreasers.

3. Terpene cleaners require enhancement methods to achieve cleaning efficiency currently obtained with Stoddard solvents.

4. When using terpene cleaners, downstrea process integrity should be tested. Potential wastewater discharge issues and regulations, should be addressed so as not to violate NPDES discharge permits. A violation of NPDES permits could result in liability and heavy fines.

5. Terpene cleaners are corrosive to elastomers and metals, therefore, careful selection of equipment and parts washed is necessary.

6. The costs associated with implementation of terpene cleaners in reality are site specific. Cost of implementation varies with configuration of existing facilities. An installation with its own treatment facility and waste solvent storage may find the use of

terpene cleaners applicable. However, for an installation without a treatment facility and/or waste solvent storage, the use of terpene cleaners is infeasible.

7. Terpene cleaners are not recyclable either by conventional methods or ultrafiltration, because the contaminants do not physically separate from the cleaners. Concentrated terpene cleaners will destroy ultrafilter adhesives and support materials. Manufacturers claim that oil completely separates when the terpene cleaners are used in diluted form, but this has not been demonstrated in the studies to date.

8. An economical analysis of the Stoddard solvent purchased through a contractor such as Safety Kleen compared to Citrikleen at various dilutions shows Stoddard solvent to be the more favorable alternative. Stoddard solvent purchased through a contractor is not only lower in cost, but also reduces the associated liabilities of storage, handling and transportation, in addition to maintenance and operation.

Appendix A

Hazardous Considerations

A.1 Stoddard Solvent

Although this chemical is not highly hazardous, caution should be used at all times when handling.[38] There are certain hazard precautions that should be known before using this chemical. Manufacturer's material safety data sheets and the U.S. Army's material specification information was used to compile this discussion.

A.1.1 Hazardous Intake Precautions

- Eye contact

This material may cause mild eye irritation. Direct contact with the liquid or exposure to vapors or mists may cause stinging, tearing and redness. If irritation or redness develops, move victim away from exposure and into fresh air. Flush eyes with clean water. If symptoms persist, seek medical attention.[46,47]

- Skin Contact

This material may cause mild skin irritation. Prolonged or repeated contact may cause redness, burning, drying, and cracking of the skin. No harmful effects have been demonstrated in skin absorption studies. Persons with pre-existing skin disorders may be more susceptible to the effects of this material.[35,46]

To avoid skin irritation, remove contaminated shoes and clothing and cleanse affected area(s) thoroughly by washing with mild soap and water. If irritation or redness develops and persists, seek medical attention.[46]

- Inhalation

This material is expected to have a low degree of toxicity by inhalation. Breathing high concentrations of vapors or mists may cause irritation of the nose and throat and signs of nervous system depression (e.g., headache, drowsiness, dizziness, loss of coordination, and fatigue). Respiratory symptoms associated with pre-existing lung disorders (e.g., asthma-like conditions) may be aggravated by exposure to this material.[25,38,46]

If respiratory symptoms develop, move victim away from the source of exposure and into fresh air. If symptoms persists, seek medical attention. If victim is not breathing, immediately begin artificial respiration. If breathing difficulties develop, oxygen should be administered by qualified personnel. Seek immediate medical attention.[38,46]

- Ingestion

While this material has a low degree of toxicity, ingestion of excessive quantities may irritate the digestive tract and signs of nervous system depression (e.g., headache, drowsiness, dizziness, loss of coordination, and fatigue). This material can enter the lungs during swallowing or vomiting and cause lung inflammation and damage.[26,38,46]

If ingestion should occur, do not induce vomiting or give anything by mouth because this material can enter the lungs and cause severe lung damage. If drowsy or unconscious, place victim on the left side with the head down. If possible, do not leave victim unattended. Seek medical attention.[38,46]

A.1.2 Special Protection Information

- Ventilation

If current ventilation practices are not adequate to maintain airborne concentrations below the established exposure limits, additional ventilation or exhaust

systems may be required. Where explosive mixtures may be present, electrical systems safe for such locations must be used.[46]

- Respiratory Protection

The use of respiratory protection is advised when concentrations exceed the established exposure limits. Depending on the airborne concentration, use a respirator or gas mask with appropriate cartridges and canisters or supplied air equipment.[46]

- Protective Equipment

The use of gloves impermeable to the Stoddard solvent is advised to prevent skin contact and possible irritation. Additionally eye protection to safeguard against eye contact, irritation, or injury is recommended. It is further suggested that clean water be available in the work area for flushing eyes and skin. Impervious clothing should be worn as needed.[46]

A.1.3 Spill and Leak Procedures

Since Stoddard solvent is combustible, it is important to keep all sources of ignition away from spill/release. Stay upwind and away from spill/release. Wear appropriate protective equipment, including respiratory protection, as conditions warrant. Prevent spilled material from entering sewers, storm drains, other unauthorized treatment drainage system, and natural waterways. Spilled material may be absorbed into an appropriate absorbent material. Notify fire authorities and appropriate Federal, state, and local agencies. Immediate cleanup of spill is recommended.[46]

A.1.4 Handling and Storage Precautions

Practice good personal hygiene when handling Stoddard solvent. Wash thoroughly after handling and do not wear contaminated clothing or shoes.[38,46,46]

Keep container(s) of Stoddard solvent tightly closed and stored in approved containers. Use and store material in cool, dry, well-ventilated areas away from heat and all sources of

ignition. Keep solvent away form incompatible materials and protect all container(s) against physical damage. The use of explosion-proof equipment is recommended and may be required when handling solvent. Outdoor or detached storage of solvent is preferred; however, indoor storage that meets OSHA standards and appropriate fire codes is also acceptable.[38,46]

"Empty" containers retain residue (liquid and /or vapor) and can be dangerous. Do not pressurize, cut, weld, braze, solder, drill, grind, or expose such containers to heat, flame, sparks, or other sources of ignition; they may explode and cause injury or death. "Empty" drums should be completely drained, properly bonded, and promptly shipped to the supplier or a drum reconditioner. All other containers should be disposed of in an environmentally safe manner and in accordance with government regulations.[46]

A.1.5 Fire and Explosive Hazard Data

Stoddard solvent is listed as a combustible material, easily ignited by heat, sparks, flames, or other sources of ignition (e.g., static electricity, pilot light, mechanical/electrical equipment). Vapors given off by Stoddard solvent may travel considerable distances to a source of ignition where they may ignite, flashback, or explode.[46] Vapor/air explosions can happen indoors, outdoors, or in a sewer because the solvent vapors are heavier than air and thus accumulate in low areas.[21]

A few extinguishing media recommended for Stoddard solvent fires are dry chemical, carbon dioxide, halon, or foam or water spray.[38,46,47]

- Special Fire Fighting Procedures

  Wear appropriate protective equipment including respiratory protection as conditions warrant. Stop spill/release and move undamaged containers from fire areas. Water spraying will minimize or disperse vapor while cooling equipment exposed to heat and flame, however, be careful to avoid spreading burning liquid with the water.[38,47]

- Fire and Explosion Hazard Data

The National Fire Protection Association (NFPA) ranks Stoddard solvent as only slightly hazardous to human health, only a moderately flammable material, and with the lowest reactive rate following hazard classification system.[46]

NFPA -Hazard Classification

Health Hazard:	1
Flammability:	2
Reactivity:	0

Hazard Ranking: 0=least, 1=slight, 2=moderate, 3=high, 4=extreme,
*=chronic health effects

The lower explosive limit for Stoddard solvent in percent volatile is 1.0, while the upper exposure limit is 7.0.[46]

A.2 Terpene Cleaners

Although terpene cleaners as a class are not highly hazardous, strict caution should be taken at all times when handling, especially when the cleaner is in concentrated form. There are certain hazard precautions that should be known before using this chemical. Several manufacturers' material safety data sheets were referenced to compile this information.

A.2.1 Hazardous Intake Precautions

- Eye Contact

This material may cause eye irritation. Direct contact with the liquid or exposure to vapors or mists may cause stinging, tearing, and redness. If irritation or redness develops, immediately flush with water for several minutes. Seek medical attention.[27]

- Skin Contact

This material may cause skin irritation. Prolonged or repeated contact may cause redness, drying, burning, and cracking of the skin. Persons with pre-existing skin disorders may be more susceptible to the effects of this material. To avoid skin irritation, remove contaminated shoes and clothing and cleanse affected area(s) by thoroughly flushing with water for several minutes. If irritation develops or persists, seek medical attention.[27]

- Inhalation

Breathing high concentrations of vapors or mists will result in corrosive effects to the nose, throat, and esophagus on contact and cause signs of dizziness, drowsiness, and irritation to the mucous membrane. Respiratory symptoms associated with pre-lung disorders may be aggravated by exposure to this material. If respiratory symptoms develop, move victim away from the source of exposure and into fresh air. If symptoms persist, seek medical attention. If victim is not breathing, immediately begin artificial respiration. Seek immediate medical attention.[27]

- Ingestion

Ingestion of this material may cause irritation in the digestive tract and signs of drowsiness or dizziness. It is corrosive to mouth and esophagus on contact. If ingested, give large amounts of milk or water to victim. Seek medical attention.[27]

A.2.2 Special Protection Information

- Ventilation

Ventilation requirements when using terpene cleaners in confining areas call for adequate local exhaust. For respiratory purposes, adequate ventilation must be present to maintain airborne concentrations below the established exposure limits.[27,28]

- Protective Equipment

Gloves that are solvent resistant, preferably rubber/neoprene, should be used when handling this material. Additionally, splashproof goggles should be worn for eye protection. It is also suggested that clean water be available in the work area at all times for flushing eyes and skin.

A.2.3 Spill and Leak Procedures

If terpene cleaners are released or spilled in high concentration, collect material on absorbent material or mop up with water. Since the material is highly combustible in its concentrated form, it is important to keep all ignition sources away from the spill. Stay upwind and away from spill, and prevent spilled material from entering sewer, storm drain, or unauthorized treatment drainage system and natural waterways.[27,28]

A.2.4 Handling and Storage Protection

Precautions to be taken in handling and storage are very important. Keep container(s) tightly closed and store material in cool, dry, well-ventilated area, away from heat and all sources of ignition. Keep away from incompatible material and protect all container(s) against physical damage. The use of explosion-proof equipment is required when handling this solvent.

Do not reuse empty containers since they retain residues (liquid and/or vapor) which are highly combustible. Do not pressurize, cut, weld, braze, solder, drill, or expose such containers to heat, flame, sparks, or other sources of ignition; they may explode and cause injury or death. Dispose of containers in accordance with local, state and Federal EPA regulations.[27,28]

A.2.5 Fire and Explosive Hazard Data

Terpene cleaners in concentrated form are highly combustible and may be ignited by heat, sparks, flame, or other sources of ignition. Vapors of this product can travel considerable distances to a source of ignition where they may ignite, flash back or explode.[28]

Special care must be taken with rags used in wipe-on and wipe-off cleaning procedures; they are usually saturated with concentrated cleaner and are highly combustible.

Fires involving terpene cleaners must be treated as an oil-type (Class B) fire by firefighters. To extinguish the flames, use carbon dioxide, dry powder, or foam.[27]

Appendix B

Case Studies

B.1 General Dynamics Study[18]

In 1987 General Dynamics at Fort Worth, TX (GD/FW) began an investigation to find an alternative solvent to eliminate "Safety-Solvent"—a Stoddard solvent derivative, used in cold cleaning applications—plant wide. An indepth program was initiated involving soil identification and classification, preliminary cleaner/optimization, performance confirmation (corrosion material compatibility, coating, and adhesion), and a pilot scale and factory evaluation on the citrus terpene cleaners.

