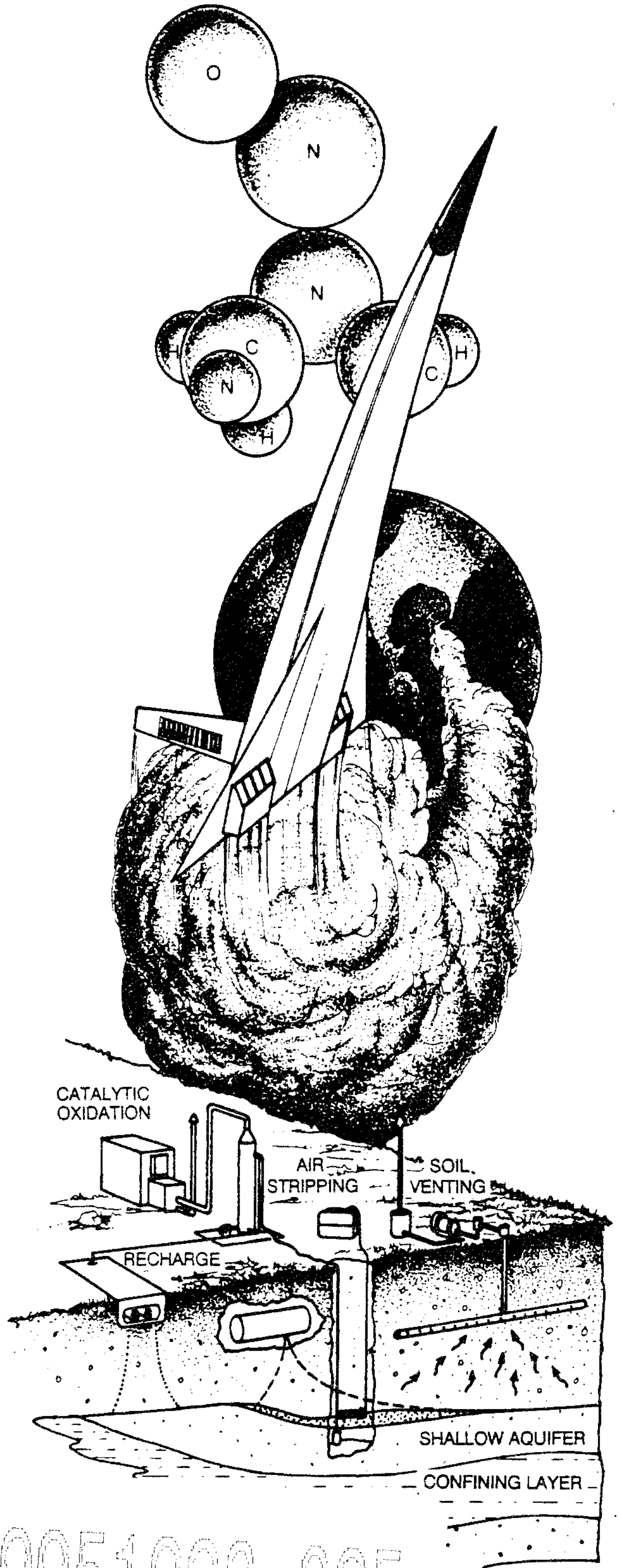


ESL-TR-91-38

SUBSTITUTION OF CLEANERS WITH BIODEGRADABLE SOLVENTS - PART 1

G.A. HULET, B.D. LEE, J.M. ESPINOSA, D.J. LARSEN, H.K. GILBERT, P.A. PRYFOGLE, L.S. BELLER, P.M. WIKOFF

IDAHO NATIONAL ENGINEERING LABORATORY
EG&G IDAHO, INC.
IDAHO FALLS, IDAHO 83415-2050

AUGUST 1995

FINAL REPORT

SEPTEMBER 1990 - AUGUST 1992

APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED

ENVIRONICS DIVISION
Air Force Civil Engineering Support Agency
Civil Engineering Laboratory
Tyndall Air Force Base, Florida 32403

NOTICE

PLEASE DO NOT REQUEST COPIES OF THIS REPORT FROM HQ AFCESA/RA (AIR FORCE CIVIL ENGINEERING SUPPORT AGENCY). ADDITIONAL COPIES MAY BE PURCHASED FROM:

NATIONAL TECHNICAL INFORMATION SERVICE
5285 PORT ROYAL ROAD
SPRINGFIELD, VIRGINIA 22161

FEDERAL GOVERNMENT AGENCIES AND THEIR CONTRACTORS REGISTERED WITH DEFENSE TECHNICAL INFORMATION CENTER SHOULD DIRECT REQUESTS FOR COPIES OF THIS REPORT TO:

DEFENSE TECHNICAL INFORMATION CENTER
CAMERON STATION
ALEXANDRIA, VIRGINIA 22314

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
August 1995

3. REPORT TYPE AND DATES COVERED
Final

4. TITLE AND SUBTITLE
Substitution of Cleaners With
Biodegradable Solvents, Part 1 of 2

5. FUNDING NUMBERS
DE-AC07-76ID01570

6. AUTHOR(S)
G. A. Hulet, B.D. Lee, J.M. Espinosa, D.J. Larsen,
H.K. Gilbert, P.A. Pryfogle, L.S. Beller, P.M. Wikoff

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Idaho National Engineering Laboratory
EG&G Idaho, Inc.
Idaho Falls, Idaho 83415-2050

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
HQ AFCESA
Tyndall AFB, FL 32403

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
ESL-TR-91-38
Part 1 of 2

11. SUPPLEMENTARY NOTES
Prepared for the United States Air Force through the U. S. Department of Energy

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Distribution Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

This report is divided into parts. Part 1 consists of the front matter, text, and Appendixes A through F, pages 1-224. Part 2 consists of Appendixes G through K, pages 225-380. The overall objective of this program, titled Substitution of Cleaners with Biodegradable Solvents, is to (a) replace the toxic chemicals currently in use with solvents that are biodegradable, can be processed at Air Force IWTPs, are less hazardous to personnel, and reduce or eliminate toxic wastes and other harmful emissions; (b) demonstrate at Tinker AFB, the solvents/processes identified or developed that meet the specified requirements; and (c) establish procedures for future testing of solvents for these applications. In Phase I, many candidate solvents were screened, and several were chosen for extended performance testing in Phase II. In phase III the most promising solvents from Phase II were tested with Air Force parts in full-scale processes. Phases II and III are reported here. The work was performed through the U.S. Department of Energy by EG&G Idaho Inc., personnel of the Idaho National Engineering laboratory.

14. SUBJECT TERMS
Biodegradable Solvents (U)
Toxic wastes (U), Solvents (U),
Cleaners (U)

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
UNCLASSIFIED

18. SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

19. SECURITY CLASSIFICATION OF ABSTRACT
UNCLASSIFIED

20. LIMITATION OF ABSTRACT
UL

NSN 7540-01-280-5500

(The reverse of this page is blank.)

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

PREFACE

This report was prepared by Idaho National Engineering Laboratory, EG&G Idaho, Inc., Idaho Falls, Idaho 83415-2050, DE-AC07-76ID01570, for the U.S. Department of Energy (DOE) and the Air Force Civil Engineering Support Agency (AFCESA), Suite 2, 139 Barnes Drive, Tyndall Air Force Base, Florida 32403-5319.

The overall objective of this program, titled Substitution of Cleaners with Biodegradable Solvents, is to (a) replace the toxic chemicals currently in use with solvents that are biodegradable, can be processed at Air Force IWTPs, are less hazardous to personnel, and reduce or eliminate toxic wastes and other harmful emissions; (b) demonstrate at Tinker AFB, the solvents/processes identified or developed that meet the specified requirements; and (c) establish procedures for future testing of solvents for these applications. In Phase I, many candidate solvents were screened, and several were chosen for extended performance testing in Phase II. In phase III the most promising solvents from Phase II were tested with Air Force parts in full-scale processes. Phases II and III are reported here. The work is being performed through the U.S. Department of Energy by EG&G Idaho Inc., personnel of the Idaho National Engineering laboratory.

This technical report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service, where it will be available to the general public, including foreign nationals.

This report has been reviewed and is approved for publication.

Phillip P. Brown
PHILLIP P. BROWN, 1LT, USAF, BSC
Environmental Engineer

Michael G. Katona
MICHAEL G. KATONA
Chief Scientist

Edward N Coppola
EDWARD N. COPPOLA, Maj, USAF
Chief, Environmental Compliance Division

Neil J. Lamb.
NEIL J. LAMB, Colonel, USAF, BSC
Chief, Environics Directorate

Accesion For
NTIS CRA&I ☑
DTIC TAB ☐
Unannounced ☐
Justification
By
Distribution /
Availability Codes

Dist	Avail and/or Special
A-1	

(The reverse of this page is blank.)

SUMMARY

Solvents and cleaners are used at the Air Force Air Logistics Centers (ALCs) to remove wax, grease, oil, and carbon from aircraft parts before repairing or electroplating. Most of these solvents are classified as toxic, and many cannot be treated in industrial waste treatment plants (IWTPs) that remove organic chemicals by biological processing. Process wastes must be shipped to approved treatment sites for disposal. Other solvents will soon be placed under strict EPA control because of their possible ozone-depleting effects.

The purpose of this program is to (a) identify solvents for removing wax, grease, and oil that can be replaced by biodegradable solvents, (b) identify the biodegradable solvents that can be used, (c) develop procedures for, and implement, their use, and (d) develop procedures for testing future solvents. The program is being conducted by EG&G Idaho, Inc. scientists and engineers of the Idaho National Engineering Laboratory.

All three phases of the program, Phase I, Solvent Selection and Performance Evaluation, Phase II Extended Performance Testing, and Phase III, Full-Scale Testing have been completed. Phases II and III are reported here.

Phase I, included five major tasks:

- Identification of the industrial processes at the ALCs in which solvents/cleaners are used, the procedures for their use, and the processes following their use such as rinsing, electroplating, etc.
- Development of quality assurance methods and procedures
- Identification of the available biodegradable solvents
- Literature review of process enhancement methods

- Screening of solvents to evaluate the performance of the biodegradable solvents for (a) removing wax, oil, grease, and carbon, (b) biodegradability, and (c) corrosiveness.

Phase I evaluation of the solvents chosen for screening was divided into four elements: biodegradability, solubility, cleaning efficiency, and corrosivity. If a solvent passed the first three evaluations, it was then tested for corrosiveness.

In Phase II, extended performance tests were conducted at the field test facility at Tinker AFB, Oklahoma. Tests included enhancement methods (effects of temperature, mixer agitation, and ultrasonic agitation); cleaning capacity for wax, oil, and grease as a function of solvent loading; rinsing and drying requirements; and impact on the heavy metal and biological treatment plant at Tinker AFB's IWTP.

Information on the toxicity of six biodegradable solvents selected for Phase II testing was obtained from the manufacturers and entered in a database.

The selected solvents were tested to determine their cleaning efficiency. Preliminary tests showed that process enhancement is needed if aircraft parts are to pass the "white glove" test. Hence, tests were conducted using ultrasonic and mixer agitation at various temperatures, with and without rinsing.

To test solvent performance, the selected solvents were loaded with various amounts of masking wax, carbonized oil/xylene, or hydraulic fluid and their cleaning efficiency was measured as a function of solvent loading.

Biological acclimation tests were started on Exxon Exxate 1000 loaded with oil/xylene. In the pilot-scale solids contact clarifier at Tinker AFB, the metal sludge floated to the surface. Subsequent jar tests showed that all of the selected solvents either float or disperse the sludge. However, flotation of the metal sludge can be prevented by adding aluminum sulfate, ferric ion, or magnesium ion. Magnesium ion addition allows the plant to be more susceptible to upsets from influent changes. Addition of these chemicals substantially increases the sludge output of the treatment plant and in some cases interferes with the removal of heavy metals and organics.

Fremont 776, added to the program during Phase III, did not float or disperse the sludge. It was added at the request of the Air Force and is currently in use at Tinker AFB.

Extended corrosion testing indicated that general corrosion occurred in some cases with enhancement techniques, especially with the aqueous solvents. None of the solvents selected for Phase II testing met the corrosion limit for magnesium, with all but Orange Sol corroding it heavily. To be safe, the corrosion information should be reviewed carefully before any of the solvents are released for general use. In all cases, no hydrogen embrittlement occurred. Fremont 776 was not tested for hydrogen embrittlement in this program.

In the ASTM work, analysis of the Phase I screening procedure and an 8-day protocol was completed. Protocol testing began by examining the selection of phenol as a test control compound. Also, tests were conducted to define the percentage of error associated with chemical oxygen demand (COD) measurements. The relative error increases as the lower limit of detection is approached and decreases at higher COD analyses. The error appears to be linear. Repeatability tests were also conducted, and COD and adenosine triphosphate (ATP) averages were plotted. The data from the TIC/TOC (total inorganic/total organic carbon) analyses had less variability than the data from COD and TOC analyses. A set of guidelines will be developed by the ASTM task group on Biological Effects and Environmental Fate. The set of guidelines will include the screening test, the 8-day test protocol and the 21-day test as steps in a series of logical events that industry can use in determining the biodegradability of solvents for use in individual waste treatment plants.

Research was conducted aimed at developing a sensor to be used in measuring soil concentration in solvent baths. The sensor was developed to the point that its sensitivity was high enough to detect day-to-day changes in nanopure water quality and that the speed of sound depends on individual ions. Results indicate that the sensor will be a viable method for qualitative determinations.

The solvents to be used in the full-scale tests were selected early in Phase III. They included:

- Exxon Exxate 1000
- Bio-Tek # 140 Saf-Solv
- Orange-Sol De-Solv-It
- 3-D Supreme
- Fremont 776.

The testing included cleaning Air Force production parts in a 100-gallon agitated tank at the Tinker AFB test facility, in a cabinet spray washer in Building 3001 and in a full-scale cleaning tank in the Building 3001 Gear Box Shop.

The Bio-Tek product was eliminated due to poor performance in the 100-gallon tank test. It removed much less soil than any of the other solvents in this test. 3-D Supreme out performed Fremont 776 in the cabinet spray washer tests, though the difference was not great. The organic-based solvents, Orange-Sol De-Solv-It and Exxon Exxate 1000 were not tested in the cabinet spray washer due to explosion hazards. Orange-Sol proved to be the best wax remover in the 100-gallon tank tests. Exxate 1000 also removed wax effectively. 3-D Supreme cleaned parts very well in the full-scale tests, removing oil, grease and carbon well enough for 81% of the parts to pass normal Air Force inspections. 100% of the parts with only oil and grease passed. When soiled with oil, grease and carbon, 64% of the Fremont 776 cleaned parts passed the inspections. The organic-based solvents did not remove the oil, grease and carbon as well as the water-based solvents. 20% of the Orange-Sol parts and 20% of the Exxate 1000 parts passed the inspections. The organic-based solvents did remove wax well. Some parts were successfully painted without blasting, a normal paint preparation step.

TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

TABLE OF CONTENTS
(Concluded)

Section Title Page

APPENDIX

LIST OF FIGURES

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

Figure Title Page

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Concluded)

LIST OF TABLES

(The reverse of this page is blank.)

SECTION I
INTRODUCTION

A. OBJECTIVE

Growing environmental and operational concerns have focused attention on solvents and cleaners in use at the Air Force Air Logistics Centers (ALCs). These chemicals, many of which are toxic, are applied in aircraft maintenance processes for removal of oil, grease, carbon, and wax during refurbishment. Solvents such as 1,1,1-trichloroethane cannot be treated in Industrial Waste Treatment Plants (IWTP) because of their impact on the biological treatment systems used for removal of organic compounds. Tightening governmental regulations will eliminate or severely restrict the use of other halogenated hydrocarbons because of their atmospheric-ozone depleting effects and cancer-related risks. Operations are being closely scrutinized and possibly terminated due to operational hazards and the solvents involved. The purposes of this program are to (a) identify solvents for removing wax, grease and oil that can be replaced by biodegradable solvents, (b) identify the biodegradable solvents, and (c) develop procedures for and implement their use.

This program has been performed in three phases: Phase I--Solvent Selection and Performance Evaluation, Phase II--Extended Performance Testing, and Phase III--Full-Scale Demonstration/Implementation of Solvents in Industrial Processes. In Phase I, reported in Reference 1, ALC processes were studied to determine which solvents should be replaced. Approximately 200 chemical companies were asked to submit samples to be tested as potential replacements. These samples were subjected to screening tests to determine their capabilities in the following areas: biodegradability, cleaning efficiency, and corrosiveness. Methods to enhance the solvents cleaning effectiveness were also investigated.

In Phase II, reported here, solvents selected in Phase I were put through an intensive performance-testing program. These tests included the following:

- Solvent cleaning capacity as a function of loading, using various component parts soiled with wax, grease or oil.
- Rinsing requirements.
- Drying requirements.
- Potential impact on the Tinker Air Force Base IWTP, including the heavy metals and organic material removal processes.
- Cleaning enhancement, including the investigation of temperature effects, mixer agitation and ultrasonic agitation.
- Solvent-loading probe research.

Tests determining the IWTP impact were performed using a 3.5-gal/min pilot-scale wastewater treatment system that modeled the IWTP processes. The effluent was analyzed to ensure compliance with the National Pollutant Discharge Elimination System (NPDES) requirements.

Solvents that performed well in the Phase II cleaning and corrosion tests were selected for Phase III testing. The work in Phase III, also reported here,started with the processing of Air Force production parts in a 100-gallon, hydraulically-agitated tank with each of the candidate solvents. These 100-gallon tank tests provided the final data necessary to select solvents for full-scale testing. Additional information was obtained from Tinker AFB personnel regarding potential applications of the solvents and processes. Two full-scale applications were chosen and tested: cleaning full-scale Air Force production parts in a Rotojet spray cabinet parts washer and in a hydraulically and mechanically agitated 300-gallon process tank. Following cleaning, inspectors from Tinker AFB examined the parts to see if any solvent residues were present that could affect further processing and usage of the parts.

B. BACKGROUND

Solvent cleaning is a surface preparation process designed to remove grease, oil, carbon, and soil from metal surfaces before further processing of the parts by inspecting, painting, or machining. Several types of solvent cleaning can be used--cold cleaning, immersion, or vapor degreasing. Cold cleaning consists of submerging the part in a tank of solvent, spraying the part with solvent, scrubbing the parts with solvent, or wiping solvent on the part. Some of the solvents used for cold cleaning and immersion are 1,1,1-trichloroethane, perchloroethylene, PD-680 (Stoddard Solvent), methylene chloride, Freon 113 and a 30 percent cresol/60 percent benzene solution. Cold cleaning includes paint removal.

Vapor degreasing, a widely used cleaning method at Tinker AFB, removes solvent-soluble soils and other entrapped soils from metals. The metal (at room temperature) is dipped into the solvent's vapor in a vapor degreaser (Figure 1). The vapor zone is controlled by the height of the tank and a cooling water jacket. The vapor condenses on the part; soluble and insoluble soil is carried away by gravity as the solvent drains. When the part reaches the temperature of the vapor, the process is complete. One major advantage of vapor degreasing is that the part always contacts clean solvent. At Tinker AFB, perchloroethylene is one of the solvents used for vapor degreasing.

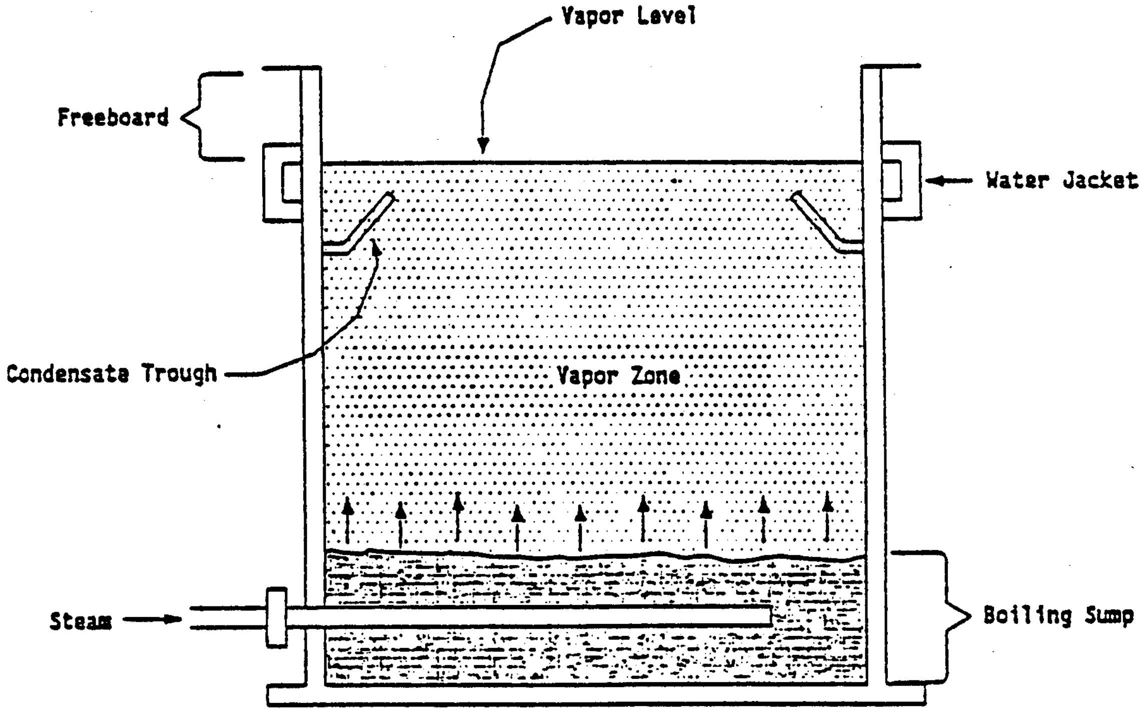


Figure 1. Schematic of a Vapor Degreaser.

Masking wax is used in electroplating various component parts. After being cleaned, the parts are dipped into the masking wax (Petrolite Amber B-Squared 175, melting point 175°F). A thick coating is deposited on the part. The wax is scraped off the areas that are to be electroplated and the surface of the scraped area is polished with pumice. Surface preparation is completed by hand cleaning with perchloroethylene. The part is then processed through the appropriate plating line for deposition of the required metal. After electroplating and rinsing, dipping the part again into the hot wax removes most of the wax; the thin layer remaining is removed by vapor degreasing.

The chlorinated hydrocarbons, including perchloroethylene, are preferred for this process because they have good solvency for organic materials and low rates of evaporation and because they are nonflammable, noncorrosive, and stable. These chlorinated hydrocarbons are not easily treated by the activated sludge system in the IWTP at Tinker AFB and they have recently fallen under scrutiny as potential hazards to the environment, workers, and the general population. The sludge (wax, dirt, oil, and grease) from the vapor degreaser is placed in drums and shipped to a RCRA-permitted disposal site.

Another environmental problem adding to operation costs is solvent loss by evaporation to the atmosphere, which occurs by four major routes for both cold solvent cleaning and vapor degreasing:

- Bath evaporation
- Solvent carryout and subsequent evaporation
- Waste solvent evaporation
- Spray evaporation.

Such emissions are hazardous to the operator and to the environment. Engineering controls and chemical replacement are two alternatives for controlling these emissions.

Many of these solvents will soon be strictly controlled by the EPA, making their use more expensive and less desirable. Chemical substitution with nontoxic or biodegradable solvents is the most favorable solution to the present problems with solvent cleaning. The substitution chemicals ultimately selected will be effective for removing greases, oils, carbon, and many other soils and may be treated in the IWTP. However, some of the solvents may require water rinsing of the parts after treatment to ensure a clean surface. In some cases, the solvents may cause oxidation on metal parts and may not clean small cracks and holes effectively due to high surface tension. These problems can be mitigated with additives to reduce surface tension and inhibit corrosion and oxidation. Some of these solvents may not be stable or may have a shorter life cycle than the chlorinated solvents.

Replacement solvents meeting the process criteria may require an enhancement process before they can clean efficiently. The processes available for enhancement can be divided into several general categories with several subcategories, including:

- Immersion Cleaning. Immersion cleaning is the simplest method of cleaning. A part is simply submerged in a tank containing the solvent until the soil is removed. To enhance this process, several methods are available: (a) air agitation, consisting of air diffusers in the tank forcing air through the solvent; (b) mechanical agitation, in which a mixer or pump increases the mass transfer of the solute into the solvent by breaking down the boundary layers; (c) tank heating to increase the solubility of the solute; and (d) ultrasonic agitation.

  Ultrasonic agitation, caused by high frequency pressure waves, causes two phenomena: microstreaming and cavitation. Microstreaming, simple eddy currents created by the standing pressure waves, works much like mechanical and air agitation, but the microstreaming cells create currents that are much more intense. High-energy ultrasound can also pull apart a liquid, leaving a cavity of vapor, dissolved gases or both. When these cavities collapse, they create extremely high, localized temperatures and pressures. Cavitation increases a solvent's cleaning effectiveness by introducing fresh solvent into hard-to-reach areas and by breaking soil loose. Ultrasonic agitation also greatly increases mass transfer rates. Its major drawbacks are equipment cost and operating costs.

- Spray Washers. Spray washers are available in several varieties including cabinet washers, conveyorized washers, and high-pressure steam washers. The basic principle of each is the same; the solvent is delivered to the part at high pressure. The high pressure breaks soil loose and forces solution into the cracks and crevices of hard-to-reach places. Cabinet sprayers use a principle similar to that of a dishwasher, with parts being cleaned in a batch mode. In conveyorized systems, a conveyor provides a continuous feed of parts to the washer.

  High-pressure steam systems are usually hand-held devices that operate in a batch mode similar to the cabinet washers, but at much higher pressures and temperatures. Cleaning solution may be added for more effectiveness, but this is required only if water alone will not do the job.

Many of these processes, including cabinet washers and high-pressure steam systems, are currently being used at the ALCs.

C. PHASE I RESEARCH SUMMARY

The Phase I research, described in Reference 1, was divided into the following six tasks:

1. Identification of the industrial processes at the ALCs in which solvents/cleaners are used, the procedures for their use and the processes following solvent use (rinsing, painting, etc.).

2. Development of quality assurance methods and procedures.

3. Identification of the available biodegradable solvents.

4. Determination of the biodegradability of these solvents.

5. Evaluation of process enhancement methods.

6. Screening of solvents to determine the performance of the biodegradable solvents for: (a) removing wax, oil, grease and carbon, (b) biodegradability, and (c) corrosiveness.

In the first task, using Air Force Technical Orders (TOs) and military specifications (MIL-SPECs), a computerized database was compiled to evaluate effects of replacement solvents and cleaners. The TO of major importance to this data system is Process Instructions Metal Surface Treatments to Meet Air Force Maintenance Requirements, (TO 42C2-1-7) (Reference 2). This manual contains information on the aircraft maintenance processes used at the five ALCs. Each process is divided into specific tasks (cleaning, masking, plating, etc.) and explained in detail. The information presented for each task includes the chemical solution used, its composition, its preparation, the procedure used to test it, process conditions, and how and where that task fits into the complete process. This information serves as the basic reference for the database system.

Along with the process information from the TOs, the information specific to each of the five ALCs was requested. These data, where supplied, include tank numbers, volumes, and the type and supplier of the solution in the tank. The data for Tinker, Kelly, McClellan, and Warner Robins AFBs have been entered into the database. In many cases, this ALC specific information does not match that specified in the TOs. However, where differences exist, both sets of information are contained in the database.

The solvent selection tasks were initiated with a request to approximately 200 chemical manufacturers for information on potential replacement solvents. Appendix A contains a list of the products chosen for evaluation. These solvents were subjected to a series of tests to screen for the most promising replacement candidates.

The Phase I evaluation of the solvents chosen for screening was divided into four subtasks:

1. Biodegradability
2. Solubility
3. Cleaning Efficiency
4. Corrosion Testing.

Figure 2 is a flow diagram of the solvent evaluation. As shown in the figure, each solvent was evaluated simultaneously for biodegradability, solubility and cleaning efficiency. The methods described in Reference 1 were used for the evaluations. If a solvent passed each of these evaluations, it was then tested for corrosiveness. A brief description of each of the evaluation criteria follows. Details of the evaluation criteria and analyses can be found in Reference 1.

- <u>Biodegradability</u>. For this program, solvents that could be biologically degraded to NPDES discharge limits by the activated sludge treatment system at Tinker AFB's IWTP were considered biodegradable. The measure of biodegradability is 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), a measure of the concentration of materials in the wastewater that are amenable to chemical oxidation. COD is also a criterion of the Tinker AFB NPDES discharge permit (the daily maximum allowable concentration

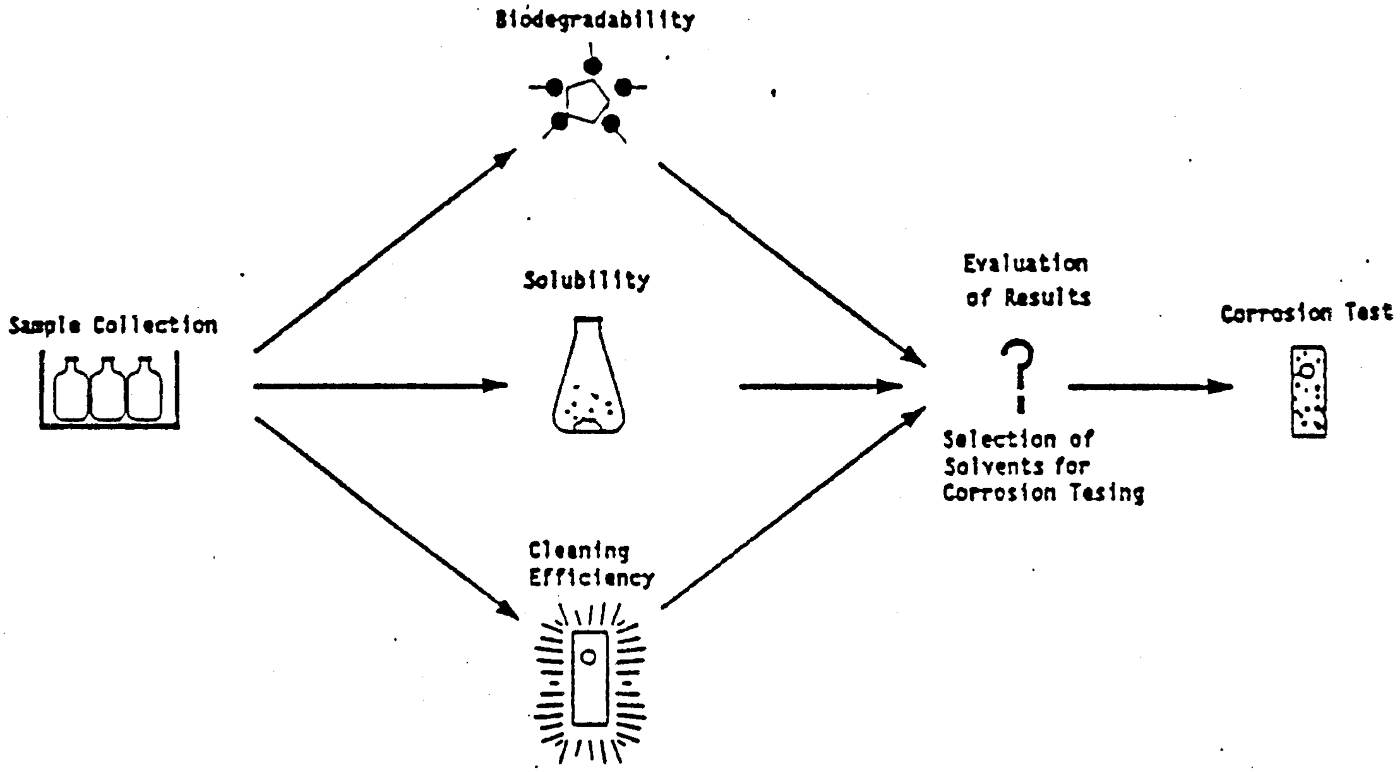


Figure 2. Flow Diagram of Solvent Evaluation Process.

is 150 milligrams/liter COD). A modification of ASTM's standard test method (<u>Biodegradability of Alkylbenzene Sulfamates</u>, Reference 3) was used to screen the biodegradability of the solvents proposed for substitution. Protocol changes were made to permit what was believed to be a more direct association of testing conditions to those conditions at the IWTP at Tinker AFB.

- <u>Solubility Testing</u>. Cleaning solutions work in two general ways to remove soil from a part. They can either solubilize the soil or they can break down the adhesion of the soil to the part, which allows the soil to be mechanically removed. The solubility of a solid in a liquid is determined by the intermolecular forces between the solute and solvent and also by the melting point and the enthalpy of fusion of the solute. The chemical compositions of many of the solvents are proprietary; therefore, the percent solubility was determined experimentally, using the method described by McCoy (Reference 4).

- Cleaning Efficiency. The cleaning efficiency test measured the ability of the solvent to remove wax, oil, or grease from metal coupons. The cleaning efficiency was defined as the average percentage of soil removed from the coupons or parts in a test run. The potential replacement solvents were evaluated for cleaning efficiency as a function of time. As a baseline, 1,1,1-trichloroethane, perchloroethylene, and PD-680 were used to clean the coupons. The solvents tested included both aqueous (water containing) and nonaqueous solvents.

- Corrosion Performance of Biodegradable Solvents. The purpose of this task was to determine the corrosion characteristics of the treated metals in the replacement solvents. The initial corrosion trials were total immersion tests as recommended in ANSI/ASTM F 483-77 (Reference 5). Only solvents that met the biodegradability and solubility criteria and were adequate in the initial cleaning performance tests were evaluated. The metals (Table 1) were selected from those commonly serviced at Tinker AFB. An arbitrary cutoff limit of 0.3 mils/year was established for both general and pitting types of corrosion.

Approximately 40 solvents passed the cleaning and biodegradability tests (Table 2). The solvents that were applicable to all of the Table 1 metals were corrosion tested. Those solvents that could be used with only a limited number of the metals were not included in the corrosion tests. The solvents tested are listed in Table 3. Reference 1 reported that all of the solvents passed the corrosion test, although discoloration was noted on some coupons. Later analysis of the data and technique indicated that the performance of some of the solvents was questionable. Reportedly, coupons that gained weight during the test were listed as having no corrosion. No record was kept of those coupons that gained weight so a full reanalysis of the data could not be performed.

TABLE 1. METAL SAMPLES USED FOR CORROSION TESTING.

Copper, CDA110 ETP
Nickel 200
Aluminum, AL2024
Steel, C4340
Aluminum AL7075
Aluminum AL1100
Stainless, 410
Admiralty Brass, CDA443
Carbon Steel, C4340, C1020
Stainless, 310S
Inconel 750
Monel MK-500
RMI Titanium
Waspaloy Alloy
Magnesium AZ31B

TABLE 2. SOLVENTS PASSING THE CLEANING AND BIODEGRADATION TESTS.

3-D Supreme
Bio-Tek Inc. 134 Hi-Solv
Bio-Tek Inc. Safety Solvent
Degreaser
Brulin CL-500
Calla Chemical Corp. Calla 301
Crowley Chemical Company Methyl Naphthalene #5
Dober Chemicals Inc. Fabulene
Elgene Chemicals Inc. Fabulene
Elgene Chemicals Inc. #22 Skidoo
Exxon Chemicals Exxate 600
Exxon Chemicals Exxate 700
Exxon Chemicals Exxate 800
Exxon Chemicals Exxate 900
Exxon Chemicals Exxate 1000
Exxon Chemicals Exxate 1300
Exxon Chemicals Norpar 13
Exxon Chemicals Norpar 15
Exxon Chemicals Aromatic 150
Exxon Chemicals Exxsol D80
Exxon Chemicals Exxsol D110
Exxon Chemicals WS2443
Frederick Gumm Chemicals Clepo 136-R
Graymills Corp. Aquatene 571
Graymills Corp. Aquatene 581
Huntington LHTS
International Products Co Micro
Kiesow International Corp. Ekasit E-231
Kiesow International Corp. Ekasit S-261
Magnuson Products Permag #406
Mitchell-Bradford, International MI-Clean 100
Mitchell-Bradford, International MI-Clean 14
Mitchell-Bradford, International MI-Clean 31
Mitchell-Bradford, International MI-Clean 59
Oakite Products, Inc. Oakite 162
Oakite Products, Inc. Oakite 2327
Oakite Products, Inc. Oakite 24
Oakite Products, Inc. Oakite Anoprep
Oakite Products, Inc. Oakite HD 126
Orange Sol Inc. De-Solv-It
Panther Chemical Co. RR 50
Parker Chemical Parco Cleaner 2033
Parker Chemical Parco Cleaner 2053
Patclin Chemical Co. #309
Patclin Chemical Co. #348
Progress Chemical Inc. AC-1
Triton Hemo-Sol

TABLE 3. SOLVENTS PASSING THE CORROSION TESTS.

3-D Supreme
Bio-Tek Inc. 134 Hi-Solv
Bio-Tek Inc. Safety Solvent Degreaser
Calla Chemical Corp. Calla 301
Crowley Chemical Company Methyl Naphthalene #5
Exxon Chemicals Exxate 600
Exxon Chemicals Exxate 700
Exxon Chemicals Exxate 800
Exxon Chemicals Exxate 900
Exxon Chemicals Exxate 1000
Exxon Chemicals Exxate 1300
Exxon Chemicals Norpar 13
Exxon Chemicals Norpar 15
Exxon Chemicals Aromatic 150
Exxon Chemicals Exxsol D80
Exxon Chemicals Exxsol D110
Exxon Chemicals WS2443
Orange Sol De-Solv-It
Triton Hemo-Sol

Six solvents, Exxon Exxate 1000, Triton Hemo-Sol, Calla 301, 3-D Supreme, Orange Sol De-Solv-It, and Bio-Tek 140 Safety Solvent, were selected for Phase II testing. Triton Hemo-Sol was later dropped because of its low flash point. The data generated for these solvents in Phase I are in Appendix B.

SECTION II
WORK SCOPE FOR PHASES II AND III

A. PHASE II SCOPE

In Phase II of the solvent substitution program the solvents selected in Phase I were tested on a 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. The new equipment included a 1-cubic-foot tank that could be heated to 200°F for coating parts with wax, a 100-gallon (379-liter) tank equipped with ultrasonics, a mixer and a heater for solvent testing, a 100-gallon rinse tank equipped with an agitator and a heater, and a drying area. Solvent cleaning performance and enhancement methods were tested with this equipment. The biodegradability of the loaded solvents was tested in the pilot water-treatment facility described in Reference 6. The tasks to be completed in Phase II were:

- Human Toxicity Data Gathering
- Enhancement Method Testing
- Solvent Performance Testing
- Biological Acclimation Testing
- Extended Corrosion Tests
- ASTM Procedure Evaluation
- Sensor Development.

A brief description of each of the Phase II tasks follows.

- Human Toxicity Data Gathering. Replacing chlorinated solvents with substances that are biodegradable but potentially more hazardous to humans will not solve the problems facing the Air Force. To avoid such a situation, existing toxicology 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. These data were collected and evaluated for further screening of the solvents. The data for solvents tested in Phase II are included in Appendix C.

- 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 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 attractive at the pilot scale 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 volatile organic compound emission problem associated with air agitation. Investigation of ultrasonic applications in large tanks was required before recommendation for full-scale testing.

- 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 milliliters of the solvent heated to the temperature determined in the previous task and mixed or agitated. Preweighed coupons were soiled with wax, grease or oil and dipped in heated solvent for a specified time, until the soil was no longer removed. The coupons were then dried and weighed to determine the amount of soil removed. This indicated the approximate amount of soil that could be removed in the pilot-scale testing. This approximation was used in the pilot-scale life expectancy testing.

Next, a 100-gallon tank was filled with solvent and heated to the solvent manufacturer's recommended temperature. Ten parts, coated with the soil to be tested, were cleaned in the solvent to determine the solvent's initial cleaning efficiency. The solvent was loaded to increasing percentages of its capacity (as estimated from the beaker tests) 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 parts-cleaning process. In this way, cleaning efficiency was determined. This procedure was performed for 0, 25, 50, 75 and 90 percent of the solvent's capacity.

- Solvent-Rinsing Requirements. The solvents currently used for vapor degreasing and for removing wax, oil and grease vaporize at room temperature. Therefore, the parts do not require rinsing or drying. However, the replacement solvents, especially those composed of solids dissolved in water, may require rinsing, drying or both to remove the solvent and any remaining soil. 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 removed as a function of time in a spray chamber and an agitated rinse tank.

- Biological Acclimation. The objective of this task was to determine the impact of introducing the new solvents into the IWTP pilot-plant (i.e., metal precipitation, microbe acclimation and toxicity). Typical activated sludge basin parameters were measured to track the changes imposed on the basin. After a test, the pilot plant was emptied and rinsed. Fresh activated sludge from Tinker's activated sludge system was introduced and a new sludge blanket was built in the solids contact clarifier.

The major components of the solvent were tracked throughout the system as part of the task.

The pilot-scale biological acclimation tests were initiated but not completed in fiscal year 1989. However, due to a change from aluminum sulfate to ferric chloride (added to prevent flotation of the sludge in the solids contact clarifier) the previously performed Exxate 1000 run had to be redone. The change to ferric chloride was made because iron is a better coagulant than aluminum or magnesium, therefore requiring a lower concentration. Also, ferric ion can be added after the sulfide and ferrous ion addition, instead of at the front of the plant. Jar tests were conducted before each run to determine the concentration of ferric chloride required to prevent the solvent from affecting the sludge bed in the solid contact clarifier (SCC).

Initially, the pilot-scale biological acclimation runs were scheduled to last for three sludge ages (approximately 21 days). However, the periods were later shortened to approximately 8 days, 3 days to establish a system baseline, followed by 5 days of solvent flow. For runs in which the system performance was marginal, the run time was to be extended to allow for the gathering of more determinant data. The 5 days of solvent exposure were considered sufficient because the IWTP would not see a continuous flow of the solvents. A solvent would be present only intermittently as solvent tanks were drained upstream of the IWTP. The microbes would not have 21 days to become acclimated to the solvent.

The solvents to be tested in the acclimation tests changed from those selected at the end of Phase I for several reasons. First, the Phase III 100-gallon tank tests were performed prior to the start of pilot-scale bioacclimation tests. Data from these tests were examined and the solvents were prioritized for full-scale implementation. Biotek's #140 Saf-Solv performed poorly in the 100-gallon tests and was eliminated as a candidate for full-scale implementation, with the concurrence of the Air Force contract representative. Because the Saf-Solv was removed from further full-scale testing, the Air Force agreed to delete it from the bioacclimation tests.

A second change was made at the Air Force request. Calla 301 was eliminated because of its toxicity. It contains 2-butoxyethanol, which can cause damage to the kidneys, liver, and bone marrow. The Air Force representative was concerned that restrictions on products containing 2-butoxyethanol might soon be instituted, eliminating Calla 301 from use in Air Force programs after it had been taken through the Phase II and III tests.

The Air Force requested that a different solvent, Fremont 776, be substituted into the pilot-scale bioacclimation and Phase III tests in place of Calla 301. The Fremont 776 is presently in use in the Roto-Jet cabinet spray washer used for cleaning fuel assemblies. As a preliminary, the Fremont 776 was subjected to the 6-hour biodegradability test and then the extended corrosion tests. Following those, it was initiated into the pilot-scale biological acclimation trial and Phase III test sequence. Additionally, when time allowed, the soil-loading tests were performed to provide a means for economic comparison.

Eliminating the Biotek #140 Saf-Sol and the Calla 301 and adding the Fremont 776 produced the final list of solvents for the pilot-scale bioacclimation and Phase III tests. This final list of candidate solvents contained 3-D Supreme, Exxate 1000, Orange Sol De-Solv-It, and Fremont 776.

- Extended Corrosion Tests. The objective of this task was to determine the hydrogen embrittlement effects of the replacement solvents. The tests were performed according to the ANSI/ASTM procedure F 519-77, Mechanical Hydrogen Embrittlement Testing of Plating Processes and Aircraft Maintenance Chemicals (Reference 7). 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 (Reference 5). This is the same ANSI/ASTM procedure as that was used in the Phase I corrosion tests except enhancement was added. Enhancement methods included tests with ultrasonics and mixer agitation at temperature.

- ASTM Procedure Evaluation. This task was directed at standardizing the procedure used in Phase I to determine solvent biodegradability. This will allow use of the procedure at other installations with similar requirements. Although these procedures are based on accepted methodology, this effort provided sufficient data to determine the relative sensitivity of the testing protocol. The procedures have been discussed in ASTM meetings and ASTM committee E-47, providing a perspective on our activities in relation to similar programs at other organizations and government agencies. An EG&G Idaho, Inc. representative acted as task committee chairperson for the November 1990 E-47 committee meeting. In this meeting, the development of ASTM guidelines including applicable portions of this program's biodegradability procedures was pursued. Due to the many, varied means of biodegrading chemicals, only guidelines were discussed or will be developed, rather than a more specific and binding ASTM method.

- Sensor Development. The objective of this task was to understand and quantify the effects of "spheres of influence" of the various solutes in water and in organic solvents for use in an on-line sensor. The speed of sound in a solution is an easily measured function of solute concentration, which extends well into the parts-per-million regime. The time for sound to traverse a fixed flight path is an increasing linear function of solute concentration. This inverse dependence of acoustic velocity on solute concentration implies a relaxation of the solvent's intermolecular forces (which determine the speed of sound) with increasing solute concentration. Previous work shows that the magnitude of the effect depends on several properties of the solute in addition to number density. The slope and magnitude of the time-vs-concentration line of polar solutes are different from that of organic solutes such as glucose. Yet, glucose's response differs from that of sodium borate, which has essentially the same molecular weight. The various effects can be lumped into a "sphere of influence" of the solute in a given solvent. These differences in response imply that the effect may be useful as an on-line qualitative and quantitative analytical tool.

The measurements were performed by serial dilution, in fully temperature-controlled baths. The speed of sound was measured as the time required for short pulses of ultrasound to traverse and be reflected in turn from two reflectors placed a fixed distance apart. Each measurement was compared to the velocity measured in the pure solvent.

Based on the theoretical and experimental discoveries in this program, further efforts in this field could yield an on-line probe that could provide temperature-independent solute concentration and composition data. Phase III did not pursue these discoveries further, although a program to do so is recommended.

B. PHASE III SCOPE

Because of Phase II program delays, the biological acclimation and IWTP impact task from Phase II was not completed prior to the commencement of Phase III. Considering that solvents that could perform well in Phase III tests would be useful to the Air Force even if they could not be processed through the IWTP, the Air Force agreed to allow Phase III testing to start before Phase II was completed. The Phase III tasks were as follows:

- 100-Gallon Tank Tests. Large-scale tests for candidate solvents with enhancement, cleaning Air Force production parts.

- Cabinet Spray Washer Tests. Application of solvents in cabinet spray washer cleaning Air Force production parts.

- 300-Gallon Tank Tests. Full-scale tests for candidate solvents in an Air Force cleaning line with enhancement engineered to fit the tank.

- Oil and Grease Tests. Determination of the impact of loaded solvent processing on oil and grease in plant effluent.

A description of the scope of the Phase III tasks is as follows:

- 100-Gallon Tank Tests. The objective of the 100-Gallon Tank Tests was to determine if the candidate solvents could clean Air Force parts. In the 100-gallon tank tests, a turbo washer manufactured by Bowden Industries was installed in the tank previously used for the large-scale loading tests. Air Force parts were cleaned in the bath, using the white-glove test and visual inspection as the criteria for successful soil removal. Initial runs were used to establish the method that was used in the subsequent tests.

- Cabinet Spray Washer Tests. Not all of the solvents were included in the cabinet spray washer tests. The manufacturer of the spray washer, Roto-Jet Inc. was contacted to determine if the organic solvents could be safely run in a modified version of the cabinet spray washer currently in use at Tinker AFB. Subsequent discussions with several Roto-Jet personnel, including a company vice president, determined that organic solvents would create an explosion hazard that could not be corrected by any modification that Roto-Jet would recommend. As stated, Fremont 776 was already used in the Roto-Jet, leaving only 3-D Supreme to be tested.

The parts typically cleaned in the cabinet spray washer are fuel controls being prepared for disassembly. Loose soil is removed to prevent contamination of the internal portions of the equipment during refurbishment. A visual inspection is sufficient to determine whether the unit is clean enough. In the 3-D Supreme tests, production assemblies were cleaned following the methods normally used in the shop. Cycle times were varied initially to determine what effects they might have. Later runs were held to 20 minutes. Inspections were performed by shop personnel.

- Full-Scale Tests. Mountain States Energy, Inc. (MSE), of the Idaho National Engineering Laboratory was contracted to design an ultrasonic enhancement system to be installed in a large-scale cleaning tank for the Phase III full-scale tests. MSE conducted a study of the methods and technology available and determined that currently, ultrasonics is not a practical cleaning enhancement method. They determined that further research is required to make ultrasonics feasible for large-scale applications. When used with organic solvents in large tanks a large percentage of the agitation energy is absorbed by the gasses dissolved in the solvent. To compensate for this energy absorption, the number of the ultrasonic transducers must be increased greatly, making the cost of the equipment prohibitive. A copy of the MSE report is included in Appendix D. Based on these findings, MSE was asked to design a mechanical agitation system for the Phase III full-scale implementation tests (Appendix D).

The Phase III full-scale tests were conducted in a 300-gallon tank in the Gearbox Shop in Building 3001. The objective of these tests was to demonstrate the cleaning ability of selected solvents on a full scale. The full-scale tests had been planned to take place in the 1850-gallon tanks in the computer-controlled cleaning line. Enhancement equipment was designed accordingly. A design review meeting was held that included Air Force and EG&G Idaho personnel to cover the proposed design and the test methods. At that meeting Air Force personnel decided that the tests should not be run in the cleaning line, but that an alternate site should be selected. After considerable delay, a new location, the 300-gallon tank, was chosen and enhancement equipment was redesigned. The four remaining candidate solvents were tested in a manner similar to the 100-gallon tank tests, cleaning actual Air Force production parts. These parts were then subjected to the normal Air Force inspection sequence with special attention given to whether any solvent residue was affecting the inspection. Parts were also processed further to determine whether properties such as paint adhesion were influenced by the solvents.

- <u>Oil and Grease Tests</u> . The objective of the oil and grease tests was to determine whether the addition of loaded solvent to the influent of the pilot-plant increased the oil and grease in the effluent. Very late in the program, the Air Force requested that these tests be run. Only a portion of the Fremont 776 bioacclimation test remained, so data were gathered during the final days of that test. Samples were analyzed using a modified version of the Partition-Gravimetric method, ASTM Method 503 A from Reference 8.

SECTION III
PROCEDURES

A. PHASE II PROCEDURES

The procedures used to complete the laboratory tasks of Phase II are included in this section. More detail can be obtained by referring to the ASTM method or MIL-SPEC referenced in the descriptions.

1. Cleaning Efficiency

The soils used to coat the coupons and aircraft parts were wax, hydraulic fluid with carbon black, molybdenum disulfide grease with carbon black, and a carbonized oil/xylene mixture. The wax was Petrolyte Amber 175 B-Squared heated to approximately 200°F. The parts or coupons were immersed in the hot wax until they were at the temperature of the wax. The immersion time depended on the size of the part; the disappearance of the white (amber) wax solid at the surface of the wax where the part was immersed indicated that the desired temperature had been reached. At this time, the part or coupon was slowly removed from the hot wax, such that only a thin film of wax remained. If holes or notches were in the part, it was tipped so that the wax poured out. The part or coupon was hung on a rack and allowed to cool.

The oil/xylene was prepared according to Mil-C-43616B (Reference 9). The procedure requires concentrating the oil to 30 percent of its original weight. In talking to personnel who prepared the procedure (Phase I Report, Reference 1), during Phase I the oil was concentrated at 450 to 500°F in a shallow pan and required 4 to 10 days. In Phase III however, the 30 percent concentration was not achieved; the oil was concentrated for 3 to 4 weeks but reached only 65 to 85 percent of its original weight. The constitution of the oil obtained for Phase III seems to be significantly different from the Phase II oil. The oil, concentrated to 65 to 85 percent, was used to prepare the soil. The coupons or parts were dipped in the carbonized oil/xylene, excess was allowed to drip off, and the coupons or parts were baked for 2 hours at 120°C according to the MIL-SPEC.

The molybdenum disulfide and the hydraulic fluid soils were prepared according to MIL-C-85570B (Reference 10). The coupons or parts were painted with the grease and dipped in the hydraulic fluid. All were baked at 120°C according to the directions in the MIL-SPEC.

Each coupon or part was cleaned with trichloroethane in a laboratory ultrasonic cleaner, rinsed with acetone, dried, and weighed before application of the soil. Following application and treatment as specified by the MIL-SPEC, the coupon with the soil was weighed. In this manner, the soil initially on the coupon, the soil removed, and the cleaning efficiency of the solvent was calculated. Cleaning efficiency (as percent) is the ratio of soil removed to the soil initially on the part, times one hundred.

2. Enhancement Testing

Enhancement testing was completed using 1/2-inch carbon steel nipples, designated as parts. A number of nipples could be prepared and tested without the variations in shape and size that would occur among the aircraft parts. However, the threads and inside walls were representative of the difficult-to-clean areas of the actual parts. Enhancement testing was conducted in ultrasonic tanks (12 x 10 x 14 inches). Ten liters of the solvent at the desired concentration was placed in the tank and brought to test temperature. The tanks were equipped with variable-wattage ultrasonics and variable-speed mixers. The ultrasonics or mixers were set at test conditions. If required when using ultrasonics, a cooling loop containing propylene glycol was circulated through the solution to remove the heat generated by ultrasonics. During each test, 12 parts were immersed for a timed interval of 10, 20, and 30 minutes. At each time, four parts were removed. Two parts were rinsed under cool running tap water and all were hung to dry over low heat (the heat was low enough that the wax would not melt off the part).

3. Solvent Loading Capacity

Solvent loading capacity was tested using 500 milliliters of the solvent in a glass beaker at the optimum conditions selected from enhancement testing. Ultrasonic agitation was provided by immersing the beaker in solvent in the ultrasonic tank and setting the appropriate wattage. Mixer agitation was tested by stirring with a magnetic stir bar on a hot plate. Ten stainless steel coupons (1 x 2 x 1/16 inch) were coated with soil, immersed in the solvent for the desired time, and the cleaning efficiency determined. This was repeated until cleaning efficiency started to decrease or a great deal of data scatter occurred. At this time, the solvent was considered to be loaded. The total weight of soil required to load the solvent was calculated and used as the estimated loading capacity of the solvent for performance testing of 379 liters (100 gallons) of the solvent. Solvent performance was tested by cleaning parts coated with the selected soil. For the water-based solvents, the parts were soiled with only hydraulic fluid or molybdenum disulfide grease. In testing the performance of the organic solvents, the parts were coated with either wax or the carbonized oil/xylene soil. The performance of the solvent was tested on each soil separately. The performance of the solvent was tested on new solvent, as a function of solvent loading, and after the solvent had remained at a given loading for approximately 24 hours. The solvent was artificially loaded by adding the required amount of soil according to the estimated loading capacity. Solvent performance testing was conducted at 25, 50, 75, and 90% of the theoretical loading. However, if cleaning was not efficient at lower loading, performance testing was stopped. In Phase I, it was found that the organic solvents were not as effective as the water-based solvents in removing light oils and greases. Conversely, the water-based solvents would not remove carbonized oil/xylene or wax.

4. Rinsing Tests

Rinsing tests were conducted as a function of time using immersion jets and spray jet. The immersion jets were in immersion tanks, and the spray was representative of a spray chamber. The parts were stainless steel nipples measuring 2.5 x 5.1 centimeters (1 x 2 inches); stainless steel was used to prevent any weight changes due to rusting. The preweighed parts were soiled with the respective soils, weighed, and immersed in the solvent at the conditions found in enhancement testing. The parts were rinsed for the selected duration, dried overnight over a hot plate, reweighed, and the amount of soil removed was calculated.

5. Drying Tests

Drying tests were conducted to determine the time required to dry residual solvents off the parts. Again, stainless steel nipples were used. The drying apparatus consisted of a blower that blew hot air across a 20.3 centimeter (8-inch) pipe in which the parts were hung for the required duration and then reweighed. The amount of solvent remaining on the part was calculated.

6. Biological Acclimation

Biological treatment of the solvent was tested using the pilot field verification unit at Tinker AFB. Spent (soil-loaded) solvent was pumped into the 170-liter (45-gallon) equalization tank at a 1:600 dilution with the influent wastewater from the equalization tank of the Tinker AFB IWTP. Treatment included sodium sulfide/ferrous sulfate treatment for metal removal (described in Reference 6) and biological treatment with an activated sludge system for degradation of the organic compounds (also described in Reference 6). The testing periods ranged from 10 to 20 days. Each run was composed of a metal sludge blanket building period, followed by a biological baseline period and the actual solvent testing period.

The metal sludge blanket building period lasted from 5 to 7 days. The duration was dependant on metal concentrations found in the waste stream. Due to low hexavalent chromium concentrations in the influent, sodium dichromate was added at the equalization tank (E-tank), yielding a hexavalent chromium concentration of 5-8 milligrams/liter. A sludge blanket depth above sixteen inches and below the overflow was the target range. An effluent containing only small amounts of pin floc and of low turbidity was found to be ideal. Baseline testing was started when the SCC sludge blanket was of adequate depth and the effluent was acceptable.

The baseline period consisted of filling the pilot-scale activated sludge (AS) system with biological sludge obtained from Tinker AFB's activated sludge basin. When an adequate amount of biological sludge had been brought to the pilot plant and flows had been started, the baseline period was begun. The baseline period was used to monitor the activated sludge microorganisms while maintaining a stable biological system. Sampling intervals for the baseline run were in six-hour rotations. Samples were taken from the E-tank, the SCC effluent, the AS basin, the return activated sludge (RAS) line and the final clarifier (FC) effluent. Samples were analyzed for solids content, mineral content, total metals, biological activity and nutrient content. Analyses included COD, adenosine triphosphate (ATP), phenol, phosphate, dry weight, volatile weight, hexavalent and total chromium, cadmium, iron, zinc, copper, lead, and nickel. Total analysis, however, was not conducted at all points listed above, but was directed at monitoring the specific process. Flow and pH were monitored throughout the field verification unit. Methods used for the analyses can be found in Appendix E.

A Lotus spreadsheet was set up to calculate various operational parameters by entering basic physical and chemical parameters measured. Data from specific physical and chemical analyses were entered into designated spreadsheet cells and system control information was calculated by spreadsheet formulas using the data entered. A completed data sheet was saved, either with active formulas intact or with a range/value conversion to freeze numeric data as displayed. These spreadsheets were used to follow the loss or gain of solids in the AS system. Similarly, loading and removal efficiencies were tracked for CODs, nutrients, and specific chemicals through the AS system. The data sheets accumulated over several days of operation were sorted to evaluate trends in the AS system (i.e., determine stability or possible upset conditions).

After an adequate baseline period was completed and the plant had stabilized, the solvent testing period began. The solvent was fed into the pilot E-tank for a minimum of 5 days. Analyses were performed as during the baseline period. The run was extended if the run results were marginal and more data were required to make the final assessments.

After each solvent run was completed the pilot plant was drained and scrubbed, to remove any residual solvent that may have adsorbed to the inner surfaces of the different tanks throughout the pilot system. After the plant was cleaned, flow was restored and the sludge building period for the next biodegradation run was started.

7. ASTM Biodegradability Procedure Evaluation

A series of tests was conducted to determine the potential impact of air sparging and its relation to COD loss during the 6-hour biodegradation screening tests. The air sparging tests were similar to the biodegradation screening tests (Reference 1), except that no microorganisms were added to the test column solution. Therefore, loss of COD over the 6-hour test period was assumed to be related to absorption or volatilization. The solvents were added to make a 1:600 (solvent:water) concentration in the column and the solution was agitated by air bubbling. The tests were conducted for 6 hours with samples collected at time zero (initial addition of the solvent) and every 2 hours thereafter. Filtered and unfiltered samples were collected and analyzed for COD.

8. Extended Corrosion Tests

The corrosion tests were conducted using a procedure similar to ASTM Method F 483-77. Each test ran approximately 1 week. Coupons were precleaned and postcleaned according to the ASTM procedure. In the mixing tests, a Teflon-coated stir bar was placed in each beaker and the beakers were placed in a constant-temperature bath. Stirring was controlled by a magnetic stirrer. For ultrasonic agitation, the beakers containing the hanging metal coupons and the solvent were placed in an ultrasonic tank full of water at a constant temperature and wattage. The test conditions and results are listed in Appendix F. Coupons were examined under a microscope.

Hydrogen embrittlement testing was performed according to ANSI-ASTM Method F 519-77. The test specimens were button-end stress cylinders of C4340 steel alloy. The average notch tensile strength of two specimens was determined on the Salec Model C creep stress machine by loading the machine to capacity and recording the time taken to break the cylinders. The average notch tensile strength was 300 kilograms (660 pounds). The stress machine was loaded to 45 percent of this load for hydrogen embrittlement testing according to the ASTM method. Three specimens for each solvent were exposed to the solvent for 168 hours at the temperature indicated as optimum from enhancement tests. The solutions were not agitated. After the test, each specimen was examined visually for cracks and other defects that would indicate hydrogen embrittlement.

9. Sensor Development

In the sensor development effort, the speed of sound was measured in several different solutions. A sharp pulse of ultrasonic energy at 5 megahertz was generated by a piezoelectric transducer. A gage, containing three annular rings at fixed, known distances from the transducer, provided pulse/echo targets to define sound transit time. The time of flight was measured as the interval between the echoes from the target rings. The full waveform was recorded by an eight-bit flash analog-to-digital converter, and the time interval between target ring echoes was measured by a digital phase-matching technique that has resolving power capability approaching 100 picoseconds.

Solutions for the tests were prepared in half-decade steps in concentrations from 5×10^{-4} moles to 1.0 mole for sodium chloride, sodium iodide, calcium chloride, and cesium iodide for two test series. One series started at 1.0 mole and the other at 0.5 mole. All water for each solute plus water blanks were derived from a single batch of demineralized water.

The largest competing effect is that of temperature, which changes the speed of sound. The solution temperature was maintained constant at about 31°C ± 0.10°C in a dual (heat and refrigerate) constant-temperature bath, which contained glass bottles with all solutions being tested. The largest source of temperature change was radiation from the bottle tops, which caused convection driven by millidegrees differences in top-to-bottom temperature. With care, temperature changes during measurements were kept within ± 0.04°C.

B. PHASE III PROCEDURES

The procedures used to complete the Phase III tasks are included in this section.

1. Cabinet Spray Washer Test

A Roto-Jet Cabinet Spray Washer is presently being used by the Air Force to clean fuel controls. With a 30-cubic foot cabinet and a 100-gallon solvent reservoir, it functions much like an automatic dishwasher. Nozzles around the sides are directed toward a rotating mesh basket located in the center of the parts washer.

Soiled aircraft parts were obtained from the Air Force for the cleaning tests. A part number, part description and soil description were recorded for each part. The soil description included the type and the amount present on the part as determined by visual examination. After the solvent had been heated to the desired temperature, the part was loaded onto the rotating rack inside the Roto-Jet and the door tightly sealed. The timer was then set for the desired cycle time and the start button was engaged. Following the completion of the wash cycle, the door was opened; the part removed and allowed to dry. The part was visually inspected and wiped with a clean white cloth to determine cleaning efficiency. The type and amount of soil remaining on the part, as determined by the visual inspection, were recorded.

2. 100-Gallon Test

The 100-gallon tank is equipped with a Bowden Industries Turbocharger system that creates vigorous agitation within the tank. A stainless steel mesh basket used to hold the parts is located in the center of the tank.

Soiled aircraft parts were obtained from the Air Force for the cleaning tests. A part number, part description, and soil description were recorded for each part. The soil description included the type and the amount present on the part as determined visually. After the solvent had been heated to the desired temperature, five to ten parts were loaded into the basket and the lid was closed. The agitation was turned on and a timer was set for 15 minutes. Following 15-minute cycle, the parts were removed from the tank, visually inspected and wiped with a clean white cloth to determine cleaning efficiency. The area wiped and the amount of soil removed by the wipe were insignificant in the overall determination of cleaning efficiency. The type and amount of soil remaining on the part, as determined by the visual inspection, were recorded. The parts were placed back into the tank, cleaned for 15 minutes and again inspected for cleaning efficiency. This 15-minute cleaning and inspecting cycle was repeated five times, resulting in a total cleaning time of 75 minutes. Immediately following the 30- and 75-minute intervals, the parts were rinsed using a cold water pressure sprayer prior to inspection. Following the completion of the cleaning cycles, the parts were allowed to dry and then returned to Air Force personnel for further inspection.

3. Full-Scale Test

The 300-gallon tank used for full-scale testing is located in the Gearbox Shop in Building 3001. The tank was equipped with an agitation system consisting of a 7.5 horsepower electric pump and three spray nozzles aligned vertically in each corner. The flow rate for the system was 100 gallons per minute. The twelve nozzles were oriented towards the mesh basket used for holding the parts located at the center of the tank. After the solvent had been heated to the desired temperature, five to ten parts were loaded into the basket and the lid was closed. The agitation was turned on and a timer was set for 15 minutes. Following the 15-minute cycle, the parts were removed from the tank and visually inspected and a small area was wiped with a clean white cloth to determine cleaning efficiency. The area wiped and the amount of soil removed by the wipe were insignificant in the overall determination of cleaning efficiency. The type and amount of soil remaining on the part were recorded. After the inspection, the parts were placed back into the tank, cleaned for 15 minutes, and again inspected for cleaning efficiency. This 15-minute cleaning and inspection cycle was repeated five times resulting in a total cleaning time of 75 minutes. Immediately following the 15- and 45-minute intervals, the parts were rinsed, using a cold water pressure spray prior to inspection. After the 75-minute interval, the parts were rinsed using a high-pressure steam sprayer and then allowed to dry before final inspection.

Two of the inspection methods employed by the Air Force to detect cracks and flaws in parts were used as acceptance criteria for the solvents. Both Fluorescent Penetrant Inspection (FPI) and Magnetic Particle Inspection (MPI) involve soaking a part with a fluorescent solution which allows cracks and flaws to be detected when viewed under a blacklight. For each solvent tested, ten to fifteen cleaned parts were selected for FPI and MPI inspections. This was done to ensure that the solvents being tested were not leaving a film or residue that would interfere with the inspection procedure. For each solvent tested, several parts which are normally painted following the cleaning process were cleaned and returned to the paint shop for painting. Some of the parts were sandblasted prior to being painted, an often-used preparation step. Several other parts were not blasted to see what effect the solvent would have on the paints ability to adhere to the metal surface.

Several parts coated with fluorescent penetrant oil were returned and cleaned using 3-D Supreme and Fremont 776. This was done to determine whether the cleaners could remove the penetrant oil.

4. Oil and Grease Test

The oil and grease content of the E-tank and FC effluent was determined using the Partition-Gravimetric Method (Method 503A. From Standard Methods for the Examination of Water and Wastewater (Reference 8). Samples sizes of 900 mL were collected in 1-L Erlenmeyer flasks. The samples were acidified to below pH 2 by adding 5 mL of hydrochloric acid (HCl), the samples were then transferred to a 1 liter separatory funnel. The flask which contained the sample was then rinsed with 30 mL of trichlorotrifluorethane, the washings were added to the separatory funnel containing sample. The solution was shaken vigorously for 2 minutes and then the layers were allowed to separate. The solvent layer was drained through a Whatman #40 filter, containing 1 gram of sodium sulfate, into a 125 mL distilling flask. The sample was extracted twice more with 30 mL of solvent, with rinsing of the sample flask with each solvent portion. The extracts were combined in the distillation flask along with 20 mL of solvent containing the washings from the filter. Solvent was distilled from the distilling flask for 2 hours in a waterbath set for 70°C. The sample was then cooled in a desiccator for 30 minutes and weighed.

5. Fremont 776 Loading Tests

The soils used to coat the parts for the Fremont loading tests were wax, hydraulic fluid with carbon black and molybdenum disulfide grease with carbon black. The wax, Petrolyte Amber 175 B-Squared, was heated to approximately 200°F. The parts or coupons were immersed in the hot wax until they were at the temperature of the wax. The disappearance of the white (amber) wax solid at the surface of the wax where the part was immersed indicated that the desired temperature had been reached. At this time, the part was slowly removed from the hot wax, such that only a thin film of wax remained. The parts were then tipped so that the excess wax could run out of the grooves. Finally, they were hung on a rack and allowed to cool.

The molybdenum disulfide and the hydraulic fluid soils were prepared according to MIL-C-85570B (Reference 10). The parts were painted with the grease and dipped in the hydraulic fluid. All were baked at 120°C according to the directions in the MIL-SPEC.

Each part was cleaned with 1,1,1-trichloroethane in a laboratory ultrasonic cleaner, rinsed with acetone, dried, and weighed before application of the soil. Following application and treatment as specified by the MIL-SPEC, the part with the soil was weighed. In this manner, the soil initially on the part, the soil removed, and the cleaning efficiency of the solvent was calculated. Cleaning efficiency (as percent) is the ratio of soil removed to the soil initially on the part, times one hundred.

Solvent loading capacity was tested using 500 milliliters of the solvent in a glass beaker at the optimum conditions recommended by the solvent label. Mixer agitation was tested by stirring with a magnetic stir bar on a hot plate. Parts for the loading tests were represented by 1/2-inch carbon steel nipples which were coated with soil, immersed in the solvent for the desired time, and the cleaning efficiency determined. The solvent was held at 140 to 150 degrees Fahrenheit during each test. Each test was conducted using three soiled parts, which were immersed for a timed interval of 10, 20, and 30 minutes. At each time, the cleaning progress was visually checked. Soils were not being removed after 30 minutes so the parts were allowed to remain in the solvent for a total of 60 minutes, and then removed. After removal from the solvent, the parts were dried over low heat for a 24-hour period. The final weight was then taken. In each test after the parts had been removed, 5 milliliters of soil was added artificially to the solvent, but in all cases the soil was not dissolved. Therefore, the loading capacity of the solvent was considered negligible.

SECTION IV
PHASE II RESULTS

Figures referred to in this section can be found in Appendix G.

A. TOXICITY

The toxicity information available from the manufacturers of the six biodegradable solvents selected for Phase II testing has been gathered and entered in a usable manner on the database (Reference 1). Data gathered included the data listed in Appendix C. These data were reviewed to eliminate any candidate solvents that would be hazardous to operators.

Calla 301 was eventually dropped from further consideration because it contains 2-butoxyethanol, which when absorbed by the body, damages the bone marrow, liver, and kidneys. When used under normal operating conditions, no excursions above recommended exposure levels should occur. In conditions where overexposure occurs, it is primarily absorbed through the skin. It is also highly irritating to the mucous membranes and upper respiratory tract. Exposure may cause headaches, nausea, dizziness, and vomiting. Though the hazard level is low when using Calla 301 as directed, the Air Force representative was concerned that future Air Force restrictions might eliminate its use. The decision was made early in Phase III to remove Calla 301 from the test program.

B. ENHANCEMENT

To define the solvents' required cleaning efficiency, a meeting was held with Tinker AFB Process personnel. Results of the meeting indicated that for a part to be considered clean, it must pass the "white glove" test. Specifically, if any residue can be wiped off the part, it is not considered clean. Using the white glove method in measuring cleaning efficiency required special care to ensure that the results of the test were not influenced by the removal of soil with the "white glove."

Residue interferes with a fluorescent penetrant oil used for examining parts for cracks or defects. Additionally, vapor degreasing is used primarily for wax, grease, or oil removal, but does not necessarily remove carbon deposits, scale or corrosion. These soils are removed by blasting or cleaning in strong-chemicals processes. Vapor degreasing represents only a minor portion of the cleaning processes conducted at Tinker AFB.

Preliminary cleaning tests of jet engine parts soiled with wax, grease, carbonized oil, or hydraulic fluid indicated that the parts could not be cleaned as well as the metal coupons. These tests were conducted by immersing metal coupons, measuring 2.5 x 5.1 x 0.15 centimeters (1 x 2 x 1/16 inches),and the parts in tanks of solvent at temperature but with no enhancement. Table 4 shows a percent-clean comparison after a 10-minute exposure to several of the solvents. A review of these data indicates that enhancement will be required for the solvents to clean the parts to pass the white glove test. This comparison was not conducted for all solvents.

Initial tests conducted using ultrasonics to enhance cleaning efficiency indicated that ultrasonics require cooling to maintain the solvents' temperature. Ultrasonics at 900 watts increased the temperature of the solvents and/or water to 194°F. Figure G-1 shows the temperature curve of the solvents as a function of time for ultrasonic agitation of Exxate 1000 and water at 900 watts and for water at 600 and 300 watts. For the remainder of the ultrasonic testing, the ultrasonics were operated in a range that maintained the temperature of the solvents below 140°F or a safe operating temperature. Communication with a representative of Exxon

TABLE 4. A COMPARISON OF PARTS AND COUPON CLEANING.

		Cleaning Efficiency (percent)	
	Soil	Parts	Coupons
Exxate 1000 at 140°F	Oil/Xylene	71	91
Exxate 1000 at 140°F	Wax	37	95
Orange Sol De-Solv-It at 140°F	Oil/Xylene	71	98
3-D Supreme 1:3 at 100°F	Hydraulic Fluid	69	98

Chemical Corporation indicated that the safe temperature for a solvent's use is 50°F below the flash point of the solvent. This prevents formation of a flammable mixture in the vapor zone around the bath (Reference 11). A review of the flash points of the solvents revealed that the safe operating temperature for five of the solvents selected for Phase II testing is 140 to 150°F. The review also showed that Triton Hemo-Sol has a flash point of 116°F; therefore, this solvent was eliminated from any further testing.

Figure G-2 shows the baseline established with 1,1,1-trichloroethane vapor for the coupons and the parts for wax removal. Perchloroethylene has the same baseline. A similar baseline exists for removal of the other soils as shown in the Phase I report. The parts, including a Waspaloy ejector nozzle, and metal coupons were examined with an electron microscope by Esso Chemical Canada (a part of Exxon Chemical Corporation) to determine if the surface characteristics of the part affects cleaning efficiency (Reference 12). The ejector nozzle has a wide variety of surface types. Some appear porous, i.e., like cast material. Others have definite grooves, i.e., machined surfaces, and yet other areas have grooves that run in a number of directions, probably as a result of grinding. Other areas appear to be welded or machined.

The solvents were tested at higher temperatures without ultrasonics or agitation to determine the effects of time and temperature on cleaning efficiency. As shown in Figure G-3, wax can be removed from the parts without enhancement but with extended exposure time. However, a great deal of scatter appears in the data. At 170°F, the parts were nearly 100 percent clean within 2 hours as shown in Figure G-4 (170°F is an unsafe operating temperature). Conversations with a process engineer at Tinker AFB* indicated that a maximum allowable cleaning time of 30 minutes should be considered.

Enhancement testing results for the Exxon Exxate 1000 are shown in Figures G-5 through G-15. Enhancement tests were conducted using 51 x 19-millimeter (2 x 3/4-inch) carbon steel nipples (representative of some of

---

* Personal communication with Anne Copeland, Tinker AFB, October 1988.

the most difficult parts to clean). Figure G-5 shows the effect of temperature increase on wax removal at 500 rpm mixer agitation after immersion for 10 minutes. Cleaning efficiency increased from 3 percent at 65°F to 28 percent at 140°F. Increasing mixer agitation to 650 rpm at 140°F resulted in little change in cleaning efficiency (Figure G-6). Ultrasonic agitation of 300 watts at 140°F increased cleaning efficiency to near 62 percent after 20 minutes immersion with no rinsing (Figure G-7). Nearly 80 percent cleaning efficiency was achieved with rinsing. A 30-minute immersion resulted in 95 percent cleaning efficiency. At 600 watts ultrasonic agitation with rinsing, wax removal was approximately 98 percent after 30 minutes immersion (Figure G-8). Ultrasonic agitation of 900 watts at 140°F resulted in 100 percent wax removal after a 20-minute immersion with no rinsing (Figure G-9).

Oil/xylene was 100 percent removed after immersion in Exxate 1000 for 20 minutes at 120°F with ultrasonic agitation at 300 watts and with rinsing (Figure G-10). At 600 watts ultrasonic agitation, the oil/xylene removal with and without rinsing was 98 percent after 10 minutes immersion, and 100 percent after 20 minutes (Figure G-11). Increasing the temperature to 140°F resulted in 100 percent oil/xylene removal after 10 minutes immersion with ultrasonic agitation at 300 watts (Figure G-12). Figures G-13, G-14, and G-15 show cleaning with mixer agitation at 650 rpm as a function of temperature. At 100°F only 96 to 98 percent cleaning efficiency was achieved (Figure G-13). Cleaning efficiency was 100 percent in 30 minutes at 120°F (Figure G-14), and with rinsing was 100 percent in 20 minutes at 164°F (Figure G-15). In Phase I, the organic solvents were generally more effective in removing the carbonized oil/xylene and wax than light oils and greases such as hydraulic fluid and molybdenum disulfide soils, and were therefore tested only with these soils.

Enhancement studies were completed with 3-D Supreme Solvent, which is an aqueous solvent, at a 1:3 solvent-to-water ratio. Phase I testing showed it to be effective for only hydraulic fluid and molybdenum disulfide grease. Figures G-16 through G-24 show the cleaning efficiency of the solvent for hydraulic fluid. With no agitation, cleaning efficiency without rinsing was about 56 percent after 10 minutes immersion at 120 or 140°F and increased to approximately 70 percent after 30 minutes (Figures G-16 and G-17). Rinsing increased cleaning efficiency to approximately 95 percent after 10 minutes immersion and 98 percent after 30 minutes. Mixer agitation (500 rpm) at room temperature, 77°F, increased efficiency to 86 percent after 10 minutes and to near 95 percent after 20 minutes without rinsing (Figure G-18). With rinsing, the cleaning efficiency was 99 percent after 30 minutes.

Increasing the temperature to 100°F (Figure G-19) increased cleaning efficiency without rinsing to 90 percent and to near 100 percent with rinsing after 20 minutes immersion. Increasing the temperature to 120°F increased cleaning efficiency to 92 percent without rinsing and 100 percent with rinsing in 10 minutes (Figure G-20). A temperature of 140°F (Figure G-21) did not further enhance cleaning efficiency. Hydraulic fluid removal at a mixer agitation of 650 rpm is shown for 77 and 100°F in Figures G-22 and G-23. Cleaning efficiency was approximately 90 percent after 20 minutes with no rinsing at either temperature. With rinsing, cleaning efficiency was approximately 90 percent after 10 minutes and near 98 percent after 20 minutes. Ultrasonic agitation at 300 watts and 77°F (Figure G-24) resulted in a cleaning efficiency of approximately 95 percent after 20 minutes immersion. Increasing the immersion time to 30 minutes did not further increase cleaning efficiency. Rinsing resulted in a cleaning efficiency of 100 percent after 20 minutes.

Molybdenum disulfide grease (MoS soil) removal with 3-D Supreme solvent is shown in Figures G-25 through G-36. At 140°F with no agitation (Figure G-25), approximately 50 percent of the MoS soil was removed with no rinsing after 10 minutes and 65 percent after 30 minutes. Rinsing increased cleaning efficiency to near 90 percent. Mixer agitation at 500 rpm increased cleaning efficiency to 63, 75, and 90 percent after 10, 20, and 30 minutes immersion at 100°F (Figure G-26). With rinsing, cleaning efficiency was 100 percent after 30 minutes. At 120°F (Figure G-27), cleaning efficiency was 75, 83, and 88 percent after 10, 20, and 30-minute immersion, and at 140°F (Figure G-28), cleaning efficiency was approximately 95 percent at all immersion times with no rinsing and near 100 percent after 20 minutes with rinsing.

Cleaning efficiency with mixer agitation at 650 rpm as a function of temperature is shown in Figures G-29 through G-32. At 77°F, cleaning efficiency with no rinsing (Figure G-29) was 49, 50, and 70 percent at 10, 20, and 30 minutes and 56, 83, and 90 percent with rinsing. At 100°F (Figure G-30), cleaning efficiency increased approximately 20 percent with no rinsing at 10 and 20 minutes over cleaning at 500 rpm (Figure G-26). At 120°F (Figure G-31), the increase was approximately 7 percent over cleaning at 500 rpm (Figure G-27) with no rinsing. At 140°F (Figures G-28 and G-32), there was little difference in cleaning efficiency at 500 and 650 rpm mixer agitation.

MoS soil removal with ultrasonic agitation at 300 watts as a function of temperature is shown in Figures G-33, G-34, and G-35. Cleaning efficiency ranged from 89 to 97 percent with no rinsing, at all temperatures and immersion times. With rinsing, cleaning efficiency was 100 percent after 20 minutes immersion at 77°F (Figure G-33) and 10-minute immersion at 100°F (Figure G-34).

Enhancement studies for the cleaning efficiency of Orange Sol De-Solv-It were completed for carbonized oil/xylene and wax removal. Oil/xylene removal with 650 rpm mixer agitation at 140°F is shown in Figure G-36. Cleaning efficiency ranged from 25 percent at 10 minutes to 60 percent at 30 minutes with rinsing. Ultrasonic agitation at 300 watts at 120 and 140°F is shown in Figures G-37 and G-38. After 30 minutes with rinsing, soil removal was approximately 78 percent at 120°F and 100 percent at 140°F. At 600 watts and 120°F (Figure G-39) cleaning efficiency after 30 minutes without rinsing was approximately 88 percent, and 100 percent with rinsing. Increasing the temperature to 140°F (Figure G-40) increased cleaning efficiency to near 97 percent after a 20-minute immersion with no rinsing. Increasing ultrasonic agitation to 900 watts increased cleaning efficiency to near 100 percent with rinsing after 20 minutes immersion at 120°F (Figure G-41). At both 120 and 140°F (Figures G-41 and G-42), cleaning efficiency ranged from 90 to 100 percent without rinsing, but there is scatter in the data.

Wax removal with Orange Sol De-Solv-It is shown in Figures G-43 through G-47. At 140°F with mixer agitation at 500 and 650 rpm (Figures G-43 and G-44), cleaning efficiency was less than 50 percent after 30 minutes agitation with and without rinsing. At 140°F and 300 watts ultrasonic agitation (Figure G-45), cleaning efficiency without rinsing was approximately 75 percent. With rinsing, cleaning efficiency increased from 80 percent after 20 minutes to near 95 percent after 30 minutes. At 600 watts ultrasonic agitation (Figure G-46), cleaning efficiency was 96 percent without rinsing and near 100 percent with rinsing after 20 minute immersion at 120°F. Ultrasonics agitation at 900 watts (Figure G-47) increased cleaning efficiency without rinsing to 97 percent after 10 minutes immersion at 120°F.

Enhancement testing of Bio-Tek Safety Solvent for wax and carbonized oil/xylene removal was completed. Figures G-48 through G-55 show wax removal with the solvent. At ambient temperature (77°F) with mixer agitation at 650 rpm or ultrasonic agitation at 300 watts, less than 10 percent of the wax was removed even with rinsing (Figures G-48 and G-49). At 140°F with no agitation, the wax was approximately 45 percent removed with rinsing after 30 minutes immersion in the solvent (Figure G-50). Mixer agitation at 650 rpm, (Figure G-51) did not increase cleaning efficiency. Ultrasonic agitation at 300 watts (Figure G-52) increased cleaning efficiency to approximately 60 percent without rinsing and 80 percent with rinsing. At 600 watts (Figure G-53) wax removal was approximately 85 percent after 20 minutes immersion and 96 percent with rinsing after 30 minutes. Increasing ultrasonic agitation to 900 watts (Figure G-54), increased cleaning efficiency to 97 percent with rinsing after 10 minutes immersion and 100 percent after 20 minutes. Increasing the temperature to 150°F at 600 watts (Figure G-55) did not achieve the cleaning efficiency attained at 140°F and 900 watts ultrasonic agitation. However, after 30 minutes immersion, cleaning efficiency was near 97 percent.

Oil/xylene removal with Bio-Tek Safety solvent is shown in Figures G-56 through G-61. Mixer agitation (650 rpm) at 120°F resulted in approximately 96 percent cleaning efficiency in 10 minutes with and without rinsing (Figure G-56). After 20 and 30 minutes immersion, cleaning efficiency was only 98 percent. Ultrasonic agitation at 300 watts at 120°F (Figure G-57) did not increase cleaning efficiency over mixer agitation at that temperature. Increasing the temperature to 140°F resulted in approximately 99 percent soil removal in 10 minutes with 650 rpm mixer agitation (Figure G-58).

Enhancement studies for cleaning efficiency of Calla 301 were completed for molybdenum disulfide grease and hydraulic fluid removal. Testing was conducted with a 50 percent solution. Molybdenum disulfide grease removal with mixer agitation at 120 and 140°F is shown in Figures G-59 and G-60. At both temperatures, considerable scatter occurred for the unrinsed data with efficiency ranging from 40 to 67 percent. With rinsing, the cleaning efficiency was near 99 percent after 20 minutes immersion at 140°F. Ultrasonic agitation at 300 watts and 100°F (Figure G-61) resulted in 26 to 34 percent cleaning efficiency without rinsing. Approximately 97 percent soil removal was achieved with rinsing at 300 watts and 120°F (Figure G-62), 55 to 68 percent of the soil was removed without rinsing, and 100 percent of the soil was removed with rinsing after 10 minutes immersion.

Removal of hydraulic fluid with Calla 301 is shown in Figures G-63 through G-66. Mixer agitation at 650 rpm resulted in a cleaning efficiency of 76 to 89 percent unrinsed and 96 to 99 percent at 120°F (Figure G-63). At 140°F (Figure G-64), 20-minute immersion resulted in a cleaning efficiency of 84 percent without rinsing and 91 percent with rinsing. Rinsing resulted in a cleaning efficiency of approximately 100 percent after the 20-minute interval. Ultrasonic agitation at 300 watts and 100°F (Figure G-65) resulted in 76 to 88 percent cleaning efficiency without rinsing and 95 to 99 percent with rinsing at all times. At 120°F (Figure G-66), cleaning efficiency was 79 percent at 10 minutes and 96 percent at 30 minutes without rinsing. With rinsing, cleaning efficiency was 100 percent at all times.

C. PERFORMANCE TESTING

The performance tests included experiments to determine solvent soil capacity, rinsing requirements, and drying requirements. The results from each of these tests are reported here.

1. Solvent Capacity Tests

Solvent capacity testing was conducted for carbonized oil/xylene using Exxon Exxate 1000 at 120°F with mixer agitation for enhancement. Figure G-67 shows cleaning efficiency as a function of solvent loading. At 34 grams/liter of the soil in the solvent, cleaning efficiency decreased to less than 90 percent. With 42 grams/liter of the oil/xylene in the solvent, cleaning efficiency decreased to less than 50 percent.

Performance testing of Exxate 1000 with the oil/xylene soil mixture was completed. These data are presented in Figure G-68. At 75 percent of the estimated loading capacity, the solvent cleaning efficiency decreased to 95 percent.

At a temperature of 140°F with 500 watts ultrasonic agitation and rinsing, the estimated loading capacity of Exxate 1000 with wax was approximately 10 milligrams/liter with an immersion time of 20 minutes. Parts cleaning efficiency decreased to 89 percent at 90 percent of the estimated loading capacity (Figure G-69).

The loading capacity of Calla 301 for molybdenum disulfide grease is shown in Figure G-70. At 140°F using mixer agitation and rinsing, the loading capacity for hydraulic fluid was 23 grams/liter (Figure G-71). The performance of Calla 301 in cleaning parts soiled with hydraulic fluid is shown in Figure G-72. At 75 percent of the estimated loading capacity, cleaning efficiency decreased to approximately 98 percent for the hydraulic fluid.

The loading capacity of 3-D Supreme is shown in Figures G-73 and G-74. At 120°F using mixer agitation and rinsing, the loading of hydraulic fluid was approximately 60 grams/liter with an immersion time of 10 minutes. The loading capacity for molybdenum disulfide grease was 10 grams/liter at 140°F with mixer agitation and 10 minutes immersion.

The performance of 3-D Supreme in cleaning parts soiled with molybdenum disulfide grease and hydraulic fluid is shown in Figures G-75 and G-76. At 100 percent of the estimated loading capacity, cleaning efficiency decreased to 95 percent for the molybdenum disulfide grease. At 75 percent of the estimated loading capacity, cleaning efficiency decreased to approximately 92 percent for hydraulic fluid.

The theoretical loading capacity of Bio-Tek 140 Safety Solvent is shown in Figures G-77 and G-78. At 140°F using mixer agitation and rinsing, the loading capacity of oil/xylene was approximately 70 grams/liter with an immersion time of 10 minutes. At 140°F using 900 watts ultrasonic agitation and rinsing, the loading capacity of wax was approximately 20 grams/liter with an immersion time of 10 minutes. Performance test results are shown in Figures G-79 and G-80. Performance for oil/xylene remained near 98 percent through 90 percent of the theoretical loading; however, at zero loading, cleaning efficiency was only 95 percent. For wax, performance was 100 percent until 90 percent of the loading capacity, when cleaning efficiency decreased to 98 percent.

Orange Sol De-Solv-It's estimated loading capacity at 140°F with ultrasonics agitation at 600 watts is shown in Figures G-81 and G-82 for the carbonized oil/xylene and wax. The solvent's capacity was approximately 60 grams/liter for the oil/xylene soil and 50 grams/liter for the wax.