B.1.1 Soil Identification

Soil identification and classification were evaluated through defining how and where Safety-Solvent was used in the plant. Safety-Solvent was found to be used mainly for maintenance procedures to clean parts, tools, machines, and surfaces by either dipping and wiping, spraying and wiping, or soaking to remove mostly oil and grease from parts. It was also used for small auto parts and on garage floors to remove Cosmoline, a tar-like soil.

B.1.2 Cleaning Application Evaluation

The commercial formulations were evaluated for all types of cleaning applications. GD/FW concluded through testing that, according to their cleaning specifications, terpenes could only satisfy a few specific cold cleaning processes. It was found that terpene cleaners could not be used in vapor degreasers due to the residues that formed and the volatile organic compounds (VOCs) instabilities. Terpene cleaners were found to be insufficient in manual cleaning due to residues, VOCs and poor cleaning efficiency. However, the terpene cleaners were found to be a sufficient alternative for cleaning difficult to remove Cosmoline from floors and metal nonproduction parts.

B.1.3 Solubility Testing

In a solubility comparison, using Mobil Grease 28 as the soil to be removed, the terpenes on average dissolved slightly lower percentages of soil than the Safety-Solvent. However, the terpenes dissolved a slightly higher percentage of the soil when compared to the Stoddard solvent tested (Table B.1).[18]

SOLVENT	% DISSOLVED
Safety-Solvent	99
Cirtus Terpene	96
Naphtha Terpene Blend (Quaker BB-68)	92
Pine Terpene	91
Stoddard Solvent	88

Table B.1 - Solubility Comparison

B.1.4 Cleaning Efficiency Testing

In the cleaning efficiency test, the contaminant used as the baseline soil was machine hydraulic oil. The terpene cleaners were applied to the contaminated surface and then wiped with a dry cloth. The concentrations versus the cleaning efficiency were recorded (Table B.2). The conclusion was to use at least 10 percent concentrated terpene material in water to achieve satisfactory cleaning efficiency for light and medium grease and soil. For heavy greases and oils, a straight concentrate of terpene was recommended in addition to soaking parts in cleaner for up to 1 hour and spraying lightly as needed (Table B.3).

Following factory feedback evaluation, laboratory-derived cleaner dilution rates were insufficient in factory cleaning operations. The laboratory tests failed to accurately account for field oils and grease found in typical maintenance cleaning. The plant personnel reported that much higher concentrations of the cleaner were needed to achieve workable and acceptable cleaning efficiencies. It was then concluded that lower dilution rates would be necessary. See Table B.4 for GD/FW final dilution recommendations.

TERPENE DILUTION	CLEANING EFFICIENCY
Straight - 100%	Excellent
50% in water	Good
20% in water	Good
10% in water	Passed
5% in water	Failed

Table B.2 - Cleaning Efficiency - Light and Medium Soil[18]

TERPENE DILUTION	CLEANING EFFICIENCY
Straight - 100%	Good
50% in water	Failed

Table B.3 - Terpene Cleaning Efficiency - Heavy Soil[18]

SOIL	% CITRUS TERPENE	RESULTS
LIGHT	10-20	SUPERIOR CLEANING
MODERATE	10-20	ADEQUATE CLEANING
HEAVY	100	ADEQUATE CLEANING WITH SPRAY/BRUSH
GARAGE	--	CLEANERS DO NOT WORK

Table B.4 - Factory Feedback - GD/FW Conclusions

B.1.5 Terpene Cleaner Selection

Only three commercial terpene formulations, out of hundreds tested, were considered by GD/FW to be acceptable alternatives for Safety-Solvent. However, it was concluded that the selected cleaners would be suitable for just one narrow line of cleaning applications at GD/FW plants. For selected cleaners see Table B.5.

Terpene cleaners were found to be suitable for maintenance cleaning of nonproduction parts in selected factory areas. Currently, the terpene cleaners are being used at GD/FW only as a bridging material. The cleaners have allowed GD/FW to eliminate perchloroethylene and methylene chloride use (found in Safety-Solvent), from the production plants. A similar selective substitution of solvents was reached by the group at Tinker AFB.

Citrikleen was considered in the GD/FW study on terpene cleaners. However, due to its formulation and listed threshold limit value (TLV), it was eliminated. Early in their evaluation of the commercial terpenes, GD/FW set a criterion to eliminate any formulation containing documented TLV's. This was done to avoid trading one environmental problem for another (in this case air pollution for water pollution).

SOLVENT	MANUFACTURER
Bioact DG-1	Petroferm
Citri-Sol	3M
SE 373	Rochester Midland

Table B.5 - GD/FW - Accepted Commercial Terpene Cleaners

B.1.6 Concerns

General Dynamics Corporation has strong concerns over the use of terpene cleaners in large applications, industries, or installations because of their many unfavorable characteristics and multiple unknown possibilities. Of concern are the following characteristics:

1. severe degradation of nonfluorinated elastomers
2. 10 to 5 percent nonvolatile residue that is found in most terpene formulations

3. rapid and severe crazing of plastics parts and equipment when using terpene cleaners

4. poor rinsing efficiencies of cleaners

5. most photochemically reactive substances known

6. terpenes tend to form gels or polymerize in aqueous emulsions

7. terpene cleaners auto-oxidize

8. combustibility of cleaners.

It is also reported by General Dynamics that workers using the material more that 30 to 45 minutes without interruption complained of skin and mucous membrane irritations. In addition, recent testing on laboratory animals is raising health concerns similar to those of the halogenated solvents.

B.2 Air Force Engineering and Services Center (AFESC) Study[39,40]

Hundreds of terpene cleaners were evaluated as potential substitutes for halogenated (i.e., chlorinated) and nonhalogenated (i.e., Stoddard) solvents used by the U.S. Air Force in the program titled "Substitution of Cleaners with Biodegradable Solvents" in 1987. This program was conducted by the AFESC at Tyndall AFB in Florida.

Because of the solvents used in both cold cleaning and vapor degreasing cleaning processes, this program began. The purpose of the program was to:

1. Identify solvents for removing wax, grease, and oil that can be replaced by biodegradable solvents

2. Identify the biodegradable solvents that can be used

3. Develop procedures for, and implement, their use

4. Develop procedures for testing future solvents

A sensor, based on the speed of sound, was developed to identify solvent solution components and concentrations. This program has three main phases: Phase I - Solvent Selection and Performance Evaluation, Phase II - Extended Performance Testing, and Phase III - Full-Scale Demonstration/Implementation of the Solvent Into Industrial Processes at the Air Force Logistic Centers.

B.2.1 Phase I - Solvent Selection and Performance Evaluation

Phase I has been completed, the five major task accomplished included:

1. identification of the industrial processes at the Air Logistic Centers (ALC) in which solvents/cleaners are used, the procedures for their use, and the processes following their use such as rinsing, electroplating, etc.
2. development of quality assurance methods and procedures
3. identification of the available biodegradable solvents
4. literature review of process enhancement methods
5. screening the candidate solvents to evaluate their performance for (a) removing wax, oil, grease, and carbon, (b) biodegradability, and (c) corrosiveness.

Alternative cleaning agents were selected based on their compatibility with the facilities' current cleaning processes such as cold cleaning tanks, immersion cleaning, and spray washing. Evaluation of the solvents chosen for screening were divided into four elements: biodegradability, ability to dissolve soils, cleaning efficiency, and corrosiveness. If a solvent passed the first three evaluations, it was tested for corrosiveness (Figure B.1). Each of the evaluation criteria and testing methods are described as follows:

- **Biodegradable**

  For this program, solvents that could be biologically degraded to meet the NPDES discharge limits by the activated sludge treatment system at the Tinker AFB's industrial wastewater treatment plant (IWTP) were considered biodegradable. At the Tinker AFB, the retention time of the activated sludge system is 6 hours. On average, this retention time is low, however the testing and evaluations were geared to the existing facilities at Tinker AFB. A modification of American Society of Testing and Materials' (ASTM's) standard test method (Biodegradability of Alkylbenzene Sulfonates) was used to screen the biodegradability of the solvents proposed for substitution at Tinker AFB.

  The measure of biodegradability was also defined as the ability of microorganisms to oxidize the solvent or toxic compounds in solution. This was measured as indicated by the decrease in soluble chemical oxygen demand (COD), which is a measure of the concentration of oxidized materials in the wastewater that are

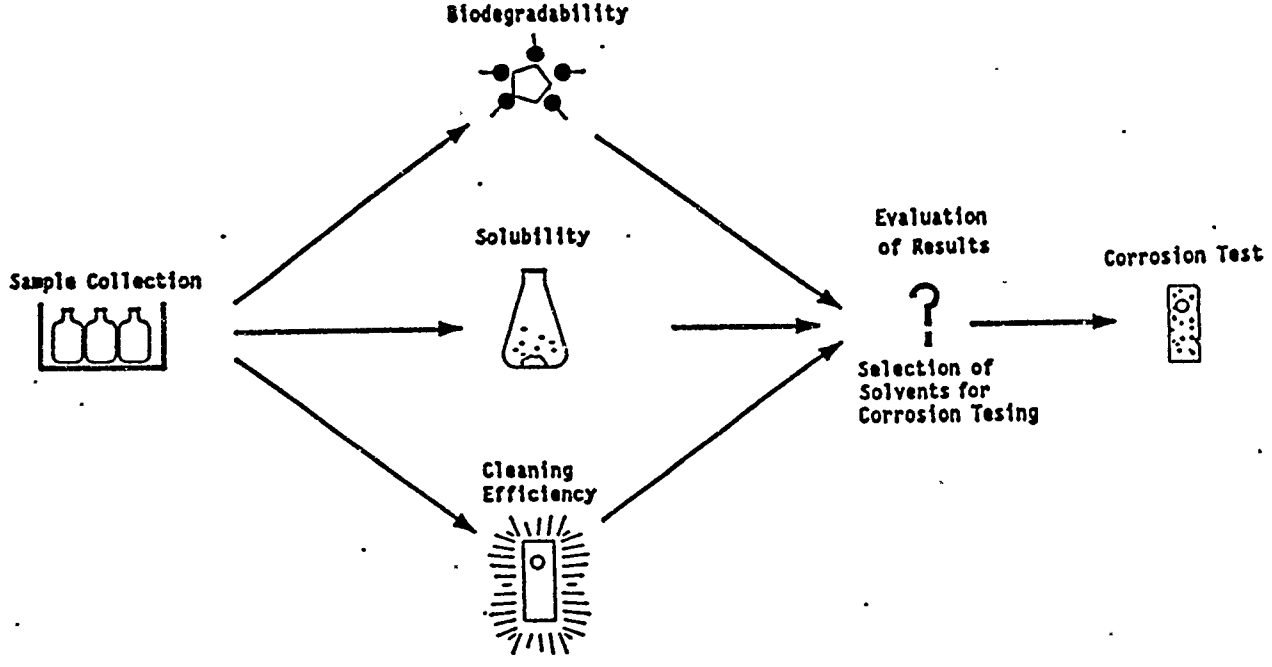

Figure B.1 - AFESC's Flow Diagram for Solvent Evaluation

amenable to chemical oxidation. COD is also a criterion of the Tinker AFB NPDES discharge permit (the limit is 150 mg/L COD). A culture of bacteria from Tinker AFB's activated sludge system was maintained in a bench-scale sludge column located in the Idaho National Engineering Laboratory's Idaho Research Center (IRC) in Idaho Falls, Idaho. This culture was used in biodegradation tests of candidate replacements for currently used solvents.