The performance of Orange Sol De-Solv-It in cleaning parts soiled with the carbonized oil/xylene is shown in Figure G-83. The solvent was loaded with the soil to the levels tested. With new solvent and solvent loaded to 6 kilograms/100 gallons (representing 25 percent of the estimated loading capacity), cleaning efficiency was 100 percent with 600 watts ultrasonic agitation at 140°F. At 50 percent of the estimated loading capacity (12 kilograms soil/100 gallons), cleaning efficiency decreased to less than 80 percent. Orange Sol De-Solv-It's wax removal performance is shown in Figure G-84. There is considerable scatter in the data. Cleaning efficiency ranges from 87 to 100 percent and down to 75 percent with from zero to 90 percent loading.

Fremont 776 performed poorly in the cleaning capacity tests. These tests were conducted after Fremont 776 was added to the program during Phase III. Of the three types of soil tested in the loading tests, hydraulic fluid was the only soil that was even partially removed by Fremont 776 from the parts tested. An average of 61.5 percent of the hydraulic fluid was removed. The soil that was removed did not go into solution. It floated on the surface of the solvent. After the parts were removed from the bath, 5 milliliters of hydraulic fluid were added directly to the solvent and the mixture was agitated for an hour. Following the hour of agitation, the hydraulic fluid still floated on the surface of the solvent. From these results, the determination was made that the hydraulic fluid was, at most, very slightly miscible with Fremont 776 solution at this concentration. As a solvent for hydraulic fluid, under these conditions, Fremont 776 was poor.

The molybdenum disulfide and wax soiled parts that were tested gained weight after remaining in solvent for one hour. By visual inspection, no soil was removed in this one-hour period. The molybdenum disulfide soil increased by 70.6 percent and the wax soil increased by 13 percent. After the soiled parts were removed, 5-milliliters of the respective soil were added to each beaker. The mixtures were agitated for one hour. After one hour, both soils floated on the surface of the solvent. Again, for both molybdenum disulfide and wax, under these conditions, Fremont 776 solvent performance was poor.

2. Rinsing Tests

The results of rinsing the respective soils from the parts after cleaning with the solvents at the conditions of the performance tests are shown in Figures G-85 through G-94. For parts soiled with wax (Figure G-85) and cleaned by immersion in Exxate 1000, rinsing removed more than

99 percent of the soil in 1 minute for both impact and immersion rinsing and 100 percent after 5 minutes. With Exxate 1000 and oil/xylene, 99 percent clean was not achieved; however, impact rinsing achieved greater than 98 percent clean. Immersion rinsing resulted in 92 to 97 percent cleaning efficiency. With Orange Sol De-Solv-It as the solvent, approximately 94 percent wax removal (Figure G-87) was achieved after 10-minute immersion rinsing and 99 percent at 10 minutes with impact rinsing. Cleaning efficiency reached 91 percent after 1 minute and 97 percent after 10 minutes. Greater than 99.9 percent soil removal (Figure G-88) was achieved with either impact or immersion rinsing after oil/xylene removal with Orange Sol De-Solv-It.

Rinsing after cleaning wax-soiled parts with Bio-Tek Safety Solvent (Figure G-89) resulted in greater than 93 percent cleaning after 1 minute to 99 percent at 10 minutes with immersion rinsing. With impact spray rinsing, 91 percent cleaning efficiency was achieved after 1 minute, increasing to 97 percent after 10 minutes. Impact rinsing resulted in 100 percent oil/xylene removal after 1 minute (Figure G-90), while immersion resulted in 97 percent soil removal after 1 minute and 100 percent after 10 minutes. Rinsing after cleaning parts soiled with hydraulic fluid (Figure G-91) resulted in greater than 99.9 percent soil removal after 1 minute with immersion rinsing, while impact rinsing resulted in 98.9 percent after 1 minute. Immersion or impact rinsing of parts soiled with molybdenum disulfide grease and cleaned with 3-D Supreme resulted in 82 percent cleaning efficiency after 10 minutes for immersion rinsing and 74 percent for impact spray rinsing (Figure G-92). For the Calla 301 removal of molybdenum disulfide grease (Figure G-93), immersion rinsing resulted in 40 percent soil removal and impact rinsing resulted in 96 percent soil removal at all times. For hydraulic fluid (Figure G-94), 100 percent soil removal was achieved with the impact spray rinse and immersion rinsing achieved 99 percent in 1 minute.

3. Drying Tests

The results of the drying tests are shown in Figures G-95 through G-98. A part dipped in water (Figure G-95) was approximately 93 percent dry after 5 minutes and 100 percent dry after 30 minutes. Water was tested in order to represent drying of a rinsed part. Drying of a part immersed in Exxon Exxate 1000 achieved approximately 92 percent solvent removal after 30 minutes (Figure G-96). The graph does, however, show extended drying or higher temperatures result in complete solvent removal. Approximately 85 percent solvent removal was achieved for the Bio-Tek 140 Safety Solvent (Figure G-97) after 30 minutes drying. The relative humidity had increased from 4 to 5 percent to 38 percent and the temperature had dropped from the 82°F of the prior test to 74°F. Drying of parts dipped in Orange Sol De-Solv-It resulted in 82 percent solvent removal (Figure G-98).

With 3-D Supreme (Figure G-99), 93 percent solvent removal was achieved after 5 minutes drying, and approximately 99 percent after 20 minutes. The relative humidity was 37 percent and the temperature was 73°F. Drying after immersion in Calla 301 (Figure G-100) resulted in 95 percent solvent removal after 30 minutes. The relative humidity was 42 percent and the temperature was 83°F.

D. ASTM BIODEGRADABILITY GUIDELINE EVALUATION

The basic screening test of the solvents was completed in Phase I of this program, and the results are reported in Air Force Document No. ESL-TR-89-04 (Reference 1). The 6-hour Biological Screening Test was developed primarily to permit a comparison of solvent treatability under a common set of conditions because of the various definitions of "biodegradable." Different solvent manufacturers use different criteria on which to base their claims of biodegradability. For example, most solvents are composed of several components, each performing a specific function of the degreasing/stripping operation. Each component may, in turn, be composed of several chemical compounds. If the individual compounds are biologically degradable, it may be feasible to assume that the combined material would also be biodegradable.

Also, many tests can be used to determine the susceptibility of a solvent/material to biodegradation. The literature contains many techniques that have been used to measure the extent of biodegradation. Swisher (Reference 13) has compiled a reference containing an extensive review of methods commonly used to measure biodegradation. The complexity of available biodegradation testing techniques also reflects the diversity of microorganisms and their differing abilities to adapt to new environments and use the compounds as a food source, either directly or indirectly.

The 6-hour screening test was developed to screen a large number of candidate replacements for the solvents (classified as hazardous and recalcitrant) used in degreasing operations at Tinker Air Force Base. The screening test was based on several assumptions:

- Failure of a solvent to pass the test did <u>not</u> mean the solvent was not biodegradable.
- The 6-hour test period was based on a typical 6-hour fluids retention time in the activated sludge basin at Tinker AFB's Industrial Waste Treatment Plant (IWTP).
- An aerobic test system was selected because the IWTP has an activated sludge (AS) system for biological treatment.
- Tinker AFB's activated sludge was used as the test inoculum because the solvents tested were planned for implementation at Tinker's operation.
- Phenol was selected as a control solvent, since phenol is commonly discharged to the IWTP for treatment and Tinker's AS system is acclimated to this solvent.
- Solvents were diluted 1:600 in the test columns, because materials are typically diluted to that ratio during travel to the IWTP.
- Degradation could be measured indirectly by chemical oxygen demand (COD) and soluble total organic carbon (TOC) analyses. A loss in solution COD and TOC over time would indicate that the solvent was

degraded. Also, Tinker AFB's National Pollution Discharge Elimination System (NPDES) permit contains a COD discharge limitation.

- Activated sludge activity could be measured by adenosine triphosphate (ATP) analyses on the biomass exposed to the solvent. An ATP increase would indicate that the solvent was a suitable substrate and could support biological growth. No increase or a decrease in ATP levels would indicate that the solvent was not a suitable substrate to support activated sludge growth.

- A 1/10 dilution of the culture was selected on the basis of:

    - Reduction of the amount of solids introduced, thus minimizing potential solvent loss due to sorption onto the biomass (solids)

    - Maintenance of a sufficient concentration of biomass to permit an observable degradation during the 6-hour exposure period

    - Reduction of the solution complexity (possible chemical/solid interference) during the analysis.

A conclusion of Phase I was that additional tests would be required for definitive biodegradability determination of the solvent tested.

The speed of the 6-hour biological degradation screening test was helpful in the selection process because more than 200 solvents were received for evaluation. The impact of the solvents on the IWTP was only one concern. Other criteria were solubility, cleaning efficiency, and corrosiveness. In reviewing the initial testing of Phase I and in view of potentially broader and continued applications, the need became evident to reevaluate some of the basic assumptions of the screening test. As a result, Phase II efforts were directed at determining the reproducibility of 6-hour tests, the justification of the selected controls and systems calibration.

1. Controls and Calibration

One area of interest was the immediate loss of the test compound during the 6-hour test and no increase in the activated sludge's biological activity. Another area of interest was the comparison of seed cultures used during the biological screening tests. Activated sludge samples were sent to the laboratory at the Idaho National Engineering Laboratory every other week. Samples were collected from the return activated sludge (RAS) line at Tinker AFB, packed in ice, and shipped overnight to the laboratory in Idaho Falls. Upon delivery, the sludge was concentrated by centrifugation at 8 k rpm and refrigerated. Dry-to-wet-weight ratios were determined. The culture column was set up to contain approximately 2.5 grams (dry weight) solids per liter of volume, which is a common solids/liquids ratio for most treatment plants.

As mentioned previously, ATP and COD analyses were used to measure the activity of the biomass and the extent of solvent degradation. Figures G-101 and G-102 exhibit the ATP and COD variability associated with the culture column over a series of test dates. There was a need to establish criteria as to when a test should be considered abnormal and either reevaluated or rerun. Therefore, the use of standard deviation about the mean was selected to determine the limits of "normal" operating conditions. For the seed cultures, the initial ATP values were calculated for a 1:100 dilution of the biomass. The area between one standard deviation above and below the mean was selected as the region of acceptable test response for ATP analyses (Figure G-103 and Table 5).

Each test included a control column that was spiked with a phenol solution to create a final phenol solution concentration of 100 milligrams/liter. The region of acceptable test response was the same as for the seed culture tests (Figure G-104 and Table 5). This number is

TABLE 5. LIMITS OF RELIABILITY FOR THE 6-HOUR BIODEGRADABILITY SCREENING TEST.

	Mean	+Std. Dev.	-Std. Dev.
Culture seed ATP	1.345 E-06	2.100 E-06	0.590 E-06
Phenol control column:			
ATP change	2.19 E-06	3.61 E-06	7.77 E-07
COD regression slope	-35.84	-23.47	-48.20

the change in ATP over the 6-hour period. For phenol, this was expected to be a positive number, because Tinker's activated sludge was acclimated to phenol. The indirect measurement of phenol loss over time by COD analysis created a plot with a characteristic negative slope (Figure G-105). Regression analysis of the decreasing COD values provided a slope calculation that was also used to set limits of acceptability for test conditions. These limits are exhibited in Figure G-106 and Table 5. Therefore, whenever a test resulted in one or more of the baseline and control conditions outside the acceptable limits, the test was reevaluated and a decision was made whether or not to conduct the test again.

The selection of phenol as a suitable control was examined further by running side-by-side test columns, each containing 100 milligrams/liter phenol additions. This test was conducted several times on different days using different seed culture preparations. The first test resulted in four of the six test columns with acceptable ATP increases over the 6-hour exposure period (Figure G-107) and all six columns had acceptable COD losses (Figure G-108). The second test produced results showing all six columns with acceptable changes in ATP (Figure G-109) and COD losses (Figure G-110). The overall data collected on the phenol control column indicate that the general health of the culture seed material can be assessed by the control column's response.

During the test periods, a set of controls was used to check and calibrate ATP, COD, and TOC analyses. Quality control samples were obtained from the Quality Assurance Research Division, Environmental Monitoring

Systems Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio. The ATP standards are no longer available from this agency; however, oxygen demand, linear alkylbenzene sulfonate (LAS), and phenol standards are available upon request. In addition, calibration and internal checks were conducted using materials prepared in the laboratory (see 6-Hour Test Protocol, Appendix E).

a. ATP Calibration

A Turner luminometer was used for ATP analyses and the internal standard procedure was used to minimize solution interference. The technique was checked by using U.S. EPA standards. Two separate concentrations (at the upper range of instrument detection) were made from different EPA standards. Intermediate and low range solutions were made from each initial solution preparation. The results were reproducible and linear over the range tested (Figure G-111).

b. COD Calibration

The Hach COD System for Wastewater Testing was used during the 6-hour testing. Most of the solvents tested possessed a high COD value even at the 1:600 dilution in the test column. Ferrous ammonium sulfate was used as a COD standard and a 1000-milligrams/liter phenol solution was used as another standard. These solutions were prepared each day (see 6-Hour Protocol, Appendix E for preparation information). In addition, an EPA oxygen demand sample was used to check the systems calibration. Again, results indicated good reproducibility of the analysis (Figure G-112). A measurement of the error associated with the range of COD standards is exhibited in Figure G-113. A lower percentage of error was associated with higher range values.

c. TOC Calibration

The TOC instrument provided analyses within a range of 0 to 50 milligrams/liter carbon. The instrument uses a one-point standard calibration; however, additional standards were used throughout every analytical operation to check the system's calibration. Typically, three standards (5, 10, and 20 milligrams/liter carbon, as potassium biphthalate) were part of each sample set. Analyses demonstrate reproducibility of the results and linearity within the range of interest (Figure G-114). Also, a check of the system with U.S. EPA QA samples supported previous calibrations and exhibited linearity within the range of 0 to 40 milligrams/liter carbon (Figure G-115).

2. Bioacclimation Testing

a. ASTM 8-Day Tests

An 8-day test series was devised as another check in developing an ASTM test protocol and to obtain more information than the 6-hour test provided. This additional step decreased the amount of pilot testing needed. As mentioned earlier, the 6-hour test was a screening test and not a definitive test to evaluate the biodegradability of a solvent. One reason for this is that the relatively short 6-hour exposure does not allow the microorganisms to acclimate to the test compounds. Also, the indirect measurements of TOC and COD losses during the test do not allow tracking of a specific compound during the test. Degradation analysis using such techniques becomes difficult because many possible interferences and conditions may confuse the interpretation of test results. The fate of the chemical in solution depends on many parameters other than the biological. The solubility of the compound in water will determine its transport to the microorganisms for degradation. Also. since the activated sludge is suspended in the water column by air sparging, the compound's volatility is another consideration, i.e., the potential to be lost by air stripping.

A series of air sparging tests were conducted to look at the potential compound loss due to air stripping. During this testing, the number of solvents to be tested had been reduced to six. These solvents were selected for further evaluation based upon their results from previous efficacy, corrosion and pitting, and biological tests. The solvents were:

Calla 301, Calla Chemical Corp.
De-Solv-It, Orange Sol, Inc.

Exxate 1000, Exxon Chemicals, Inc.
Safety Sol, Bio-Tek, Inc.
Hemo-Sol, Triton
3-D Supreme, 3-D Corp.

The air sparging tests were conducted in a manner similar to the biodegradation screening tests of Phase I except that no microorganisms (activated sludge) were added to the test column solution. Therefore, loss of COD over the 6-hour test period was assumed to be related to adsorption or volatilization. The solvents were added to make a 1:600 (solvent:water) concentration in the column. The solution was agitated by air bubbling through the column and the tests were conducted for 6 hours with COD samples collected at time zero (initial addition of the solvent) and every 2 hours thereafter until the completion of the test. Filtered and unfiltered samples were collected and analyzed for COD.

Two sets of tests were completed. The results of the first test exhibited no change of COD for both phenol and the control, nanopure water (Figures G-116 and G-117). Exxate 1000 filtered samples exhibited a gradual loss over time, while unfiltered COD values exhibited an initial decrease followed by an increase at the end of the test (Figure G-118). De-Solv-It exhibited an increase in COD in both filtered and unfiltered samples over the entire testing period (Figure G-119). Safety Sol exhibited a rapid decrease in the COD associated with unfiltered samples and a very gradual loss in filtered material (Figure G-120). Hemo-Sol showed a rapid decrease in the unfiltered COD, which approached the filtered value. The two values then mirrored each other for the remainder of the test (Figure G-121).

The second set of tests showed similar results for both phenol and water (Figures G-122 and G-123). 3-D Supreme also showed close association of the filtered and unfiltered COD analyses (Figure G-124). De-Solv-It again exhibited an increase in both filtered and unfiltered COD values over time (Figure G-125), while Calla 301 showed a gradual decrease (Figure G-126). Ideally, one would expect the analyses to exhibit no change in COD over the test period. A decrease in COD may indicate potential loss of the solvent due to air stripping. (This same condition could occur if the solvent adsorbed onto the test chamber wall.) An increase over time may indicate that the solvent may have initially sorbed to the test vessel or was not miscible in water and floated on top of the test column at the bubble zone, then gradually dissolved into solution. A wide difference between filtered and unfiltered COD analyses for a solvent indicates the ability of the COD to be filtered from solution.

These tests are helpful in understanding, at least initially, the complexity of the biodegradation tests by permitting a look at nonbiological factors imposing conditions on the test procedure. Additional information could be obtained if direct analysis of the compounds were possible. This information would be helpful in determining the compartmentalization of the compounds, i.e., hydrolyzing, sparging, and sorption.

Additional tests were completed to determine biodegradability of the selected solvents. The ASTM 8-Day test for the determination of biodegradability of alkylbenzene sulfonates (Method D 2667-82) was adapted for application in the lab. The test includes two 3-day periods of initial exposure of the inoculum to the solvent, and thus includes acclimation as part of the biodegradation test. A laboratory protocol was established (Appendix E) that was based upon the ASTM method. The data are presented in Appendix H. The solvents tested by this procedure were:

Exxate 1000	January 31 through February 14, 1989
De-Solv-It	April 4 through April 18, 1989
3-D Supreme	June 13, through June 27, 1989
Calla 301	July 11 through July 25, 1989

Although the biodegradation test is 8 days long, two 3-day periods of acclimation are required before the biodegradation test begins. The entire test requires 15 days. The ASTM procedure calls for sampling at the beginning and end of each inoculation period. The current laboratory protocol increased sampling frequency to every day during the acclimation period and to every other day during the degradation testing period. The exception to this practice was the first test with Exxate 1000. During this test, samples were collected every day during the 8-day test period for ATP and COD analyses. The following paragraphs contain a brief description of each test and the results obtained.

(1) Exxate 1000. This test proved to be valuable because many of the initial results pointed to areas that needed additional attention. One of the concerns was the comparability of COD and TOC analyses. The COD analyses exhibited a greater amount of variability (Figure G-127) during the 8-day test than did the TOC analyses (Figure G-128). This, coupled with results received from the next tests, led to the eventual elimination of COD analyses during the 8-day test period. The ATP analyses of the acclimation period exhibited higher ATP levels for phenol during the first acclimation period (Figure G-129), with equal ATP levels for Exxate and phenol flasks during the second acclimation period, followed by higher ATP levels in the Exxate flasks each day of the final 8-day test (Figure G-130). This indicates that the organisms were able to adapt to the Exxate and maintain a high level of activity. However, the COD and ATP values increased over time (Figures G-127 and G-128), which suggests a buildup of the solvent. Because Exxate 1000 was not specifically analyzed and identified, saying that the organisms degraded the Exxate is not possible. Nor is it possible to determine whether the increases in TOC and COD were due to increased Exxate in solution or the buildup of secondary metabolites resulting from the solvent's degradation. Gas chromatographic analyses were performed but failed to produce results that could clarify the interactions in the flasks. There were no characteristic peaks for Exxate 1000 for the samples processed with the gas chromatograph (GC).

(2) De-Solv-It. Because the original ASTM 8-day test protocol included the use of LAS as a suitable control for comparison, a LAS standard was included in this test and the following tests to provide additional comparability of results. (Note: LAS/QC samples are available from the U.S. EPA Laboratory, Cincinnati, Ohio.) The ATP analyses indicated an initial ability of the activated sludge to use De-Solv-It as a substrate for growth. During the initial acclimation period, the ATP levels in the test flasks were higher than in the phenol flask for the first two days (Figure G-131). It appeared as though the organisms were adapting to the

phenol. COD and TOC data support the activity by exhibiting decreasing values over the initial test period (Figures G-132 and G-133). During the second adaptation period, both COD and TOC analyses indicated a continuous loss of soluble COD and TOC from the samples collected over the 3-day exposure period (Figures G-134 and G-135). During the 8-day biodegradation test, phenol exhibited the greatest activity of ATP production followed by LAS and De-Solv-It (Figure G-136).

One interesting point is the obvious peak of ATP in the De-Solv-It test flasks on Day 2 followed by a gradual decline to almost background levels by the last day. This peak coincides with the reversal of initial TOC loss (Figure G-137) into an increasing trend. This is somewhat mirrored by the COD analyses (Figure G-138), except that the COD shows an increasing soluble COD up to Day 6 and then drops at Day 8.

(3) <u>3-D Supreme</u>. During the initial acclimation period, the activated sludge's ATP values indicated no substrate inhibition upon exposure to all test solutions (Figure G-139, basal w/o: uninoculated basal medium solution). COD and TOC data supported this conclusion because all solutions lost COD and TOC over the 3-day period. The second acclimation period exhibited some confusion. First, the LAS solution concentration in the flask was greater than required by test protocol (the stock solution bottles had been switched). This resulted in COD values beyond detection limits for all samples analyzed during the period (Figure G-140). Another interesting point was the increasing ATP values each day (Figure G-141) coinciding with increasing TOC values for LAS (Figure G-142). This again points out the limitation of analyses based on indirect determination of solvent biodegradation. This increase in TOC is probably related to an increase in metabolites resulting from the high amount of biological activity. The limitations of the analyses do not permit the distinction of these components; therefore, the issue becomes clouded. During the 8-day test period, the ATP, COD, and TOC analyses supported the general idea that microorganisms were active (the COD and TOC values decreased over time). Figure G-143 exhibits the confusion of data interpretation caused by in indirect analysis of the solvents tested. The uninoculated basal medium has a characteristic soluble TOC background level due, in part, to the yeast extract and other components of the medium. Each test flask contained this

medium initially. Therefore, it may be assumed that at time zero, the flasks contained the same amount of TOC associated with the basal medium plus any TOC associated with the solvent added. From Time Zero, it is not possible to resolve with any accuracy the degradation of the solvent versus utilization of the basal medium. The trend of TOC loss for 3-D Supreme, LAS, and inoculated basal medium (basal w/b) parallel each other throughout the test period. Because it is not possible to distinguish the basal medium TOC loss from TOC loss associated with the added solvents, the TOC loss means very little. The microorganisms may have been using the basal medium only, the solvent only, or any combination.

(4) Calla 301. During the first acclimation period, the activated sludge exhibited an increase in ATP upon exposure to each medium tested (Figure G-144). Similarly, the COD and TOC analyses indicated a loss of soluble COD and TOC during this test period (Figures G-145 and G-146). The second acclimation period showed similar trends.

During the 8-day test, TOC analyses only were made on the samples collected and the COD analyses were discontinued: (a) to reduce the sample load, (b) because the COD and TOC analyses commonly exhibited the same trends, (c) the COD analyses typically showed more variability among replicate samples, and (d) the COD test solution was made up of a chromate with a mercuric salt. The solution remaining after analysis is classified as a hazardous waste and must be disposed of accordingly. The reduction in the number of COD analyses reduced the volume of hazardous waste generated in the laboratory. This change had no perceptible effect on the research goals.

The ATP levels in each solvent preparation exhibited an increase by the second day, followed by a gradual decline to the end of the test (Figure G-147). This may be related to utilization of available substrates and inhibition by a buildup of secondary metabolites in the test solution. The loss of soluble TOC supports the previous idea concerning the utilization of available substrate (Figure G-148). However, as previously stated, without specific identification of the substances present in the mixed medium it is not possible to distinguish accurately between basal medium utilization and solvent degradation.

(5) Gas Chromatograph Techniques. To solve the problem of the inability to make positive identification of solvents in the test solutions, an analytical technique using a GC was developed. This technique was developed to help distinguish between basal medium utilization and solvent degradation.

b. Pilot Plant Activated Sludge Test

This test was set up to look at pilot-plant scale implementation of waste solvent discharge to the activated sludge (AS) system. It was a follow-up to the laboratory ASTM 8-day test.

Initially, testing was to be initiated by establishing steady-state conditions in the pilot plant and maintaining a stable baseline for the activated sludge system for 3 days. This requires filling the pilot plant AS system with solids from Tinker AFB's AS system, and operating and monitoring the AS system to obtain operating conditions. Next, the test solvent was to be introduced to the top of the treatment system. The solvent flow was to be continued for 21 days. The first week permitted acclimation, the second week permitted further acclimation, and the third week provided a period of stabilized treatment conditions. Following a test, the AS system was to be drained and thoroughly cleaned to remove any residual solvent and materials before starting the next test.

After further consideration, the solvent test period was shortened from 21 days to 5 days with the option to extend the test if results were marginal. The establishment of the AS system baseline was to remain the same. The 5-day period better represented the actual operating conditions at the IWTP. In most cases the microorganisms in the AS system would not have 14 days to acclimate to the solvent. The AS system would process slugs of the solvent after a solvent tank was dumped upstream. Depending on how the IWTP equalization basins were operated, these slugs could last for several days at varying concentration. Unless solvent tanks were dumped very frequently, the microorganisms would not see a constant flow of solvent to which they could become acclimated. Tests runs were attempted with Exxon Exxate 1000 before the test period was shortened.

E. PILOT-SCALE BIOLOGICAL ACCLIMATION TESTS

Two 21-day tests were attempted using Exxon Exxate 1000 before the time requirement for the biological acclimation test was reduced. Neither test was successfully completed because of problems with the SCC sludge bed. However, in attempting the tests considerable useful information was gathered. A description of these attempts is included here.

The shorter-length test runs were performed for Exxate 1000, 3-D Supreme and Fremont 776. Orange-Sol De-Solv-It was not tested in the pilot plant because of expected problems with the SCC, based on jar test results. Descriptions of the jar tests and test runs are included here.

1. 21-Day Test with Exxate 1000

Two attempts were made to conduct a 21-day test with Exxate 1000. The first was during February and March 1989 and the second was during August and September 1989. The first test suffered several complications due to flotation of the metal sludge in the solids contact clarifier in the presence of the solvents, so a second test was run during the summer of 1989 after the problem had been addressed. Even with measures added to prevent flotation of the sludge, the second attempt was unsuccessful again because of SCC sludge-blanket breakup.

Jar testing had indicated that the addition of either aluminum sulfate or magnesium sulfate to 50 milligrams/liter of the aluminum or magnesium prevented flotation of the metal sludges with all the solvents tested except Orange Sol De-Solv-It. The addition of both coagulants before adding the metal precipitation treatment chemicals was pilot tested. An organic solvent, Triton Hemo-Sol, at a 1:600 dilution, was fed during the tests. Each test duration was approximately 4 days, during which time the solids contact clarifier effluent was monitored for the heavy metals. With aluminum sulfate, effluent quality changed little. Use of magnesium resulted in much more susceptibility to upsets due to changes in solvent concentration or changes in the influent wastewater. The economics of the aluminum addition has not been determined, but the chemical cost should be no more than an additional polymer. However, the use of the aluminum sulfate would add significantly to the sludge produced in the metals removal process at the IWTP. The sludge removal costs would increase proportionately to the amount of aluminum added.

Later jar tests indicated that the addition of ferric iron, either as ferric chloride or as a coagulant in a Burmah 8170 cationic polymer would prevent flotation of the metal sludges. Ferric ion can be added after the sulfide and ferrous ion addition instead of at the front of the plant. Normally, iron is a better coagulant than aluminum or magnesium; therefore, a lower concentration may be required. Also, the use of the polymer may eliminate the requirement for the Betz cationic polymer currently in use. Ferric chloride was selected for use in the pilot plant runs.

The second bioacclimation test of Exxon Exxate 1000 was attempted beginning in August and continuing into September 1989. Sodium aluminate was added to prevent metal sludge flotation. Even with the sodium aluminate the SCC sludge bed broke up after the solvent was added. The sodium aluminate was difficult to work with because of its tendency to clump up and plug lines. After three attempts with the same problems with the sludge bed, the test was stopped.

In addition to ATP, respirometry analyses were applied to the pilot plant's AS system during the test. The respirometer measures the rate of oxygen uptake and carbon dioxide release of the microorganisms as they metabolize components of the waste. (Again, the activated sludge biological activity is an aerobic process requiring oxygen for the metabolism.) If a substance (in this case a solvent) is used by the microbes, the respiration rate should be positive and relatively high. However if a substance is not easily used by the microorganisms or may be toxic to the biomass, respiration would decrease. Respirometric measurements collected during the August-September test indicated an increase in respiration over a period of time (Figure G-149). This may indicate acclimation of the activated sludge bed to the solvent, Exxate 1000, discharged through the basin. The lack of chemical analyses for Exxate 1000 in the system prevents the acceptance of this conclusion since there was no way of examining the mass balance of the solvent for this consideration.

A particular point of interest was the common starting point of each day's respirometric rates. This led to the speculation that bed performance or operation may be the criteria for direct consideration and not acclimation. Typically, some inherent problems are associated with maintaining a continuous return activated sludge (RAS) and wasted activated sludge (WAS) flow on the pilot plant. The return and waste lines were susceptible to blocked flow, and they needed frequent attention to maintain the split flows. Because the respirometric sampling of the AS system was regulated to daytime operations, the common starting point may indicate some background level of the system. The increase in respiration rate by the end of the day's operation may indicate the ability to maintain RAS and WAS flows. If such conditions are true, the data similarly indicate better AS system performance over time.

Operation of the respirometer proved extremely difficult. Continual respirometer equipment failures tied up personnel and made the respirometer data hard to obtain and somewhat questionable in quality. The respirometer was eliminated in subsequent testing.

Samples for solvent analysis were collected through out the test period. When these samples were analyzed and evaluated no characteristic peaks could be found for the Exxate 1000 with the GC. Without the GC peak data, verification of actual degradation of the solvent was not possible. The acclimation of the AS system to the Exxate 1000 could be determined only by indirect means.

2. Orange-Sol De-Solv-It

Prior to starting a bioacclimation run, jar tests were conducted to determine the impact of the solvent on the heavy metal precipitation portion of the system. The results of the Orange-Sol jar tests showed that Orange-Sol floated the metal-bearing sludge, even if sodium aluminate or ferric chloride ($FeCl_3$) was added. When the stirring rate of the emulsified sample was decreased to 70 rpm, a ring of emulsified solvent formed on the surface of the solution in the beaker. The control beaker (no $FeCl_3$ added) showed a clear supernatant but all of the sludge floated to the top. Subsequent beakers, with increasing amounts of $FeCl_3$ showed larger amounts of sludge being formed, but, in all cases, the sludge floated. When the $FeCl_3$ concentration increased to above 300 mg/liters the solution became a cloudy orange color. As more $FeCl_3$ was added the pH of the jar test mixtures decreased. As pH decreased, floc size decreased, probably due to the solubilization of the metals in the sludge because of the low pH.

From the results of the Orange-Sol jar tests, it was determined that the solvent would upset the pilot plant irreversibly, so the solvent was not considered for testing in the pilot plant. Previous testing showed that the addition of aluminum sulfate did not keep the metal-sludge bed from achieving an upset condition.

The microorganisms present in the activated sludge may have been able to acclimate to the solvent, as shown in the 8-day ASTM test, but the decrease in pH from $FeCl_3$ additions would lead to an eventual upset of the biological system. The pH problem could be overcome by pretreating the AS influent with caustic to increase the pH to approximately 7.0. The biological system may show acclimation to Orange-Sol, if solvent were added to the waste stream at some point after the metals precipitation process. Though the De-Solv-It is immiscible with water, the agitation in the activated sludge basin should be sufficient to expose the solvent to the microorganisms. Its immiscible nature would allow the oil and water separating system to remove nearly all of it, if the solvent were to enter the wastewater system upstream of the IWTP.

During acclimation testing, the biological sludge obtained from the industrial waste treatment plant's (IWTP's) activated sludge (AS) system was not metabolically healthy. The IWTP was having trouble with little or no phenol coming through the plant, due to pump outages. When the biological sludge was pumped into the pilot-scale AS basin there was a large amount of floating sludge on the surface of the inner ring of the final clarifier (FC). As the pilot-scale AS system was operated, the sludge wastage rate had to be increased to remove this unhealthy sludge. The increased wastage led to the low, but constant, biological solids concentrations seen during the solvent testing periods. The decreased amount of microorganisms yielded a better food-to-mass ratio for the AS process, as indicated by the disappearance of the floating sludge in the FC. If too little food (organics) is applied for the amount of microorganisms present, effluent quality may deteriorate.

3. Exxon Exxate 1000

Sludge formed in the jar tests performed on Exxate 1000 began settling when the $FeCl_3$ concentration was between 300 and 400 mg/liters. After all ingredients were added to the jar test mixtures the following results were obtained: the 200 mg/liters $FeCl_3$ sludge floated immediately, the 300 mg/liters $FeCl_3$ sample showed some suspended floc, and the 400 mg/liters sample showed that the sludge had settled. The supernatant of the 400 mg/liters $FeCl_3$ sample was slightly cloudy and had an orange tint. The pH of the 300 mg/liters sample was 3.6, the 400 mg/liters sample was pH 1.6. A concentration of 350 mg/liters $FeCl_3$ was determined to be suitable for the stabilization of the sludge bed when Exxate 1000 was being pumped through the pilot plant.

The solvent/industrial wastewater emulsion was very turbid. After addition of chemicals, the supernatant was very clear, showing that the solvent had been absorbed into the metal sludge floc.

The pilot plant was run for two days with 40 percent $FeCl_3$ solution being pumped at a rate of 8.4 mL/minutes, giving a final concentration of 350 mg/liters. In two days the pH dropped from approximately 6.8 to 4.7. The drop in pH slowly decreased the metabolic activity of the microorganisms in the activated sludge system, as seen in the adenosine triphosphate (ATP) data (Figure G-150). Microscopic examination showed that there were no acid intolerant microorganisms such as rotifers or other protozoans, present in the basin. Acid intolerance causes the microorganisms in the sludge to die, yielding a sludge with low metabolic activity. Low metabolic activity means the solvent will not be degraded.

Chemical oxygen demand (COD) values showed only a small amount of decrease throughout the baseline period. A decrease in COD concentrations was seen between the E-tank and solids contact clarifier (SCC), and between the SCC and FC (Figure G-151). Incoming total organic carbon (TOC) values were constant as seen in the E-tank. Values in the SCC stayed steady during baseline testing and dropped to zero after Exxate was added (Figure G-152).

During baseline testing before the Exxate was added no increase in concentrations of NH_4-N, NO_3-N and phosphorus were seen in the final clarifier, The data were an indicator that the biomass present was not showing signs of endogenous decay (Figures G-153, G-154, and G-155).

Phenol concentrations coming into the AS basin fluctuated widely, but concentrations in the final clarifier were at or near zero, showing that the microorganisms were physiologically healthy (Figure G-156).

Addition of $FeCl_3$ to the waste stream caused a large increase in total iron concentrations that were seen coming out of the SCC and FC (Figure G-157). Amounts of chromium and zinc coming out of the SCC and FC were not affected by the decrease in pH caused by the addition of $FeCl_3$ (Figures G-158 and G-159).

Solvent flow was started to the E-tank at 11 a.m. on Saturday September 22. At 7 p.m. the same day the metal sludge floc had increased in size. The SCC sludge was drained for a short time to bring the sludge blanket depth down to desirable levels. Within 2 hours the sludge had built up to a level where sludge was almost overflowing the weir of the SCC. By 5 a.m. the next morning the sludge bed was beginning to disperse. The SCC was drained for 10 minutes, and the sludge level was back up to overflow in 20 minutes. The floc were very large and the sludge blanket at the top of the clarifier was not uniform. The sludge bed appeared to be disintegrating. The overflowing sludge problem could not be handled by the actuator system on line. Further operation would have put large amounts of metal-bearing sludge into the AS basin.

GC tests were used to monitor the concentration of the principal constituents of the solvent. Analyses were run on samples taken from the E-tank, the SCC effluent and the FC effluent. Samples from an earlier run that had been stored in a refrigerator, showed no solvents. Those from the present test also gave similar results.

4. 3-D Supreme

Jar testing showed that 50 mg/liters $FeCl_3$ was adequate to stabilize the metal-sludge bed. Results from the test showed that there was a small amount of suspended sludge in the 25 mg/liters $FeCl_3$ sample, and none in the 50 mg/liters sample.

Testing of the solvent was done from September 22 to September 30. Originally the solvent was started and no $FeCl_3$ was added to the waste stream. Six hours after the solvent was started the sludge was found overflowing the weirs of the SCC. The metal-bearing floc appeared to be large and light. Floc was overflowing at a rate much faster than it would have been generated by incoming metal concentrations. The SCC was drained to lower the sludge-bed level and the flow of the 3-D Supreme was stopped. The sludge-bed continued to recede over the next several hours.

$FeCl_3$ was added and the plant was allowed to stabilize for 1 day. After sludge-bed stabilization the solvent was started and an actuator program for SCC sludge wasting was optimized. The sludge was drained for 4 minutes every 5 hours, to keep the sludge bed from overflowing the SCC weir.

The small amount of SCC sludge that was dumped into the activated sludge decreased metabolism slightly, but the microorganisms recovered and ATP concentrations were fairly steady throughout the testing period. No increases or decreases in ATP production, due to the presence of the solvent were noted. ATP concentrations present were fairly constant (Figure G-160).

Nutrient profiles for the testing period showed that the same amounts of nitrogen and phosphorus were coming into the activated sludge system, as were going out (Figures G-161, G-162, and G-163). An increase in the amount of these elements in the effluent would be an indicator that the solvent was having adverse effects on the microorganisms present in the AS basin. As with previous solvent testing, the protozoans seen in the system when sludge was first obtained from the IWTP were not present after the solvent and $FeCl_3$ had been run through the plant.

Phenol was present in the waste stream during the solvent testing (Figure G-164). With the methods used, no determination could be made whether the microorganisms were selectively using the phenol, were using small amounts of both phenol and solvent, or were using the solvent present. In the absence of phenol, the microorganisms can become acclimated to the solvent. An intermittent flow of phenol in the plant may have enabled acclimation to occur. However, this was not observed in the acclimation tests.

Fluctuation in COD concentrations seen during the pilot run were more likely due to fluctuations with oxidizing agents coming through the plant than to the addition of solvent. There was no significant increase in COD values when solvent was added to the waste stream (Figure G-165). Data from the 6-hour tests and ASTM 8-day tests showed that water soluble solvents yielded only small increases in COD concentrations. The small decrease in COD removal seen between the SCC effluent and the FC effluent, could be accounted for by the utilization of phenol by the microorganisms or by a decrease in solids content.

TOC concentrations coming into the pilot plant started out at 62 mg/liters dropped off to zero and then increased to nearly 120 mg/liters. Concentrations from the SCC were similar to the E-tank. TOC concentrations determined for the FC showed no significant decrease from values seen coming into the biological system (Figure G-166).

Chromium concentrations seen in the SCC effluent were not affected by the addition of solvent or $FeCl_3$ to the waste stream (Figure G-167). Iron concentrations in the SCC and FC effluent increased due to the addition of $FeCl_3$ (Figure G-168). Zinc concentrations in the SCC and FC effluent were not affected by addition of solvent or $FeCl_3$ (Figure G-169).

Gas-chromatography methodology produced chromatograms that contained a phenol peak at a retention time of 2.6 minutes and a solvent peak at a retention time of 3.2 minutes with a satellite peak at 3.3 minutes. The solvent was not picked up in the samples from the E-tank in the first five days of the run after solvent had been added. Apparently, the solvent was absorbed into suspended solids in the solutions that settled out prior to the GC analysis. Phenol peaks were detected in all three samples tested, concentrations usually decreasing between the SCC effluent and FC effluent. Solvent peaks were seen in the SCC effluent and the FC effluent. No noticeable decreases or peaks from metabolic by-products were seen in the samples run (Table 6).

Data obtained throughout the 3-D Supreme testing period showed that in the five-day testing period the microorganisms did not acclimate to the solvent. Ideally, if a waste stream could be isolated that did not contain phenolics, the ability of the microorganisms to switch cellular metabolic systems could be followed. A switch of metabolic systems would allow utilization of the solvent. Phenol tests and GC data showed that the microorganisms were utilizing the phenol present in the waste stream.

TABLE 6. RESULTS OF GAS CHROMATOGRAPHY RUNS.

10/22/90
Gas Chromatographic Data for 3-D Run 8/25/90-8/31/90
Injection: 0.5 uL on-column
Column: 30 m SPB-5
Method/Instrument: PE Sigma 2000/2100
Inj. 280 C Det.(FID) 300 C
Temp. program: 65 deg. C for 3 min, then 10 deg./min to 120 deg. C, then 30 deg./min until 250 C. Recycle.
Data stop at 8.0 min. Attn.=8
Carrier: He Flow rate=25 Column Head Pressure=20

Date	Time	Sample	Phenol Area	3D Area
8/25	1100	E-tank	***	***
8/25	1100	SCC	***	***
8/25	1100	FC	***	***
8/26	1100	E-tank	<10000	18441
8/26	1100	SCC	45755	80825
8/26	1100	FC	***	***
8/26	1700	E-tank	79461	***
8/26	1700	SCC	57063	15006
8/26	1700	FC	***	10566
8/26	2200	E-tank	106977	***
8/26	2200	SCC	65388	23934
8/26	2200	FC	***	***
8/27	0500	E-tank	502234	***
8/27	0500	SCC	295263	29938
8/27	0500	FC	29108	10558
8/27	1100	E-tank	46307	***
8/27	1100	SCC	119970	23436
8/27	1100	FC	19822	<10000
8/27	1700	E-tank	74776	***
8/27	1700	SCC	210778	69875
8/27	1700	FC	<10000	17941
8/27	2200	E-tank	77541	***
8/27	2200	SCC	125762	57160
8/27	2200	FC	***	70452
8/28	0500	E-tank	82809	63220
8/28	0500	SCC	100691	40706
8/28	0500	FC	***	***
8/28	1700	E-tank	***	***
8/28	1700	SCC	***	***
8/28	1700	FC	***	16970
8/29	0500	E-tank	11115	13417
8/29	0500	SCC	12825	15831
8/29	0500	FC	***	13090
8/29	1100	E-tank	13334	24742
8/29	1100	SCC	10138	14727
8/29	1100	FC	***	13843
8/29	1700	E-tank	10381	***
8/29	1700	SCC	<10000	15989
8/29	1700	FC	***	14427
8/29	2200	E-tank	71727	***
8/29	2200	SCC	43344	40487
8/29	2200	FC	***	52608
8/30	0500	E-tank	***	50568
8/30	0500	SCC	38865	54828
8/30	0500	FC	***	49951
8/30	1100	E-tank	***	54501
8/30	1100	SCC	***	53099
8/30	1100	FC	***	56909
8/31	0500	E-tank	11373	60672
8/31	0500	SCC	***	53932
8/31	0500	FC	***	51614
8/31	1100	E-tank	73090	68017
8/31	1100	SCC	51539	65949
8/31	1100	FC	***	21253
8/31	1700	E-tank	96519	***
8/31	1700	SCC	55941	52184
8/31	1700	FC	***	51029
8/31	2200	E-tank	24903	***
8/31	2200	SCC	57299	51013
8/31	2200	FC	***	47937

*** = None detected.
<10000 = Present but not integrated because peak was less than 10000 area units.

Switching cellular metabolic systems would have been an inefficient step in energy utilization for the microorganisms present in the AS system, when a readily metabolizable substance,such as phenol, was already present in the wastewater.

5. Fremont 776

$FeCl_3$ was not needed for SCC sludge-bed stabilization for Fremont 776, differing from the previous solvents tested. The sludge in the control sample settled, showing no $FeCl_3$ was needed. No increase in settling characteristics was seen by the addition of $FeCl_3$ to the solvent containing wastewater. The only adverse effect seen by the addition of the solvent to the wastewater was the supernatant became murky after the sludge had settled.

The solvent testing period was form October 3 until October 14. After solvent was added to the plant influent, the SCC effluent became cloudy. Several days elapsed before the sludge blanket in the SCC began to filter out the particles that were making the effluent cloudy.

Fremont 776 does not contain any organic constituents, the formulation is mostly sodium metasilicate. The absence of organic constituents was seen by running a control on the GC, which yielded no peaks of any type.

As seen with the 3-D Supreme, there was no adverse effect of the solvent on the biological system of the pilot plant. Ammonia, nitrogen and phosphorus concentrations were consistent between the SCC and FC throughout the testing period (Figures G-170, G-171 and G-172). ATP levels at the beginning of the run decreased due to a small solids control problem. During the testing period, the microorganisms were able to recover and ATP concentrations were constant through the rest of testing period (Figure G-173).