To evaluate biodegradability, twelve small columns were fabricated. These columns used air diffusion for solids suspension and have sample ports which closely represent those of the actual treatment system. Samples of each solvent were mixed to recommended concentrations (as prescribed by the manufacturer) and then diluted with a nutrient medium so as to represent the concentration that might be expected at the IWTP.

- **Solubility Testing**

Solvents remove soil from a part in two general ways. They can either solubilize the soil or they can break down the adhesion of the soil to the part, allowing the soil to be mechanically removed. Therefore, the chemical composition of many of the solvents evaluated in this program was proprietary and, thus, the percent solubility was determined experimentally using the methods described by McCoy.[40]

The solubility test was used to determine the extent that wax was soluble in the solvent tested. At the greater solubilities, the solvent was more likely to clean efficiently. Following the procedure recommended by McCoy, a 1-gram sample of the wax was placed in a 250 mL round-bottom flask and 100 mL of solvent at concentrations recommended by the manufacturer was added. The flask heated for 4 hours at the temperature suggested by the manufacturers. The solution was filtered and the undissolved residue was dried and weighed. From this weight the percent solubility was calculated. The standards, 1,1,1-trichloroethane and Stoddard solvent, were evaluated first to establish a baseline for comparing the potential replacement solvents and cleaners. Since there was no easy way of filtering the grease and oils, they were not screened.

- Cleaning Efficiency

Cleaning efficiency was evaluated by the ability of the solvent to remove wax, oil, or grease from metal coupons. A selection of eight alloys (A12023, A17075, Az31B, C1020, 310S, Incone1750, CDA433, and Monel K-500), representative of the alloys that are presently being cold cleaned and vapor degreased, were used to determine cleaning efficiency. The potential replacement solvents were evaluated for cleaning efficiency as a function of time. As a baseline, trichloroethane and Stoddard solvent were used to clean coupons.

The solvent cleaning efficiency was determined for four different soils. The soils included Petrolyte Amber B-squared 175 wax, a carbonized oil/xylene mixture, a hydraulic fluid/carbon mixture, and a molybdenum sulfide/carbon mixture. The method for applying the soils onto the coupons can be found in Reference 40.

Coupons were coated with the representative soils and then cleaned in potential replacement solvents. The cleaning efficiency was determined by the change in the weight of the soil on the coupon. These cleanings were then measured against baseline solvents.

- Corrosion Testing

The corrosion testing was only performed on those solvents that proved to be biodegradable and were adequate in the initial cleaning performance evaluations. The main purpose of this task was to determine the corrosion characteristics of the treated metals in the replacement solvents. Initial corrosion tests were the total immersion tests recommended in ANSI/ASTM F 483-77.

Fifteen metals, commonly serviced at Tinker AFB, were corrosion tested in each solvent that met biodegradability and cleaning criteria. The metals are listed in Table B.6. According to the test procedure, the metals were tested for 168 hours in the concentrated solvents or in the solvent at the recommended concentration and temperature. After 168 hours, the coupons were cleaned by scrubbing with a soft-bristle brush under running hot water, rinsed with distilled water, and then rinsed with acetone. The excess acetone was removed by wiping with a paper towel and the coupon was dried for 15 minutes in a vacuum desiccator. The coupons were cleaned according to the acid cleaning procedure for the respective metal and then reweighed.

The appearance of the coupons was recorded after removing the solvent, after scrubbing under water, and again after acid cleaning. The cleaned coupons were examined under a microscope at 480X for pits and surface attack. Three coupons of each metal were tested in each solvent.

B.2.2 Results of Phase I Testing

Approximately 40 solvents passed the cleaning and biodegradability test. The solvents that were applicable to all the metals were corrosion tested. Ten passed the test criteria, however, only six solvents (Exxon Exxate 1000, Triton Hemo-Sol, Calla 301, 3D Supreme, Orange Sol De-Solv-it, and Bio-Tek 140 Safety Solvent) were selected for Phase II evaluation.

	METAL	TYPE
1	Copper	CDA110 EPT
2	Nickel	200
3	Aluminum	AL2024
4	Steel	C4340
5	Aluminum	AL7075
6	Aluminum	AL1100
7	Stainless	410
8	Admiralty Brass	CDA443
9	Carbon Steel	C4340, C1020
10	Stainless	310S
11	Inconel	705
12	Monel	MK-500
13	Titanium	RMI
14	Waspaloy Alloy	--

Table B.6 - Metal Samples Used for Corrosion Testing

Results from each of the characteristics tested are described as follows.

- **Biodegradability**

To establish a basis for comparison, the biodegradability tests of the solvents were run with appropriate controls and standards. Changes in biomass, biological activity, and biodegradation were compared to the controls in the test columns, which contained phenol. Examination of the data indicated the activities discussed below.

Acclimation of the organisms to some solvents tested was apparent. This acclimation was evidenced by a delay of biodegradation activity for 2 to 3 hours followed by a period of sustained degradation (see Figure B.2).

Another condition that became evident was toxicity or recalcitrance of certain solvents. This was indicated by no loss of COD during the entire testing period, which showed that the material was resistant to biological degradation during the contact time permitted. Adenosine Triphosphate (ATP) was used to determine if the solvent was toxic to the microorganisms. A severe decrease of the ATP over the test period indicated that the material was particularly toxic to the activated sludge used as seed in the test columns (Figure B.2). A minor decrease in ATP was expected to occur in test solvents that were resistant to degradation, but were not toxic. Additional testing was necessary to distinguish between actual toxicity and recalcitrance in areas of possible overlap of these conditions.

Air stripping and sorption of certain solvents was also evident (Figure B.2). Large losses in COD over the testing period may represent loss due to biological activity, sorption of the solvent to the biomass or container walls, or solvent volatility. Again, the ATP data were used to determine if the loss of solvent indicated increased biological activity.

- **Solubility Screening**

As an indication of the required solubility and cleaning temperatures, tests were run to determine the temperature at which the wax and grease starts to go into solution. Wax solubility tests were run at temperatures 5 to 10 °F greater than the initial dissolution temperature. For the most part, these temperatures indicated the temperature at which the solvent would remove the wax efficiently from the coupons.

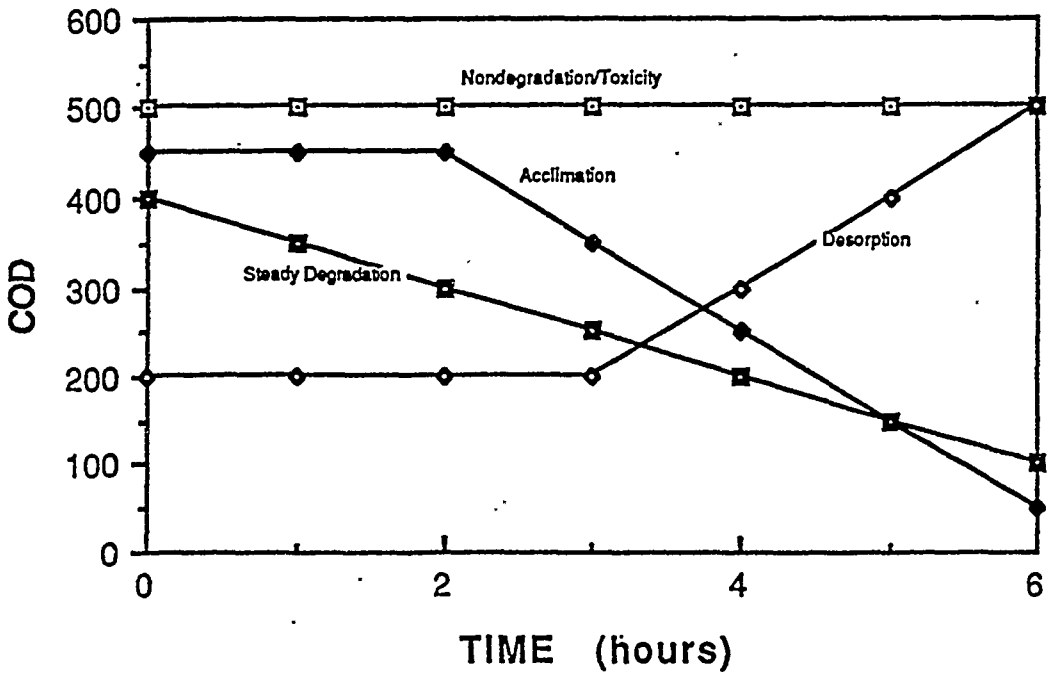

Figure B.2 - AFESC's Example of Biodegradation in the Biodegradability Test

It was found, when testing all the solvents, that unless the solubility of the wax in the solvent was greater than 70 percent, good cleaning efficiency could not be achieved. Solubility testing could not be performed on the grease/carbon mixture, the carbonized oil/xylene mixture, or hydraulic fluid/carbon mixture since there was no way to filter. However, the initial temperature of dissolution of the grease/carbon mixture was not indicative of the temperature at which good cleaning efficiency could be achieved. It is assumed that stirring during heating dispersed the grease rather than dissolved it.

- **Cleaning Efficiency**

The baseline solvents used for comparison purposes included 1,1,1-trichloroethane at ambient temperature, PD-680 at ambient temperature, and the cresol benzene mixture at 140°F. The coupons cleaned with these three solvents were treated in the same manner as the cleaning test procedures for the replacement solvents. The cleaning efficiencies obtained using baseline solvents for 10 minutes at ambient temperatures are shown in Table B.7.

SOIL	TCE	STODDARD	BENZ/33% CRE
Wax	75	55	100
Hydraulic Fluid	100	95	100
Grease/Oil	86	95	100
Oil/Xylene	86	86	100

Table B.7 - Baseline Solvents Cleaning Efficiencies
% Removal at Ambient Temperature (10 minutes)

To define clean, or to select solvents for further testing, a criterion of 80% removal in 10 minutes was established. In addition, if more that 60 percent removal occurred in 10 minutes, the solvent was selected as one for which cleaning could be improved by one of the enhancement process. Several of the solvents were tested at temperatures at which enhancement could be recommended by stirring the solution with a magnetic stirrer. In some cases stirring made a significant difference in cleaning efficiency, increasing the efficiency to more than 80 percent clean in 10 minutes. In other cases, there was little difference, even with stirring.

In many cases, cleaning efficiency increased from 0 to 10 percent with no rinsing to nearly 100 percent with rinsing.

B.2.3 Phase II - Extended Performance Testing

Phase II was completed in November of 1989. The tasks completed in this phase include:

1. Human Toxicity Data Gathering
2. Enhancement Method Testing
3. Solvent Performance Testing
4. Bioacclimation Testing
5. Extended Corrosion Tests

Phase II of this program was primarily pilot-scale testing of the solvents selected from Phase I. Pilot-scale tanks were installed at the pilot test facility at Tinker AFB for coating aircraft parts with soil (wax, grease, or oil), cleaning, rinsing, and drying the parts. Installation included a 1-cubic-foot tank that can be heated to 200 °F for coating parts with wax, a 100 gallon (379 liter) tank equipped with ultrasonics, mixer, and heater for solvent testing, a 100 gallon rinse tank equipped with agitator and heater, and a drying area. Solvent cleaning performance and enhancement methods was tested in this area. The biodegradability of the loaded solvents was tested in a pilot water treatment facility. A brief description of the task completed in Phase II is as follows.

- **Human Toxicity Data Gathering**

  Existing toxicological data were gathered on solvents to be tested in Phase II from the manufacturers and the National Library of Medicine (NLM) Toxicology Information Program database. For many of the solvents, the manufacturers had already completed toxicology testing on their respective solvents. These data were collected and evaluated for further screening of the solvents.

- **Enhancement Method Testing**

  To enhance cleaning and reduce operating temperatures, two enhancement methods (ultrasonic and mechanical agitation) were evaluated. These methods enhance soil removal by increasing the mass transfer and abrasive effects of the solvent, thus removing soil faster and at lower temperatures. High operating temperatures will increase the operating expense of the replacement solvents and

increase danger to operating personnel. Each solvent was evaluated at several ultrasonic and mixing enhancement conditions and temperatures. The approximate energy input was then calculated for the enhancement methods to establish the economics of maintaining the solvent. Ultrasonic enhancement was selected because of the high currents created by the microstreaming cells and cavitation. Ultrasonic agitation is much like mechanical agitation in its effects, but is more intense and does not create the VOC emission problem associated with air agitation.

- **Solvent Performance Testing**

The objective of this task was to determine solvent performance, including life expectancy, rinsing requirements, and drying requirements.

Life Expectancies/Efficiency/Capacity - Initial solvent soil-holding capacity was determined in beaker tests with 500 mL of the solvent heated to the temperature determined in the previous task and mixed/agitated. Pre-weighed coupons were soiled with wax, grease, or oil and dipped in the solvent for the time determined in Task 3 until the soil was no longer removed. The coupons were then dried and weighed to determine the amount of soil removed, which indicated the approximate amount of soil that can be removed in the pilot-scale testing. This approximation was used in the pilot-scale life expectancy testing.

Next, ten parts were coated with the soil and cleaned in the solvent to determine the solvent's initial cleaning efficiency. The solvent was then loaded to 25 percent of its capacity by adding the required amount of soil to the tank of solvent. The soil was added in amounts and at time intervals simulating the actual part-cleaning process. This determined cleaning efficiency. This procedure was repeated for 50, 75, and 90 percent of the solvent's capacity.

Solvent Rinsing Requirements - Each solvent's rinsing and drying requirements were investigated. Drying without rinsing was investigated by dipping aircraft parts in the solvent, suspending the parts from a suitable support, and allowing them to dry at ambient temperature or blow-drying the parts with hot air. The extent of drying was determined as a function of time. Rinsing requirements were established by determining the soil removal as a function of time in a spray chamber and an agitated rinse tank.

- **Bioacclimation**

The objective of this task was to determine the impact of introducing new solvents to the pilot IWTP (i.e., metal precipitation, acclimation, and toxicity). Typical activated sludge basin parameters were measured to track the changes imposed on the basin. The duration of each test was planned to be three sludge ages (approximately 21 days), which is the number of cycles generally required to obtain a stable acclimated basin following a change. However, because the amount of time available for testing was shortened due to metal sludge flotation, the duration of each test was reduced to about 1 week. After a test, the activated sludge from Tinker's activated sludge system was introduced. Included with this task is tracking the major components of the solvent throughout the system and determining the effects of introducing high concentrations of solvent into the system.

- **Extended Corrosion Tests**

The objective of this task was to determine the hydrogen embrittlement effects of the replacement solvents. The test were performed according to the ANSI/ASTM procedures F 591-77, *Mechanical Hydrogen Embrittlement Testing of Plating Processes and Aircraft Maintenance Chemicals.* In addition, immersion corrosion testing of the solvents was completed. The tests incorporated the enhancement methods found applicable for the solvent and a modified ANSI/ASTM procedure F 483-77, *Total Immersion Corrosion Test for Aircraft Maintenance Chemicals.*

B.2.4 Results of Phase II Testing

Due to inner surfaces and the notches and crevices inherent to parts, enhancements were required to achieve efficient cleaning. However, once enhancement techniques are applied, the cleaners can be as effective as the chlorinated hydrocarbon solvents and the Stoddard solvents.

Rinsing was found to be required to remove the residual soil from the parts, either with water or fresh solvent, depending on the application. In some cases, the residual solvent could be completely removed by drying within 30 minutes, but in other cases rinsing with water was required. Rinsing requirements are listed in Table B.8; drying requirements in Table B.9.

Several problems were encountered in operating the small ultrasonic units and the 100 gallon (379-liter) unit. Problems included maintaining the transducer banks, maintaining fuses, and keeping enough power to the units. Ultrasonics are normally used for aqueous solutions. Some manufacturers indicated that there may be problems when ultrasonics are used with nonaqueous solutions because of the still time created when solvents are offgassing, potential problems with VOCs, and static buildup. Ultrasonics increased cleaning effectiveness by introducing microstreaming and cavitation, allowing fresh solvent to enter hard-to-reach areas and loosening soil. However, costs increase significantly when ultrasonic tanks are large.

The 8-day testing period appears to have good potential application in solvent testing program for the determination of solvent biodegradation. The two 3-day acclimation periods overcome the limitations of the 6-hour biological screening test since acclimation is an important component in biodegradability testing.

		IMMERSION		IMPACT	
SOLVENT	SOIL	CLEAN[a] (%)	TIME (MIN)	CLEAN[a] (%)	TIME (MIN)
Exxate	Wax	100	5	100	5
	Oil/Xylene	97.6	30	98.5	30
De-Solv-It	Wax	99.0	30	97.8	30
	Oil/Xylene	99.0	1	100	1
Safety-Solvent	Wax	99.1	30	98.0	30
	Oil/Xylene	100	30	100	1
Supreme	Hydr Fluid	100	1	100	5
	Grease	83	5	73.0	10
Calla 301	Hydr Fluid	100	5	100	1
	Grease	40	10	95.0	10

[a]Maximum cleaning efficiency

Table B.8 - Rinsing Requirements

SOLVENT	CLEANING EFFICIENCY (%)	TIME (MIN)
Water	100	30
Exxate	92	30
Safety Solvent	82	30
De-Solv-It	83	30
Calla 301	94	10
Supreme	100	20

Table B.9 - Drying Requirements

The results are summarized in Table B.10 which shows the optimum conditions, loading capacity, and performance of the solvents cleaning aircraft parts. Cost estimates and energy usage are also incorporated into this table. The following assumptions were used in determining these costs.

Energy consumption estimate assumptions:

- 100 gallon (379 liter) tank; fluid maintained at specified temperature
- Ultrasonic generator efficiency - 90 percent; ultrasonic transducer efficiency - 90 percent
- Electricity cost - $0.07/kWh
- Tank heat loss - 350 Btu/h
- Electric heater efficiency - 85 percent
- Rinse water recirculated and pumped (2.5 kW of power)
- Mixer with 3/4 hp motor

Estimated cost estimate assumptions:

- Use existing 100 gallon (379 liter) tank
- Purchase of a mixer, an ultrasonic generator, and a transducer set
- Purchase of an electric in-tank heater
- Purchase of a centrifugal pump for recirculation system

SOLVENT	SOIL	OPERATING TEMP. (°F)	ULTRASONICS (WATTS)	MIXERS USED	CLEANING DURATION	NEED RINSE	SOIL*	CLEANING EFFICIENCY (%)	COST ($/100gal)	ENERGY ($/hr)
EXXON, EXXATE 1000	WAX	140	500	NO	20	YES	0.74	90	20,000	0.82
	OIL/XYLENE	120	NO	YES	20	YES	0.95	95	5,500	0.64
ORANGE SOL, DE-SOLV-IT	WAX	140	600	NO	10	NO	0.74	80	17,500	0.65
	OIL/XYLENE	140	600	NO	20	YES	0.95	80	20,000	0.82
BIO-TEK, 140 SAF SOL	WAX	140	900	NO	20	YES	0.74	98	20,000	0.85
	OIL/XYLENE	140	NO	YES	20	YES	0.95	98	5,500	0.81
3D, SUPREME	HYDRAULIC FLUID	120	NO	YES	10	YES	0.85	92	5,500	0.64
	GREASE	140	NO	YES	10	YES	0.52	92	5,500	0.81
CALLA 301	HYDRAULIC FLUID	140	NO	YES	20	YES	0.85	96	5,500	0.81
	GREASE	–	–	–	–	–	–	–	–	

*Average weight of the soil on a 1 by 2 in. carbon steel nipple.

Table B.10 - Summary of AFESC Test Results

- Miscellaneous parts (piping, valves, etc.) account for 20 percent of the above items total cost
- Two types of systems:
  a. ultrasonic enhancement with heating and rinsing
  b. mixing enhancement with heating and rinsing.

The equipment cost estimates were based on retrofitting an existing 100-gallon tank. Equipment cost estimate does not include cost of installation. Also, solvent costs have not been included.

Bioacclimation testing has been started for the Exxon Exxate 1000 solvent loaded with oil/xylene. In the presence of the solvent, the metal sludge floated in the solid contact clarifier. Jar tests indicated that all the selected solvents either float or disperse the sludge. The addition of either aluminum sulfate or magnesium sulfate prevented flotation of the metal sludges with all the solvents tested except Orange Sol De-Solv-It. The use of magnesium caused the solids contact clarifier to be much more susceptible to upset conditions due to changes in solvent concentration or changes in the influent wastewater. The cost of an aluminum addition should be no more than an additional polymer. Bioacclimation testing and gas chromatograph analysis are still being completed.

Air sparging tests indicate some sparging of the Exxon Exxate 1000 and Bio-Tek Safety Solvent over the 6-hour test period. The results of Phase II indicated that solvents are available for demonstration implementation into the process lines at Tinker AFB.

B.2.5 Phase III - Full Scale Demonstration/Implementation

The solvents selected to be implemented in full scale demonstrations at Tinker AFB are:

1. Exxon Exxate 1000
2. Calla 301
3. 3D Supreme
4. Orange Sol De-Solv-it
5. Bio-Tek 140 Safety Solvent.

The solvents selected for Phase III depended on the processes at Tinker AFB, availability to accept the replacement solvents, and modification needed for implementation.

The solvents to be implemented were selected shortly after the process to be used had been identified and proven to be compatible with the enhancement techniques required. Phase III was begun in the late spring of 1990, and the evaluation is to be complete in the spring of 1991.

B.3 Kelly Air Force Base Study[43]

The Kelly AFB, TX, conducted a site-specific study on the use of terpene cleaners, in 1988. The study was initiated in the process of identifying less hazardous alternatives to solvents and cleaners currently used on management equipment at the base. The terpene cleaners were evaluated in cold cleaning process and treatment schemes currently available at Kelly AFB. Characteristics such as toxicity, flash point (safety), biodegradability, ozone depletion potential VOC content, disposal method, life cycle cost, and general requirements for Air Force cleaners were evaluated. The information on ten manufacturer's terpene-based products authorized for limited use are:

1. Penetone Corporation, Citrikleen
2. Fine Organics, Envirosolve CRX
3. M-Oil-Free, Ultra 90
4. MARC, Safe Solv OT
5. B&B Tri Tech, B&B 2030
6. Chem-Lube Corporation, X-122 Citrus Based Cleaner
7. Eldorado Chemical Company, Astromat Orange
8. Rochester Midland, SE377C
9. Safe Performance, Safe-T-Solve
10. 3D Incorporated, Citrigold.