Phenol was present throughout the solvent testing period (Figure G-174). The microorganisms present were utilizing the phenol rather than the Fremont. There were a few small prokaryotic organisms present upon microscopic examinations, but no rotifers were seen in the slide examined. The biological sludge had finger-like projections, a sign of sludge growth.

There was no increase in COD values that could be seen by the addition of solvent to the waste stream (Figure G-175). The filtered COD samples gave a better example of the soluble constituents present in the wastewater. Changes in COD concentration were attributed to the normal fluctuation of oxygen utilizing substances in the waste stream. Without solids present in the samples, the COD removal efficiency was increased to more desirable levels than those seen in the 3-D testing.

TOC values fluctuated widely over the testing period (Figure G-176). In all testing periods there was a consistent decrease in TOC between E-tank, SCC and FC.

The total chromium concentration changed substantially during the period of Fremont 776 addition to the waste stream. The amount of chromium in the SCC effluent was higher during solvent testing than in the baseline period (Figure G-177). The marked increase of chromium in the E-tank indicated a rise in chromium in the influent wastewater. The increase seen at the SCC was attributable to the change in the influent. The amount of zinc in the SCC effluent was similar to concentrations obtained in the baseline period (Figure G-178). Iron concentrations in the FC increased during the baseline period due to leaching of iron from SCC sludge that had overflowed into the AS basin (Figure G-179).

Overall the addition of Fremont 776 to the waste stream had no adverse effects on the pilot plant system. Because the solvent contained no carbon source, it was not metabolizable by the microorganisms present in the AS system. COD concentrations were not increased and the solvent did not have a negative effect on the biological system. These results indicate that the solvent could be added to a wastestream treated in the biological system, but the system would have little effect on the solvent. Solvent use would be limited by silicon discharge limits imposed on the IWTP.

F. EXTENDED CORROSION TESTING

Extended corrosion tests were conducted at those conditions shown to produce optimum results for cleaning in enhancement testing. The test conditions and results are listed in Appendix F.

Table 7 lists the metals that exhibited pitting or corrosion greater than 0.3 mils/year, which was established as the cutoff limit in Phase I. All of the solvents except Orange Sol De-Solv-It heavily corroded/oxidized magnesium. The Orange Sol exceeded the corrosion limit for magnesium but did not demonstrate the severe attack of the other solvents. Based on the 0.3 mils/year limit, none of the solvents should be used to clean magnesium. 3-D Supreme corroded aluminum alloy 1100 excessively also. Each of the solvents attacked other coupons at a rate greater than the limit. The Table 7 data should be studied closely before the solvents are released for general use to determine if they are safe for their intended application.

Hydrogen embrittlement testing was performed according to ANSI-ASTM Method F 519-77. No hydrogen embrittlement was apparent on the specimens in the five solvents tested. No hydrogen embrittlement tests were performed for Fremont 776 in this project. Fremont 776 was added to the test program after the Phase II hydrogen embrittlement tests had been completed and reported. It was already in use, cleaning Air Force production parts.

G. SENSOR DEVELOPMENT

Temperature changes and convection limited sensor sensitivity to about ± 3 nanoseconds or 0.0018 percent of the time of flight for water. A secondary limit was set by variations in the day-to-day variations in purity of the demineralized water. Together, these factors set a lower

TABLE 7. ASTM METHOD F 483-77 CORROSION TESTING RESULTS.

Solvent	Metal	Temp. (°F)	Agitation	Rate[a] (mils/year)	No. Pits	Maximum Depth (mm)
Exxon Exxate 1000	C1020	120	Mixer	0.23	12	0.034
	Mag	120	Mixer	-0.71	0	HO[d]
	Mag	140	US[b],600W	0.35	0	HO
	CDA110	140	US, 600W	0.51	418	0.006
Bio-Tek 140 Safety Solvent	CDA110	120	US, 300W	0.79	12	0.012
	Mag	120	US, 300W	0.39	0	HO
3-D Supreme	Al1100	77	US, 300W	64.9	HC[c]	0.160
	N200	77	US, 300W	0.68	19	0.080
	SS410	77	US, 300W	0.44	4	0.080
	C1020	77	US, 300W	0.58	13	0.160
	C4340	77	US, 300W	0.39	15	0.120
	Al7075	77	US, 300W	1.18	12	0.12
	Ti-2	77	US, 300W	0.75	0	HO
	Al2024	77	US, 300W	0.59	0	HO
	Mag	77	US, 300W	574	HC	
Orange Sol De-Solv-It	Al1100	140	US, 600W	0.33	0	HO
	Mag	140	US, 600W	2.01	0	LO
	C4340	140	US, 600W	4.57	0	HO
	CDA110	140	US, 600W	0.41	0	LO
	N200	140	US, 600W	0.56	0	HO
	C1020	140	US, 600W	3.07	0	HO
Calla 301	Al1100	120	US, 300W	1.85	228	0.120
	Mag	120	US, 300W	60.6	HC	0.500
	CDA110	120	US, 300W	0.91	36	0.200

---

a. Negative numbers indicate a scale that is not removed by acid cleaning or scrubbing.

b. US = ultrasonic agitation.

c. HC = heavy corrosion, coupon significantly deteriorated.

d. HO = heavy oxidation; LO = light oxidation.

limit of about 10^{-5}moles/liters to the concentrations that could be measured reliably. This limit was sufficient to detect weighing and dilution errors of less than 0.2 percent and to demonstrate milligrams/liter sensitivity.

The time of flight was an accurately linear function of concentration over almost the full range measured in all solutes (Figure G-180). The figure is a linear plot covering more than four decades of concentration. The zero-concentration intercept is the transit time for water. The time scale on the ordinate is the transit time in this particular gage.

Uncertainties of each measurement approximate the size of the plotting symbol. The slope of the transit time versus concentration is the calibration for the solute in each case, in units of microseconds/mole for this gage. The slope and intercept were computed by the least-squares method, weighted according to the experimental uncertainty at each point. Results are presented in Table 8 and plotted in Figure G-181.

The calibration for NaCl has a negative slope; the speed of sound increased with increasing concentration, with concentrations up to at least 0.5 mole/liters. The other solutes have increasingly positive calibrations. The slope for CsCl is small but positive and easily measured with accuracy, as can be seen in Figure G-182. The calibrations are shown in Figure G-183, relative to the time of flight for demineralized water, so they apply to any gage length.

TABLE 8. MEASURED CALIBRATION SLOPES.

Solute	Slope[a]	Uncertainty
NaCl	-6.7524	0.098
CsCl	0.1219	0.008
NaI	2.6577	0.091
CsI	25.6011	0.030

---

[a] Slope is expressed in microseconds/mole for the transit time of the particular gage used in these measurements; demineralized water has a transit time of 165.814 microseconds at the reference temperature of this gage.

The speed of sound in any medium is a function of the average intermolecular forces in that medium and of the mass of the individual particles. Solutes in a liquid change the intermolecular forces, which determine sound speed. This work shows that in all the cases investigated, for very dilute solutions at least, changes in intermolecular forces for a given solute are proportional to solute concentration. However, this proportionality is not always true at higher concentrations.

In a polar liquid, molecule or ion size, charge, hydration spheres, and similar variables are also expected to affect intermolecular forces, which control the speed of sound. The solution's density, proportional to the molecular weight in these measurements, is clearly not dominant. If it were, the calibration for NaCl could not be negative. The calibrations in Figure G-183 can be used directly and on-line for accurate quantitative analysis of solutions of a single known solute.

The difference in calibration slopes indicates that the technique can be used for qualitative analysis as well. At the present state of development, the analysis would proceed by serial dilution of the unknown. The curve of transit time versus dilution would not be linear, and could be fragmented into a series of straight lines that would indicate initial concentrations of each solute. Theory says that it may be possible to perform quantitative and qualitative analysis on a single concentration, and thus on-line, by combining several different kinds of acoustic fields.

Instruments can be arranged whereby the effects of temperature variations can be normalized out at the same time the temperature itself can be measured acoustically; temperature limitations need not apply to an on-line instrument.

This work suggests that an acoustic sensor could be used to determine the end of a solvent's useful life. The applications for a probe of this type would be numerous. Further work toward its development is recommended.

SECTION V
PHASE III RESULTS

A. 100-GALLON TESTS

In the 100-gallon tests, oil and grease were removed within the first 45 minutes of cleaning. Light oil was easily removed, usually within the first 15 minutes, while the grease in hard-to-reach areas (cavities, grooves, splines) required up to 45 minutes to remove. Figure 3 shows the percentage of parts with oil and grease removed after 15, 30, and 45 minutes for each solvent. After 15 minutes, 3-D Supreme had removed all of the oil and grease from 64 percent of the parts cleaned, while Fremont 776 had removed the soil from 41 percent. Exxate 1000 and Orange-Sol had cleaned just 13 percent of the parts, while Bio-Tek failed to remove oil and grease from any of the parts after 15 minutes. After 30 minutes, 3-D Supreme and Fremont 776 had removed oil and grease from approximately 94 percent of the parts. Bio-Tek had removed oil and grease from 71 percent of the parts, Exxate 1000 80 percent, and Orange-Sol 100 percent after 30 minutes.

The percentage of parts where all carbon was removed is shown in Figure 4. The water-based solvents, 3-D Supreme and Fremont 776, removed carbon from a higher percentage of parts than did the organic-based solvents. The difference in cleaning efficiency is due to the different cleaning mechanisms used by the two types of solvent. The water-based solvents seemed to attack and loosen the bonds between the carbon and the metal surface. This type of action caused the carbon to lift and flake off in pieces when rinsed with a pressure sprayer. The organic-based solvents appeared to slowly eat away at the outer surface of the soil, but never loosened it from the metal surface. This difference in cleaning efficiency can also be attributed to the fact that spray rinsing with water was more effective when used with water-based solvents. The carbon-to-metal bonds weakened by the water-based solvents were easily broken by the spray rinse.

Four waxed parts were cleaned in each solvent tested. The individual part descriptions and cleaning results are listed in Appendix I.

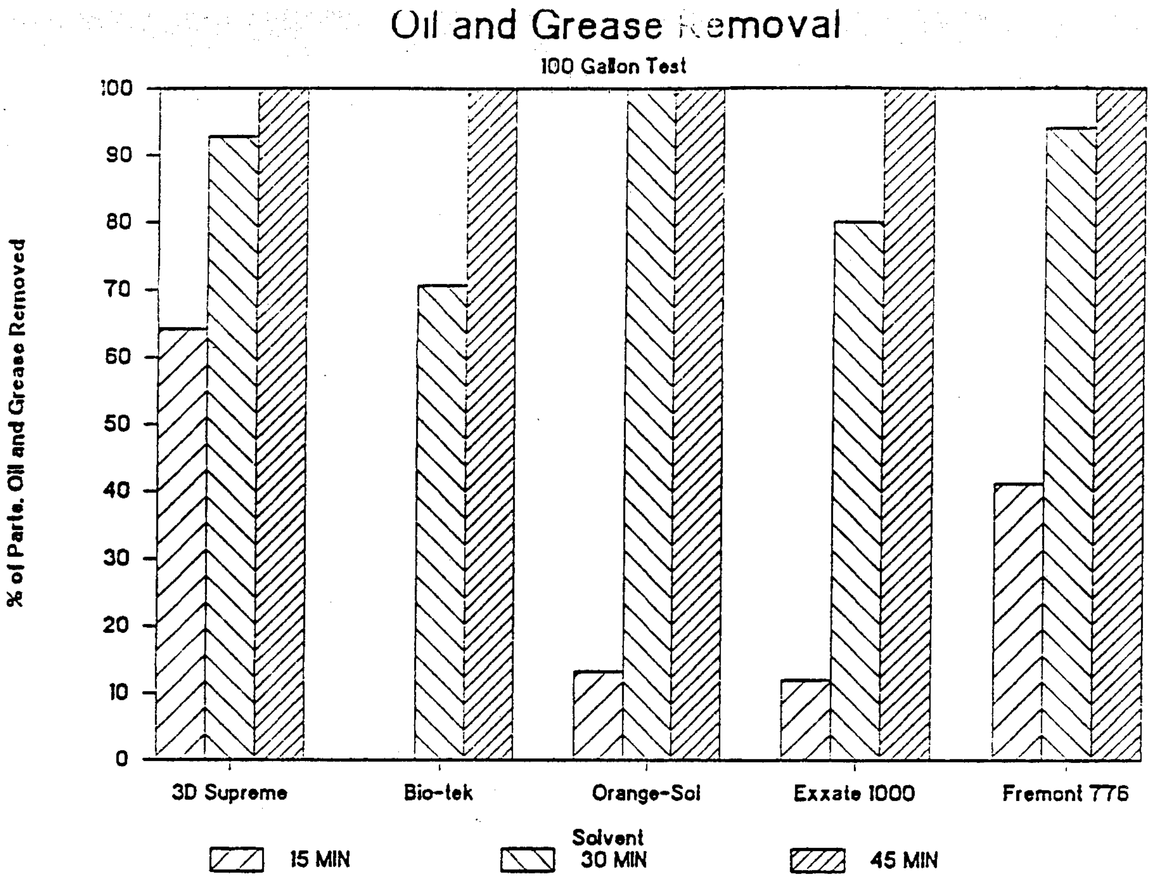


Figure 3. Percentage of Parts from which Oil and Grease Were Completely Removed in 100-Gallon Cleaning Tests in 15, 30, and 45 Minutes.

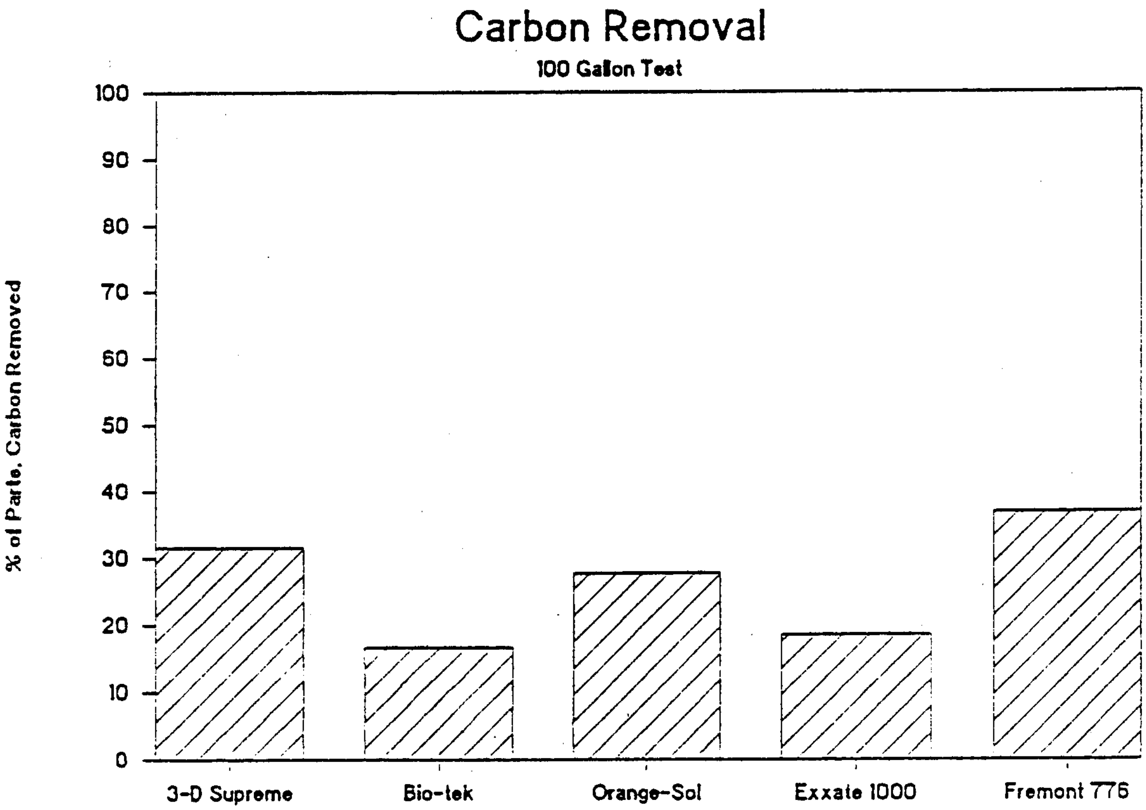


Figure 4. Percentage of Parts from which Carbon Was Completely Removed During 100-Gallon Cleaning Tests.

The water-based solvents required a significantly longer cleaning time to remove wax than did the organic based solvents. 3-D Supreme and Fremont 776 required 75 minutes or longer in order to remove all wax from cavities and hard to reach areas. The organic-based solvents averaged a removal time of 30 minutes. At the request of Air Force personnel, 3-D Supreme was tested at a dilution of 1:20 at the 100-gallon scale. Results for these tests are listed in Appendix I. Parts soiled with oil, grease and carbon were cleaned at this dilution, however, parts with wax were not available. Cleaning efficiency was not affected by the dilution.

B. CABINET SPRAY WASHER

3-D Supreme was tested in the cabinet spray washer at three different dilutions and at temperatures ranging from 140 to 160°F. Results for specific parts are listed in Appendix J.

Parts cleaned at the 1:4 dilution had a light coating of white residue after drying. It was identified as sodium metasilicate. Based on recommendations from the product manufacturer, the solvent concentration was changed to a 1:6 dilution and the temperature increased to 160°F. The residue was no longer present after making these changes, while cleaning efficiency remained constant. Oil and grease were removed after 10 minutes and only light carbon remained after 20 and 30 minutes at both the 1:4 and 1:6 dilutions.

3-D Supreme was also tested at a dilution of 1:20 with no significant decrease in cleaning efficiency. Oil and grease were removed after 10 minutes in all cases. Some carbon was removed after 20 minutes while only light carbon remained after 30 minutes. Complete carbon removal was never achieved. According to cabinet spray washer operators, this was consistent with their previous cleaning experience with other cleaners.

Two cabinet spray washer operators who were present throughout the tests, stated that the fuel controls cleaned at the 1:20 dilution were much cleaner than most fuel controls cleaned with detergents presently being used. One of the detergents presently being used in the cabinet spray washer is Fremont 776. The process engineer felt that the improvement in cleaning of 3-D Supreme as compared to Fremont 776 was insignificant.

As described previously, the organic solvents were not tested, because the Roto-Jet manufacturer predicted that a severe explosion hazard would result. The cabinet spray washer could not be modified to alleviate this hazard.

C. FULL-SCALE TESTS

Table 9 shows a partial list of parts cleaned by each of the four solvents in the full-scale tests. The list includes the part number, cleaning results, metal alloy and the name of each part cleaned. It does not represent a particular percentage of total parts cleaned. Appendix K contains a comprehensive listing for these tests.

Oil and grease were removed within the first 15 minutes of cleaning for all of the solvents tested. The increased cleaning efficiency compared to the 100-gallon tests can be attributed to spray rinsing of the parts after 15 minutes opposed to 30 minutes for the 100-gallon tests. Also, the sprayer used for rinsing during the full-scale tests had twice the pressure of the sprayer used for the 100-gallon tests and therefore, was much more effective.

The percentage of parts that had all carbon removed is shown for each solvent in Figure 5. As in the 100-gallon tests, the water-based solvents removed carbon from a higher percentage of parts than did the organic-based solvents. Again this can be attributed to the difference in cleaning mechanisms used by the two types of solvent, as explained in the 100-gallon results section. During the full-scale tests, the carbon-metal interface appeared to be attacked by the water-based, solvents causing it to lift the carbon from the metal.

TABLE 9. SUMMARY OF PARTS CLEANED.

Solvent	Part Number	Cleaning Results Pass/Fail	Metal Alloy	Part Name
3-D Supreme	385384	P	Low Alloy Steel	Gear Shaft Spur (TF-3)
	653310	F	Low Alloy Steel	Fuel Pump Dr. Gear Shaft Spur (TF-33)
	6899467	P	Low Alloy Steel	Spiral Bevel Gear Shaft (TF-41)
	416152	F	Low Alloy Steel	30 Teeth Bevel Gear Shaft (TF-33)
	516D855P1	P	Low Alloy Steel	26T Gear Spur (J-79)
	772345	F	Low Alloy Steel	Starter Drive Coupling Coupling (TF-33)
Fremont 776	234931	P	Low Alloy Steel	Gear Shaft (J-57)
	554570	F	Titanium Alloy	Grbx. Quick Disconnect (TF-30)
	502097	P	Low Alloy Steel	Spacers (TF-30)
	502724	F	Aluminum Alloy	Xfr Gearbox Tubes (TF-33)
	411573	P	Low Alloy Steel	Acc. Dr. Gearbox Spur Gear (TF-33)
	384758	F	Low Alloy Steel	50 Tooth Bevel Gear Shaft (TF-33)
Orange-Sol	502563	P	Aluminum Alloy	Xfr Gearbox Packing Tubes (TF-30)
	411587	F	Carbon Steel	Gearbox Oil Baffle Assembly (TF-33)
	502371	P	Low Alloy Steel	Grbx. Dr. Sealing Tube Assembly (TF-33)
	697217	F	Low Alloy Steel	Grbx. Quick Disconnect Adaptor (TF-30)
	501633	P	Low Alloy Steel	Gearbox Spur Gear Shaft (TF-30)
	538581	F	Heat Res. Steel	Oil Tank Guide Assembly (TF-30)
Exxate 1000	579858	P	Low Alloy Steel	Gearbox Idler Shaft (TF-33)
	308D127P1	F	Low Alloy Steel	Coupling Spline (J-79)
	411573	P	Low Alloy Steel	Acc. Dr. Grbx. Spur Gear (TF-33)
	639E453P5	F	Low Alloy Steel	Gear Shaft Bevel (J-79)
	386124	P	Low Alloy Steel	Coupling (TF-33)
	7042M95G01	F	Low Alloy Steel	Gear Shaft Assembly (J-79)

Both 3-D Supreme and Fremont 776 had a significantly higher percentage of parts come clean in the full scale testing than in the 100-gallon tests. This difference is mostly due to the high pressure steam rinse used as the final step in the full-scale procedure, which was not used for the 100-gallon tests.

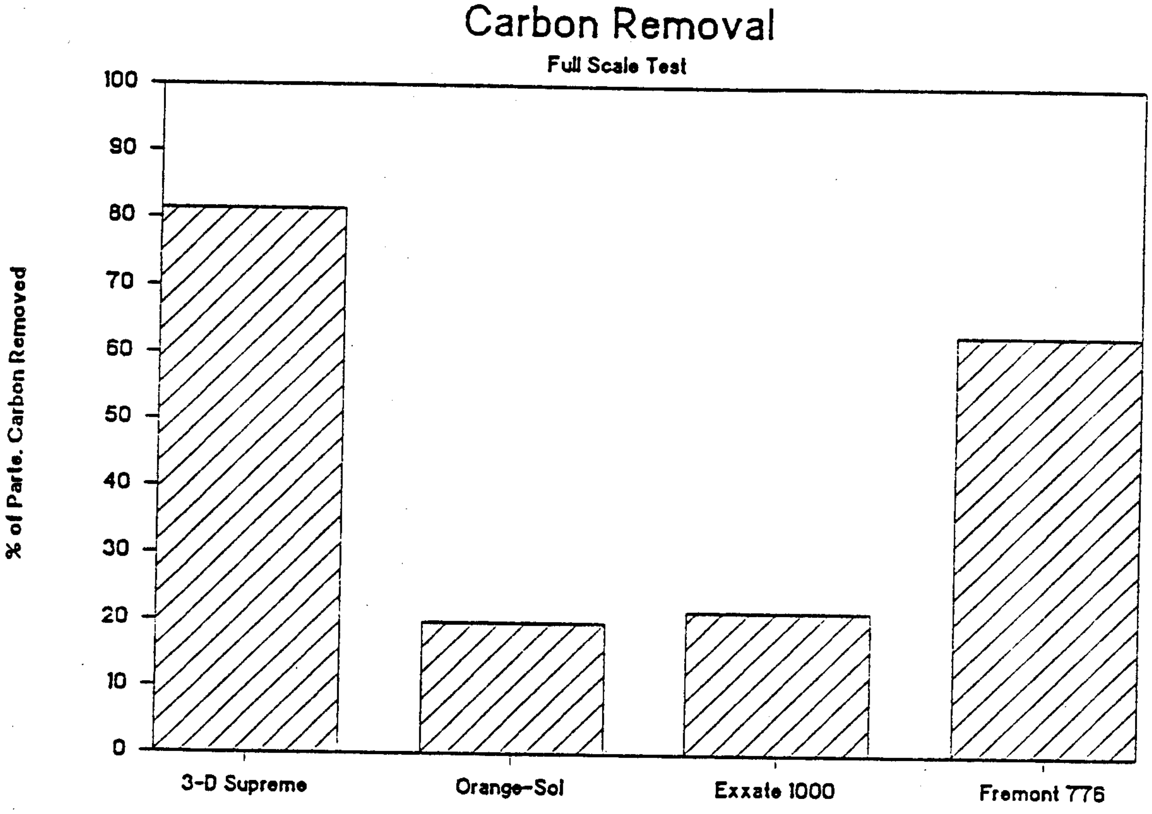


Figure 5. Percentage of Parts from which Carbon Was Completely Removed During Full-Scale Cleaning Tests.

Wax-soiled parts were cleaned using Orange-Sol and Exxate 1000 during the testing. Exxate 1000 required a maximum of 45 minutes to completely remove the wax coatings from parts having a layer of wax approximately 1/8- to 1/4-inch thick. A #5 Bearing Housing covered with wax ranging from 1/4- to 1-inch thick was cleaned using the Orange-Sol solvent. This was considered the worst case part. If it could be cleaned, any other waxed part could be. Fifty percent of the wax had been removed after 45 minutes and 90 percent had been removed after 75 minutes. Only cavities and grooves where the wax was the thickest, contained small quantities of wax. After 90 minutes, only traces of wax could be found with careful inspection. The normal time for cleaning this part is considerably less using a halogenated hydrocarbon cleaner.

All of the cleaned parts which were inspected through the FPI and MPI inspection processes passed those inspections. The solvents did not leave a residue or film which would interfere with the inspection process. Parts that were cleaned and returned to the paint shop received either Sermetel, Actithane, or enamel paint. One of the parts cleaned with Orange-Sol was not acceptable due to the paint's tendency to run. It could not be determined whether this was due to a solvent residue remaining on the part or soil that had not been removed during cleaning. All of the other parts were found to be acceptable.

Both 3-D Supreme and Fremont 776 removed the fluorescent penetrant oil in less than 15 minutes. The results are listed in Appendix K.

D. OIL AND GREASE TEST

As was previously discussed, the oil and grease samples were only obtained during the Fremont 776 pilot plant biological acclimation runs. A set of samples was drawn each shift, morning and evening, for the final two days that the solvent was added to the pilot plant. After the solvent feed was stopped, the pilot plant was operated for three additional days. Samples were drawn only during the morning shift on those last three days.

The E-Tank and FC data are graphed in Figure 6. The concentration of oil and grease in the influent was essentially constant during the run, averaging about 14 mg/liter. Except for the first sample set with Fremont added, the concentration of oil and grease in the FC samples with Fremont was lower than that without Fremont. Based on this small data set, the addition of Fremont seemed to improve the removal of oil and grease by the pilot plant.

The small size of the data set was of some concern. A second concern was the interference of suspended solids with the performance of the analyses. A considerable amount of material collected in the

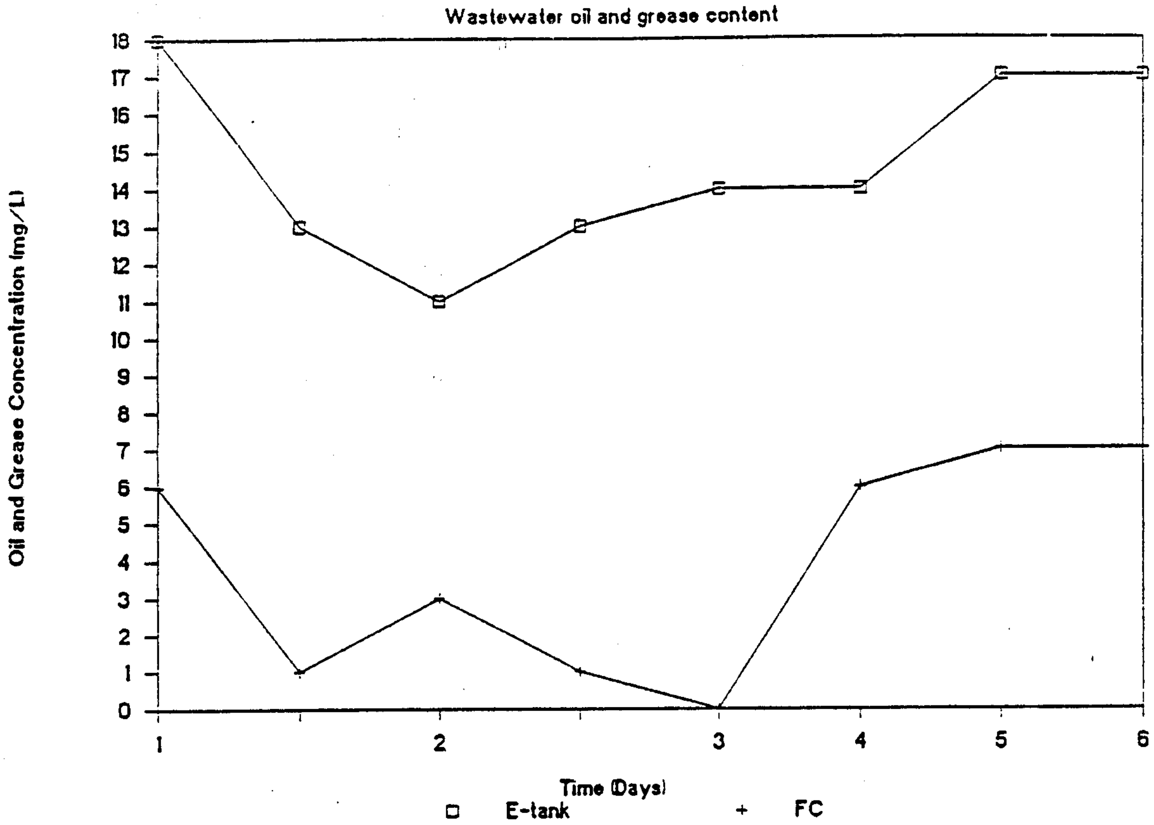


Figure 6. Results of Oil and Grease Tests

trichlorotrifluoroethane was used to extract the oil and grease from the samples. This material was strained out by the filter paper, slowing the filtration process and eventually clogging the filter paper. The chemical composition of this material was unknown. Though the material did not appear oily, oil and grease may have absorbed into it, masking the actual oil and grease concentrations. Special care was taken to ensure that each extraction was done thoroughly. This allowed the trichlorotrifluoroethane to absorb as much of the available oil and grease as possible.

Even with the interference of the unknown material, the results of the test appear to be valid. The material was present independent of the presence of Fremont, so its influence should not prejudice the results of the analyses. If it had an effect, it should have equally affected all of the samples.

SECTION VI
CONCLUSIONS

A. PHASE II CONCLUSIONS

The major discoveries and conclusions from the Phase II test program are included here. Some of these findings were utilized in developing the Phase III test series, while other conclusions were not applicable to the Phase III full-scale solvent implementation.

1. Performance Tests

Enhancement tests, performance tests, and rinsing and drying tests were completed in Phase II. The final results of these tests are listed in Table 10, which shows the optimum conditions, loading capacity, and performance of the solvents using aircraft parts. Solvent costs are also incorporated in this table. In general, parts cleaning could not be achieved at the temperatures that were efficient for cleaning metal coupons in Phase I. Because of inner surfaces and the notches and crevices inherent to parts, enhancements were required to achieve efficient cleaning. Generally, the operating temperature could not be decreased below the highest temperature at which the solvent could be safely used. Rinsing was 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. The rinsing requirements are listed in Table 11 and drying requirements in Table 12. Fremont 776 had not been added to the program at the time that the rinsing and drying tests were performed. Insufficient time and money were available to reassemble the equipment and perform rinsing and drying tests for Fremont 776.

In some applications, such as in parts storage, a film of solvent may be desirable, especially in preventing rust on steel parts. Before allowing solvent to remain on the parts, a determination of the impact on

TABLE 10. SUMMARY OF TEST RESULTS

SOLVENT	SOIL	AVG SOIL PER NIPPLE * (g)	TEMPERATURE (F)	ULTRASONICS	MIXER AGITATED	RUN DURATION (min)	RINSE APPLIED	MAXIMUM SOIL LOAD CAPACITY (g/L)	OPERATIONAL SOIL LOAD CAPACITY (g/L)	CLEANING EFFICIENCY (percent) (Soil Removed)	COST ** UNMIXED (100 GAL)
EXXON EXXATE 1000	WAX	--	140	900 W	NO	20	NO	--	--	--	$2000
EXXON EXXATE 1000	WAX	0.74	140	500 W	NO	20	YES	10	9	90	--
EXXON EXXATE 1000	OIL/XYLENE	--	120	NO	YES	30	NO	--	--	--	--
EXXON EXXATE 1000	OIL/XYLENE	0.95	120	NO	YES	20	YES	56	45	95	--
EXXON EXXATE 1000	OIL/XYLENE	--	140	NO	YES	30	NO	--	--	--	--
EXXON EXXATE 1000	OIL/XYLENE	--	140	300 W	NO	10	NO	--	--	--	--
EXXON EXXATE 1000	OIL/XYLENE	--	120	600 W	NO	20	NO	--	--	--	--
ORANGE SOL DE-SOLV-IT	WAX	--	120	600 W	NO	10	NO	--	--	--	$1490
ORANGE SOL DE-SOLV-IT	WAX	0.74	140	600 W	NO	10	NO	50	45	80	--
ORANGE SOL DE-SOLV-IT	OIL/XYLENE	--	120	600 W	NO	30	YES	--	--	--	--
ORANGE SOL DE-SOLV-IT	OIL/XYLENE	--	120	900 W	NO	30	NO	--	--	--	--
ORANGE SOL DE-SOLV-IT	OIL/XYLENE	--	120	900 W	NO	20	YES	--	--	--	--
ORANGE SOL DE-SOLV-IT	OIL/XYLENE	--	140	300 W	NO	30	YES	--	--	--	--
ORANGE SOL DE-SOLV-IT	OIL/XYLENE	0.95	140	600 W	NO	20	YES	60	30	80	--
BIO-TEK 140 SAF SOL	WAX	0.74	140	900 W	NO	20	YES	20	20	98	$1980
BIO-TEK 140 SAF SOL	OIL/XYLENE	0.95	140	NO	YES	20	YES	70	70	98	--
3D SUPREME	HYDRAULIC FLUID	--	77	NO	YES	30	YES	--	--	--	$ 602
3D SUPREME	HYDRAULIC FLUID	--	100	NO	YES	20	YES	--	--	--	--
3D SUPREME	HYDRAULIC FLUID	0.85	120	NO	YES	10	YES	58	44	92	$550
3D SUPREME	HYDRAULIC FLUID	--	77	300 W	NO	10	YES	--	--	--	--
3D SUPREME	MOS GREASE	--	100	NO	YES	30	YES	--	--	--	--
3D SUPREME	MOS GREASE	0.52	140	NO	YES	10	YES	10	8	92	$550
3D SUPREME	MOS GREASE	--	77	300 W	NO	20	YES	--	--	--	--
3D SUPREME	MOS GREASE	--	100	300 W	NO	10	YES	--	--	--	--
CALLA 301	HYDRAULIC FLUID	0.85	140	NO	YES	20	YES	23	17	96	$ 418
CALLA 301	HYDRAULIC FLUID	--	120	300 W	NO	10	YES	--	--	--	--
CALLA 301	MOS GREASE	0.52	140	NO	YES	20	YES	30	--	--	--
CALLA 301	MOS GREASE	--	120	300 W	NO	10	YES	--	--	--	--

*AVERAGE WEIGHT OF THE SOIL ON A 1 X 2 INCH CARBON STEEL NIPPLE

**COSTS SHOULD BE LOWER IF SOLVENTS ARE BOUGHT IN BULK.

TABLE 11. RINSING REQUIREMENTS.

Solvent	Soil	Immersion Cleaning Efficiency[a] (%)	Immersion Time (min)	Impact Cleaning Efficiency (%)	Impact Time (min)
Exxon Exxate 1000	Wax	100	5	100	5
	Oil/xylene	97.6	30	98.5	30
Orange Sol De-Solv-It	Wax	99.0	30	97.8	30
	Oil/xylene	99.9	1	100	1
Bio-Tek Safety Solvent	Wax	99.1	30	98.0	30
	Oil/xylene	100	30	100	1
3-D Supreme	Hydraulic fluid	100	1	100	5
	MoS grease	83	5	73	10
Calla 301	Hydraulic fluid	100	5	100	1
	MoS grease	40	10	95	10

---

a. Maximum efficiency achieved.

TABLE 12. DRYING REQUIREMENTS.

Solvent	Cleaning Efficiency (%)	Time (min)
Water	100	30
Exxon Exxate 1000	92	30
Bio-Tek 140 Safety Solvent	85	30
Orange Sol De-Solv-It	82	30
Calla 301	94	10
3-D Supreme	99	20

future processing would be required. This determination was not within the scope of this project but would be a worthwhile area to investigate.

Although enhancement is required for the efficient use of substitute solvents, when the enhancement techniques are applied, the solvents are as effective as the chlorinated hydrocarbons they are to replace, but without the hazardous characteristics of the solvents replaced. The replacement solvents were able to remove the test soils successfully on a large scale.

Several problems were encountered in operating the small ultrasonic units (Sonicor) and the 379-liter (100-gallon) unit (Ultrason X). Problems included maintaining the transducer banks, maintaining fuses, and keeping enough power to the units. Investigations into the use of ultrasonics in parts cleaning indicated poor results with the Sonicor 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 volatile organic compounds, and static buildup. However, ultrasonic agitation is used by many industries in parts cleaning. As stated earlier, ultrasonics create microstreaming and cavitation. Microstreaming operates much like mechanical and air agitation, but creates currents much more intense. Cavitation creates extremely high localized temperatures and pressures, and increases cleaning effectiveness by introducing fresh solvent into hard-to-reach areas and by loosening soil. However, costs increase significantly when ultrasonic tanks are large.

Impinger, or turbo, pump systems are available that may be nearly as efficient as ultrasonic units in removing soil, but not as costly for larger systems. These systems would be easily adapted to solvent recovery systems since a slipstream of used solvent could be diverted and recovered, e.g., filtration, and reintroduced to the system. In this manner the solvent would be retained and tank changeout decreased.

2. ASTM Biodegradation Guideline Development

Work continued on the ASTM testing protocol preparing it for submission to the ASTM committee for review. Testing indicated that the relative error with COD analysis increases at the lower limit of detection. Air sparging tests with the 6-hour test apparatus indicated some sparging of the Exxon Exxate 1000 and Bio-Tek Safety Solvent over the 6-hour test period. Care must be taken in interpreting 6-hour test data to avoid inaccurate conclusions due to air-sparging effects.

The 8-day test appears to have good potential application in the 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.

The analytical technique developed for use with a gas chromatograph provided the means to identify major components of the medium and to determine if they were degraded. With the complex matrix found in the wastewater, the technique was not as successful as hoped. 3-D Supreme could easily be traced through the pilot system using the GC, while Exxon Exxate 1000 could not be detected after it was mixed with the wastestream. With Fremont 776, which is principally inorganic, the GC was unable to detect any solvent peaks. The Orange Sol De-Solv-It was not tested in the pilot plant so the technique was not tried with it.

3. Sensor Development

Development experiments were completed for the soil-concentration sensor, confirming the feasibility of an accurate probe for measuring solute concentrations quantitatively using acoustic measurement techniques recently developed at the INEL. These techniques extend previous acoustic measurements into the milligrams/liter regime. The experiments showed that the technique would be capable of assessing the concentration and identity of individual solutes and ions. Sensor development results show that sensitivity is high enough to detect the fact that nanopure water quality changes from day to day. In addition, the sensor has been used to show that the speed of sound depends on the individual ions in a solution.

Qualitative and quantitative analysis aspects should be pursued in further development of the sensor, beginning with mixtures of several solutes of more immediate interest to this program. Temperature normalization should also be developed.

4. Bioacclimation Testing and Pilot-Plant Response

Because of the constantly varying nature of the wastewater processed at the industrial wastewater treatment plant (IWTP), determinations of whether the solvents degraded proved very difficult. Changes in other contaminants masked most of the indications for determining biodegradability. The conclusions in the following paragraphs were developed in spite of these difficulties.

a. SCC Sludge Bed Stabilizers

Bioacclimation testing was 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 ferric chloride, 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. Aluminum sulfate added considerably to the quantity of sludge precipitated in the SCC. The ferric chloride required to prevent breakup of the SCC sludge bed lowered the system pH sufficiently to impact the microorganisms in the activated sludge system and to begin to leach heavy metals from the SCC sludge. Even with the ferric chloride present, the SCC sludge bed was unstable at the pilot-scale with Exxate 1000 in the system.

b. 3-D Supreme

3-D Supreme did not biodegrade during the pilot plant run. The gas chromatography (GC) data clearly showed the presence of the solvent in the equalization tank (E-tank) and in the effluent from the final clarifier (FC). The microorganisms in the activated sludge (AS) basin feed mostly on phenol and to a lesser extent on other organic constituents of the wastewater stream. As long as phenol is intermittently available, the organisms will feed on it and will not acclimate to removing other organic constituents as efficiently or completely. Even with a full 21-day test, whether the organisms would adjust to and degrade the 3-D Supreme is questionable. The outcome would be largely dependant on the presence of phenol during the test period.

Given the constant availability of 3-D Supreme and the absence of phenol, the organisms have been shown to acclimate to the solvent, as evidenced by reduction in COD and TOC concentrations in the 8-day tests. Pilot plant influent containing large fluctuations of phenol concentrations would hamper that adjustment. If 3-D Supreme were dumped into the wastewater stream intermittently, the organisms would not adjust to it in time to degrade a significant portion. If the solvent were stored and fed into the system continuously, the microorganisms would, in the absence of phenol, acclimate to it and degrade it. Along with the problem of biodegradation, is the problem of the 3-D Supreme causing the SCC sludge to float. A solution to this problem is the addition of small amounts of ferric chloride ($FeCl_3$) to the IWTP process stream. The operator time and chemical and equipment expenses involved in adding another chemical to the process would be costly. The addition of 50 mg/liter of $FeCl_3$ would cost $391 per million gallons of water treated for the chemicals alone.

The cost could be reduced if an iron bearing polymer such as Aquatec 8170 could replace the current cationic polymer. This possibility was not tested in this test program because of time and funding limitations. Testing this option in the pilot plant is strongly recommended.

c. Exxon Exxate 1000

The GC analyses on the Exxate 1000 sample sets showed no characteristic peak for the solvent. The solvent was absorbed into or onto other constituents in the waste water stream. Its characteristic odor could be detected throughout the pilot system, showing that it was present, but not in a soluble form that could be monitored on the GC. These data came mostly from the August 1989 run of Exxate 1000 with aluminum sulfate. The run where ferric chloride was added was too short to achieve equilibrium of Exxate 1000 through the plant. Other data collected exhibited a marked change from the baseline values, providing no evidence of biodegradation of the solvent. The 8-day test data proved that microorganisms from the IWTP's AS basin could acclimate to the solvent under proper conditions. Though the pilot-scale run data failed to verify the acclimation of the microorganisms, it did demonstrate that the solvent did not disrupt the AS sludge basin operation.

As mentioned previously, concentrations of ferric chloride high enough to ensure the SCC sludge would settle lowered the pH to a level that was harmful to the activated sludge. Unless the ferric chloride treatment were coupled with a pH adjustment downstream of the SCC the activated sludge system would be upset. Low pH conditions would also shift the metal precipitation equilibrium, raising the concentration of heavy metals downstream from the SCC. For these reasons, the ferric chloride treatment is not recommended for use with Exxate 1000.

Aluminum sulfate was successful in preventing the flotation of the SCC sludge, with Exxate 1000 present in the waste stream. This method would be costly for two reasons. First, the chemical and its handling would be expensive. Second, the amount of SCC sludge would be increased substantially since the aluminum sulfate would have to be added to the E-tank or immediately downstream. A large increase in sludge generation would drive process costs up considerably. If aluminum sulfate were added at 50 mg/liter, an additional 76 tons of SCC sludge would be generated per year. Finding a different disposal method for the Exxate 1000 seems to be a better choice. Recycling should be investigated.

d. Fremont 776

Fremont 776 performed satisfactorily in the pilot-scale tests. The Fremont does not have a characteristic GC peak so the GC could not be used to track it through the pilot plant. As previously discussed, the results of the other analyses indicated that the solvent had little or no impact on the performance of the pilot system. No change in system parameters could be attributed to it. The Fremont had no adverse effects on the SCC or the activated sludge. In turn, the system had minimal, if any, effect on the solvent, especially its major constituent, sodium metasilicate. Because the sodium metasilicate is inorganic, the microorganisms in the activated sludge could not degrade it. However, sodium metasilicate has no impact on NPDES regulated chemical concentrations and does not have to be degraded. Fremont 776 is already in use in the Roto-Jet cabinet spray washer and it appears satisfactory for general use.

e. Orange-Sol De-Solve-It

The jar tests demonstrated that neither ferric chloride nor aluminum sulfate could prevent the SCC sludge from floating when Orange-Sol was present. For this reason, Orange-Sol should not be added to the Tinker AFB wastewater systems unless the oil and water separator can be shown to remove it. A second reason is that, since the cost of the solvent is high, recycling seems an obvious choice. A method for recycling Orange-Sol and like solvents should be developed.

Attempts to emulsify the Orange-Sol in the jar tests using a high-speed blender were ineffective. Being that resistant to emulsification speaks well for its removal by the oil and water separation system. A study to determine whether De-Solv-It would be removed is recommended.

5. Recommendations for Phase III Testing

The results of the Phase II evaluation indicated that solvents were available that should perform well if implemented in the process lines at Tinker AFB. To achieve cleaning efficiency of 100 percent soil removal for carbonized oil/xylene or wax using organic solvents, ultrasonic agitation was recommended. The recommendation was made that representative parts having burned-on oils (carbon) be cleaned with the substitute solvents using the 379-liter (100-gallon) tank at the pilot facility and then, if appropriate, subjecting the parts to the remaining cleaning processes at the 3001 building. The Roto-Jet parts washer was included in this recommendation. The cleaned parts should then be inspected and compared to parts cleaned with current methods. This comparison process was to be followed with organic and aqueous solvents. This recommendation served as the basis for the Phase III test program. As discussed, ultrasonic agitation was not implemented because it was unsuitable for use in large tanks of organic solvents and because of its history of undependability. If ultrasonic technology could be developed to overcome these problems, it would be an excellent source of agitation.

6. Additional Corrosion Studies

The corrosion studies from Phase II incorporating mixer or ultrasonic agitation indicated that the corrosion rate was greater than 0.3 mils/year applicable to 1,1,1-trichloroethane or perchloroethylene. The corrosion rates of other solvents or cleaners currently in use should be determined to establish a comparison.

B. PHASE III CONCLUSIONS

Each of the solvents tested in the full-scale test program could be applied in cleaning processes at Tinker AFB. The solvents differed greatly in their performance depending on soil type, but that was expected from earlier testing. Specific recommendations for solvent use are included below.

1. 3-D Supreme

The cabinet spray washer and full-scale tests both indicated that 3-D Supreme was an effective cleaner for Air Force parts. Applied in an agitated tank similar to the full scale test design, it would provide an acceptable alterative to vapor degreasers now in service. The solvent is effective in removing oils, grease, and carbon deposits but should not be considered for wax removal.

The major drawback in using 3-D Supreme is its impact on the SCC sludge bed. A study should be initiated to find a method of treating the solvent before it is released to the wastewater system. If a simple procedure could be developed to "neutralize" the solvent in the cleaning tank, the solvent could be released to the industrial wastewater system making the solvent much more convenient to use and more cost effective. Though 3-D Supreme can be applied effectively now, these improvements would substantially enhance its worth as a general cleaner.

For both 3-D Supreme and Fremont 776, rinsing the parts with steam or high-pressure spray at intermediate points in the cleaning cycle, as well as the end, would enhance the cleaning substantially and reduce the overall cleaning-cycle time. These water-based solvents seem to clean by attacking the soil-to-metal bond. Intermediate rinsing removes the loosened soil and provides the solvent easier access to the remaining soil.

2. Fremont 776

The Fremont 776 is already in use in the cabinet spray washer, which has been used for cleaning fuel assemblies. The full-scale test results showed Fremont 776 being less effective than 3-D Supreme as a cleaner. However, it did perform adequately on oils, grease, and carbon soil. The major advantage of Fremont 776 is that it would be much easier to treat at the IWTP.

Soil-loading tests conducted with the Fremont to provide cost comparison data were inconclusive. The solvent did not remove molybdenum disulfide grease or wax and did not seem to emulsify the hydraulic oil. Comparing these 500-milliliter tests to the full scale tests that had already been performed produced a major disparity. Fremont 776 performed poorly in the bench-scale trials, but adequately in the large-scale tests. Spray washer operating experience appears to be a better source for cost data than the loading tests. This experience indicates that Fremont 776 can be used effectively and economically.

3. Orange Sol De-Solv-It

Orange Sol De-Solv-It is an effective wax remover when enhanced with agitation and elevated temperature. The single "worst case" part provided by the Air Force for cleaning would take a long time to process, but given sufficient time, the wax could be removed. However, the majority of production parts would not have wax coats as thick or shapes as convoluted. For these parts, the cleaning time would be reasonable. Cleaning parts covered with an inch of wax would not be cost effective anyway, because the solvent would be exhausted in a very short time. A preliminary step could easily be devised where the part could be heated to the melting temperature of the wax, allowing the bulk of the wax to be removed before treatment with the solvent. The remainder of the wax coating could be removed easily by the solvent. Given a process of this sort, Orange Sol De-Solv-It would serve well as a cleaner.

Orange Sol De-Solv-It is expensive at $14.90 per gallon. Replacing halogenated hydrocarbons will most likely require materials of considerable expense. Larger order sizes should reduce the per-gallon cost.

4. Exxon Exxate 1000

Application of Exxon's Exxate 1000 has several drawbacks. First is the previously-discussed actions that must be taken to treat it in the IWTP. A second consideration is the distinctive odor of the solvent. Personnel working with it complained of headaches and other discomfort. Special ventilation would have to be considered in its area of use. Like Orange-Sol De-Solv-It, it is expensive, costing $6.24 per gallon.

Aside from these drawbacks, Exxate 1000 did prove effective for removing wax and could be used in applications such as those described for the Orange-Sol.

This program has not investigated solvent recovery or treatment methods other than biodegradation. Many facilities do not have biological treatment processes. Several solvents were promising in Phase I testing, but were not biodegradable. Alternative treatment methods and solvent recovery methods should be evaluated.

C. ASTM STANDARD GUIDE PREPARATION

The work on the standard guide for biodegradation of solvents has not been completed. Considerable work remains before it can be released. Currently it is entitled, "Standard Guide for: Biodegradation of Water Soluble and Poorly Water Soluble Organic Solvents." The mechanism for its approval and release is explained here.

During Phases I and II of the Biodegradable Solvents Program an ASTM standard method was being evolved utilizing the biodegradation screening tests that were developed and tested during these phases of work. After attendance at an ASTM meeting, INEL personnel determined that the document being developed would better fit the category of an ASTM standard guide. The biodegradation tests used in screening the solvents tested in Phases I and II will be integrated as part of the guide.

By definition the purpose of a guide is to offer direction, based on a consensus of viewpoints, but not to establish a fixed procedure. A guide is intended to increase the awareness of the user to available techniques in a given subject area and to provide information from which subsequent evaluation and standardization can be derived. The definition of a test method is a definitive document comprising definitions of terms; descriptions of terms; explanations of qualities, characteristics, or properties of a material, product, system, or service that produces a test result. The standard being developed is not a definitive procedure but a series of options that will give available techniques on biodegradation. The techniques will be presented in a manner that will direct the user toward an approach that will yield the most applicable results for the system being tested.

With the significant number of degradation tests developed, a researcher can get involved in degradation testing and end up with data and results that are confusing and inappropriate for the intended application of the research. The purpose of this guide is to attempt to lead the user in a direction that aids in making the most appropriate decisions for his particular application. Rating one method against another is not included in this purpose.

The scope of the guide includes degradation terminology and the advantages and disadvantages of different screening tests. The guide will also cover the different analytical methods used, direct or indirect, to follow the product through the degradation process. The guide will emphasize general principles. Only in a few instances will step-by-step instructions be given.

The guide will be significant because it will help the user develop a screening test that will permit a comparison of solvent treatability under a common set of conditions. The need has developed due to the different criteria on which solvent manufacturers base biodegradability. The degradation tests developed could then be considered for specific and general operations. General use of the test will provide an information base for many operations.

Questions that need to be answered during the development of the guide are numerous: On what is the manufacturer that developed the product basing biodegradation? Is the biodegradation of the product compliance or economics driven? Will the degradation test developed be specific to an operation? Can the results from the test method be used as an information base for several operations relating to the initial screening test, product loss, end product formation and identification, and environmental fate? What are the discharge limits and solids disposal practices of the user? And, what is the on site treatment, is it full or partial, is the system aerobic, anaerobic or combined, and is the discharge to a stream or a public sewage system?

Biodegradation testing procedures used in the Biodegradable Solvents Evaluation program will also be included in the guide. These tests include, the 6-hour test, the 8-day test and the acclimation tests using the pilot plant. The 6-hour test was developed from an EPA test (Reference 14). The test was modified by running six columns side-by-side, to allow comparison of different solvents run under similar conditions. A six hour testing period was chosen to model the retention time of the activated sludge basin at Tinker AFB. The 8-day test was developed from ASTM method D 2667-82, Biodegradation of Alkylbenzene Sulfonates (Reference 3). The test was run in the manner outlined in the standard, except for more frequent sampling. The 8-day test allowed for acclimation of the microorganisms in the activated sludge to the solvent being tested. The acclimation tests were field verification of the biodegradation techniques used in the benchscale testing. The acclimation tests allowed for determination of solvent effect on the whole industrial waste water treatment system.

Analytical tests used to follow product loss and end-product formation will also be included in the guide. A number of standard test methods can be obtained from ASTM, and also can be found in Standard Methods for the Examination of Water and Wastewater (Reference 8). The analytical tests that will adequately represent parameters found in full scale treatment are chosen by the user.

Control and calibration techniques used in the Biodegradable Solvents program were developed to determine the precision and bias of the analytical tests being used. Most ASTM documents are required to contain a statement of precision and bias. In the guide being developed, the methods used to determine precision and bias for the analytical tests will be left to the discretion of the user.

In determining the time frame that an actual ASTM standard guide will be in place the editing process of the society must be reviewed. When a guide is submitted to ASTM it is first submitted at the subcommittee level. The document is then sent out to the members of the subcommittee and the members are asked to review the document and cast a ballot for the document. The document can be balloted as affirmative, meaning the document has passed this editing stage. It can be affirmative with comments, meaning the document is scientifically accurate but there are some editorial remarks that need to be revised. Or, the document can be balloted as negative, meaning a committee member has found a scientific inaccuracy. A negative ballot does not mean the material contained in the document is bad; it usually means another researcher has run the test in a different manner. Negatives can be discussed in committee and changes, additions, or deletions can be made. After the document has been affirmed in subcommittee it is then balloted in the main committee, with the same balloting process taking place. When the main committee is satisfied, the document is balloted on the society level. Once the document has been passed on the society level it then becomes a standard guide and will be included in an Annual Book of ASTM Standards.

The ASTM committee on Biological Effects and Environmental Fate meets semiannually. The different documents and ballots are discussed. Any negatives or affirmatives with comments are covered and the resulting material is given to the writer of the document for incorporation.

At present an extensive literature search and the development of an initial outline for the guide are taking place. A wide variety of methods commonly used to measure biodegradation has been compiled by Swisher (Reference 13), but to date none have been placed in a standard guide. Literature not included in the compilation is being reviewed to make sure no recent methods will be left out of the guide, making it incomplete. The more updated and complete the guide when it is submitted for balloting the lower the probability is for a negative ballot.

The Air Force should continue to support the development of the biodegradability guideline. It is one of the most significant contributions of the solvent substitution program.

(The reverse of this page is blank.)

SECTION VII

REFERENCES

1. Beller, J. M., Carpenter, G. S., McAtee, R. E., Pryfogle, P. A., Suciu, D. F., Wikoff, P. M., Harris, T. L. and Schober, R. K., Substitution of Wax and Grease Cleaners with Biodegradable Solvents, Phase I Report, ESL-TR-89-04, Air Force Engineering and Services Center, Tyndall AFB, Florida, November 1988.

2. T. O. 42C2-1-7, Process Instructions, Metal Surface Treatments to Meet Air Force Requirements, March 1979.

3. Biodegradation of Alkylbenzene Sulfonates (Designation D2667-82, Presumptive Test), April 1982.

4. McCoy, J. W. Industrial Chemical Cleaning, Chemical Publishing Co., New York, 1982.

5. ANSI/ASTM F 483-77, Standard Method of Total Immersion Corrosion Test for Aircraft Maintenance Chemicals.

6. Wikoff, P. M., Prescott, D. S., Schober, R. K., Lloyd, F. S., Harris, T. L., Carpenter, G. S., Schutte, W. C., Pryfogle, P. A., and Wichlacz, P. L., Pilot Field Verification Studies of the Sodium Sulfide/Ferrous Sulfate Treatment Process, ESL-TR-88-13, Air Force Engineering and Services Center, Tyndall AFB, Florida, September 1988.

7. ANSI/ASTM F519-77, Mechanical Hydrogen Embrittlement Testing of Plating Processed and Aircraft Maintenance Chemicals.

8. Greenburg, A. E., Trussel, R. R., and Clesceri, L. S.(ed.), APHA 503A, "Oil and Grease Partition-Gravimetric Method," Standard Methods for the Examination of Water and Wastewater, Sixteenth ed., American Public Health Association, Washington, D.C., 1985.

9. MIL-C-43616B, Purchase Description, Remover, Activated Solvent Type, for Difficult-to-Remove Finishes for SA-ALC and OC-ALC Directorate of Maintenance, February 19, 1985.

10. MIL-C-85570B, Cleaning Compound, Aircraft Exterior, December 1986.

11. Letter from Janet Catanach, Exxon Chemical Company, Subject: Biodegradability, GC, and Safety Information to EG&G, 89PPITT0148.

12. Letter from G. P. Fawdry, Chemist, Exxon Chemical Canada, Evaluation of Metal Surface of Parts by Microscopy, 89PPITC0019, January 25, 1989.

13. Swisher, R. D., Surfactant Biodegradation, Second Edition, Revised and Expanded, Surfactant Sciences Series Vol. 18, Marcel Dekker, Inc., New York, 1987.

14. Federal Register (September 27, 1985), Vol. 50, Number 188, Page 39279.

APPENDIX A

SOLVENTS SUBMITTED FOR PHASE I TESTING

These pages contain the solvents and cleaners that were submitted by the chemical manufacturers for Phase I testing.

Mention of these products listed in this appendix does not constitute Air Force endorsement or rejection of this product, and use of information contained herein for advertising purposes without obtaining clearance according to existing contractural agreements is prohibited.

(The reverse of this page is blank.)

BIODEGRADABLE SOLVENTS
PRODUCTS RECIEVED

** 3 D INC.
3D SUPREME
747 AIRCRAFT CLEANER
BRITE BOY
CITRIGOLD
RUST ERADICATOR
SIEGE

** AMERICAN NIAGARA CORP.
ACCUSOL S/T-20

** BARTLETT CHEMICAL INC.
DOLPHIN 281
DOLPHIN TPS CODE 219
DOLPHIN WSD CODE 207
TOBY CODE 230

** BIO-TEK INC.
122 QUIK
126 SONI-CLEAN
134 HI-SOLV
710 dry clean
SAFTEY SOLVENT DEGREASER

** BRULIN
711 SC
815 QR
AQUA SAFE
CL-500
FORMULA 512M
NATURE-SOL 100

** BUILD ALL

BAC #137

** CABOT CHEMICAL CORP.

X-166

** CALLA CHEMICAL CORP

CALLA 301
CALLA 301-A
CALLA 301-A-LEMON
CALLA 626B
CALLA 800

** CHEMIQUE INC

BAR-2-NU
ION-417X
ION-420/LC
KRC-7

** CIRCUIT CHEMISTRY CORPORA

NCN-CU A,B

** CROWLEY CHEMICAL COMPANY

AROMATIC SOLVENT #58
METHYL NAPHTHALENE #5

** DIVERSEY WYANDOTTE METALS

ALDET
DIVERCLEAN LTS
DIVERSEY WYADOTTE II
NUVAT
NUVAT LT
NUVAT NP
PORENAC

** DOBER CHEMICAL CORP.

4190

8679

CD-44

CD-44HD

** DREW INDUSTRIAL DIVISION

DREW OIL AND GREASE REM.

** ELGENE CHEMICALS INC.

#22 SKIDOO

A-CD

ECONOMISER CF

FABULENE

SAFETY SOLVENT #10

** EXXON CHEMICALS

AROMATIC 150

ARCMATIC 200

EXSOL D 80

EXXAL 13 TRIDECYL ALCOHOL

EXXAL 16 -ISOCETYL ALCOHO

EXXAL 20

EXXAL L1315

EXXATE 1000

EXXATE 1300

EXXATE 600

EXXATE 700

EXXATE 800

EXXATE 900

EXXSOL D110

NORPAR 13

NORPAR 15

WS 2443 SOLVENT

WS 2444 SOLVENT

** FINE ORGANICS CORP
F.O. 2074

** FORMULA IV CORPORATION
MAGNA IV C-1000

** FREDERICK GUMM CHEM.
CLEPO 136-R
CLEPO 136-R
CLEPO 204
CLEPO 426-A
CLEPO 644-L
CLEPO 681-L
SONIC SOAK

** GRAYMILLS CORP.
AGITENE
AQUATENE 330
AQUATENE 571
AQUATENE 581

** HOLT LLOYD CORP.
CHEMPRO APC
CPS HEAVY DUTY CLEANER

** HOMESTEAD INDUSTRIES INC.
#49
#49-S
#65
AP
HDL

** HUNTINGTON
J8-10P
LHTS
ONLINE CE SD

SOLVENT EMULSION DEGREASE
THUNDER BOLT

** HYDRITE CHEMICAL CO.
HYDRI-CLEAN NPX

** HYLUBE INC.
ALKAKLEEN 658
HYKLEEN 300
HYKLEEN 312

** INTERNATIONAL PRODUCTS CO
MICRO

** JOHNSON WAX/GEM STATE PAP
BIG BARE
J-SHOP 500
J-SHOP 600

** KIESOW INTERNATIONAL CORP
EKASIT D-103
EKASIT E-231
EKASIT S-261

** KLEER-FLO COMPANY
DEGREASOL 99R
HI-T DEGREASER

** LAKE PRODUCTS CO. INC.
LAKE-97

** LEA MANUFACTURING CO.
CLEANOL

** M-OIL-FREE CO.
CITRIC

GS-A-67
M-OIL-FREE #1000
ULTRA
ULTRA 70
ULTRA 90

** MADISON BIONICS
CHEMERSE

** MAGNUSON PRODUCTS
PERMAG #404
** MAN-GILL CHEMICAL
MAGNUSOL 728

** MEQQEM
MEQQEM-CLEAN 8512
MEQQEM-CLEAN 8516

** MIRACHEM
MIRACHEM 100

** MITCHELL-BRADFORD, INTERN
MI-CLEAN 100
MI-CLEAN 14
MI-CLEAN 31
MI-CLEAN 59

** NORTH COAST CHEMICAL CO
CARBON REMOVER 730

** OAKITE PRODUCTS INC.
OAKITE 162
OAKITE 2327
OAKITE 24
OAKITE ANOPREP

OAKITE DYNADET
OAKITE HD 126

** ORANGE-SOL INCORPORATED
DE-SOLV-IT

** PACIFIC CHEMICAL
FIST
MASTER MHW
PACE S-L
RIDDALL

** PANTHER CHEMICAL CO.
759
AS-33
CR-138
CR-140
RR 50

** PARKER CHEMICAL
PARCO CLEANER 2033
PARCO CLEANER 2053

** PATCLIN CHEMICAL CO.
#309
#348
#380
#490
330 BEC

** PENETONE
CITRI KLEEN

** PETROFIRM INC.
BIOACT INDUSTRIAL DG1

** PROGRESS CHEMICAL INC.
#611
#65

AC-1
L-365

** ROCHESTER MIDLAND
SE377C

** SUTTON CORP.
TOPSALL

** TELSTAR INDUSTRIES
TELE-SOLV
TOWER 270

** TITAN CHEMICAL
OIL-FLO

** TRI TON
HEMO-SOL

** TWIN SPECIALTIES CORP.
CLEANER 54-TWIN INDUSTRIA
TWIN CITRON CLEANER 100

** U.S. POLYCHEMICAL CORP.
ST-21 POLY SPRAY JET

** UNITED LABORATORIES
UNITED 392
UNITED 395

** VAN STRAATEN CHEM CO.
21-271-A

APPENDIX B

DATA FROM PHASE I FOR THE SOLVENTS SELECTED FOR FURTHER TESTING

(The reverse of this page is blank.)

APPENDIX B

DATA FROM PHASE I FOR THE SOLVENTS SELECTED FOR FURTHER TESTING

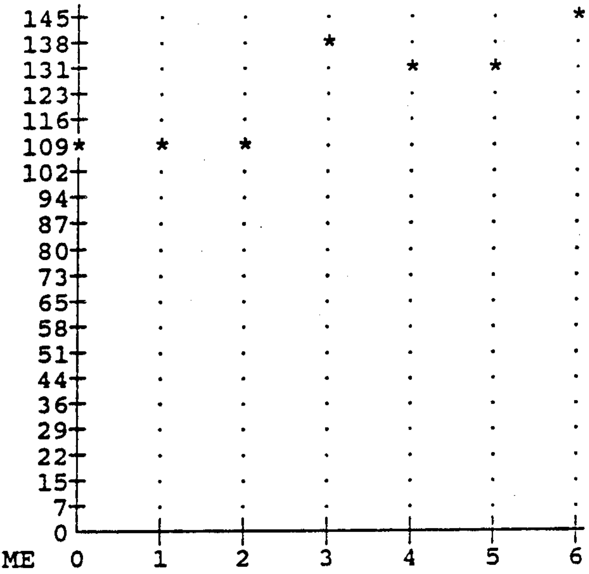
These pages contain data gathered during Phase I testing for the solvents that were selected for Phase II testing. No data is included for Fremont 776 because it was not added to the project until late in Phase II.

These figures and tables contain the test data for the biodegradability, solubility and cleaning efficiency tests. For each set of solvents the first tables contain the biodegradability tests, a plot of COD versus time, along with the change in ATP during the test. The plot directly below is the plot of the control phenol that was run during the same day. Also listed are TOC before testing, COD before testing, and TOC after testing.

Following the biodegradability plots are the plots for cleaning efficiency. The solvent is listed, the conditions at which it was tested, the alloy used and the results in table and plot form.

COMPANY - 3 D INC.
PRODUCT - 3D SUPREME
TOC INIT- 52475
TOC 2nd - 0
COD INIT- 148000
ANILINE PT - 0.0000
ATP ----- 1 E-8

SOLUBILITY DATA:
1-3 @ 180 1%



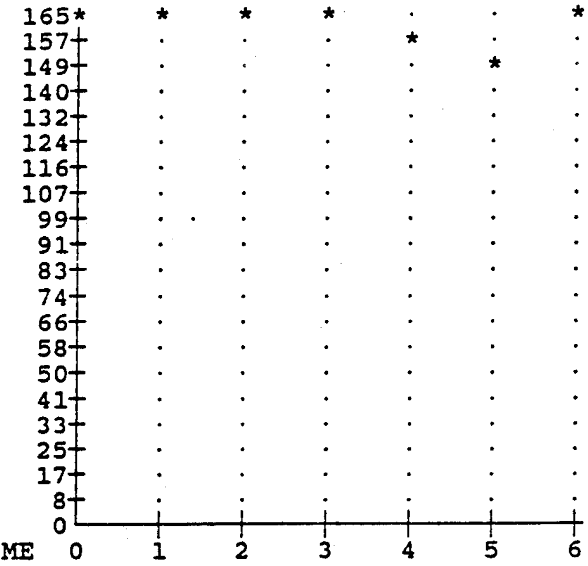
0-	112
1-	109
2-	108
3-	138
4-	134
5-	132
6-	145

DRY
WEIGHT
0.0597

DATE - 02/25/88 COD vs TIME

PHENOL
02/25/88
ATP - 16 E-8

3 D INC.
3D SUPREME



0-	165
1-	165
2-	165
3-	165
4-	154
5-	146
6-	165

DRY
WEIGHT
0.0597

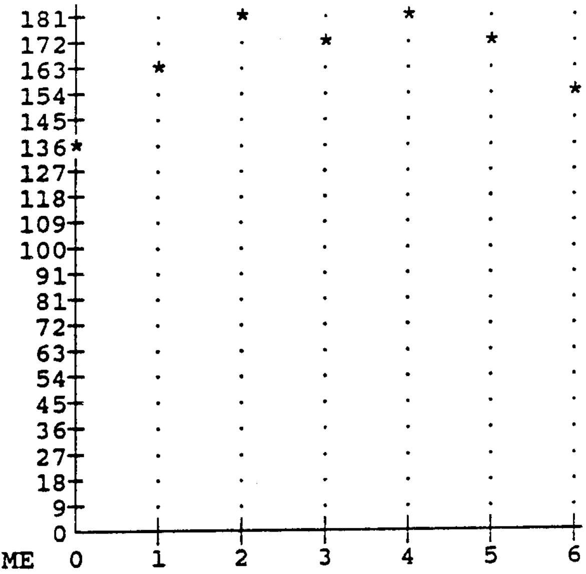
DATE - 02/25/88 COD vs TIME

```
COMPANY -  3 D INC.            246*    .    .    .    .    .    .
PRODUCT -  3D SUPREME          234+    *    .    .    .    .    .     0-  246
TOC INIT-        52475         221+    .    *    .    .    .    .     1-  232
TOC 2nd -            0         209+    .    .    .    .    .    .     2-  220
COD INIT-      148000          197+    .    .    .    .    .    .     3-  164
ANILINE PT -      0.0000       185+    .    .    .    *    .    .     4-  182
ATP -----  93 E-8              172+    .    .    .    .    .    .     5-  104
                               160+    .    .    *    .    .    .     6-  135
SOLUBILITY DATA:               148+    .    .    .    .    .    .
1-3      @ 180          1%     135+    .    .    .    .    .    *      DRY
                               123+    .    .    .    .    .    .     WEIGHT
                               111+    .    .    .    .    .    .     0.0558
                                98+    .    .    .    .    *    .
                                86+    .    .    .    .    .    .
                                74+    .    .    .    .    .    .
                                62+    .    .    .    .    .    .
                                49+    .    .    .    .    .    .
                                37+    .    .    .    .    .    .
                                25+    .    .    .    .    .    .
                                12+    .    .    .    .    .    .
                                 0+----+----+----+----+----+----+
  DATE - 03/07/88     COD vs TIME  0    1    2    3    4    5    6
```

```
                               439*    .    .    .    .    .    .
       PHENOL                  417+    .    .    .    .    .    .     0-  439
       03/07/88                395+    *    *    .    .    .    .     1-  406
       ATP - 211 E-8           373+    .    .    .    .    .    .     2-  386
                               351+    .    .    *    .    .    .     3-  356
                               329+    .    .    .    .    .    .     4-  309
3 D INC.                       307+    .    .    .    *    .    .     5-  270
3D SUPREME                     285+    .    .    .    .    .    .     6-  246
                               263+    .    .    .    .    *    .
3 D INC.                       241+    .    .    .    .    .    *      DRY
CITRIGOLD                      220+    .    .    .    .    .    .     WEIGHT
                               198+    .    .    .    .    .    .     0.0558
3 D INC.                       176+    .    .    .    .    .    .
SIEGE                          154+    .    .    .    .    .    .
                               132+    .    .    .    .    .    .
BARTLETT CHEMICAL INC.         110+    .    .    .    .    .    .
DOLPHIN 281                     88+    .    .    .    .    .    .
                                66+    .    .    .    .    .    .
BIO-TEK INC.                    44+    .    .    .    .    .    .
134 HI-SOLV                     22+    .    .    .    .    .    .
                                 0+----+----+----+----+----+----+
  DATE - 03/07/88     COD vs TIME  0    1    2    3    4    5    6
```

COMPANY - 3 D INC.
PRODUCT - 3D SUPREME
TOC INIT- 52475
TOC 2nd - 0
COD INIT- 148000
ANILINE PT - 0.0000
ATP ----- -21 E-8

SOLUBILITY DATA:
1-3 @ 180 1%



0- 140
1- 160
2- 181
3- 170
4- 180
5- 176
6- 150

DRY
WEIGHT
0.0600

DATE - 03/22/88 COD vs TIME

PHENOL
03/22/88
ATP - 69 E-8

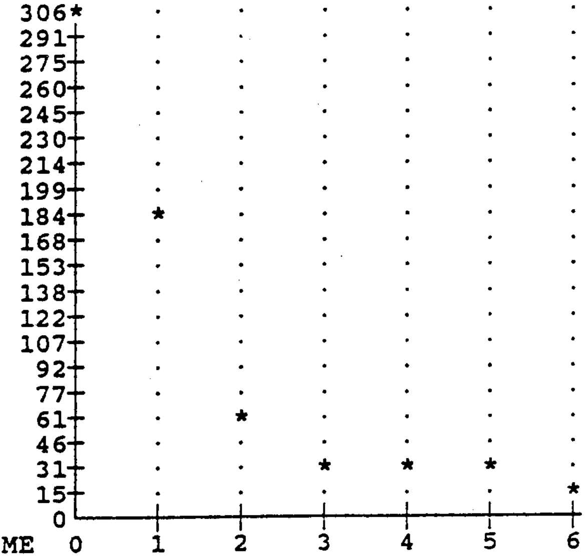
3 D INC.
3D SUPREME

3 D INC.
CITRIGOLD

ZEP MANUFACTURING CO.
BIG ORANGE

ZEP MANUFACTURING CO.
ZEP 940

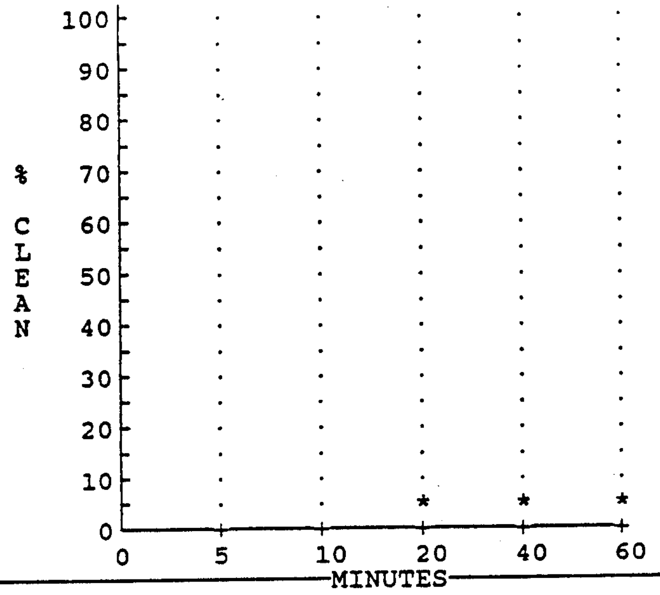
ZEP MANUFACTURING CO.
ZEPRIDE



0- 306
1- 178
2- 58
3- 36
4- 37
5- 34
6- 12

DRY
WEIGHT
0.0600

DATE - 03/22/88 COD vs TIME

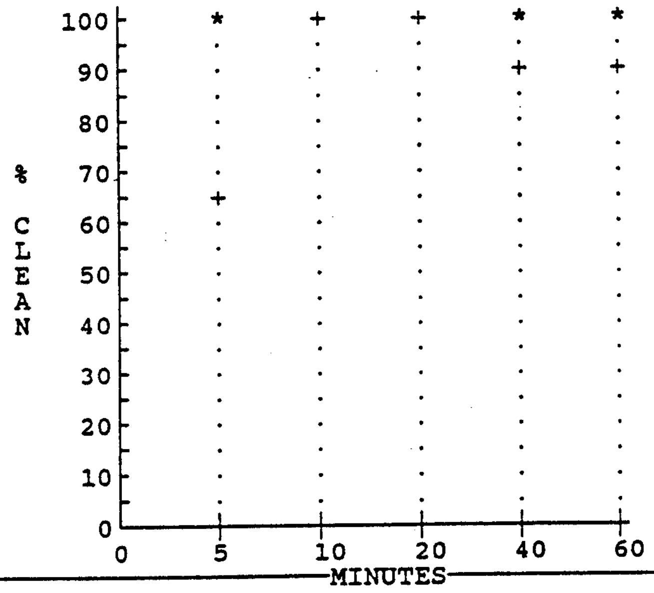


3 D INC.
3D SUPREME
1:4 AT 160 F

MONEL K-500

* -- RINSED
\+ -- UNRINSED

RINSED	UNRINSED
0%	1%
0%	0%
5%	0%
3%	0%
3%	1%

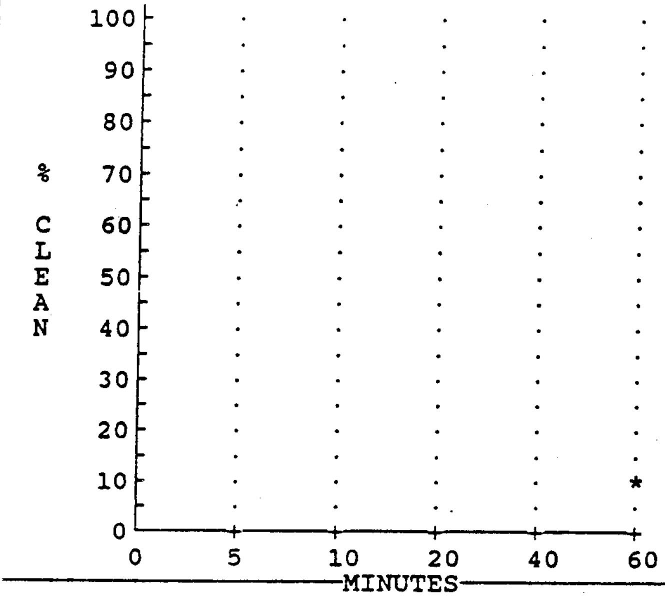


3 D INC.
3D SUPREME
GREASE: 1:3 AT 100 F

Az31B

* -- RINSED
\+ -- UNRINSED

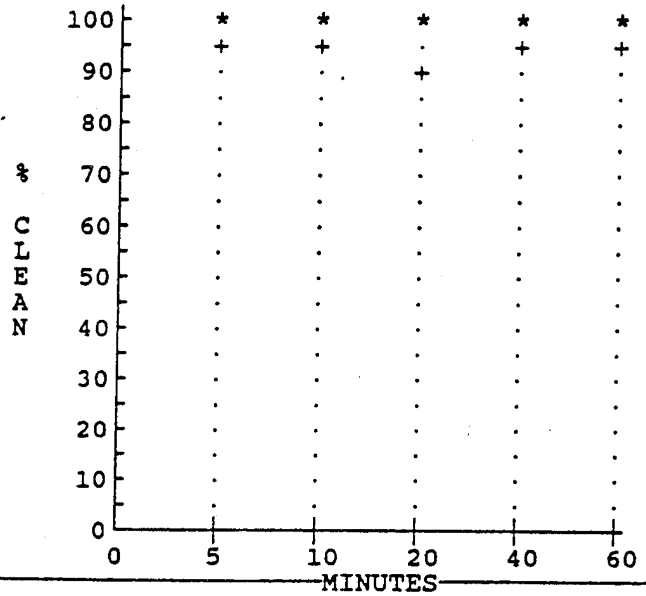
RINSED	UNRINSED
98%	65%
100%	100%
99%	100%
99%	92%
100%	91%



3 D INC.
3D SUPREME
OIL & XYLENE: 1:3 AT 100
F
A17075

* -- RINSED
+ -- UNRINSED

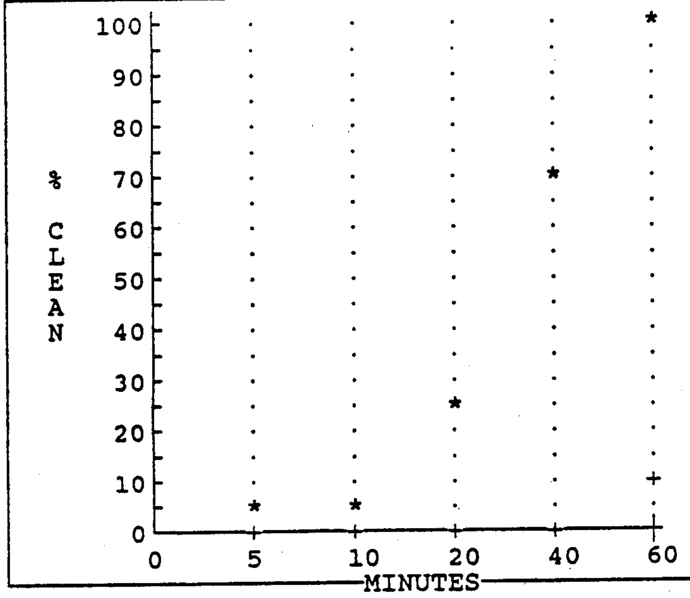
RINSED	:	UNRINSED
0%		0%
0%		0%
0%		0%
0%		0%
12%		0%



3 D INC.
3D SUPREME
HYDRAULIC FLUID: 1:3 AT 1
00 F
C1020

* -- RINSED
+ -- UNRINSED

RINSED	:	UNRINSED
100%		96%
100%		93%
99%		88%
100%		96%
100%		94%

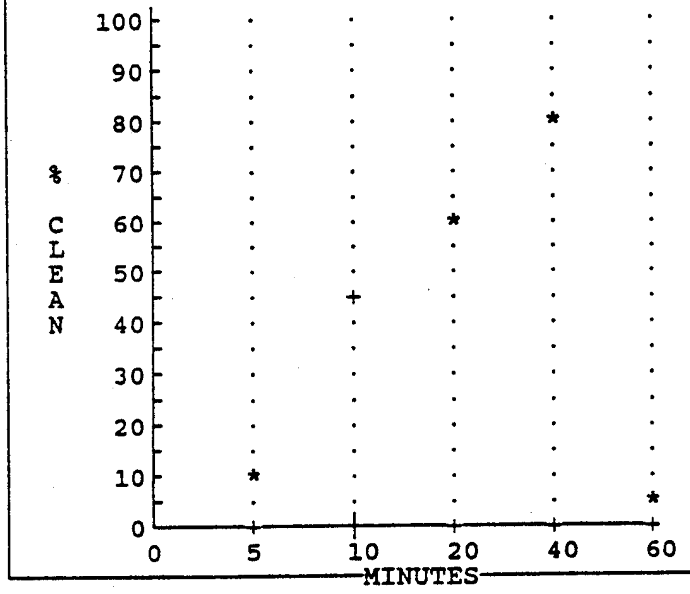


3 D INC.
3D SUPREME
OIL/XYLENE: 1:3 AT 160 F

CDA433

* -- RINSED
\+ -- UNRINSED

RINSED	UNRINSED
7%	0%
7%	0%
27%	0%
68%	0%
99%	12%

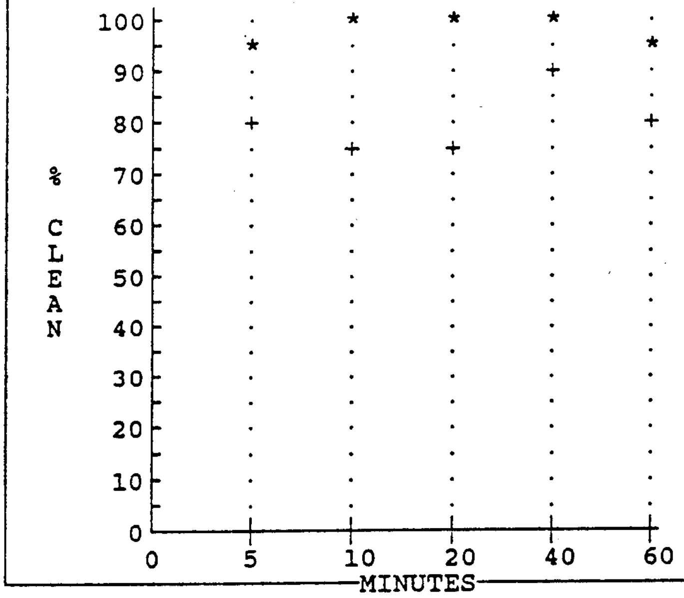


3 D INC.
3D SUPREME
OIL/XYLENE: 1:3 AT 180 F

A12024

* -- RINSED
\+ -- UNRINSED

RINSED	UNRINSED
9%	0%
43%	44%
61%	0%
82%	0%
8%	0%

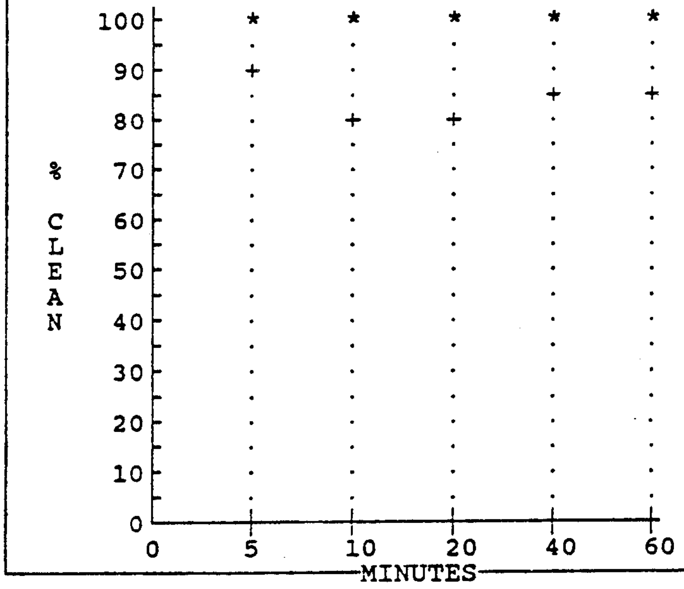


3 D INC.
3D SUPREME
GREASE: 1:3 AT 140

INCONEL 750

* -- RINSED
\+ -- UNRINSED

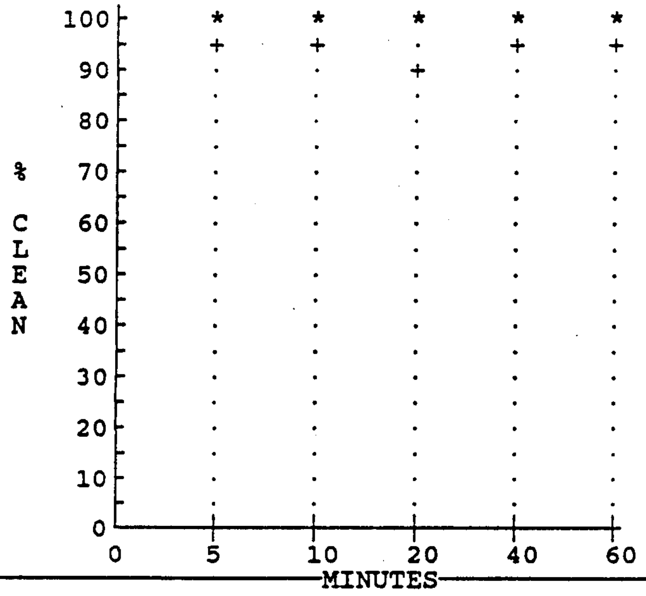
RINSED	UNRINSED
97%	80%
100%	76%
100%	77%
100%	89%
97%	81%



3 D INC.
3D SUPREME
HYDRAULIC FLUID: 1:3 AT
140 F
A12024

* -- RINSED
\+ -- UNRINSED

RINSED	UNRINSED
100%	88%
100%	81%
100%	82%
100%	84%
100%	86%



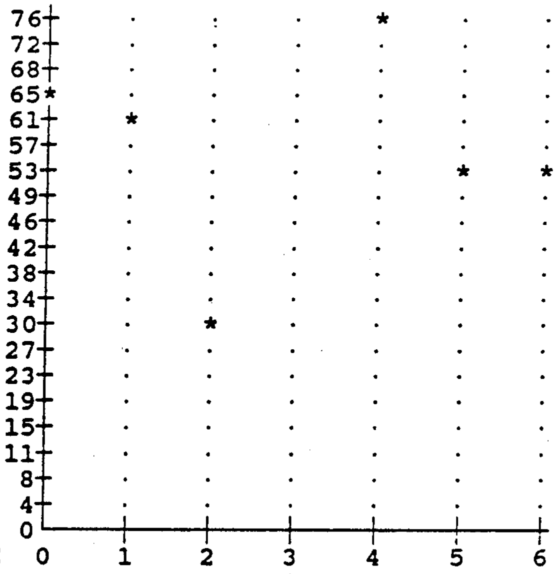
3 D INC.
3D SUPREME
HYDRAULIC FLUID: 1:3 AT
100 F
A12024