The above cleaners were selected following extensive testing in verifying the acceptability of the product for use on Air Force equipment.

B.3.1 General Findings

- Cleaning

Unlike many of the solvents currently in use (e.g., PD-680, 1,1,1-trichloroethane), the terpene-based solvents are water dilutable and in most instances require a clear

water rinse. The cleaning procedures are similar to an alkaline soap. The products are free rinsing and evaporation rates are comparable to water. After cleaning bare metals, corrosion protection will be required to prevent flash corrosion.

- **Flash point**

The flash points of the concentrated cleaners varies around 120 °F. When diluted with two parts water the resulting emulsions tested can provide a flash point higher than 140 °F can be obtained.

- **Toxicity**

Most terpene cleaners were found to contain the hazardous ingredient ethanolamine. This ingredient is hazardous due to a TLV of 3 ppm. No further testing on toxicity has been initiated, but is anticipated in the future.

Even though the products are listed as less hazardous than conventional solvents (e.g., Acetone, 1,1,1-trichloroethane), protective gloves, goggles, and apron should be worn as the terpene-based cleaners will remove the natural oils in the skin.

- **Ozone Depletion Potential**

Air sample testing for in-application use has shown concentrations within permissible exposure limits of 8.0 mg/m^3.

- **Volatile Organic Compound**

They concluded the VOC content depends on the percentage of terpene-based material and ethanolamine contained in the product. VOC content averages around 50 percent of the cleaner (approximately 500 grams/L). A two-part water to one-part cleaning solution provided an in-application VOC content of 166 grams/liter and the terpene cleaners are not listed as Ozone Layer Depleting Substances (OLDS).

- **Disposal**

Kelly AFB has found, through site investigation, that the cleaners work very well in oil/water separators. Therefore, it is suggested that spent solution can be properly

disposed of into satisfactorily operating effluent treatment facilities after soils have been released.

- Biodegradable

Although presented as biodegradable, the time required to decompose the cleaners in effluent treatment facilities varies on the method, bacteria, dilution and product used. Because each installation has unique conformance criteria for disposal of materials, an evaluation of the material safety data sheet by the installation bioenvironmental engineers, the base civil engineers, and the local Industrial Water Treatment Facility personnel is absolutely essential.

B.3.2 Cleaning Guidelines and Procedure

Kelly AFB is developing cleaning procedure guidelines for the use of terpene cleaners. The recommended guidelines and cleaning procedure have been developed for jet engine exterior washing and parts cleaning, cleaning exterior surface of T37/38 aircraft, and for aircraft exterior spray-on, wipe-off cleaning.

Jet Exterior and Parts Cleaning Guidelines:

Recommended guidelines for jet engine exterior washing and parts cleaning using the authorized terpene cleaners are as follows:

1. The terpene products can be used to clean the exterior surface of the engine and as an engine parts cleaner. They are not authorized as engine path cleaners at this time. The products can be used to remove particles, solidified grease, gelled oil, and other types of soil in cold dip tanks, sprayers, foamers, or brush-on applications.

2. Under no circumstances will the cleaners be used in concentrated form. Recommended dilution ratios depend on the amount of soil to be removed and are given within the procedures. Always read the precautions and follow the manufacturers' instructions before using these products. Also, each installation's Environmental and Safety Office must evaluate a current Material Safety Data Sheet (MSDS) for the product to ensure that it is suitable for use in their cleaning process and can be disposed of by the local waste treatment facility.

3. Unlike PD-680, these cleaners will not leave a protective oil film on the cleaned parts. For cleaned parts that will not be immediately coated with primer, it will be necessary to apply a Corrosion Prevention Compound (CPC) or light lubrication oil (i.e., VV-L-80) to the cleaned part to prevent flash rusting and corrosion.

4. Special care should be taken when implementing any new product into a cleaning process. Continuous monitoring must be accomplished during the cleaning process. Do not leave any metal exposed to the cleaner beyond the recommended time limits.

5. These products can not be heated over 115 °F. The organic solvents will evaporate and may give off a nauseous odor. These products will not be used with steam cleaners or heated ultrasonic tanks.

- Recommended Cleaning Procedure for Exterior Surface

For cleaning the exterior surface of engines, use brush-on, spray, or foam application. Follow recommended procedures for covering the intake, exhaust and other openings. Dilute the product with 4 to 10 parts water. The cleaner will be left on the equipment for no more than 10 minutes. If a second application is necessary to remove soils, completely rinse the first application of cleaner from the equipment and reapply. The cleaner must be rinsed thoroughly with water. Do not let the cleaner dry on the equipment. Agitation will speed up the cleaning process.

- Recommended Cleaning Procedures for Parts Cleaning

For dip tank operations to remove light to medium soils, dilute the product with 10 to 20 parts water. Maximum immersion time for dip tank operation is 1 hour; rinse thoroughly with water. Agitation will speed up the cleaning process.

Use parts washers, cold dip tanks, or recirculating tanks to remove heavy soils. Dilute the product with 2 to 10 parts water. Immerse the parts no more than 1 hour. Agitation or aeration will speed up the cleaning operation. Thoroughly rinse with water.

If the dip tank is left overnight, the soil will float to the surface and can be skimmed off for ease of disposal. Heavy soils will collect on the bottom of the tank and can be removed for disposal. Replenish the tank with diluted cleaner.

- Cleaning Precautions
  a. Do not use on indium, lead, or other soft metals. Approved products have met the Immersion Corrosion removal limits for cadmium.
  b. Do not mix different vendors' products.
  c. Deterioration of rubber and neoprene may result if immersed in the cleaner for extended periods.
  d. Undiluted cleaners can stress-craze acrylics. Water rinse if cleaners come in contact with acrylic materials.
  e. Do not use on electrical wiring, connectors, or equipment.

General Guidelines for Cleaning Exterior Surface of T37/38 Aircraft:

Cleaning procedures have been developed for cleaning aircraft exterior surface using Citrikleen HD, manufactured by Penetone Corporation, in a cold application. The procedures are outlined as follows:

1. Prepare the aircraft for washing per the appropriate technical order.
2. Dilute Citrikleen HD with water by volume. For foam application, dilute 9 to 15 parts water to 1 part Citrikleen HD. For spray, sponge or brush application, dilute 10 to 20 parts water to 1 part Citrikleen HD. For heavy duty cleaning of solidified grease, carbon, hydraulic fluid, and oils, dilute 4 parts water to 1 part Citrikleen HD.
3. Apply the cleaner to the surface for no more than 20 minutes. Agitation of the surface will facilitate cleaning.
4. Thoroughly rinse the cleaner from the surface with fresh water. Do not allow the cleaner to dry on the equipment.
5. If a second application is necessary to remove soils, reapply cleaner to surface and agitate with a clean cloth. Rinse thoroughly with water.

- Caution

  At the dilution ratios recommended, the cleaner should not stress-craze acrylic windshields. The cleaner has passed ASTM F484 for Acrylics, Polycarbonate, and Polysulfone materials at a 2(water).1 (cleaner) dilution. As a precaution, mask/cover the windshields and thoroughly rinse after the aircraft cleaning is accomplished.

Guidelines for Aircraft Exterior Spray-On, Wipe-Off Spot Cleaning:

Citrikleen HD has been authorized for spot cleaning the exterior surface of an aircraft. The guidelines recommended when using Citrikleen HD as a spot cleaner are as follows:

1. Using a diluted solution of 4 parts water to 1 part Citrikleen HD, lightly spray the product onto the surface of the aircraft.
2. Remove the cleaner and dirt with a dry, clean cloth. Rewipe the surface. The cleaner does not require a clear water rinse.

- Caution

  Do not use the product as a spot cleaner on windshields (acrylic, plastics, or polycarbonate materials), lacquer painted surfaces, electrical equipment, or bare metals. If the cleaner comes in contact with these materials, rinse with water. The cleaner works best on gloss polyurethane topcoats.

B.3.3 Conclusion

The terpene cleaners were not found to be a "cure all," but provide acceptable alternatives, in some instances, to the hazardous solvents currently under EPA's scrutiny. Terpenes have been approved at Kelly AFB on a limited basis for the following:

1. external and parts washing of TF39 engines
2. external washing of TF34 engines
3. external and parts washing of T56 engines
4. exterior wash of C-5 aircraft
5. exterior wash of OV-10 aircraft
6. exterior wash of A/T-37 aircraft
7. exterior wash of T-38 aircraft
8. parts washing of GTEs (Depot Level)
9. cleaning of Noise Suppressor Facilities
10. cleaning of Support Equipment, TO 35-1-12.

Ongoing projects associated with the terpene based cleaners at Kelly AFB are:

1. writing a specification; Cleaning Compound, Aerospace Equipment

2. testing for electrical/electronic equipment cleaning
3. testing for engine gas path cleaning
4. testing for bearing cleaning
5. testing for toxicity (conducted for the EPA).

B.4 U.S. Army Water Study - Aberdeen Proving Grounds[30]

Due to the widespread use of terpene solvents, the U.S. Army requested that a water study be conducted on Citrikleen. The Water Quality Engineering Consultation conducted the environmental assessment on the product. The assessment was requested by the Environmental Management Division at the U.S. Army Aberdeen Proving Grounds Support Activity.

B.4.1 Methodology

The assessment methodology used for this consultation included a preliminary toxicity screening, a simplified treatability study, and a review of the manufacturer's brochure on Citrikleen. The preliminary toxicity screening performed was a simple static biotoxicity test in which several concentrations (from 1mg/L to 1000mg/L) of Citrikleen were prepared in glass beakers. Test organisms were placed in the beakers and the results were noted.

The findings of Citrikleen's biological treatability and its compatibility with conventional domestic sewage treatment plants (STPs) in this study are only applicable to the aerobic processes with STPs. Possible impacts on anaerobic processes, such as digestors or denitrification systems were not evaluated.

B.4.2 Findings

As shown in Figure B.3, the specific growth rates for both the acclimated and nonacclimated seeds, with Citrikleen wastewater, reached a maximum at an initial COD concentration of approximately 100 mg/L and then declined significantly. This is indicative of an inhibitory substrate. This indicates that, in a domestic STP, discharging Citrikleen COD concentrations greater than 100 mg/L would cause an upset of the biological treatment system and possible permit noncompliance. In terms of 5-day biochemical oxygen demand (BOD_5) this is equivalent to approximately 30 mg/L BOD_5.

In comparison, the specific growth rate for the control batch test reached a maximum at approximately 30 mg/L, then decreased slowly, indicative of a noninhibitory substrate.

Discharges of higher concentrations of Citrikleen to an acclimated system is not recommended because of the instability of the microbial population and the greater potential for plant upset.

Figure B.3 also illustrates the impact of acclimation on the biodegradability with Citrikleen. Even a short acclimation period of 14 days drastically increases the growth rate. The major impact of this effect in a STP is that the Citrikleen degraded more quickly at the same influent concentration when compared to a nonacclimated seed.

B.4.3 Results

The preliminary screening indicates if Citrikleen is discharged directly to a receiving stream without treatment, it will adversely affect aquatic organisms.

The treatability study shows that Citrikleen is biodegradable in an aerobic biological treatment system. However, at concentrations greater than 100 mg/L as COD, it inhibits the microbial growth, which could result in noncompliance with permit limits. It was also shown that acclimation of the receiving treatment system with Citrikleen will increase the rate of its biodegradation.