* -- RINSED
+ -- UNRINSED

RINSED	UNRINSED
100%	96%
100%	93%
99%	88%
100%	96%
100%	94%

COMPANY - BIO-TEK INC.
PRODUCT - SAFTEY SOLVENT DEG
TOC INIT- 107185
TOC 2nd - 0
COD INIT- 59000
ANILINE PT - 0.0000
ATP ----- -46 E-8

SOLUBILITY DATA:
CONCENT @ AMBIE 12%
CONCENT @ 140 79%



0- 64
1- 60
2- 32
3- -7
4- 76
5- 54
6- 55

DRY
WEIGHT
0.0678

DATE - 03/08/88 COD vs TIME

PHENOL
03/08/88
ATP - 30 E-8

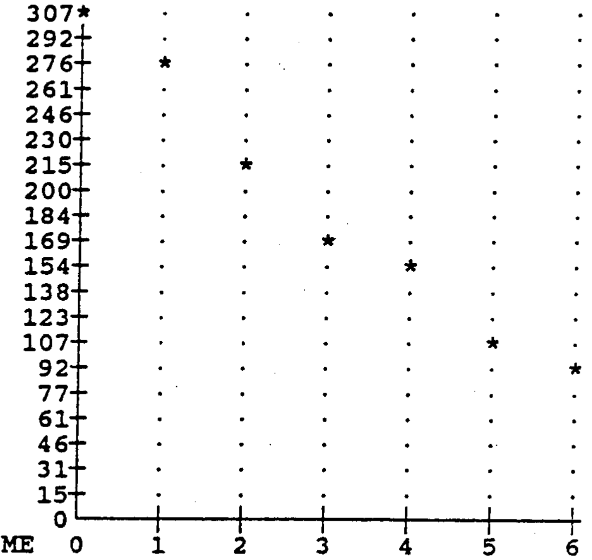
BIO-TEK INC.
SAFTEY SOLVENT DEGREASER

BRULIN
AQUA SAFE

BRULIN
NATURE-SOL 100

CALLA CHEMICAL CORP
CALLA 301-A-LEMON

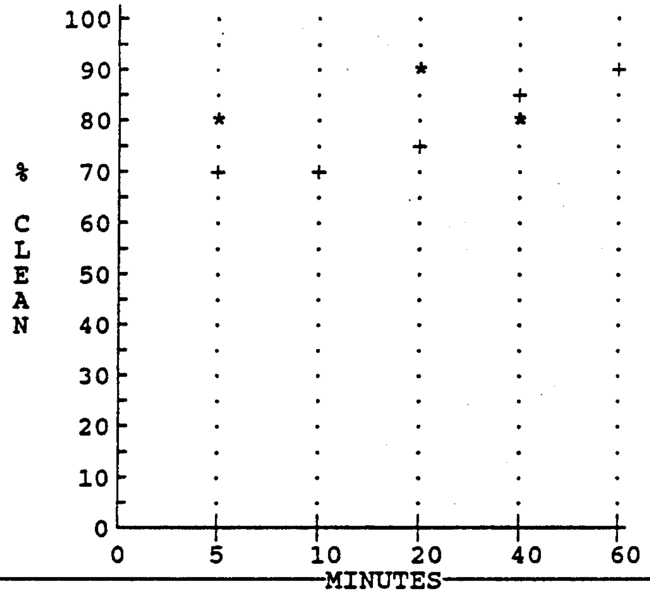
CROWLEY CHEMICAL COMPANY
METHYL NAPHTHALENE #5



0- 307
1- 276
2- 209
3- 174
4- 156
5- 108
6- 88

DRY
WEIGHT
0.0678

DATE - 03/08/88 COD vs TIME

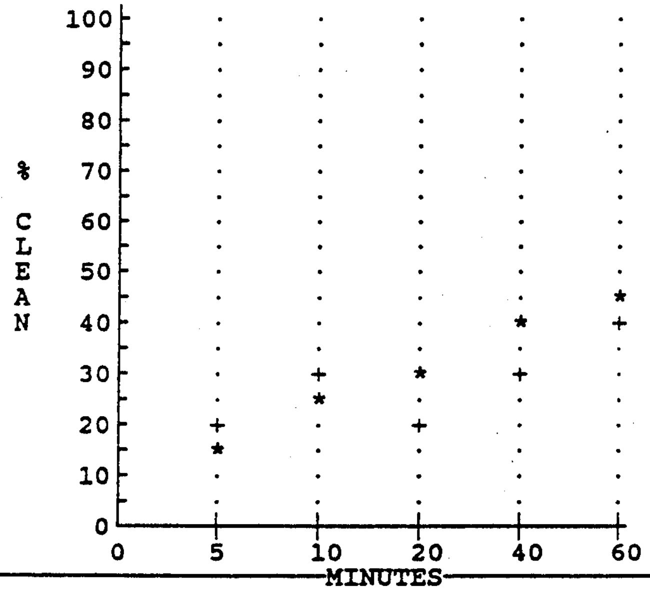


BIO-TEK INC.
SAFTEY SOLVENT DEGREASER
CONCENTRATED, 140 F

A12024

* -- RINSED
\+ -- UNRINSED

RINSED	UNRINSED
79%	69%
69%	70%
89%	73%
81%	88%
91%	89%

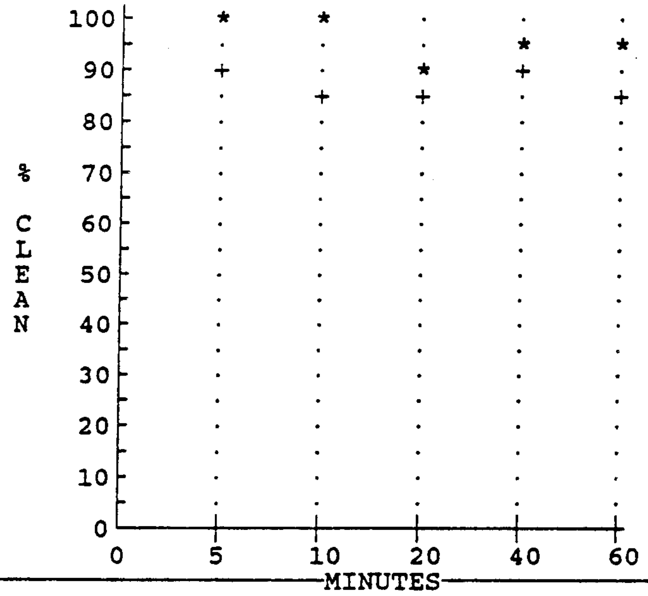


BIO-TEK INC.
SAFTEY SOLVENT DEGREASER
CONCENTRATED, AMBIENT

A17075

* -- RINSED
\+ -- UNRINSED

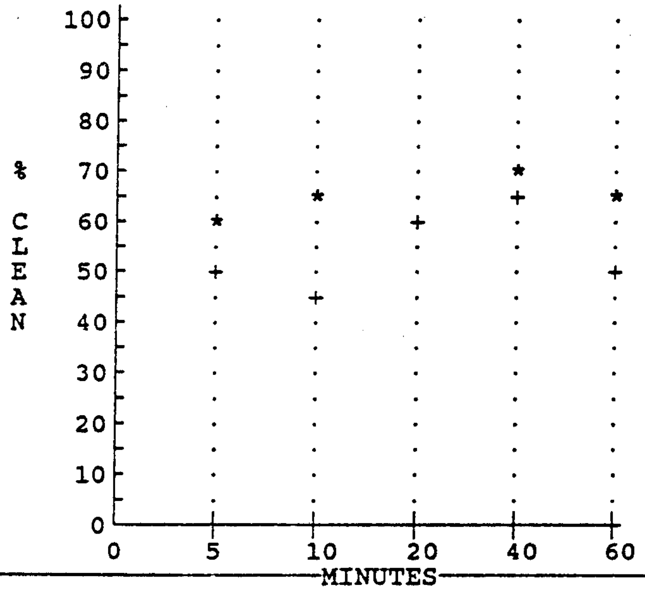
RINSED	UNRINSED
15%	18%
23%	30%
32%	21%
41%	32%
44%	42%



BIO-TEK INC.
SAFTEY SOLVENT DEGREASER
CONCENTRATE AT 140 WITH S
TIRRING
C1020

* -- RINSED
\+ -- UNRINSED

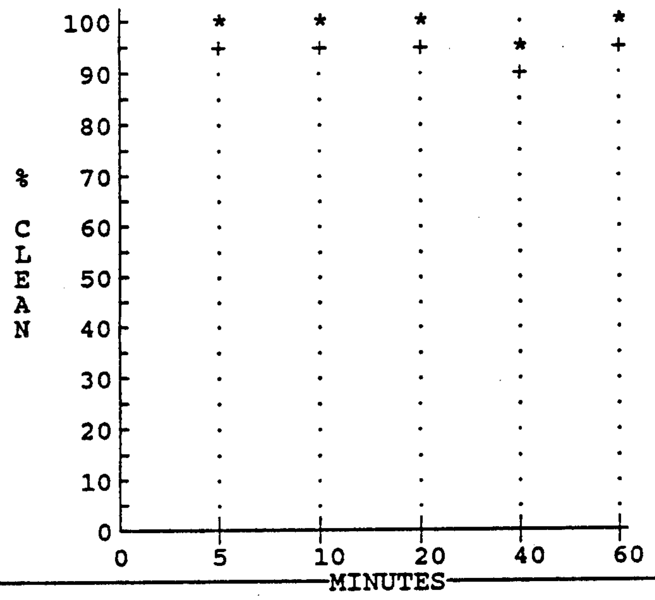
RINSED	UNRINSED
98%	91%
100%	87%
90%	85%
97%	92%
96%	86%



BIO-TEK INC.
SAFTEY SOLVENT DEGREASER
GREASE: CONCENTRATE AT AM
BIENT
A12024

* -- RINSED
\+ -- UNRINSED

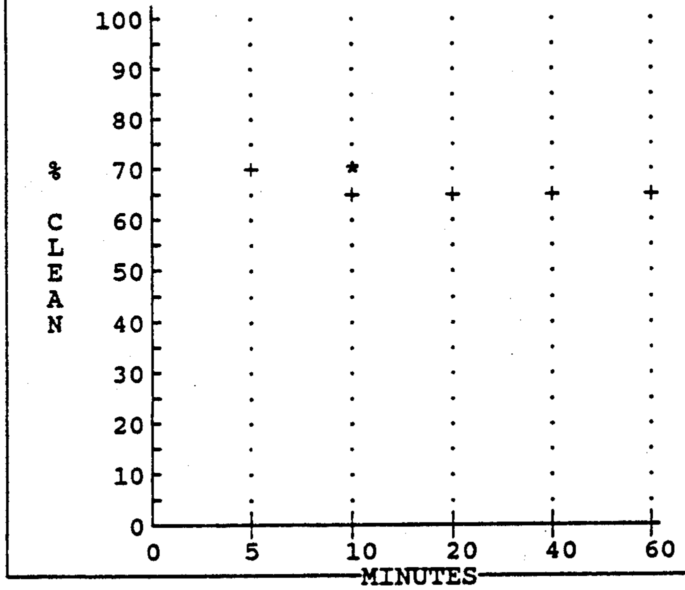
RINSED	UNRINSED
62%	48%
65%	47%
60%	61%
71%	63%
64%	51%



BIO-TEK INC.
SAFTEY SOLVENT DEGREASER
OIL/XYLENE: CONCENTRATE
AT 150 F
INCONEL 750

* -- RINSED
+ -- UNRINSED

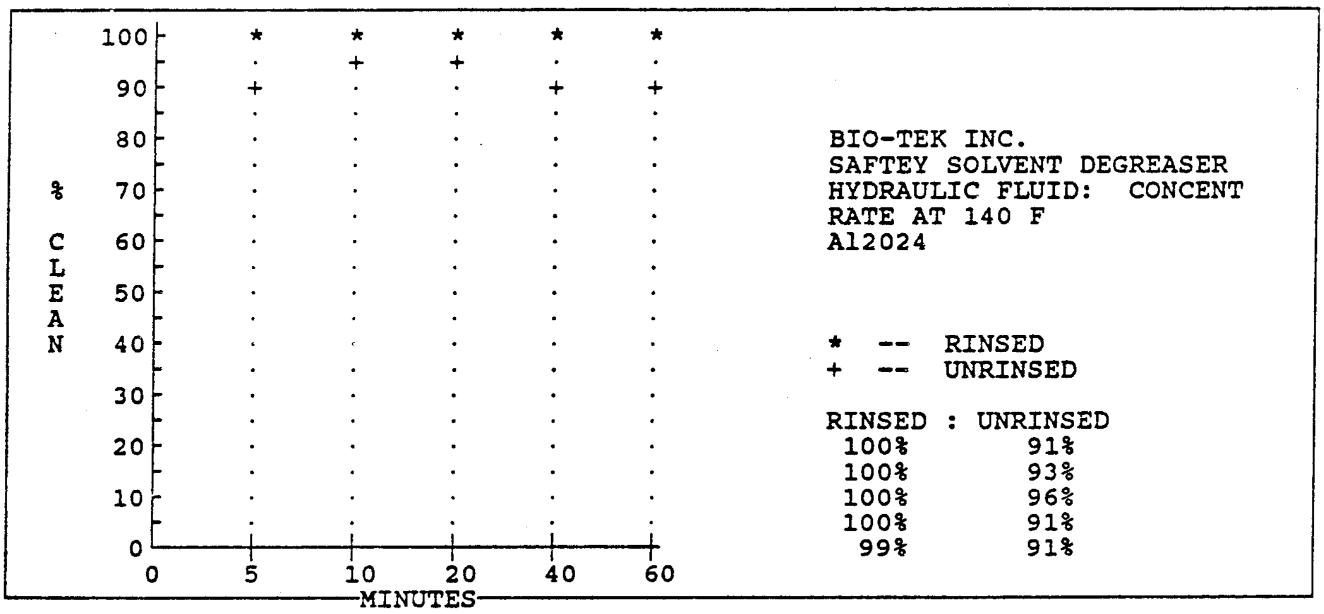
RINSED	: UNRINSED
100%	94%
99%	96%
98%	94%
98%	91%
100%	95%



BIO-TEK INC.
SAFTEY SOLVENT DEGREASER
GREASE: CONCENTRATE AT 1
40 F
Az31B

* -- RINSED
+ -- UNRINSED

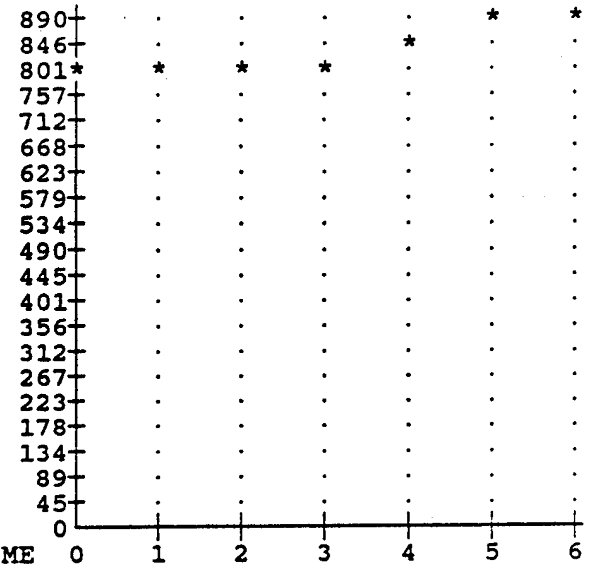
RINSED	: UNRINSED
72%	68%
68%	67%
68%	67%
66%	68%
68%	67%



BIO-TEK INC.
SAFTEY SOLVENT DEGREASER
HYDRAULIC FLUID: CONCENT
RATE AT 140 F
A12024

RINSED	: UNRINSED
100%	91%
100%	93%
100%	96%
100%	91%
99%	91%

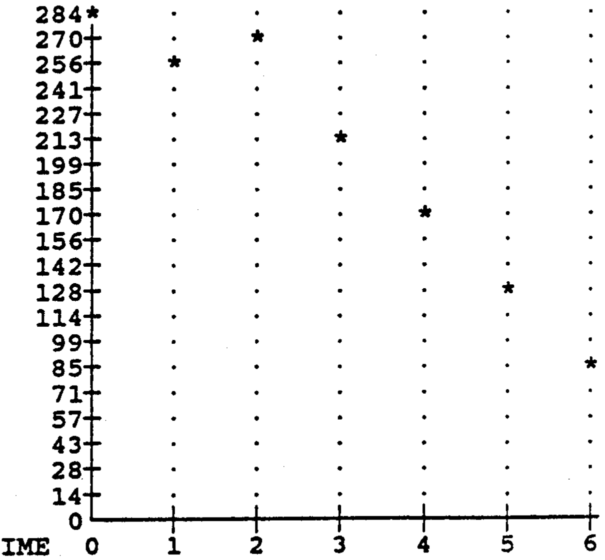
```
COMPANY -  CALLA CHEMICAL COR
PRODUCT -  CALLA 301
TOC INIT-        87188
TOC 2nd -            0
COD INIT-        32500
ANILINE PT -       0.0000
ATP -----  22 E-8

SOLUBILITY DATA:
```



```
0-  820
1-  813
2-  812
3-  789
4-  850
5-  869
6-  890

 DRY
WEIGHT
0.0607
```

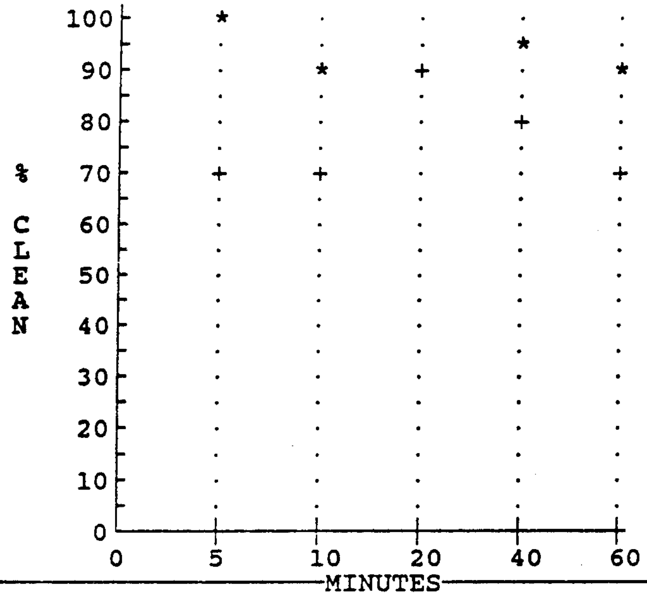
```
  DATE - 12/20/89     COD vs TIME
```

```
PHENOL
12/20/89
ATP - 185 E-8

CALLA CHEMICAL CORP
CALLA 301
```



```
0-  284
1-  262
2-  271
3-  206
4-  164
5-  133
6-   86

 DRY
WEIGHT
0.0607
```

```
  DATE - 12/20/89     COD vs TIME
```

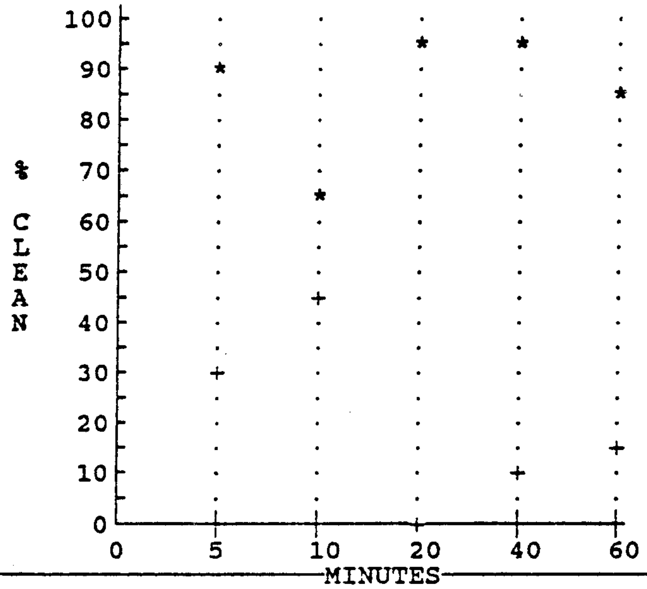


CALLA CHEMICAL CORP
CALLA 301
GREASE: 1:1 AT AMBIENT

INCONEL 750

* -- RINSED
\+ -- UNRINSED

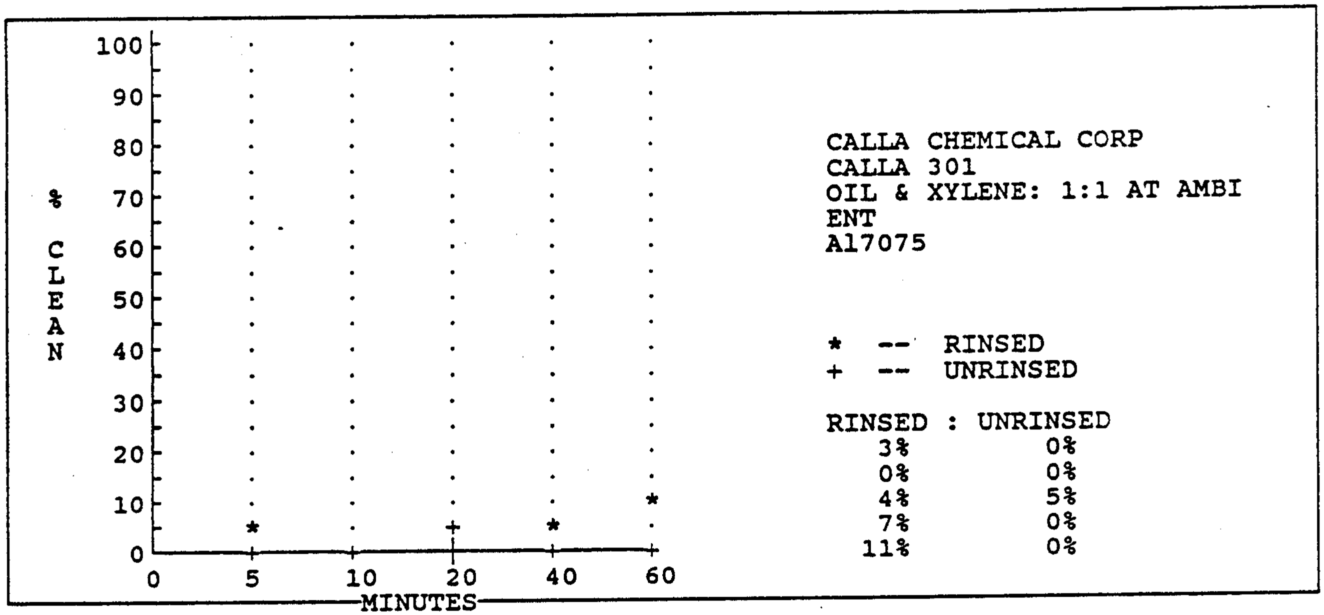
RINSED	: UNRINSED
98%	70%
90%	68%
91%	88%
94%	81%
89%	72%



CALLA CHEMICAL CORP
CALLA 301
HYDRAULIC FLUID: 1:1 AT
AMBIENT
C1020

* -- RINSED
\+ -- UNRINSED

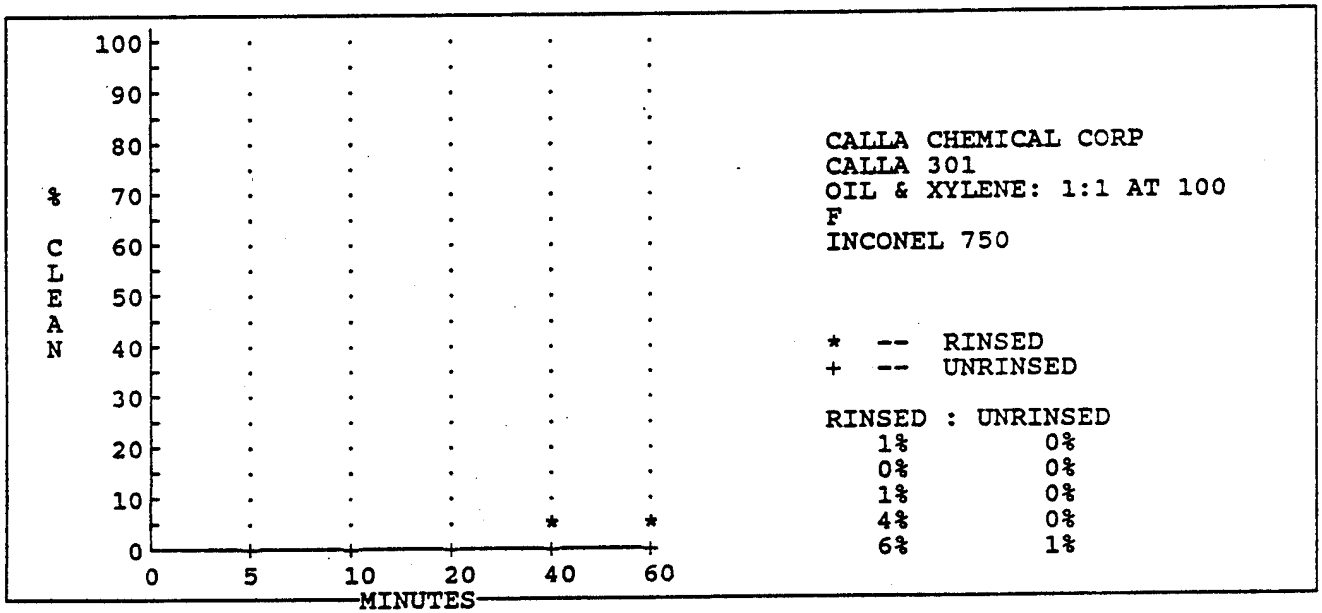
RINSED	: UNRINSED
90%	29%
65%	43%
97%	0%
97%	11%
84%	13%



CALLA CHEMICAL CORP
CALLA 301
OIL & XYLENE: 1:1 AT AMBIENT
A17075

* -- RINSED
\+ -- UNRINSED

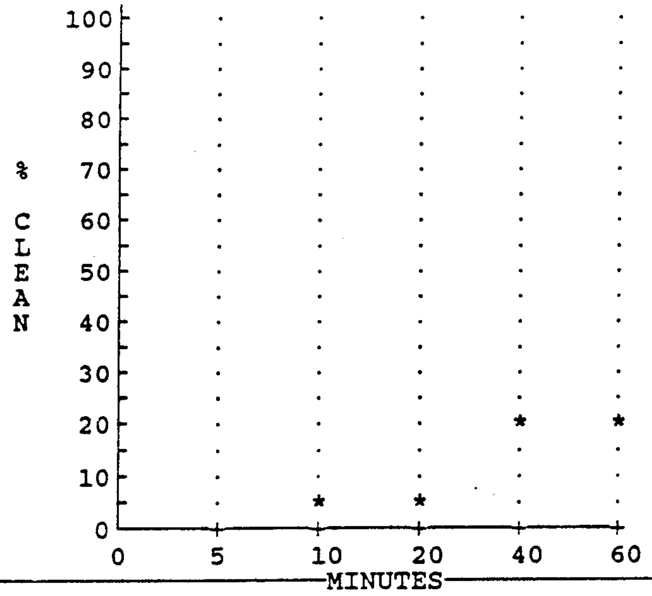
RINSED	UNRINSED
3%	0%
0%	0%
4%	5%
7%	0%
11%	0%



CALLA CHEMICAL CORP
CALLA 301
OIL & XYLENE: 1:1 AT 100 F
INCONEL 750

* -- RINSED
\+ -- UNRINSED

RINSED	UNRINSED
1%	0%
0%	0%
1%	0%
4%	0%
6%	1%

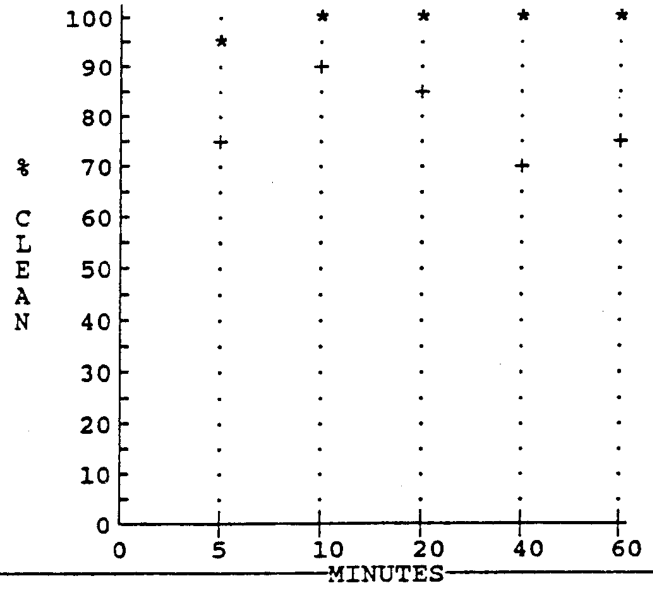


CALLA CHEMICAL CORP
CALLA 301
OIL/XYLENE: 1:4 AT 140 F

Az31B

* -- RINSED
+ -- UNRINSED

RINSED	UNRINSED
0%	0%
5%	0%
6%	0%
18%	0%
19%	0%

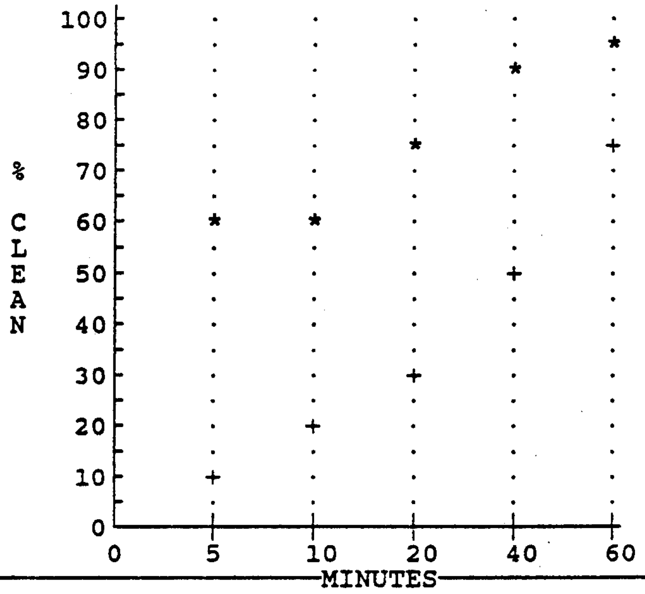


CALLA CHEMICAL CORP
CALLA 301
GREASE: 1:1 AT 100 F

310S

* -- RINSED
+ -- UNRINSED

RINSED	UNRINSED
95%	73%
100%	91%
99%	83%
98%	71%
100%	75%

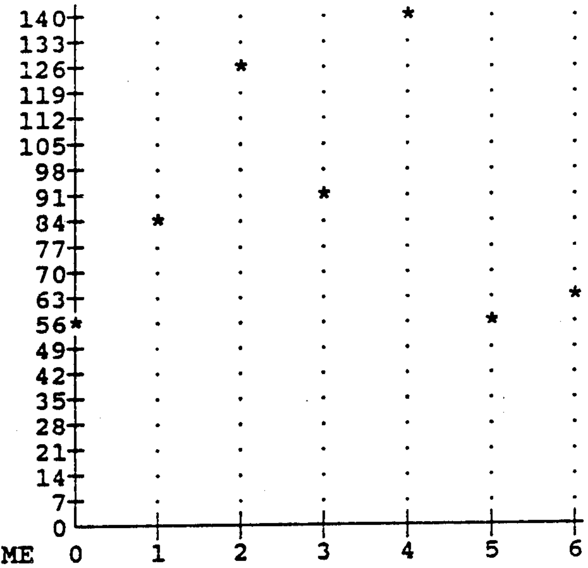


CALLA CHEMICAL CORP
CALLA 301
HYDRAULIC FLUID: 1:1 AT
100 F
A12024

* -- RINSED
\+ -- UNRINSED

RINSED :	UNRINSED
62%	12%
61%	19%
77%	30%
91%	50%
96%	76%

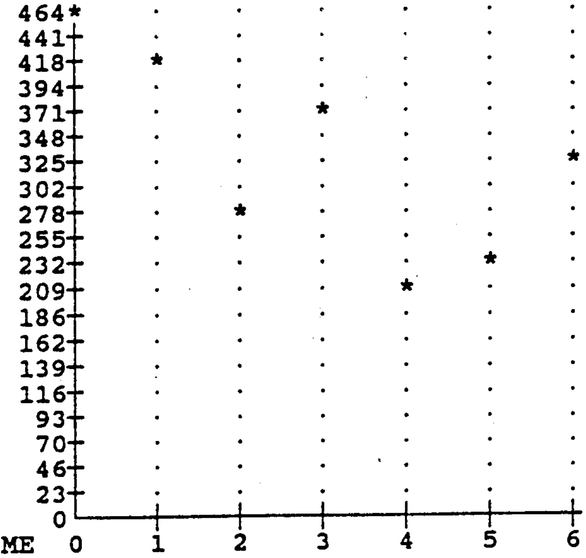
```
COMPANY -   EXXON CHEMICALS
PRODUCT -   EXXATE 1000
TOC INIT-        327872
TOC 2nd  -            0
COD INIT-        272000
ANILINE PT -        0.0000
ATP -----    -257 E-8

SOLUBILITY DATA:
CONCENT @ AMBIE            14%
CONCENT @ 100              49%
CONCENT @ 140              95%
```



```
0-   54
1-   86
2-  129
3-   90
4-  140
5-   54
6-   64

 DRY
WEIGHT
0.0691
```

DATE - 03/09/88   COD vs TIME

```
PHENOL
03/09/88
ATP - 14 E-8

DREW INDUSTRIAL DIVISION
DREW OIL AND GREASE REM.

ELGENE CHEMICALS INC.
#22 SKIDOO

ELGENE CHEMICALS INC.
ECONOMISER CF

ELGENE CHEMICALS INC.
FABULENE

EXXON CHEMICALS
EXXATE 1000
```



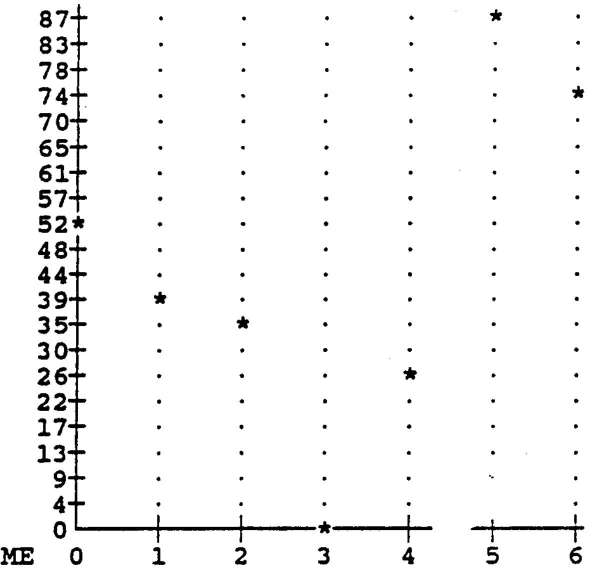
```
0-  464
1-  412
2-  284
3-  367
4-  217
5-  224
6-  314

 DRY
WEIGHT
0.0691
```

DATE - 03/09/88   COD vs TIME

COMPANY - EXXON CHEMICALS
PRODUCT - EXXATE 1000
TOC INIT- 327872
TOC 2nd - 0
COD INIT- 272000
ANILINE PT - 0.0000
ATP ----- 94 E-8

SOLUBILITY DATA:

CONCENT @ AMBIE	14%
CONCENT @ 100	49%
CONCENT @ 140	95%



DATE - 03/24/88

0- 52
1- 41
2- 36
3- 0
4- 24
5- 87
6- 76

DRY
WEIGHT
0.0776

PHENOL
03/24/88
ATP - 118 E-8

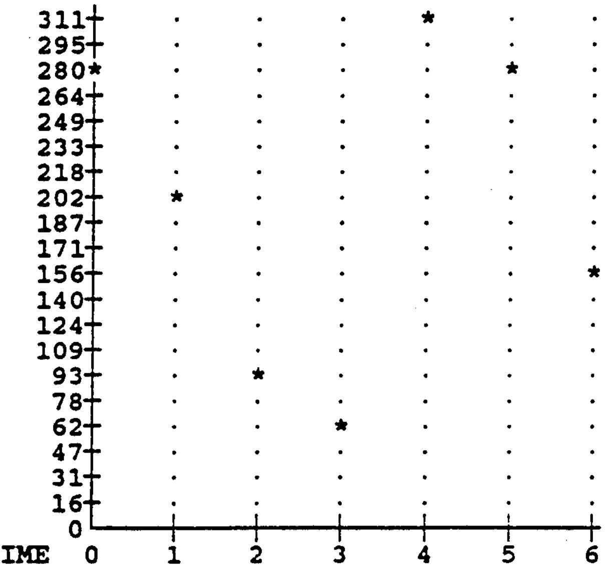
DREW INDUSTRIAL DIVISION
DREW OIL AND GREASE REM.

ELGENE CHEMICALS INC.
#22 SKIDOO

ELGENE CHEMICALS INC.
ECONOMISER CF

ELGENE CHEMICALS INC.
FABULENE

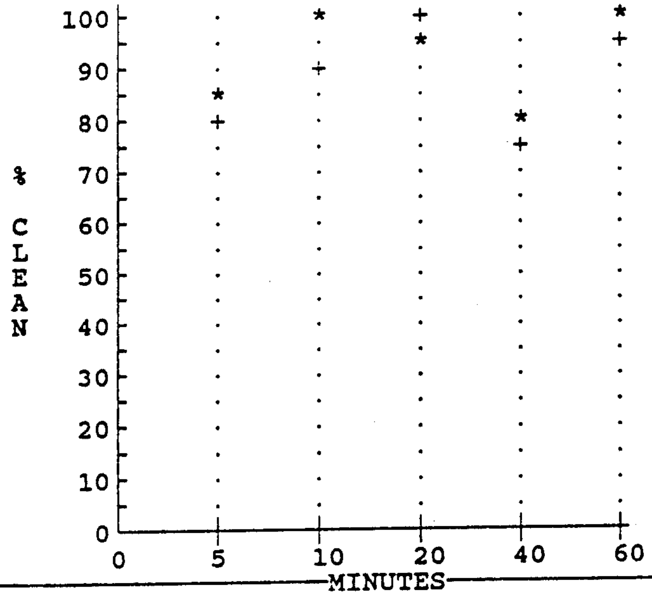
EXXON CHEMICALS
EXXATE 1000



DATE - 03/24/88

0- 282
1- 197
2- 100
3- 56
4- 311
5- 286
6- 158

DRY
WEIGHT
0.0776

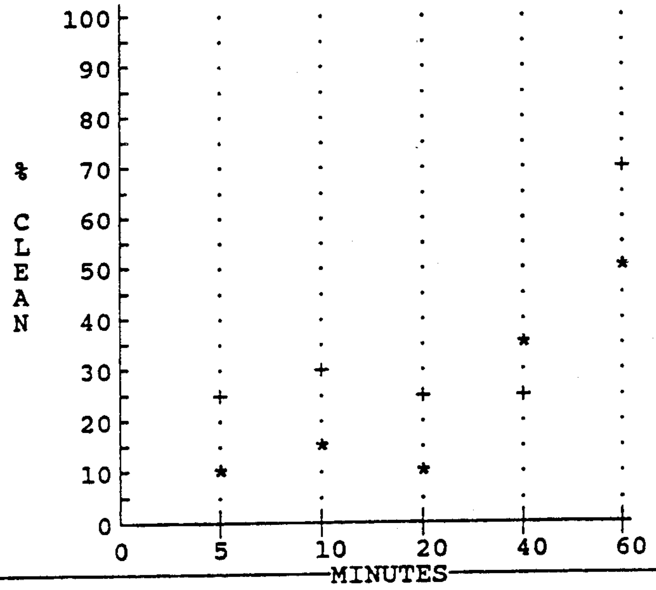


EXXON CHEMICALS
EXXATE 1000
CONCENT @ 140, NO DYE

A17075

* -- RINSED
\+ -- UNRINSED

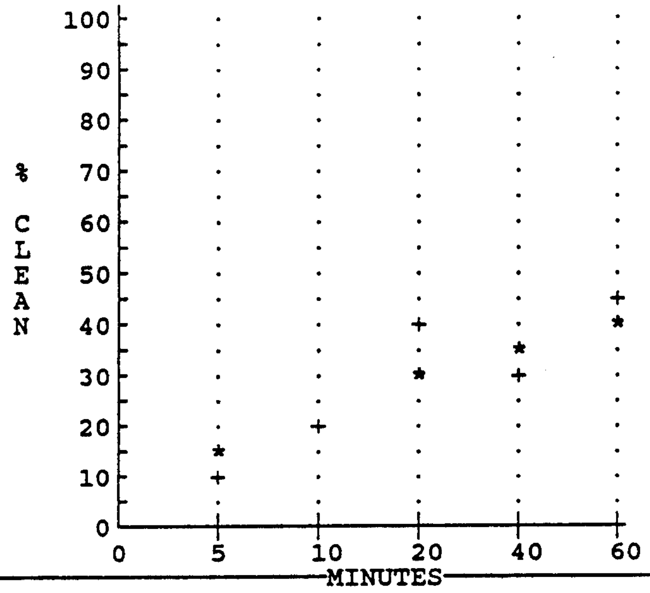
RINSED	: UNRINSED
87%	80%
100%	91%
93%	100%
79%	75%
100%	93%



EXXON CHEMICALS
EXXATE 1000
CONCENTRATE, AMBIENT, SUD
AN IV
CDA433

* -- RINSED
\+ -- UNRINSED

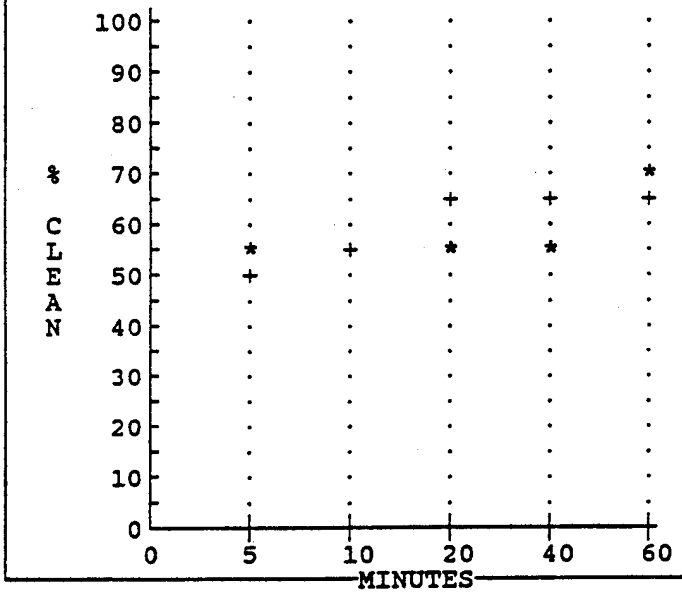
RINSED	: UNRINSED
10%	27%
13%	31%
12%	24%
37%	25%
49%	69%



EXXON CHEMICALS
EXXATE 1000
CONCENTRATE, AMBIENT, NO DYE
CDA433

* -- RINSED
+ -- UNRINSED

RINSED	UNRINSED
16%	11%
19%	22%
32%	41%
33%	30%
40%	44%

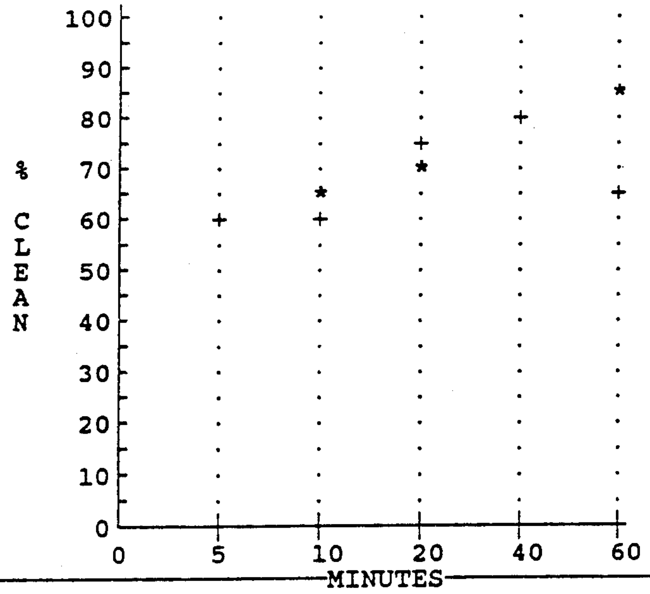


EXXON CHEMICALS
EXXATE 1000
CONCENT @ 100

A12024

* -- RINSED
+ -- UNRINSED

RINSED	UNRINSED
55%	49%
57%	57%
57%	67%
57%	63%
68%	64%

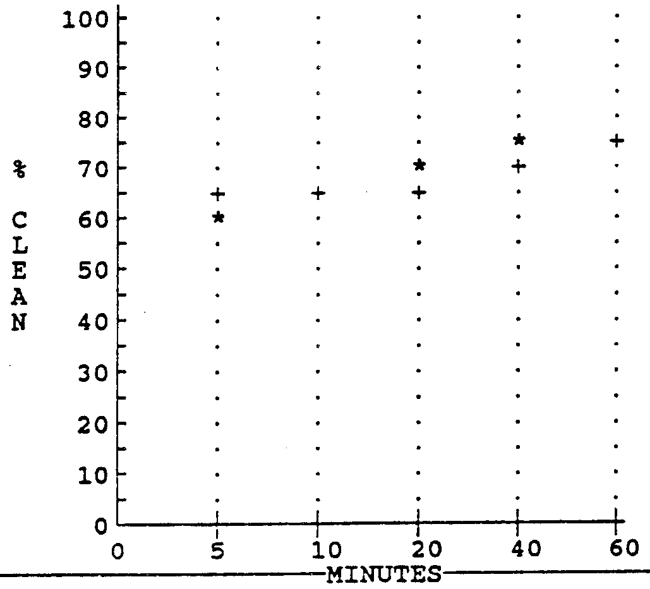


EXXON CHEMICALS
EXXATE 1000
CONCENT @ 100

A17075

* -- RINSED
\+ -- UNRINSED

RINSED	UNRINSED
60%	60%
64%	58%
71%	73%
81%	78%
85%	65%

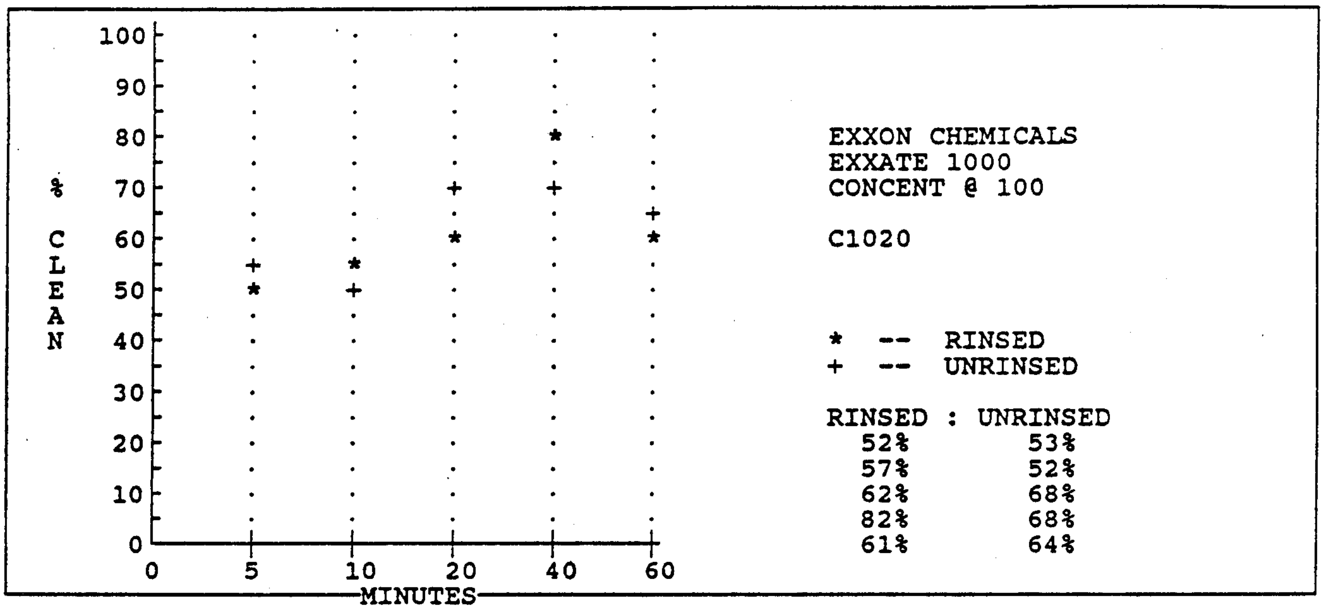


EXXON CHEMICALS
EXXATE 1000
CONCENT @ 100

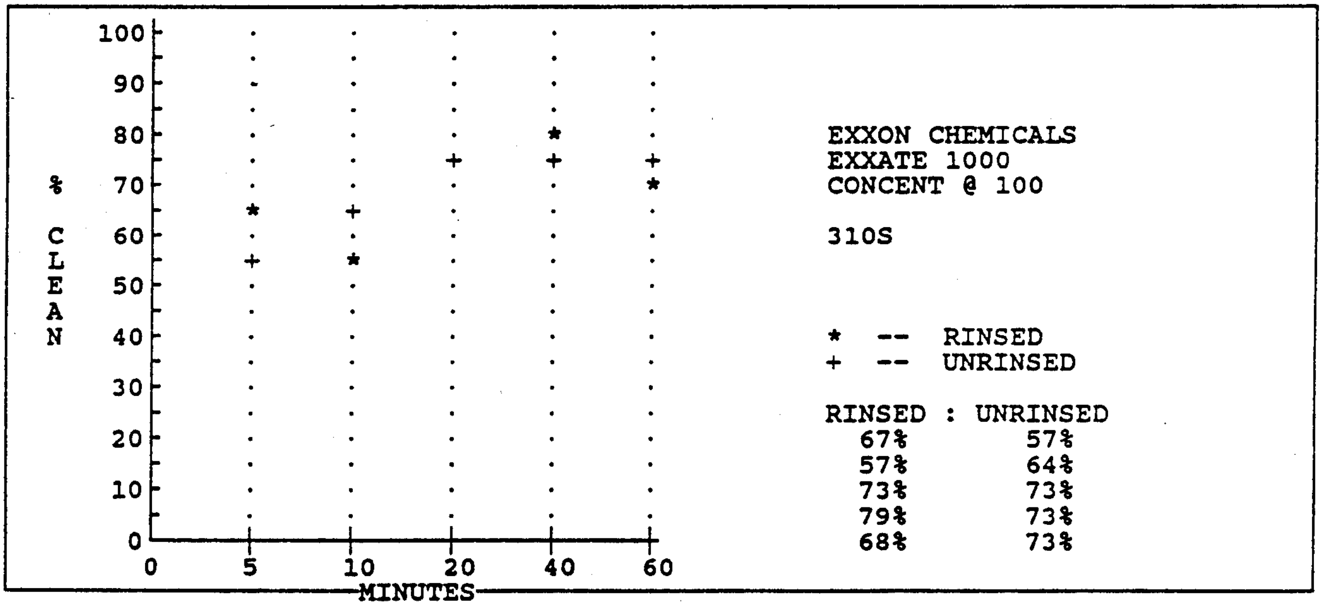
Az31B

* -- RINSED
\+ -- UNRINSED

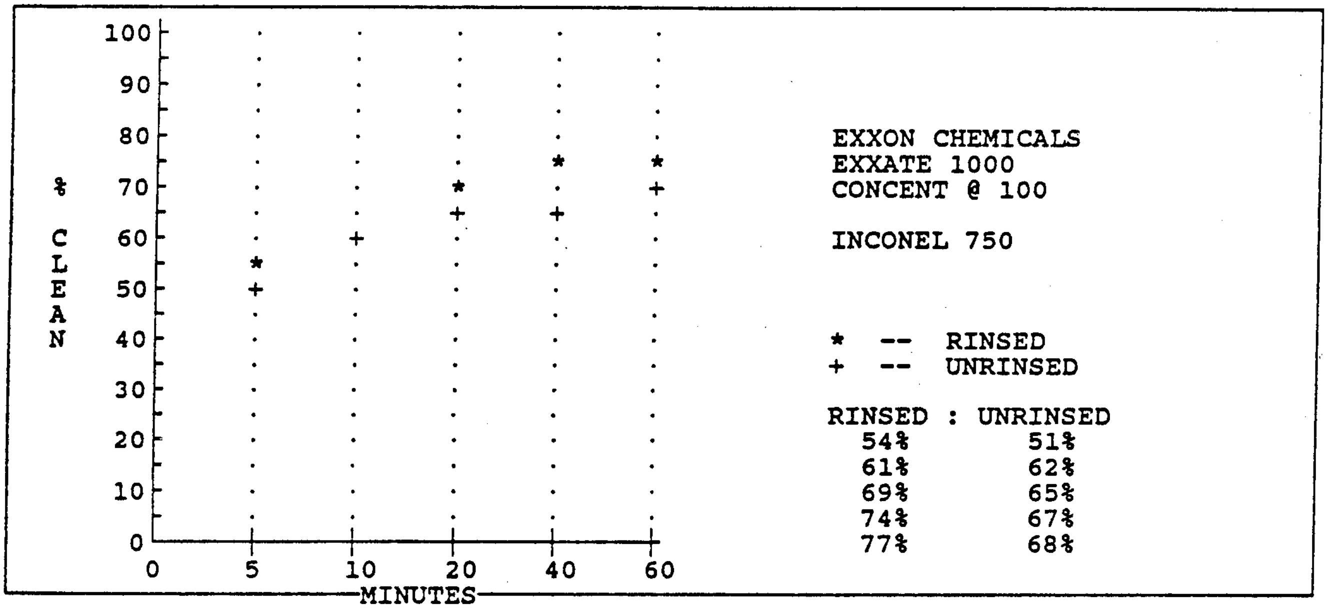
RINSED	UNRINSED
60%	64%
63%	67%
72%	67%
75%	70%
76%	76%



RINSED	UNRINSED
52%	53%
57%	52%
62%	68%
82%	68%
61%	64%



RINSED	UNRINSED
67%	57%
57%	64%
73%	73%
79%	73%
68%	73%

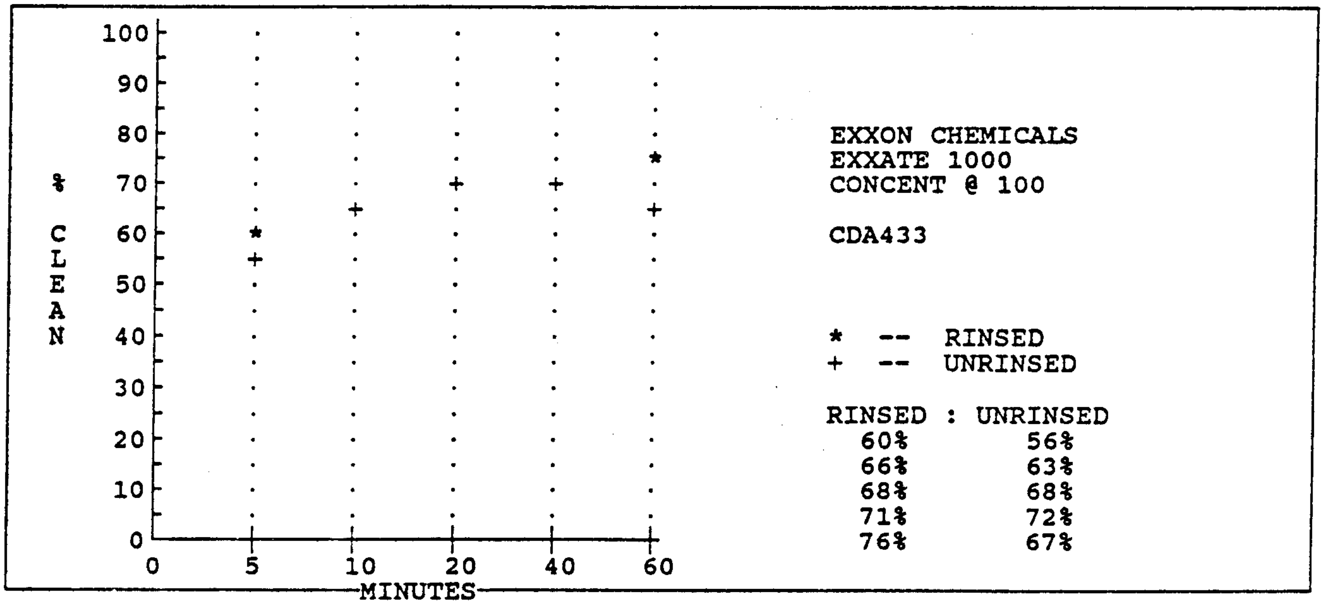


EXXON CHEMICALS
EXXATE 1000
CONCENT @ 100

INCONEL 750

* -- RINSED
\+ -- UNRINSED

RINSED	UNRINSED
54%	51%
61%	62%
69%	65%
74%	67%
77%	68%

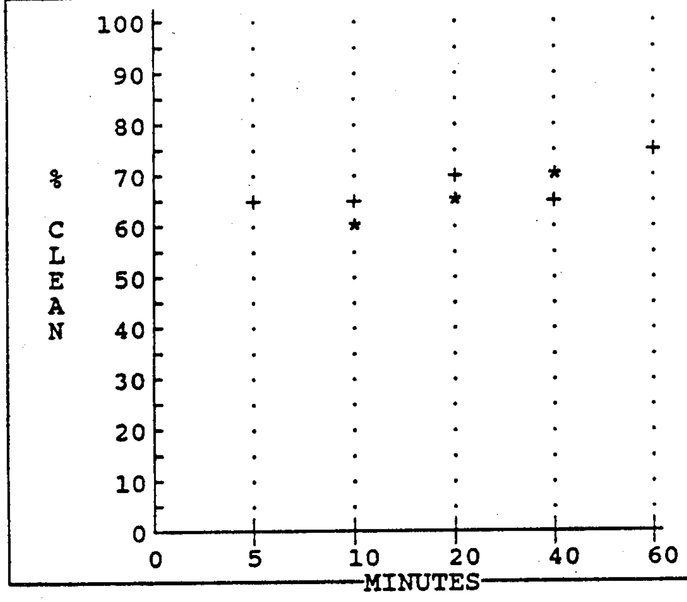


EXXON CHEMICALS
EXXATE 1000
CONCENT @ 100

CDA433

* -- RINSED
\+ -- UNRINSED

RINSED	UNRINSED
60%	56%
66%	63%
68%	68%
71%	72%
76%	67%

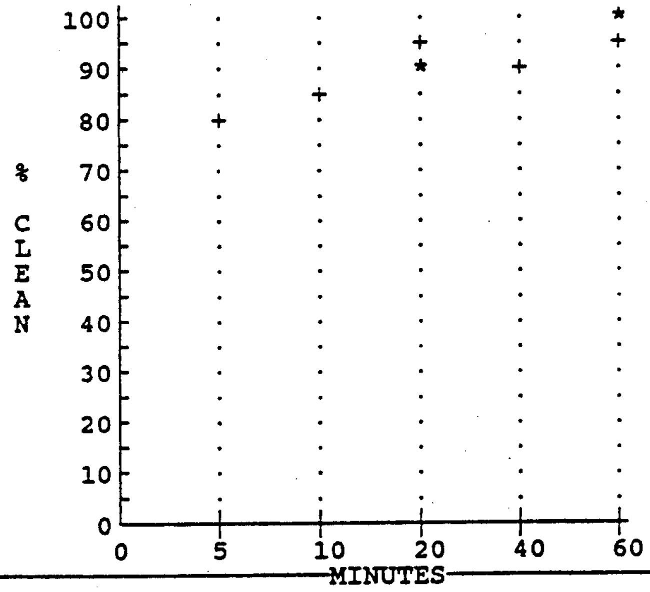


EXXON CHEMICALS
EXXATE 1000
CONCENT @ 100

MONEL K-500

* -- RINSED
\+ -- UNRINSED

RINSED	UNRINSED
63%	64%
59%	65%
65%	69%
69%	67%
76%	74%

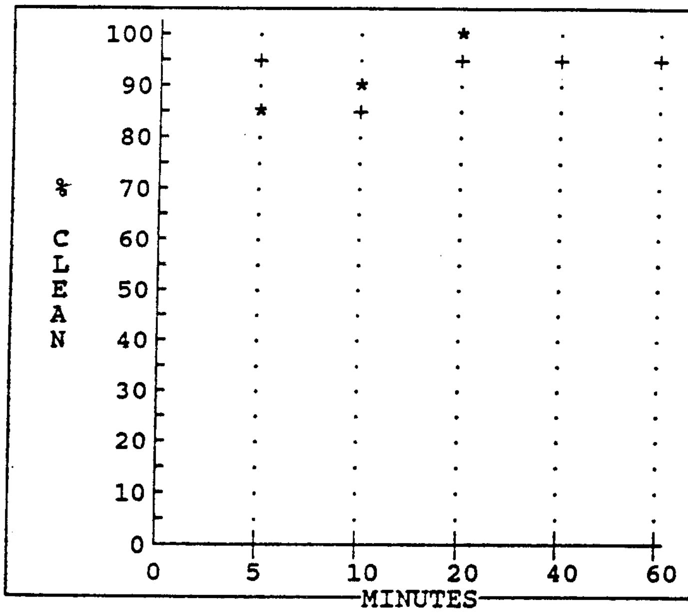


EXXON CHEMICALS
EXXATE 1000
CONCENTRATE @ 120 F

C1020

* -- RINSED
\+ -- UNRINSED

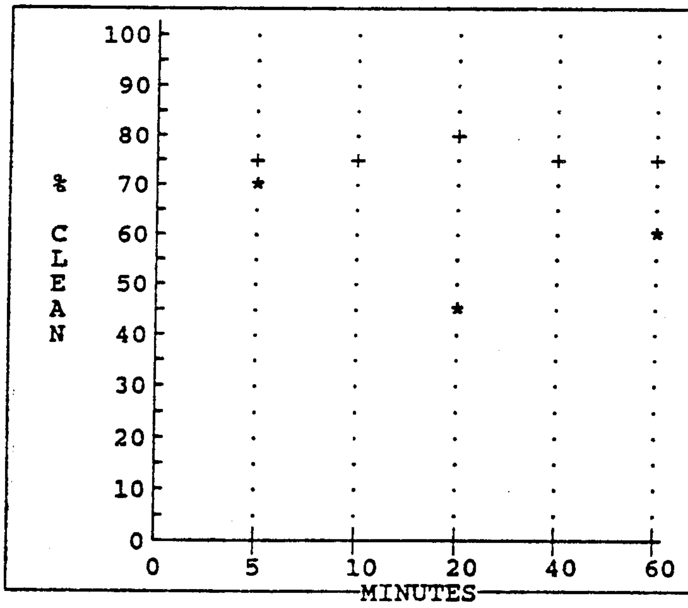
RINSED	UNRINSED
79%	80%
83%	84%
89%	97%
91%	89%
100%	94%



EXXON CHEMICALS
EXXATE 1000
CONCENTRATE AT 120 F WITH
STIRRING
Az31B

* -- RINSED
\+ -- UNRINSED

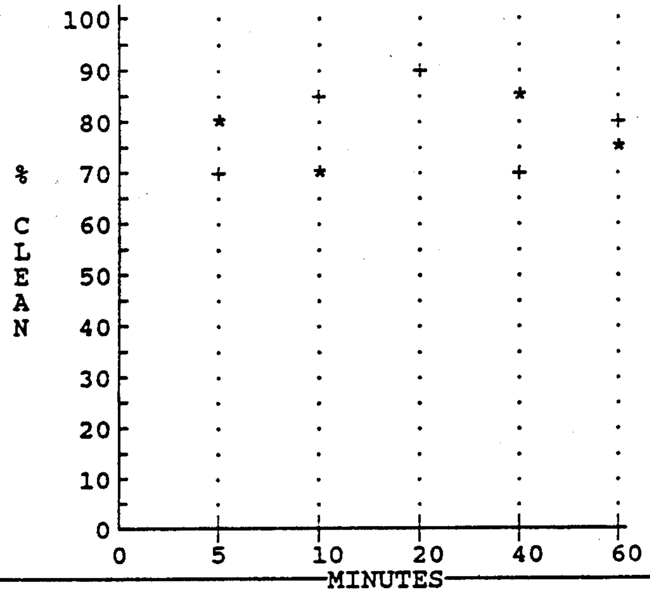
RINSED	UNRINSED
87%	93%
90%	88%
98%	93%
95%	96%
97%	94%



EXXON CHEMICALS
EXXATE 1000
GREASE: CONCENTRATE AT A
MBIENT
C1020

* -- RINSED
\+ -- UNRINSED

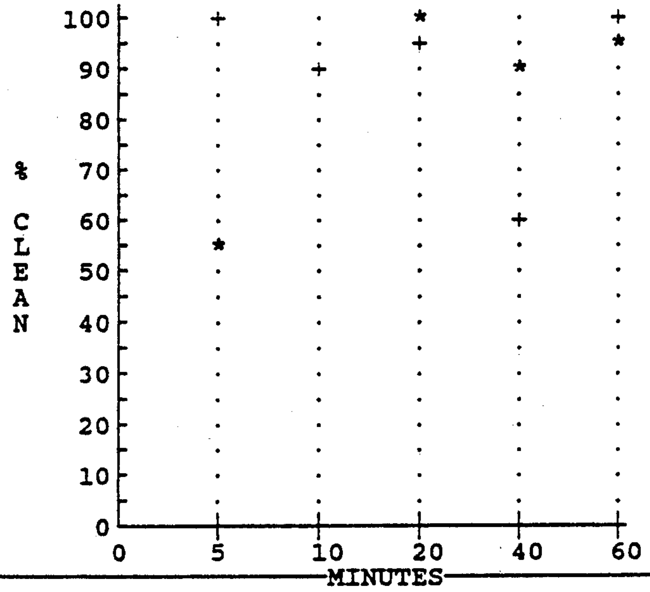
RINSED	UNRINSED
71%	73%
77%	73%
47%	79%
73%	77%
60%	75%



EXXON CHEMICALS
EXXATE 1000
GREASE: CONCENTRATE AT 12
0 F
MONEL K-500

* -- RINSED
\+ -- UNRINSED

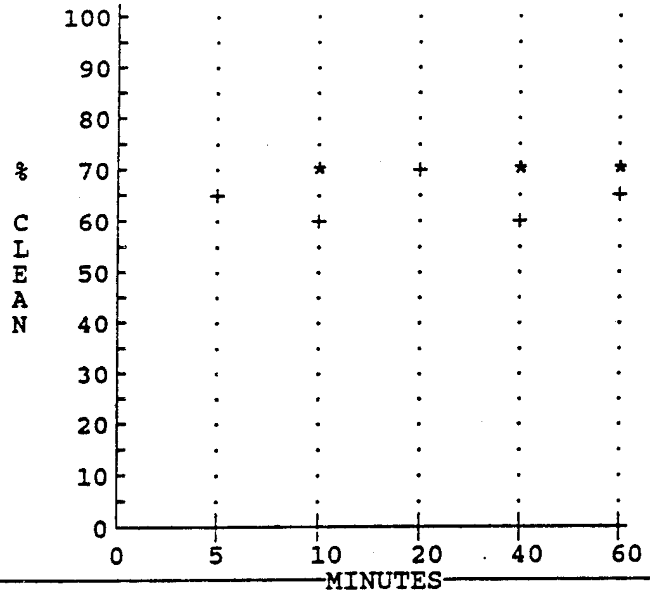
RINSED	UNRINSED
79%	69%
71%	85%
88%	88%
87%	72%
76%	82%



EXXON CHEMICALS
EXXATE 1000
OIL/XYLENE: CONCENTRATE
AT 140 F
A17075

* -- RINSED
\+ -- UNRINSED

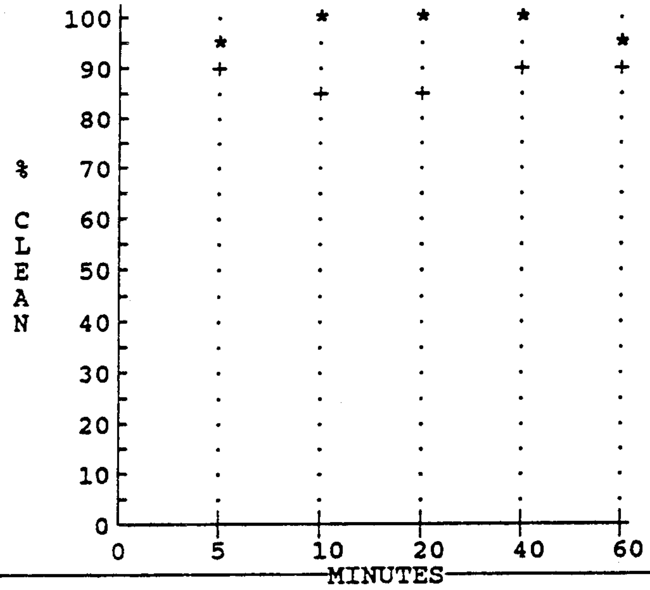
RINSED	UNRINSED
57%	100%
92%	90%
100%	97%
91%	63%
94%	100%



EXXON CHEMICALS
EXXATE 1000
GREASE: CONCENTRATE AT 1
20 F
Az31B

* -- RINSED
\+ -- UNRINSED

RINSED :	UNRINSED
67%	67%
70%	59%
71%	72%
72%	62%
68%	64%



EXXON CHEMICALS
EXXATE 1000
HYDRAULIC FLUID: CONCENT
RATE AT 120 F:
INCONEL 750

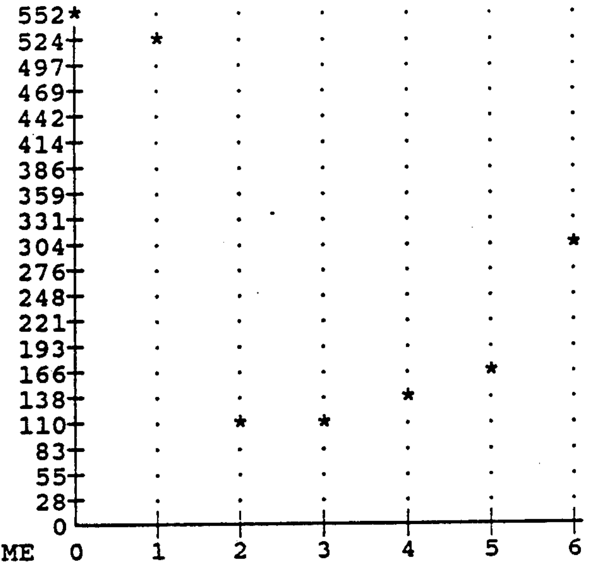
* -- RINSED
\+ -- UNRINSED

RINSED :	UNRINSED
96%	91%
100%	84%
99%	87%
100%	88%
96%	88%

COMPANY - ORANGE-SOL INCORPE
PRODUCT - DE-SOLV-IT
TOC INIT- 251425
TOC 2nd - 0
COD INIT- 1255000
ANILINE PT - 0.0000
ATP ----- 9 E-8

SOLUBILITY DATA:

CONCENT @ AMBIE	18%
CONCENT @ 100	60%
CONCENT @ 140	99%



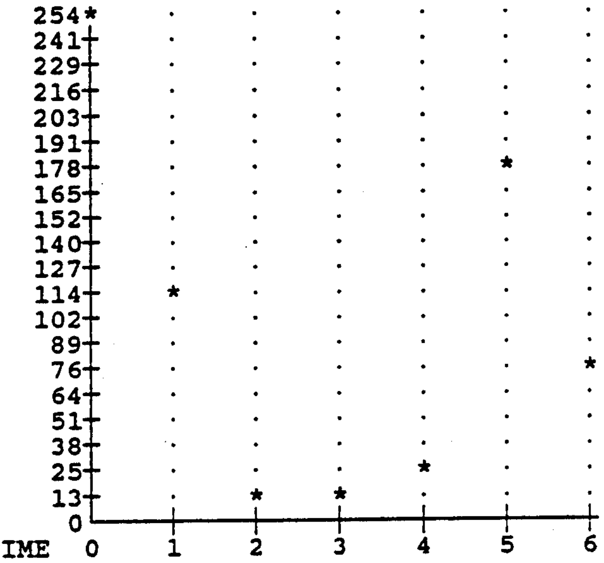
0- 552
1- 533
2- 107
3- 117
4- 142
5- 162
6- 301

DRY
WEIGHT
0.0030

DATE - 02/23/88 COD vs TIME

PHENOL
02/23/88
ATP - 34 E-8

ORANGE-SOL INCORPERATED
DE-SOLV-IT



0- 254
1- 112
2- 10
3- 16
4- 22
5- 172
6- 82

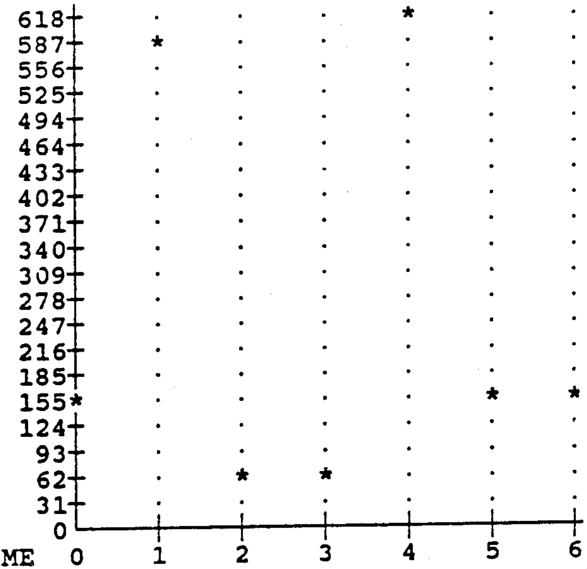
DRY
WEIGHT
0.0030

DATE - 02/23/88 COD vs TIME

COMPANY - ORANGE-SOL INCORPE
PRODUCT - DE-SOLV-IT
TOC INIT- 251425
TOC 2nd - 0
COD INIT- 1255000
ANILINE PT - 0.0000
ATP ----- 47 E-8

SOLUBILITY DATA:

CONCENT @ AMBIE	18%
CONCENT @ 100	60%
CONCENT @ 140	99%



DATE - 03/17/88 COD vs TIME

0-	160
1-	584
2-	60
3-	56
4-	618
5-	153
6-	159

DRY
WEIGHT
0.0610

PHENOL
03/17/88
ATP - 60 E-8

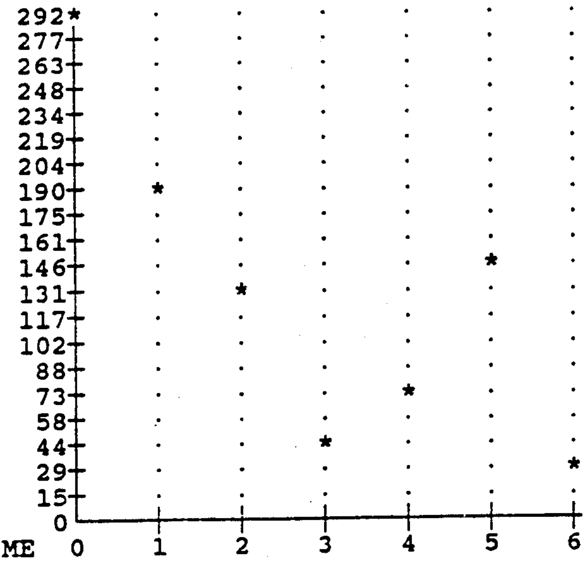
HYLUBE INC.
HYKLEEN 300

INTERNATIONAL PRODUCTS CO
MICRO

ORANGE-SOL INCORPERATED
DE-SOLV-IT

PACIFIC CHEMICAL
RIDDALL

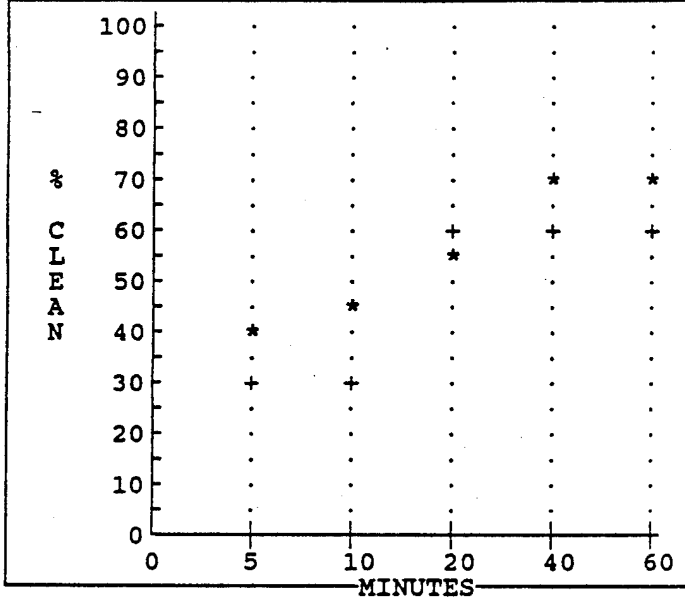
PANTHER CHEMICAL CO.
759



DATE - 03/17/88 COD vs TIME

0-	292
1-	195
2-	135
3-	46
4-	76
5-	140
6-	32

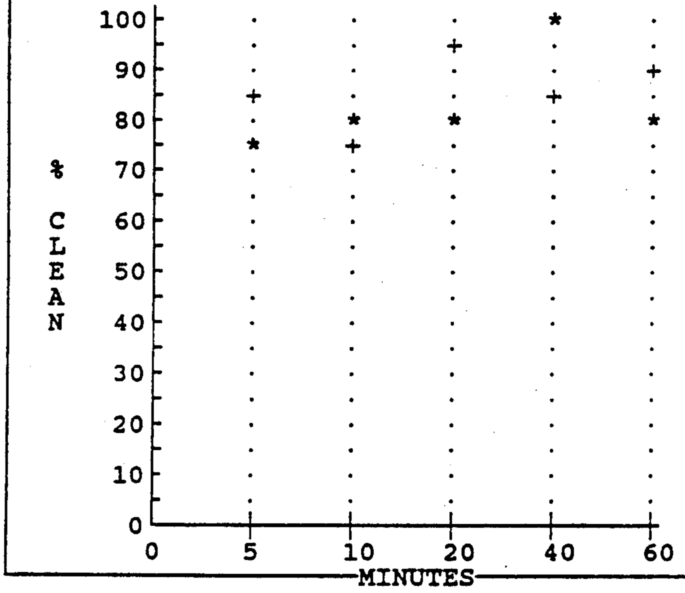
DRY
WEIGHT
0.0610



ORANGE-SOL INCORPERATED
DE-SOLV-IT
CONCENTRATED, AMBIENT, NO DYE
A12024

* -- RINSED
\+ -- UNRINSED

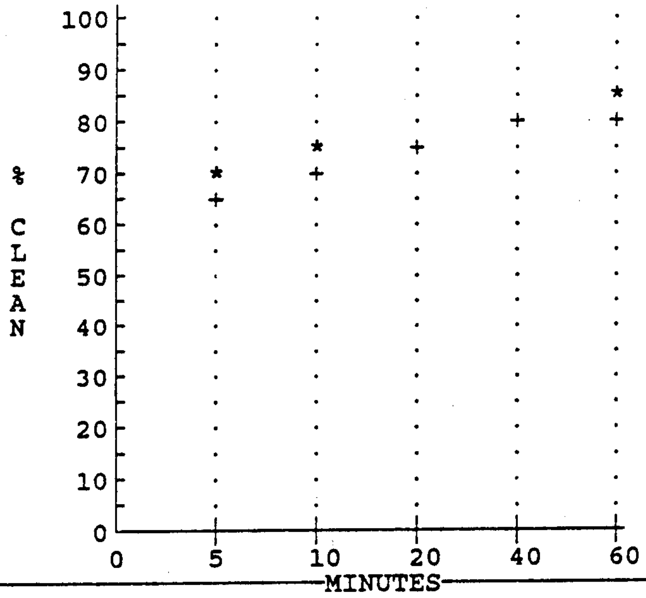
RINSED :	UNRINSED
41%	33%
44%	29%
54%	60%
70%	62%
70%	62%



ORANGE-SOL INCORPERATED
DE-SOLV-IT
CONCENTRATE, 140 F, NO DY
E
A17075

* -- RINSED
\+ -- UNRINSED

RINSED :	UNRINSED
76%	83%
81%	75%
81%	94%
100%	85%
79%	92%

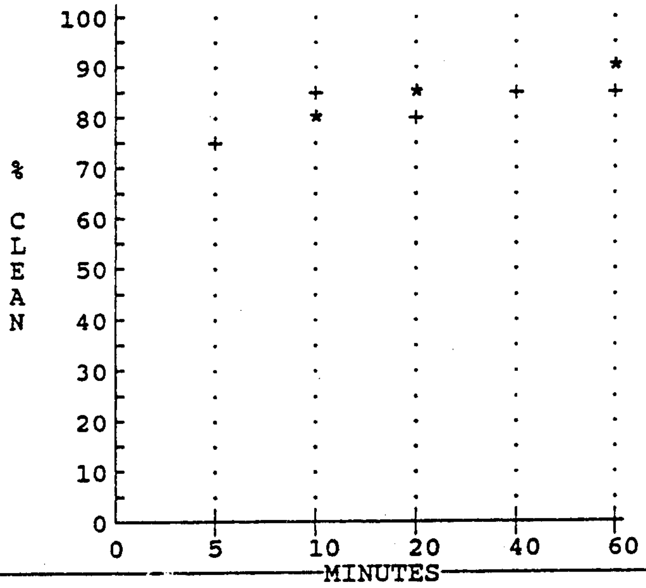


ORANGE-SOL INCORPERATED
DE-SOLV-IT
CONCENT @ 100

A12024

* -- RINSED
\+ -- UNRINSED

RINSED	UNRINSED
71%	63%
75%	72%
77%	77%
81%	80%
85%	81%

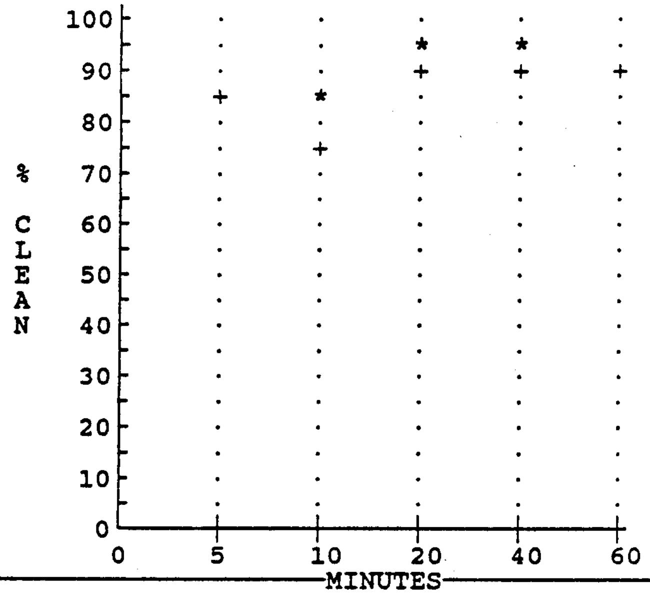


ORANGE-SOL INCORPERATED
DE-SOLV-IT
CONCENTRATE @ 120 F

A12024

* -- RINSED
\+ -- UNRINSED

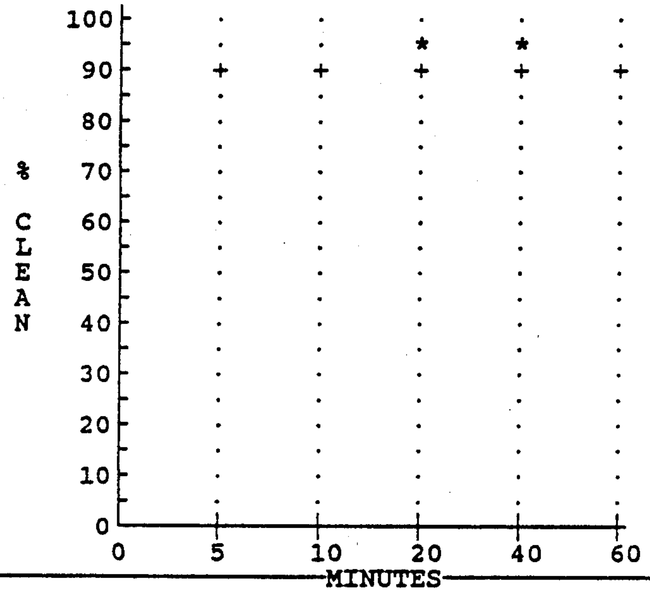
RINSED	UNRINSED
74%	75%
79%	83%
86%	81%
87%	86%
90%	87%



ORANGE-SOL INCORPERATED
DE-SOLV-IT
CONCENTRATE AT 120 WITH S
TIRRING
Az31B

* -- RINSED
\+ -- UNRINSED

RINSED	UNRINSED
84%	86%
87%	74%
95%	89%
96%	90%
90%	92%

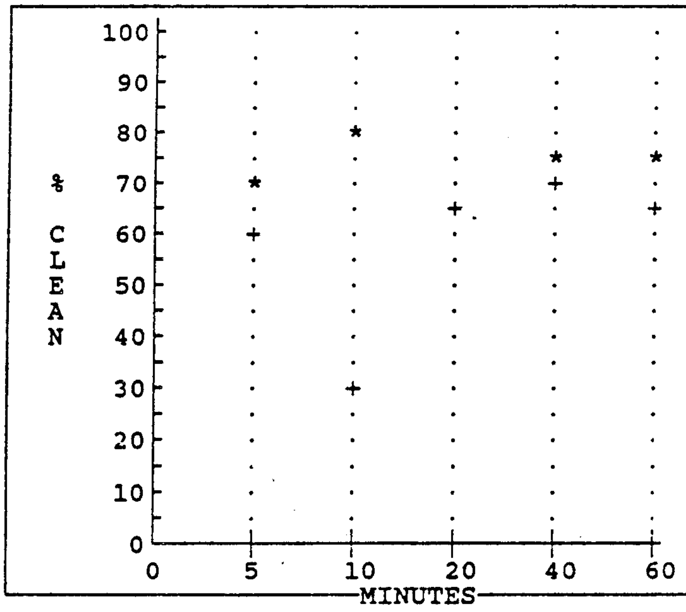


ORANGE-SOL INCORPERATED
DE-SOLV-IT
CONCENTRATE AT 150 F

310S

* -- RINSED
\+ -- UNRINSED

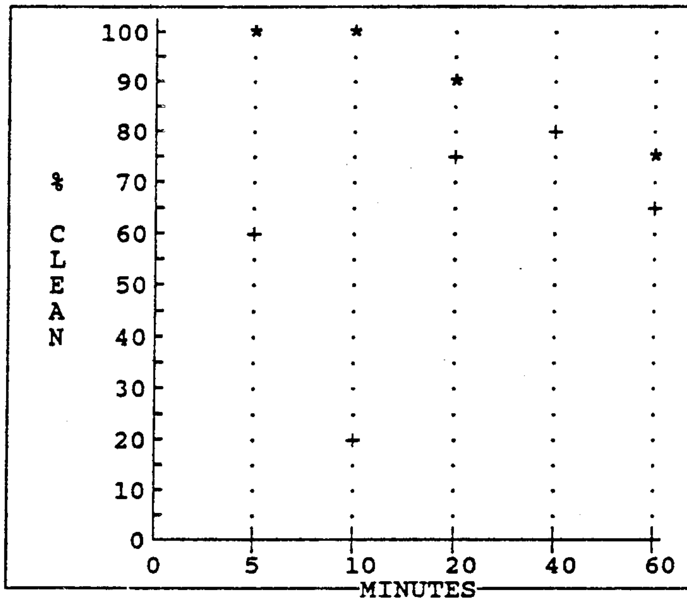
RINSED	UNRINSED
92%	91%
92%	92%
98%	90%
96%	90%
92%	91%



ORANGE-SOL INCORPERATED
DE-SOLV-IT
GEASE: CONCENTRATE AT AM
BIENT
310S

* -- RINSED
+ -- UNRINSED

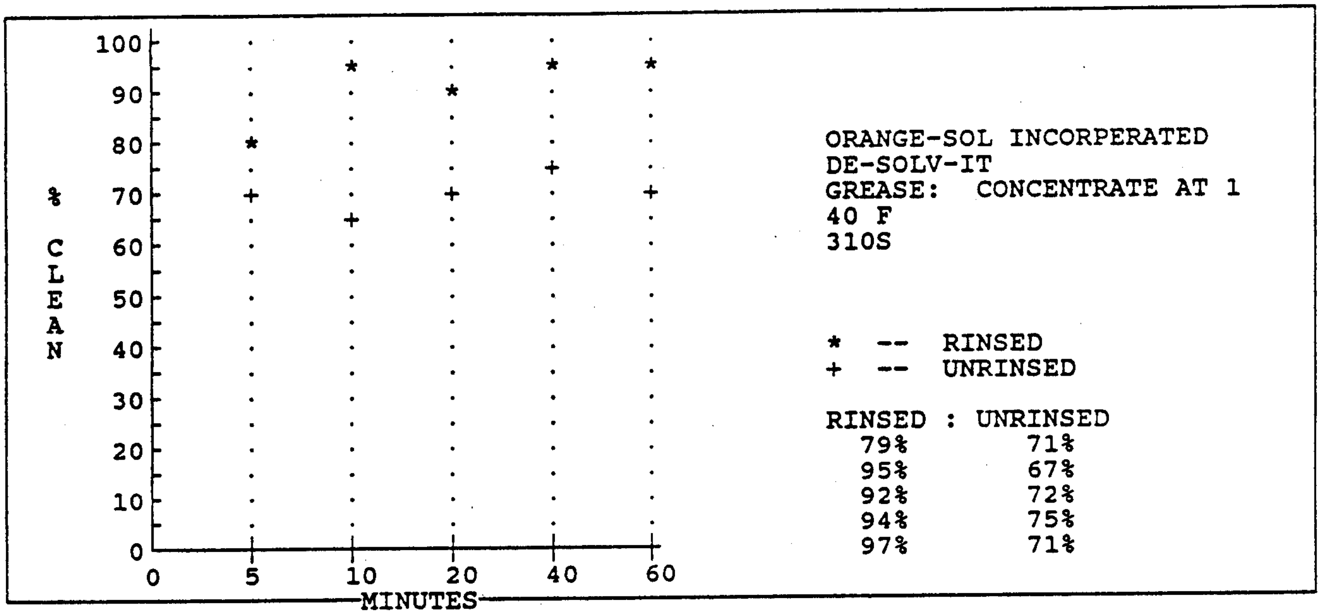
RINSED :	UNRINSED
69%	58%
79%	29%
63%	63%
75%	69%
76%	63%



ORANGE-SOL INCORPERATED
DE-SOLV-IT
OIL/XYLENE: CONCENTRATE A
T 140 F
C1020

* -- RINSED
+ -- UNRINSED

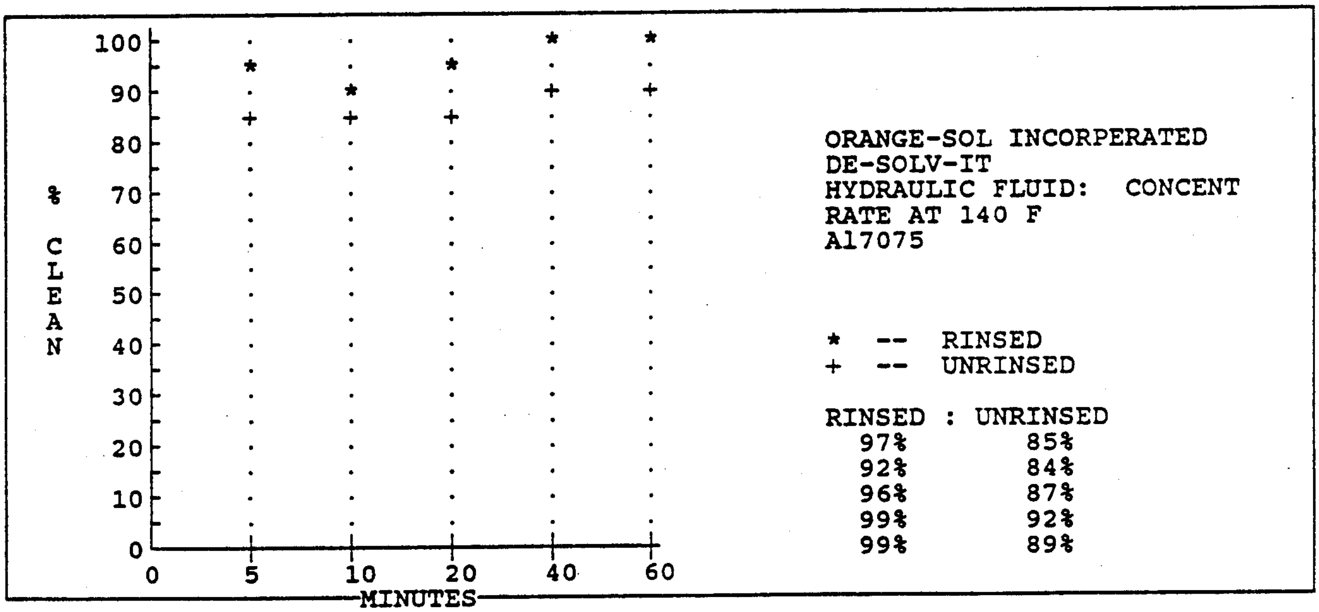
RINSED :	UNRINSED
98%	60%
98%	20%
92%	77%
79%	79%
75%	65%



ORANGE-SOL INCORPERATED
DE-SOLV-IT
GREASE: CONCENTRATE AT 1
40 F
310S

* -- RINSED
\+ -- UNRINSED

RINSED	UNRINSED
79%	71%
95%	67%
92%	72%
94%	75%
97%	71%



ORANGE-SOL INCORPERATED
DE-SOLV-IT
HYDRAULIC FLUID: CONCENT
RATE AT 140 F
A17075

* -- RINSED
\+ -- UNRINSED

RINSED	UNRINSED
97%	85%
92%	84%
96%	87%
99%	92%
99%	89%

(The reverse of this page is blank.)