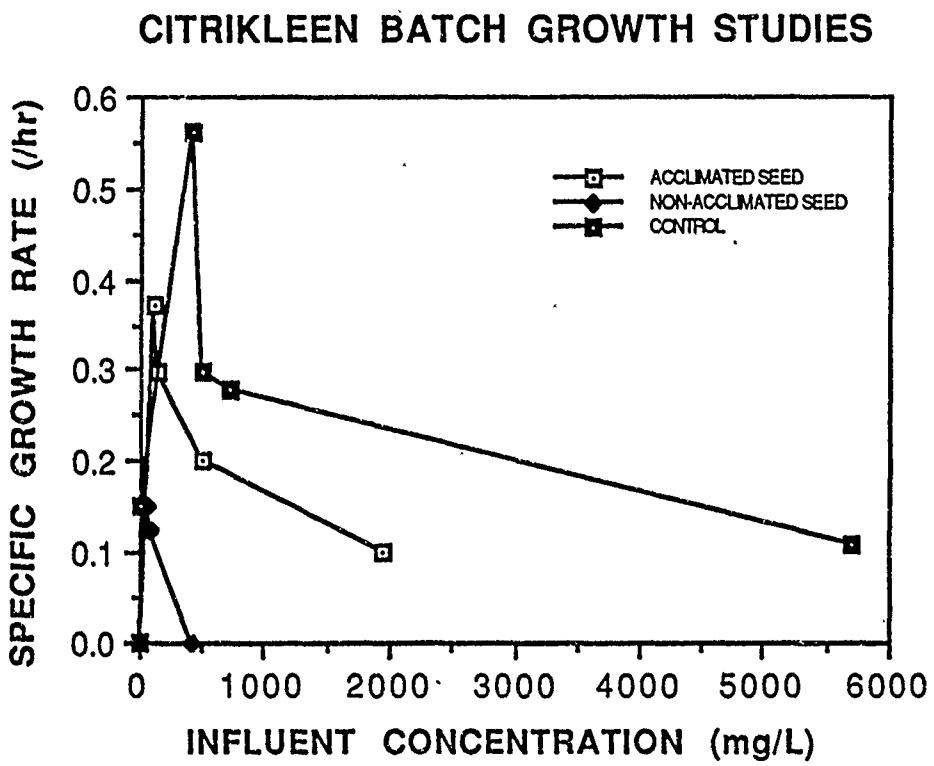

Figure B.3 - Impact of Acclimation on the Biodegradability

In a treatment plant, the discharge of Citrikleen in concentrations greater than 100 mg/L as COD could cause an upset of the biological treatment system. In terms of BOD_5, the 100 mg/L COD is equivalent to approximately 30 mg/L. The recommended amount of concentrated Citrikleen to be discharged to the sanitary sewer system should not exceed 40 gallons per one million gallons of sewage flow at the STP.

Citrikleen was also found to be an effective oil solvent. It is expected that more emulsified oil (chemical emulsion) will enter the sanitary sewer with Citrikleen use. It must be noted that emulsified oil cannot be removed in a gravity-type oil water separator and that oil in concentrations greater than 100 mg/L has been known to inhibit the biological treatment system at STP.

B.4.4 Conclusion

It is recommended that the discharge of Citrikleen rinsewater to the sanitary sewer should not exceed 40 gallons (concentrate) per million gallons of sewage flow. If the Citrikleen wastewater can be collected, it is advisable to have it transported to the STP and have the STP personnel handle the bleed-in operation to ensure conformance with the recommended rate of discharge.

B.5 Fort Hood U.S. Army Base Study[48]

Fort Hood initiated a study of terpene cleaners following a base demonstration of Cirtikleen HD conducted by a representative from the Penetone Corporation in 1988.

A cleaning demonstration with Citrikleen was conducted at the vehicle washracks. An Environmental Protection Specialist at the Environmental Management Office on base took samples of the effluent from the washracks' out falls. The samples were sent to a laboratory for evaluation and consultation.

B.5.1 Results

The results received from the laboratory testing of the effluent from the washracks can be seen in Table B.11. (Note: this is the actual data obtained and evaluated.)

	TSS[a] (mg/L)	OIL & GREASE (mg/L)	COD[b] (mg/L)
GRAB SAMPLE	98	121.9	1725.3
NPDES STANDARDS	30	15	200

[a]Total Suspended Solids
[b]Chemical Oxygen Demand

Table B.11 - Test Results of Effluent Citrikleen Sample Following Demonstration

This evaluation indicated that indiscriminate use of cleaning compounds, even biodegradable ones, can cause NPDES violations by exceeding standards for oil and grease and chemical oxygen demands.

B.5.2 Recommendations

Since the effluent of the vehicle washracks is generally a point source, out falls are regulated under NPDES provisions. According to a typical NPDES permit, water samples are to be collected and analyzed weekly. NPDES violations can lead to the assessment of fines of $25,000 per day of violation. Thus, close supervision must be kept over effluents.

The failure of a product, such as Cirtikleen, to pass NPDES permit limits and to adversely affect aquatic life downstream can create major problems if implemented installation-wide. Due to these problems, base officials have banned terpene cleaners for use in cleaning operations until further notice.

Steam cleaning without the use of chemicals is recommended for degreasing. The steam alone will, in most instances, do a reasonably good degreasing job. Generally, a degreasing job takes just as much elbow grease, with or without chemicals.

Fort Hood recommends the use of detergents and solvents at vehicle washracks should not be authorized unless the product is specifically evaluated through the local Environmental Management Office. Before a cleaning agent is approved for use on or near NPDES-permitted facilities, environmental consequences and disposal requirements must be considered. Water samples should be taken at the out fall and analyze them for NPDES

compliance. The Fort Hood Environmental Management Office has developed a questionnaire for solvent sales representatives to complete before conducting a demonstration on base.

This is the format used at Fort Hood when a sales representative comes to sell any so-called, "Biodegradable-Environmentally Safe-EPA Approved" cleaners. Put the name of the product in the blanks.

1. How much time does _____ solution take to biodegrade when mixed according to label and is it discharged into surface waters?

2. Under what specific conditions is _____ environmentally safe?

3. Under what specific conditions, or at what concentration, will _____ become damaging to the environment.

4. Is it safe and legal to discharge _____ solution into surface waters after using such solution for degreasing vehicles, without first collecting the oil and grease?

5. How does _____ affect the chemical composition of motor oils and automotive greases?

6. Does _____ have the ability to negate the polluting characteristics of automotive fuels and lubricants? If yes, please explain how.

7. Does _____ improve or hasten petroleum biodegradation? What time measurement?

8. If effluent is discharged into surface waters under provision of NPDES permit, will the surfactants and emulsifiers in _____ affect compliance with oil and grease standards?

9. Is it safe and legal to discharge unused _____ solution into surface waters?

10. How much time does it take for oily contaminants to separate and rise to the fluid surface in _____ solution?

11. Must _____ be disposed of through the sanitary sewer?

12. What are the specific consequences of _____'s biodegradation?

13. What is the chronological sequence of _____'s biodegradation? When does it change to what?

14. What is the chemical composition of _____?

15. What specific State, Federal, and local regulations are applicable to disposal of _____ and _____ -solutions?

16. In relation to NPDES permit, how does _____ affect the chemical oxygen demand standards when _____-solution is used for degreasing at vehicle washracks?

17. How much do 5 gallons and 55 gallons of _____ cost, respectively?

18. Does your company have a GSA contract?

19. Can you provide a sample of _____ at no cost to the Government?

B.6 National Toxicity Program Study[36]

A study of the terpene cleaners toxicity study was conducted by the NTP due to the concern that several of these new cleaners primarily contain the chemical d-limonene. D-limonene has a low order of toxicity, has been used in medical treatment, and is approved by

the Food and Drug Administration as a chewing gum base (2300 ppm). There is no evidence to suggest that this compound is mutinogenic or teratogenic, however, studies have shown that it is carcinogenic.

Terpene formulas containing d-limonene were suggested for NTP testing because of the increasingly widespread exposure in cleaner for use in industry.

B.6.1 Findings

Commercial grades of d-limonene were found to cause contact dermatitis due to contamination with other terpenes and related materials. Therefore, it is suggested that the cleaners be formulated with high grade or medical grade d-limonene of 99 percent minimum purity. The principal manifestations of poisoning with d-limonene were found to be similar to the Stoddard solvents, by producing pulmonary irritation and central nervous system depression, but requiring much higher doses.

D-limonene may also cause aspiration pneumonia due to pulmonary aspiration during episodes of omitting in cases of accidental ingestion. Probably lethal dose in humans would be between one pint and one quart of material.

Biodegradability of d-limonene products is dependent on the dilution and degree of contamination with soluble components. Representative samples should be taken periodically to determine hazardous waste characteristics as defined by applicable Federal and state regulations.

B.6.2 Study

Toxicity and carcinogenicity studies were conducted on d-limonene. The d-limonene used in these studies was more than 99 percent pure and was administered in corn oil by gavage. Short-term studies were conducted in rats and mice to identify toxic effects and affected sites and to establish doses for the 2-year study. The genetic toxicity studies were conducted in *Salmonella typhimurim*, mouse cells, and chinese hamster ovary (CHO) cells.

The doses selected for the 16-day studies ranged form 413 to 6600 mg/kg for both rats and mice. death and reduction in body weight gain occurred at the two highest doses. No compound-related clinical signs or histopathologic lesions were observed in any of the surviving dose groups.

The doses selected for the 13-week studies ranged from 150 to 2400 mg/kg for rats and from 125 to 2000 mg/kg for mice. Deaths occurred in the high dose group of each species and sex. Greater that 10 percent reduction in body weight gain was observed in the two highest dose groups of male rats and male mice, the high dose female rats and male mice; and the high dose female rats. Rough coats and decreased activity were observed at the two highest doses in both rats and mice.

B.6.3 Study Results

The NTP panel agreed that d-limonene showed clear evidence of cancer in male rats but no evidence of cancer in female rats or either gender of mice tested. The 2-year study concluded that the kidney was confirmed as the primary target organ for chemically-related lesions. The studies concluded there was no evidence of carcinogenicity of female rats that received 300 to 600 mg/kg of d-limonene. There was no evidence of carcinogenic activity of d-limonene in male mice receiving 250 to 500 mg/kg, or in female mice receiving 500 to 1000 mg/kg.

Appendix C

Telephone Contacts

C.1 Military/ Government Citrikleen Customer List

US Army

Corps Engineers
Newburgh, NY
Fort Bliss, TX
Fort Bragg, NC
Fort Campbell, KY
Fort Eustis, VA
Fort Hood, TX
Fort Lewis, WA
Fort Ord, CA
Fort Riley, KS
Fort Rucker, AL
Fort Sill, OK
Fort Stewart, GA
Hunter AAF, GA
USMA West Point, NY

US Army National Guard

Arkansas
California
Kansas
Maryland
Montana
New Jersey
New York
Oklahoma
Wyoming

US Army Depots

Bellmore, NY
Letterkenny, PA
Red River, TX
Sacramento, CA
Seneca, NY
Watervliet Arsenal, NY

US Army Reserve

90th ARCOM, TX

US Air Force Depot

McClellan, CA

US Air Force

Andrews, VA
Beale, CA
Bergstorm, TX
Carswell, TX
Castle, CA
Charleston, SC
Dover, DE
Fairchild, WA
Hill, UT
Langley, VA
Mather, CA
McChord, WA
McGuire, NJ
Pope, NC
Travis, CA

US Air Force National Guard

CA Air Guard
DC Air Guard
Missouri Air Guard
Montana Air Guard
Nevada Air Guard
NY Air Guard
ND Air Guard
Washington State, Tacoma
Wyoming Air Guard

US Marines

Camp Lejeune, NC
Camp Pendleton, CA
Cherry Point, NC
New River, NC
Quantico, VA
San Diego, CA
Twentynine Palms, CA

US Coast Guard

Elizabeth City, NC
Fort Macon, NC
McClellan, CA

US Navy

Colts Neck, NJ
Dahlgren, VA
Mayport, FL
Mitamar, CA
Moffett Field, CA
Pacific Strike Team, CA
Patuxent, MD
Point Mugu, CA
Port Hueneme, CA
Seal Beach, CA
Sealift Command, NJ
Suisan Bay Reserve, CA

Navy Shipyards

Bremerton, WA
Charleston, SC
Honolulu, HI
Mare Island, CA
Philadelphia, PA

US Navy Aviation Depots

Alameda, CA

Post Offices/ Veterians Admin.

USPO, Binghomton, NY
USPO, Fishkill, NY
USPO, Kearny, NJ
USPO, Newark, NJ
VA, Albany, NY
VA, Bath, NY
VA, Battle Creek, MI

C.2 Contacts

George Bollaine
March Air Force Base, CA

Ann Copeland
Department of Engineering and Housing
Tinker Air Force Base
Phone: (405)736-5871

Ann Engleburger
Department of Engineering and Housing
Fort Hood, TX
Phone: (817)287-6499

Stephen Evanoff
Environmental Resource Management
General Dynamics-Ft. Worth Division
Ft. Worth, TX
Phone: (817)777-3772

Charles Harris
Environmental Management and Operations
Ft. Riley
Phone: 856-2630 (Autovan)

Stan Mitchell
Department of Engineering and Housing
Fort Gillem, Georgia
Headquarters FORSCOM
Phone: (404)362-7197

Christopher Parent
Fort Lee, VA
Phone: (804)734-1764

John Riggs
Natural Resources Office
Camp Ligon, NC
Phone: 484-1690 (Autovon)

H.A. John Rivera
Environmental, Engineering and Housing
Fort Hood, TX
Phone: (817)287-6499

John Roudebush
Brulin Corporation - Chemist and Sales
Indianapolis,IN
Phone: (800)776-7149

George Samples
Ft. Bragg, NC
Phone: (919)396-3341

Brian Spindor
Engineering and Housing - Water Treatment
Fort Lewis, WA
Phone: (206)967-5237

Dr. Charles Stagg
Fort Polk
Phone: (318)535-6244

Robert Stark
Department of Engineering and Housing
Ft. Carson, CO
Phone: 691-4828 (autovan)

Chad Tennant
Citrikleen Military supplier and Consultant
Tenefly, NJ
Phone: (609)234-4229
(800)992-8226

Henry Weltman
General Dynamics Chemist
General Dynamics-Ft. Worth Division
Ft. Worth, TX
Phone: (817)777-3772

Captain Witt
Kelly Air Force Base
Phone: (512)925-8745

Appendix D

Site Visits

D.1 Fort Carson

Fort Carson, located in Colorado Springs, CO, is a large U.S. Army Base. It is very active and uses a large amount of solvents annually for equipment cleaning, maintenance, and rebuilding. The primary solvent used on the base is Stoddard solvent, purchased through off-site contractor Safety-Kleen. The spent Stoddard solvent liquid and sludge are released for removal and disposal through the Safety-Kleen contractor. The contractor collects, reclaims, recycles, and replaces the spent solvent every 4 weeks. The base has been using this system for 2 years, and is ready to sign the third-year contract.

As a result of consultation and testing by Reinhart Laboratories in Denver, CO, Citrikleen was not recommended for use.

A primary reason Fort Carson decided not to use Citrikleen was the likelihood of damage to treatment facilities. The cleaner could cause an increase in the pH level of the treatment system or create a high BOD, causing an upset in the system. The terpene cleaner tends to form emulsions with oils and greases that do not separate efficiently in the oil/water separator. Furthermore Citrikleen is very expensive at an estimated rate of $15.00/gallon. The management felt that misuse of the solvent could be expensive with regard to treatment and maintenance cleaning.

The decision to purchase Stoddard solvent through an off-site contractor such as Safety-Kleen was based on a number of issues. Through the use of an off-site closed-loop contractor, the installation is relieved of many responsibilities such as solvent treatment, collection, cleaning tank maintenance, and disposal. These responsibilities are under taken on by the contractor. Data for solvent cost, quantities, and number of tanks were collected, as was personnel cleaning time.

D.2 Fort Lewis

Fort Lewis, located in Tacoma, WA, is an active installation with a large population. Uses of solvents are primarily for equipment, vehicle, and small arms maintenance. Fort Lewis is currently investigating a number of different optio to degrease metal machinery in motor pools and vehicle maintenance facilities. Solvents under investigation include the Stoddard solvent contracts and the terpene cleaners. The cleaning procedures are listed below.

D.2.1 Central Wash Facilities

At the wash facilities, pressurized hoses are used to dislodge soil and remove grease from vehicles and tanks. No detergent or soap is allowed to aid in cleaning at the washrack. The rinsewater is sent through an oil/water separator and recycled to the water pumps to be reused. Besides going through the oil/water separator, this water is not treated.

D.2.2 Vehicle Maintenance

Water is heated to 160 °F and is applied at high pressure to clean vehicles. The rinsewater is then sent to an oil/water separator or the plate pack oil/water separator. This rinsewater goes in to the storm sewer.

Solvents are used to clean small parts and soils that are not removed by the hot water. Both Stoddard solvent and Citrikleen cleaner are used to clean parts.

Stoddard solvent is supplied by a contractor, WESCO Incorporated (same as Safety Kleen). After the solvent is spent, it is reclaimed, recycled, and replaced by the contractor.

D.2.3 Motor Pool

A number of solvents are used in Motor Pool facilities. They have not adopted one product, but are in the process of experimentation with a number of cleaners.

They are using Stoddard solvent, supplied by WESCO Incorporated, in maintenance and rebuilding. Cleaning procedures include hand-dipping and hand-wiping in a cold cleaning tank. A brush is also used to aid in cleaning procedures. The solvent is continuously recycled until it is completely spent. The supplier reclaims, recycles, and replaces the spent solvent with fresh solvent. The solvent is collected every 4 weeks.

Citrikleen HD is used in the Motor Pool to perform the same cleaning processes for which the Stoddard solvent is used, however, the solvent must be thoroughly rinsed off the

parts being cleaned. Citrikleen is also used in a spray cleaning procedure. The maintenance personnel made a spray tank apparatus from an old fire extinguisher. The parts are sprayed and wiped with a rag and then rinsed.

Citrikleen was used at full strength in all cleaning procedures. There was no collection system to receive the rinsewater; it is allowed to flow to storm sewers or land.

D.2.4 Wastewater Treatment Plant

The wastewater treatment plant has both primary and secondary treatment facilities. The operator of the plant did not witness any effects on the plant since the cleaner was implemented, probably due to its limited use. He indicated that there is a chance of the cleaner upsetting the plant if it is used base-wide.

D.2.5 Comments

Plant personnel expressed concern about the use of Citrikleen at Fort Lewis. It was indicated that the Citrikleen products break down the oil and greases, and they are not captured in the oil/water separator. This defeats the purpose of using an oil/water separator for treatment purposes, so more treatment will be required before water is released to outlets.

In order to keep water and oil from emulsifying, Fort Lewis has initiated a plan throughout the base to eliminate soap and detergents from vehicle washrack facilities. By keeping the oil and water from emulsifying, the oil can be more efficiently removed and collected for recycle and reuse. The collected oil is currently used by the school, and depending on the flash point of the oil, it can be sold for as much as $1.00/gallon. The average price per gallon is usually $0.20 to $0.40.

D.3 Washington National Guard

At the National Guard facility, located just outside Fort Lewis, Citrikleen is being used. The Environmental Division has approved the use of the product only on a trial basis.

Citrikleen is currently being used only over the washracks to clean tanks, trucks, and other large vehicles. It is applied to the vehicle using a high pressure spray unit purchased specifically for the use of Citrikleen. The unit dilutes the Citrikleen with hot water and is sprayed at high pressure onto the vehicle engine, wheels, brakes, and other parts in need of

maintenance. The unit has the option of being simply a hot water/high pressure sprayer or a steam cleaner.

At $6000 to $7000 per machine, 13 of these solvent applicator units have been purchased by the National Guard to use Citrikleen. Approximately 15 gallons of Citrikleen are used per month at the price of approximately $600 per 55 gallons (approximately $12/gallon).

Citrikleen is used for no other cleaning purposes, and the applications in which it is used are minimal. There have been no user complaints.

References

1. Annual Book of ASTM Standards, Petroleum Products, Lubricants and Fossil Fuels, Vol. 5.01, D56-D-1947, American Society of Testing and Materials [ASTM], 1988.

2. Arnts, Gay, "Sources, Lifetime, and Fates of Species in the Natural Troposphere," Atmospheric Chemistry-Fundamentals and Experimental Techniques, 1979.

3. Brulin Corporation, "Nature-Sol - Manufacturer Literature," Indiana, 1989.

4. C.P. Carpenter, et al., Toxic Application Pharm. Vol. 32 p. 282-297, 1976.

5. C.P. Carpenter, et al., Toxic Application Pharm. Vol. 44, p. 54, 1978.

6. A. Chavez, et al., "Substitution of Cleaners With Biodegradable Solvents, Phase II, Extended Performance Testing," Air Force Engineering and Services Center [AFESC], Tyndall Air Force Base, FL, November 1989.

7. Chemical Regulations Reporter, The Bureau of National Affairs, Inc. Vol. 4, No. 4, April 1988.

8. K. Chylla, G. Zipfel, "Economic Analysis for Minimizing Hazardous Wastes, Version 2.1: User's Manual," U.S. Army Construction Engineering Research Laboratory [USACERL] ADP Report N-90/07/ADA219670, March 1990.

9. K. Darnall, "Reactivity Scale for Atmospheric Hydrocarbons Based on Reaction with Hydroxyl Radical," Environmental Science and Technology, Vol. 10, pp. 692-6, 1976.

10. S. Dharmavaram, "Hazardous Waste Minimization Assessment: Fort Campbell, KY," USACERL Technical Report (TR) N-91/09, February 1991.

11. B.A. Donahue, "Solvent 'Cradle-to-Grave' Management Guidelines for Use at Army Installations," USACERL TR N-168/ADA137063, December 1983.

12. B.A. Donahue, "Used Solvent Testing and Reclamation, Volume I: Cold-Cleaning Solvents," USACERL TR N-89/03/ADA204731, December 1988.

13. B.A. Donahue, "Used Solvent Testing and Reclamation, Vol II: Vapor Degreasing and Precision Cleaning Solvents," USACERL TR N-89/03/ADA204732, December 1988.

14. S. Evanoff, "Alternatives to Chlorinated Solvent Degreasing - Testing, Evaluation, and Process Design," Process Technology, August 15-18, 1989.

15. S. Evanoff, H. Weltman, "A Methodology for Developing Alternatives to Halogenated Solvent Degreasing," General Dynamics Fort Worth, TX, 1989.

16. S. Evanoff, H. Weltman, "General Dynamics Forth Worth Division's Program to Eliminate Halogenated Solvents," General Dynamics Fort Worth, October 1989.

17. S. Evanoff, "Hazardous Waste Reduction in the Aerospace Industry," Chemical Engineering Progress, April 1990.

18. S. Evanoff, H. Weltman, T. Araiza, "Terpenes as Potential Substitutes for Safety Solvent," MIL-C-18718; General Dynamics, Fort Worth, January 1989.

19. Exxon Chemical, "Hydrocarbon Solvents," Material Safety Data Sheet, Exxon Chemical Company, February 1988.

20. C. Fromm, S.Budaraju, S.Cordery, "Minimization of Process Equipment Cleaning Wastes," EPA Seminar Publication - Solvent Waste Reduction, Chapter 5, September 1989.

21. A. Gordon, "The Chemist's Companion, A Handbook of Practical Data, Techniques, and References," New York, 1972.

22. M. Hayes, "Chlorinated and CFC Solvent Replacement in the Electronics Industry: The Terpene Hydrocarbon Alternative," The Third Annual Hazardous Materials Management Conference/West, Long Beach, California, December 1-3, 1987.

23. M. Hayes, "Naturally Derived Biodegradable Cleaning Agents: Terpene-Based Substitutes for Halogenated Solvents," The Fourth Annual Hazardous Materials Management Conference/West, Long Beach California, November 8-10, 1988.

24. Jacobs Engineering Group, "Waste Minimization Audit Report: Case Study of Minimization of Solvent Waste from Parts Cleaning and From Electronic Capacitor Manufacturing Operations," Pasadena, CA, 1987.

25. NOISH, "Criteria for a Recommended Standard - Occupational Exposure to Refined Petroleum Solvents," DHEW Pub. No. (NOISH) 77-192, 1977.

26. Organic Industrial Solvents-Handbook, Fifth Edition, New Jersey, 1980.

27. Penetone Corporation, "Citrikleen HD," Material Safety Data Sheet, Tenafly, New Jersey, October 1989.

28. Penetone Corporation, "Citrikleen - Manufacturer Literature," Tenafly, New Jersey, 1989.

29. "Regular Mineral Spirits Product Data," Material Safety Data Sheet, Unocal Chemical Distribution, 1989.

30. J. Resta, "Citrikleen Treatability Study, Environmental Assessment on the Use of Citrikleen at Aberdeen Proving Ground," Aberdeen Proving Grounds, Maryland, October 1988.

31. E. Rodzewich, "Source Reduction - Parts Cleaning," EPA Seminar Publication - Solvent Waste Reduction, Chapter 6, September 1989.

32. Safety-Kleen Corporation, "Features and Specifications of Parts Cleaners," Safety-Kleen Distributions, 1986.

33. R. Salvesen, "On-Site Reuse and Recycle of Solvents," EPA Seminar Publication - Solvent Waste Reduction, Chapter 10, September 1989.

34. R. Salvesen, "Treatment: Solvent Wastestreams," EPA Seminar Publication -Solvent Waste Reduction, Chapter 13, September 1989.

35. M. Sittig, "Stoddard Solvent," Handbook of Toxic and Hazardous Chemicals and Carcinogens, Second Edition, New Jersey, 1985.

36. F. Slavich, "D-Limonene Containing Degreasers," US Air Force Occupational and Environmental Health Laboratory Newsletter, Vol. 12., No. 1, March 1988.

37. T. Stanczyk, "What To Do With Hazardous Wastes: Regulations, Management, and Disposal," EPA Seminar Publication - Solvent Waste Reduction, Chapter 8, September 1989.

38. G. Weiss, "Stoddard Solvent," Hazardous Chemical Data Book, Second Edition, New Jersey, 1986.

39. P.M. Wikoff, "Biodegradable Solvent Substitution - Quick Look Report," U.S. Air Force, June 1988.

40. P.M. Wikoff, R.K. Schober, T.L. Harris, D.F. Suciu, R.E. McAtee, G.S. Carpenter, P.A. Pryfogle, J.M. Beller, "Substitution of Wax and Grease Cleaners with Biodegradable Solvents," Air Force Engineering and Services Center, September 1989.

41. M. Windholz, S. Budavari, Merck Index, "An Encyclopedia of Chemicals, Drugs and Biologicals," Tenth Edition, Merck & Co., Inc, 1983.

42 Winer, "Contributions to Ozone Formation," Atmospheric Chemistry-Fundamentals and Experimental Techniques, 1984.

43. D. Witt, "SA-ALC/MMETM Recommended Guidlines for Jet Engine Exterior Washing and Parts Cleaning with Terpene Based Products," Kelly Air Force Base, TX, June 1990.

44. Unocal Chemicals, "Mineral Spirits 75," Material Safety Data Sheet, Unocal Chemical Distributions, 1989.

45. Unocal Chemical, "Naphthol Spirits 66/3 Product Data," Material Safety Data Sheet, Unocal Chemical Distribution, 1989.

46. Unocal Chemical, "140 Solvent 66/3," Material Safety Data Sheet, Unocal Chemical Distribution, 1989.

47. U.S. Army, "Dry Cleaning and Degreasing Solvent P-D-680A," Federal Specification, February 16, 1989.

48. U.S. Army, "Water Quality Assessment of Citrikleen," Environmental Engineering and Housing, Fort Hood, TX, October 1988.

Acronyms

AFESC	Air Force Engineering and Services Center
ASTM	American Society of Testing and Materials
ATP	Adenosine Triphosphate
BOD	biochemical oxygen demand
CEAMHW	CERL Economic Analysis for Minimizing Hazardous Wastes
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CHO	chinese hamster ovary
COD	chemical oxygen demand
CPC	corrosion prevention compound
DOD	Department of Defense
EPA	U.S. Environmental Protection Agency
GD/FW	General Dynamics at Fort Worth, TX
GRAS	generally recognized as safe
HSWA	Hazardous and Solid Waste Amendments of 1984
IRC	Idaho Research Center
IWTP	Industrial Wastewater Treatment Plant
MSDS	Material Safety Data Sheet
NFPA	National Fire Protection Association
NLM	National Library of Medicine
NPDES	National Pollution Discharge Elimination Standards
NPV	net present value
NTP	National Toxicity Program

O&M	operations and maintenance
OLDS	ozone layer depleting substances
OSHA	Occupational Safety and Health Administration
R&D	research and development
RCRA	Resource Conservation and Recovery Act
STP	sewage treatment plant
TLV	threshold limit value
TSCA	Toxic Substance Control Act
USACERL	U.S. Army Construction Engineering Research Laboratory
USAF	U.S. Air Force
VOC	volatile organic compounds

DISTRIBUTION

Chief of Engineers
ATTN: CEMP-ZA
ATTN: CEHEC-IM-LH (2)
ATTN: CEHEC-IM-LP (2)
ATTN: CERD-L

CEHSC
ATTN: CEHSC-FU
ATTN: CEHSC-FB

US Army Engineer District
New York 10278
ATTN: Chief, NANEN-E
ATTN: Chief, Design Br
Pittsburgh 15222
ATTN: Chief, Engr Div
Philadelphia 19106
ATTN: Chief, NAPEN-E
Norfolk 23510
ATTN: Chief, NAOEN-D
Huntington 25701
ATTN: Chief, ORHED-H
Wilmington 28402
ATTN: Chief, SAWEN-PM
ATTN: Chief, SAWEN-E
Savannah 31402
ATTN: Chief, SASAS-L
Jacksonville 32232
ATTN: Envr Res Br
Mobile 36628
ATTN: Chief, SAMEN-C
Vicksburg 39180
ATTN: Chief, Engr Div
Chicago 60606
ATTN: Chief, NCCCO-R
ATTN: Chief, NCCED-H
ATTN: Chief, NCCPD-ER
ATTN: Chief, NCCPE-PES
St. Louis 63101
ATTN: Chief, ED-D
Kansas City 64106
ATTN: Chief, Engr Div
Omaha 68102
ATTN: Chief, Engr Div
Tulsa 74101
ATTN: SWTED
Fort Worth 76102
ATTN: Chief, SWFED-D
ATTN: Chief, SWFED-MA
Galveston 77553
ATTN: Chief, SWGAS-L
ATTN: Chief, SWGCO-M
Los Angeles 90053
ATTN: Chief, SPLED-E
San Francisco 94105
ATTN: Chief, Engr Div
Sacramento 95814
ATTN: Chief, SPKED-D
Far East 96301
ATTN: POFED-L

Seattle 98124
ATTN: Chief, NPSEN-FM
ATTN: Chief, NPSEN-DB-SE
ATTN: Chief, NPSEN-PL-WC
ATTN: Chief, NPSEN-PL-ER
Walla Walla 99362
ATTN: Chief, Engr Div
Alaska 99506
ATTN: Chief, NPAEN-G-M

US Army Engineer Division
New England 02254
ATTN: Chief, NADED-E
North Atlantic 10007
ATTN: Chief, NADEN-T
South Atlantic 30335
ATTN: Chief, SADEN-TE
Huntsville 35807
ATTN: Chief, HNDED-CS
ATTN: Chief, HNDED-SY
ATTN: Chief, HNDED-SR
Lower Mississippi Valley 39180
ATTN: Chief, PD-R
Ohio River 45201
ATTN: Chief, Engr Div
North Central 60605
ATTN: Chief, Engr Planning Br
Missouri River 68101
ATTN: Chief, MRDED-T
Southwestern 75242
ATTN: Chief, SWDED-T
South Pacific 94111
ATTN: Chief, SPDED
Pacific Ocean 96858
ATTN: Chief, Engr Div
ATTN: Chief, PODED-MP
ATTN: Chief, PODED-P
North Pacific 97208
ATTN: Chief, Engr Div

79th US ARCOM 19090
ATTN: AFKA-ACB-EN

7th US Army 09407
ATTN: AETTM-DTT-MG-EH

US Army Foreign Science & Tech Ctr
ATTN: Charlottesville, VA 22901
ATTN: Far East Office 96328

USA ARRADCOM
ATTN: DRDAR-LCA-OK 07801

West Point, NY 10996
ATTN: Dept of Mechanics
ATTN: Library

Ft. Belvoir, VA 22060
ATTN: Learning Resources Ctr
ATTN: CECC-R

US Army Garrison 94004
ATTN: SOCO-EHD-E

NAVFAC 22332
ATTN: Code 04

Ft. A. P. Hill 24502
ATTN: Facility Engineer

Ft. Leavenworth, KS 66027
ATTN: ATZLCA-SA

Ft. McPherson, GA 30330
ATTN: AFEN-CD

Ft. Monroe, VA 23651
ATTN: ATEN-FE-US
ATTN: ATEN-FE-E
ATTN: ATEN-AD

Aberdeen Proving Ground, MD 21010
ATTN: HSHB-ME-W
ATTN: NGB-ARI-E

US Naval Oceanographic Office 39522
ATTN: Library

Naval Training Center 32813
ATTN: Technical Library

Bolling AFB, DC 20332
ATTN: AF/LEEEU

Little Rock AFB 72099
ATTN: 314/DEEE

Tinker AFB, OK 73145
2854 ABG/DEEE

Building Research Board 20418

Dept of Transportation
Tallahassee, FL 32301

US Dept of the Interior 98304

Dept of Transportation Library 20590

Transportation Research Board 20418

Defense Technical Info. Center 22304
ATTN: DTIC-FAB (2)

100
+2
03/91