APPENDIX C

TOXICITY DATA

These pages contain toxicity data for the solvents selected for Phase II testing.

Company	Solvent	Vapor Pressure (MM HG)	Flash Point	Comments
Exxon	Exxate 700	0.8 @ 68°F	150°F	Oral LD50 (rat) > 5 g/Kg. Low order of toxicity. Dermal LD50 (rabbit) > 3 g/Kg. Low order of toxicity. Mildly irritating. Eye irritation: (rabbit) judged to be slight. Maximum draize scores out of possible 110: 4 at 1 hour, 6 at 4 hours, 2 at 24 hours and 0 thereafter.
Exxon	Exxate 800	0.75 @ 68°F	141°F	Oral LD50 (rat) approximately 5 g/Kg. Low order of toxicity. Dermal LD50 (rabbit) > 3 g/Kg. Low order of toxicity. Dermal irritation (rabbit): slight irritation. Eye irritation (rabbit): judged to be slight. Maximum draize scores out of possible 110: 4 at 1 and 4 hours, 2 at 24 and 48 hours and 0 thereafter. 90 day subchronic: rats received undiluted solvent via oral gavage at doses of 0.1, 0.5 or 1.0 g/Kg 5 days/week for 13 weeks. Several treatment-related effects were observed in the high dose group. These included slight reductions in body weight and food consumption, and increased liver and kidney weights in the mid-dose group, no other significant treatment related effects were observed in the mid or low dose animals. These results are indicative of an overall low degree of toxicity Teratology: pregnant rats received undiluted solvent via oral gavage at doses of 0.1, 0.5 and 1.0 g/Kg on days 6 through 15 of gestation. The high dose produced maternal toxicity which was accompanied by a slight increase in malformations and embryotoxicity. Adverse effects were not observed in the mid or low dose groups. No teratogenic effects were observed at maternally nontoxic doses.
Exxon	EXXATE 1000	0.1 @ 68°F	212°F	Oral LD50 (rat) > 5 g/Kg. Low order of toxicity. Dermal LD50 (rabbit) > 3 g/Kg. Low order of toxicity. Dermal irritation (rabbit): mildly irritating. Eye irritation: judged to be slight. Maximum draize scores out of possible 110: 6 at 1 hour, 4 at 4 hours, 2 and 24 and 48 hours and 0 thereafter.

Company	Solvent	Vapor Pressure (MM HG)	Flash Point	Comments
Exxon	Exxate 1300	0.03 @ 68°F	261°F	Oral LD50 (rat) > g/Kg. Low order of toxicity. Dermal LD50 (rabbit) > 3 g/Kg. Low order of toxicity. Dermal irritation (rabbit) mildly irritating. Eye irritation: judged to be slight. Maximum draize scores out of possible 110: 6 at 1 and 4 hours, 4 at 24 hours, 2 at 48 and 72 hours, 0 thereafter. 90 day subchronic: rats received undiluted solvent via oral gavage at doses of 0.1, 0.5 or 1.0 g/Kg, 5 days/week for 13 weeks. Several treatment-related effects were observed in the mid and high dose groups. None were considered to be of significant toxicological concern.
Tri Ton	Hemo-Sol	1 @ 20°C	115°F	Harmful if swallowed. May cause eye damage. Can cause skin irritation. Fema-Gras: FAD-GRAs: RIFM lists acute LD50 (rat) > 5 g/Kg acute dermal LD50 (rat) .5 g/Kg. Mild irritant - None in 10% petrolatum. Sensitization - none in 10% petrolatum.
Orange-Sol	De-Solv-It	0.15 @ 20°C	205°F	Oral Toxicity Test: LD50 = 17,750 mg/Kg (160 mL/Kg). Inhalation toxicity test: no toxic manifestations. Draize eye irritation test: test score 0.00. Primary skin irritation test: tested at a low irritation index of 0.2. Muscle tissue test: no deleterious effects. All tests are available on request.
Bio-Tek	Safety Solvent	0.6 @ 20°C	215°F	Oral limit LD50 (rat) 5 g/Kg. Low order of toxicity. Dermal toxicity LD50 (rabbit) 3 g/Kg. Low order of toxicity. Dermal irritation (rabbit). Mildly irritating. Eye irritation Draize test. Judged to be slight. 90 day subchronic: rats received undiluted solvent via oral gavage at doses of 0.1, 0.5 and 1.0 g/Kg, 5 days/week for 13 weeks. Some treatment-related effects were observed in the mid and high dose groups. None were considered to be of significant toxicological concern. The results are indicative of an overall low

Company	Solvent	Vapor Pressure (MM HG)	Flash Point	Comments
				degree of toxicity. Teratology: pregnant rats received same doses as above with no suggestive signs of fetotoxicity or teratogenicity. Considered to be non-teratogenic. TLV has not been established for product.
Bio-Tek	134 Hi-Solv	0.325 @ 20°C	215°F	TLV has not been established for product.
Exxon	Exxate 6000	1.403 @ 68°F	135°F	Oral LD50 (rat) > 10 g/Kg. Low order of toxicity. Dermal LD50 (rabbit) .3 g/Kg. Low order of toxicity. Eye irritation (rabbit) judged to slight to moderate. Maximum draize scores out of possible 110: 12 at 1 hour, 14 at 4 hours, 10 at 24 hours, 6 at 48 and 72 hours, and 2 at 4 days. Inhalation limit: in high concentrations the vapor is irritating and anesthetic. Rats, mice and guinea pigs were exposed to nominal concentrations of 11,800 ppm for 6 hours. No rats died, 1/10 guinea pigs and 10/10 mice died. The results are indicative of an overall low degree of toxicity. Teratology: pregnant rats received undiluted solvent via oral gavage at doses of 0.5, 1.3 and 2.5 g/Kg on days 6 through 15 of gestation. Signs suggestive of fetotoxicity or teratogenicity were not observed in any of the dose groups. Non-teratogenic.

(The reverse of this page is blank.)

APPENDIX D

MSE REPORTS

These pages contain the reports from MSE concerning the poor performance of ultrasonic agitation in large-scale applications and the design for the hydraulic agitation system used in the full-scale tests.

(The reverse of this page is blank.)

Project: Tinker AFB, MSE Process Engineering Subcontract to EG&G

Subject: Comments on Use of Ultrasonics for Enhancement of Solvent Cleaning

The Solvent Substitution program testing has identified organic solvents as the most likely replacement candidate. To achieve acceptable cleaning performance, these solvents require physical enhancements such as heating, mechanical agitation and/or ultrasonic agitation. As part of a vendor contact effort to identify suppliers of enhancement equipment, several ultrasonic vendors were approached. Conversations with them to detail the proposed utilization of ultrasonics to enhance the performance of the organic solvents revealed potential problems with using systems larger than 100 gallons. A discussion of ultrasonic operations and how organic solvents are affected follows, including a list of the vendors who detailed the potential problems.

Discussion

Ultrasonic equipment suppliers state their testing has shown that organic solvents will not cavitate successfully in large tanks (capacities greater than 100 gallons). The problem is the dissolved gases in the fluid. A partial solution is heating the liquid to a high temperature, nominally 80 percent of its normal boiling point. Small, bench-scale test have been successful without high temperatures due to the ability to introduce enough cavitation intensity to overwhelm the dissolved gases. The suppliers concur that to produce adequate intensity in large tanks, liquid heating to the 80 percent of normal boiling point is required along with high power inputs. While technically feasible, the number of transducers required results in excessive costs, somewhere on the order of $100,000+ for just the transducers for a tank similar in size to current Air Force equipment.

The reasons for the organic solvents incompatibility with ultrasonics lies in how the cleaning impact is created. Ultrasonic cleaning effects are produced by cavitation energy. High frequency sound waves (20 to 100 kHz) introduce microscopic voids (bubbles) in the fluid. When these bubbles implode due to alternating waves of compressive energy, extremely small but highly intense shock waves are produced. This is what generates the surface cleaning. Cavitation intensity is a function of the power transmitted to the liquid and properties of the cleaning fluid. The power is related to the ultrasonic frequency utilized, with most available equipment operating in the 20 kHz to 45 kHz range. Test performed for DOE by the General Electric Co., Neutron Devices Department indicated the cavitation intensity was higher at the 40 kHz level, giving better overall cleaning. However, the frequency can be varied within the 20 to 45 kHz range to maximize cleaning in cases such as small areas to be penetrated and parts sensitive to certain frequencies.

The properties of the cleaning liquid effecting cavitation intensity include vapor pressure, surface tension, viscosity, density and dissolved gases. The most important factor is the dissolved gases. Gas in a fluid will diffuse into the cavitation bubble and cushion the implosion, reducing or eliminating the desired shock waves. Dissolved gases can be removed by drawing a vacuum on the liquid or application of intermittent pulses of ultrasonic energy. However, when exposed to air, the degassed liquid will immediately reabsorb gas. Heat can be used to enhance the degassing process because heating reduces the ability of the fluid to hold dissolved gas. But, maximum cavitation intensity is usually achieved in a narrow temperature range, nominally 80 percent of the normal boiling point.

Summary

Use of ultrasonic energy to enhance cleaning with organic solvents, while technically feasible, is cost prohibitive and would result in operations at fluid temperature levels higher than deemed safe by the Air Force. Other types of fluid agitation such as mechanical or fluid jets should be investigated.

References

-Delta Sonics, Jim Halbert, 15341 Texaco Ave., Paramount, CA 90723, (213) 634-7140

-Blackstone Ultrasonics, Richard Thies, 1111 Allen St., Jamestown, NY 14701, (716) 665-2620

-Zenith, Edward Pedzy, 90 Herbert Ave., Closter, NJ 07624, (201) 767-1332

-"Ultrasonic Cleaner Evaluation," T.J. Gillespie, General Electric Co., Neutron Devices Dept., P.O. Box 11508, St. Petersburg, FL 33733

MSE, Inc. Corporate Office P.O. Box 4078 Butte, MT 59702 (406) 723-8213
Component Development and Integration Facility (CDIF) P.O. Box 3767 Butte, MT 59702 (406) 494-7100

August 7, 1990

90CDIF-570

John Espinosa
EG&G Idaho, Inc.
P.O. Box 1625, MS 1500
Idaho Falls, ID 83415

Greg Hulet
EG&G Idaho, Inc.
Tinker AFB Pilot Plant
Bldg. 62516
Oklahoma City, OK 73145

Dear John/Greg:

Attached is the proposed design for the solvent substitution full-scale test tank agitation. The objective is to provide agitation which is both vigorous and uniform. Other options using fewer nozzles and/or tank mixing eductors are available, but the flow distribution can not be predicted and the size of the eductors is too large when the basket is in place.

The design and construction is detailed in the attached sheets, as is the materials required. However, a few details should be emphasized to ensure satisfactory performance:

1) Nozzles: The maximum effective penetration of a jet of fluid is about 100 nozzle diameters. Placing the nozzles in each corner of the tank with the nozzles pointed toward the center of the tank and assuming 36" of total penetration gives a nozzle diameter of 3/8". Using 10 psi drop across this nozzle will give a bulk velocity of 0.86 feet/sec. which is well within the recommended range for vigorous agitation of 0.7 to 1.0 feet/sec. The nozzle calculations are based on the Spraying Systems Co. Veejet nozzle which was chosen because of its one-piece construction - multiple-part nozzles are more difficult to keep operating. The necessary ordering information from the Spraying Systems Co. catalog are attached.

2) Flow Straighteners: To provide predictable flow patterns, Jet Stabilizers should be installed between the manifold and the nozzle.

3) Adjustable Ball Fittings: To provide flexibility with the spray nozzles, Adjustable Ball Fittings should be installed as per the Spraying System Co. catalog. The fittings provide 40° of total movement, allowing experimentation with the nozzle directions for best tank agitation.

4) Pump Inlet: Use 45° elbows for directing the piping from the tank drain to the pump suction, as shown on the attached "Pump Suction Detail" figure. This will minimize the pressure drop from the piping and will enable fitting the suction pipe so it clears the existing 2" IWTP line. Install a screen on the interior opening of the 2" tank drain line to prevent large debris from being sucked into the pump.

5) Nozzle Runs: At least 1 1/2" diameter pipe should be used - a smaller diameter pipe would tend to increase the fluid flowrate through the first nozzles and increase the pressure drop, causing an increase in pump head required.

I've contacted the pump vendor recommended by Bill Martin so they can begin searching for a pump. When I hear from them (Bush Sales in Salt Lake City, (801)322-1058, ask for Norm), I will pass the information along.

If you have any questions, comments, or changes on the design, please call.

Sincerely,

E.L. Rademacher, Jr.

E.L. Rademacher, Jr.
MSE, Inc.

ELR/bh

Attachment

cc: Tink 99.05

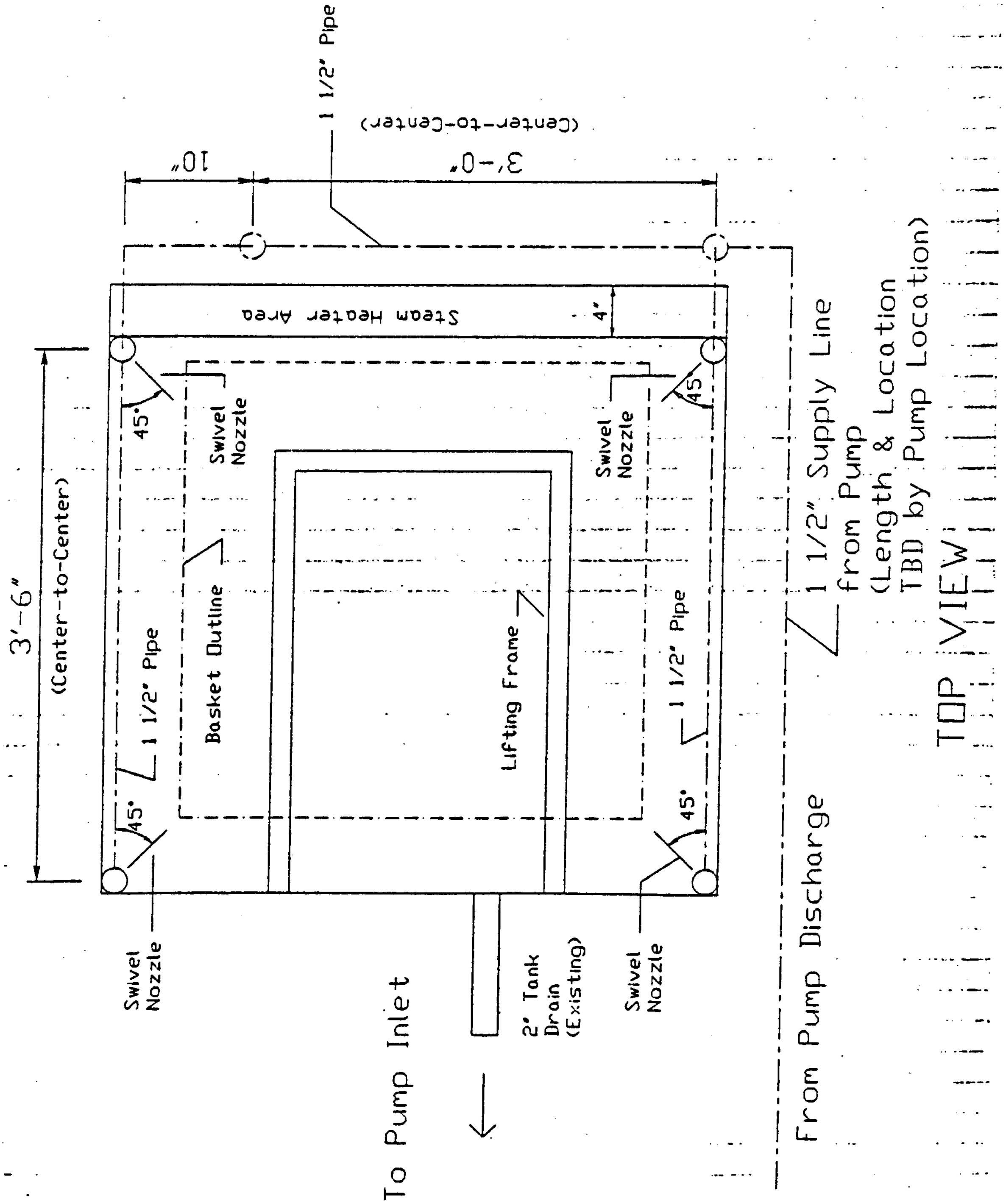
EER

PREPARED E.L. Rademacher, Jr. 9-6-90
CHECKED
FILE
PROJECT Tinker/EG&G
SUBJECT Tank Agitation

PAGE ____ OF ____

MSE INC.
COMPONENT DEVELOPMENT AND
INTEGRATION FACILITY (CDIF)
P.O. BOX 3767 (406)494-7100
BUTTE, MONTANA FTS 587-7100

NOTE: Tank Inside Dim. = 48"LX48"WX39"H
Assumed Basket Dim. = 36"LX36"WX12"H



ESK

PREPARED E. L. Rademacher, Jr 8-6-90

CHECKED

FILE

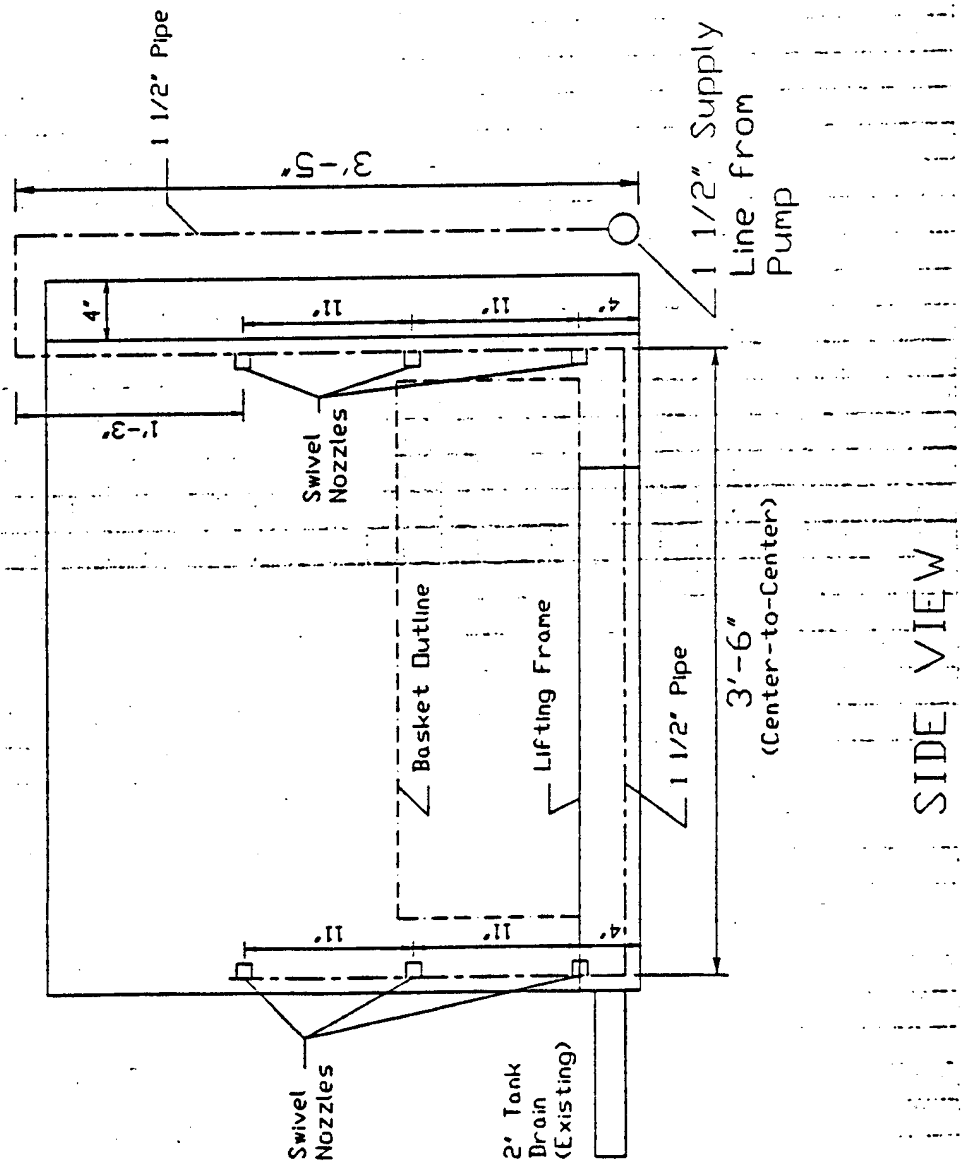
PROJECT Tinker / EG&G

SUBJECT Tank Agitation

PAGE ____ OF ____

MSE INC.

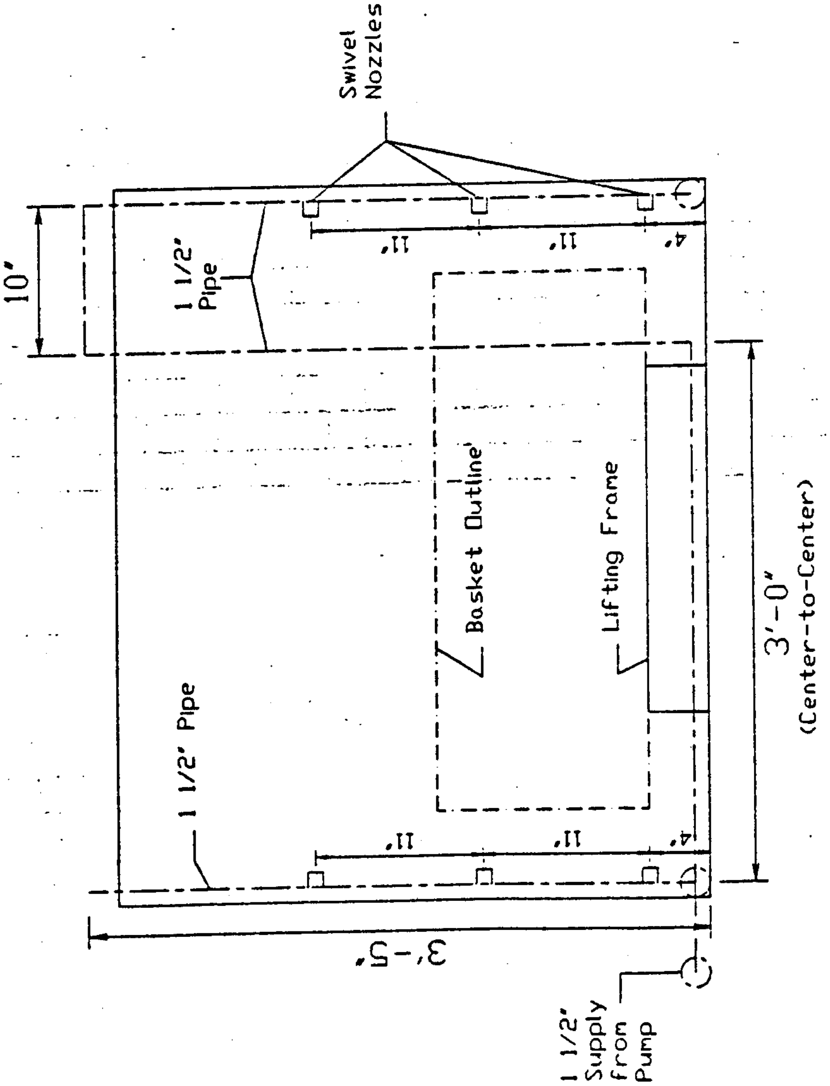
COMPONENT DEVELOPMENT AND
INTEGRATION FACILITY (CDIF)
P.O. BOX 3767 (406)494-7100
BUTTE, MONTANA FTS 587-7100



PREPARED E. L. Rademacher, Jr ESR 8-6-90
CHECKED
FILE
PROJECT Tinker / EG+G
SUBJECT Tank Agitation

PAGE ___ OF ___

MSE INC.
COMPONENT DEVELOPMENT AND
INTEGRATION FACILITY (CDIF)
P.O. BOX 3767 (406)494-7100
BUTTE, MONTANA FTS 587-7100

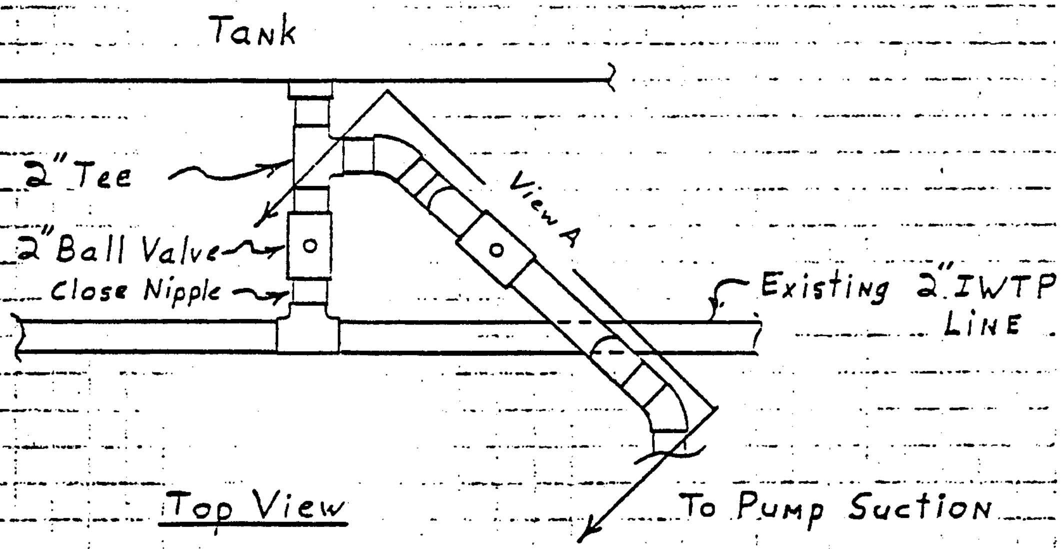


END VIEW

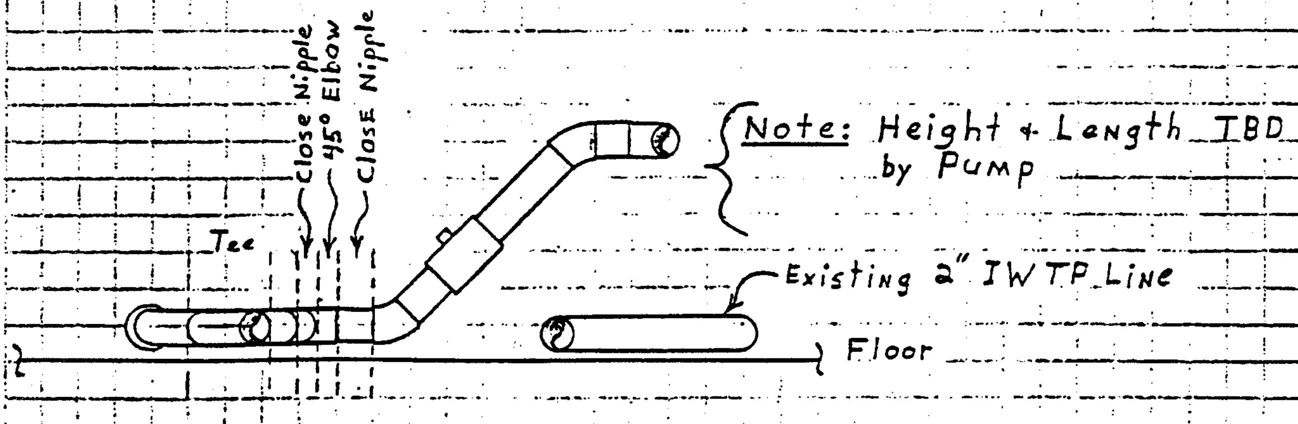
PREPARED E.L. Rademacher, Jr. ESR 8-6-90
CHECKED ______ ______
FILE ______ ______
PROJECT Tinker/EG+G
SUBJECT Pump Suction Detail

PAGE ____ OF ____

MSE INC.
COMPONENT DEVELOPMENT AND
INTEGRATION FACILITY (CDIF)
P.O. BOX 3767 (406)494-7100
BUTTE, MONTANA FTS 587-7100



Top View

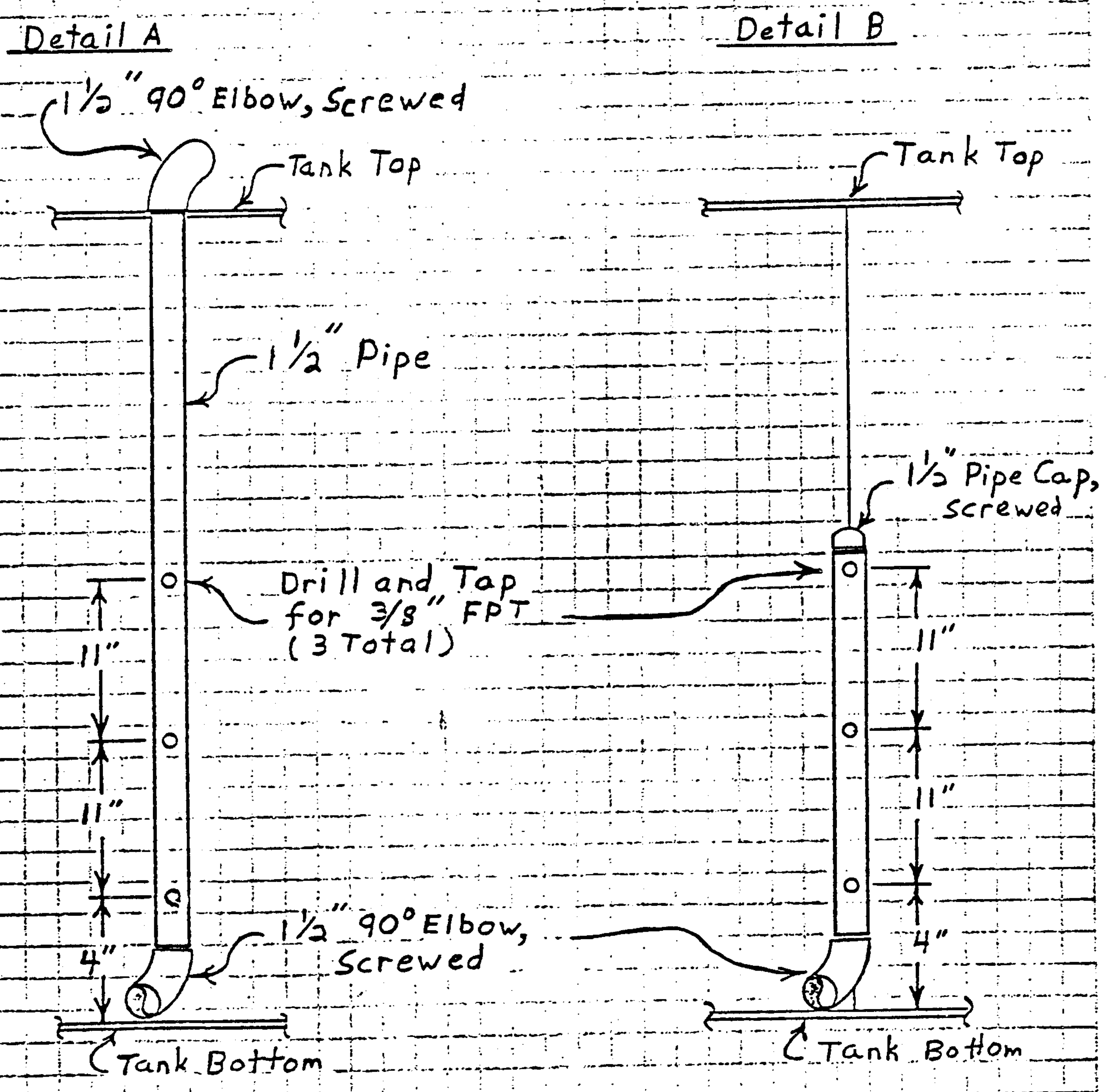


View A

PREPARED E.L. Rademacher, Jr. ESR 8-6-90
CHECKED
FILE
PROJECT Tinker/EG&G
SUBJECT Tank Agitation

PAGE ___ OF ___
MSE INC.
COMPONENT DEVELOPMENT AND INTEGRATION FACILITY (CDIF)
P.O. BOX 3767 (406)494-7100
BUTTE, MONTANA FTS 587-7100

Nozzle Run Detail



APPENDIX E

TESTING PROTOCOLS

These pages contain the protocols used for the Phase II biological acclimation tests.

6-HOUR TEST PROTOCOL

(The reverse of this page is blank.)

Test Configuration

Time (hours)	Test Columns 1	2	3	4	5	6 (Phenol)
0	2F 2ATP	2F 2ATP	2F 2ATP	2F 2ATP	2F 2ATP	2F 2ATP
1	2F 2UF	2F	2F	2F	2F	2F
2	2F	2F	2F	2F	2F	2F
3	2F	2F	2F	2F	2F	2F
4	2F	2F	2F	2F	2F	2F
5	2F 2UF	2F	2F	2F	2F	2F
6	2F 2ATP	2F 2ATP	2F 2ATP	2F 2ATP	2F 2ATP	2F 2ATP

2F	2 Filtered (2-mL) samples for COD analysis
2ATP	2 unfiltered (1-mL) samples for adenosine triphosphate
2UF	2 unfiltered (2-mL) samples for COD analysis

The activated sludge from Tinker AFB is maintained in a culture column with air circulation, with siphon activated maximum volume overflow wasting, and with constant nutrient additions. Solids are maintained at approximately 2.5 grams/liter.

Solids

Activated sludge, brought to this lab from Tinker AFB's IWTP, is concentrated by centrifugation at 5°C and 5000 rpm. The elutrient is discarded and the pellet is collected in a container which is stored in a refrigerator at 5°C. The moisture content of the concentrated sludge is determined by adding 1.0 grams of wet concentrated sludge to a preweighed pan. The material is dried to a constant weight at 105°C in a drying oven. The percent of solids is determined by:

$$\frac{\text{dry weight}}{\text{wet weight}} \times 100 = \%\ \text{Solids}$$

This value is used to determine the amount of concentrated sludge added to the column.

$$\frac{\text{2.5 grams Solids/Liter}}{\%\ \text{Solids}} \times \text{4 Liters of column} = \begin{array}{l}\text{amount of wet solids}\\ \text{added to the column}\end{array}$$

Column Setup

1. The column is set up by initially adding 4-liters of dilution media to the column and turning on the air agitation in the column.
2. The column is allowed to mix for 5 minutes to permit mixing and oxygenation of the solution prior to the addition of solids.
3. The preweighed solids are added to the column.
4. Nutrient feed is started to the column.
5. Following 1/2 hour mixing period, a 50 mL sample is pulled in a glass beaker, a magnet bar is added, and placed on a stirring plate. The pH of the solution is measured using a calibrated pH probe. This solution is discarded following the pH determination.
6. A 25 mL sample of the culture column material is added to a preweighed drying tin. The sample is placed in a 105°C drying oven and dried to a constant weight.

Comments:

The air-flow in the column should be adjusted to prevent excessive bumping, yet provide adequate mixing.

Check all feed and waste discharge lines for proper flow.

Prepare a slide for microscopic observation of the column material.

The medium used for maintaining the activated sludge will be made up of the following materials (*):

1- liter deionized water (DIW)
1- milliliter solution I
1- milliliter solution II
1- milliliter solution III

Solution	Compound	g/L
I	NH_4Cl	35
	KNO_3	15
	$K_2HPO_4 \cdot 3H_2O$	75
	$NaH_2PO_4 \cdot H_2O$	25
II	KCl	10
	$MgSO_4$	20
	$FeSO_4 \cdot 7H_2O$	1
	(adjust pH to 3.0)	
III	$CaCl_2$	5
	$ZnCl_2$	0.05
	$MnCl_2 \cdot 4H_2O$	0.5
	$CuCl_2$	0.05
	$CoCl_2$	0.001
	H_3BO_3	0.001
	MoO_3	0.0004

*Federal Register (September 27, 1985), volume 50, number 188, page 39279.
Refrigerate the solutions.

Nutrient Supplement Preparation

The following addresses the nutrient feed concentration of phenol, nitrogen, and phosphorus added daily. The ratio of 10:5:1 (C:N:P) is the operating premise. Iron is added as an additional supplement for good floc growth.

The average phenol feed is assumed to be 100 mg/L (similar to pilot plant maintenance feed requirements). The feed rate of 16 L per day would offer a 4.0 turnover rate of the column (4 L volume), similar to the pilot plant and IWTP at Tinker AFB.

100 mg/L - Carbon, (100-mg/L)(16.0 L) = 1.60-g C/day

50 mg/L - Nitrogen, (50-mg/L)(16.0 L) = 0.80-g N/day

10 mg/L - Phosphorus, (10-mg/L)(16.0 L) = 0.16-g P/day

5 mg/L - Iron, (5-mg/L)(16.0 L) = 0.08-g Fe/day

For the source of carbon, phenol will be added at a rate of 1.60 g of phenol daily.

Ammonium chloride (NH_4Cl) is used as the source of nitrogen. The nitrogen in ammonium chloride represents approximately 26% of the formula weight; therefore, (0.8-g N/day)/(26% N/NH_4Cl) = 3.077-g NH_4Cl/day is required in the nutrient feed.

Potassium phosphate (KPO_4) is used as the source of phosphorus. The phosphorus in potassium phosphate represents approximately 13% of the formula weight; therefore, (0.16-g P/day)/(13% P/KPO_4) = 1.231-g KPO_4/day is required in the nutrient feed.

Ferric Chloride ($FeCl_3$) is used as the source of iron. The iron in ferric chloride represents approximately 34.5% of the formula weight; therefore, (0.08-g Fe/day)/(34.5% Fe/$FeCl_3$) = 0.232-g $FeCl_3$ is required in the nutrient feed.

Feed/Flow Rate Calculations

Based on a feed flow rate of .75 mL/min, the amount of materials needed to be in a liter of the biodegradation solution can be calculated by:

(0.75mL/min)(60min/hour)(24hours/day) = 1080mL/day, or 1.08 liters/day

Therefore, in making up the nutrient feed for the columns, the following compounds must be added in the amounts indicated.

$$\frac{(1.60\text{g Phenol/day})}{(1.08\text{L's/day})} = \underline{1.481\text{-g/L}}$$

$$\frac{(3.077\text{-g Ammonium Chloride/day})}{(1.08\text{L's/day})} = \underline{2.849\text{-g/L}}$$

$$\frac{(1.231\text{-g Potassium Phosphate/day})}{(1.08\text{L/day})} = \underline{1.140\text{-g/L}}$$

$$\frac{(0.232\text{-g Ferric Chloride/day})}{(1.08\text{L/day})} = \underline{0.215\text{-g/L}}$$

Volume Prepared (liter)	Phenol (grams)	Ammonium Chloride (grams)	Potassium Phosphate (grams)	Ferric Chloride (grams)
1	1.481	2.849	1.140	0.215
2	2.962	5.698	2.280	0.430
3	4.443	8.547	3.420	0.645

1) The ammonium chloride and potassium phosphate (monobasic) are added to the basic nutrient media.
2) The solution is sterilized, 121°C, 20 psi, 20 minutes.
3) The nutrient solution is cooled to room temperature.
4) Dissolve the phenol additive in 50 mL of nanopure water and filter sterilize the solution (Note: You may need to swirl the phenol back into solution in the filter cup before emptying the contents into the nutrient media.
5) Dissolve the ferric chloride in 50 mL of nanopure water and filter sterilize the solution (see the note under step #4).
6) The nutrient media is attached to the nutrient feed pump using the feed tubing (that has previously been autoclaved/sterilized).

(Note: Use good microtechniques to reduce possible contamination of nutrient feed and feed lines.)

Test Setup Procedures

The during the biodegradation test the basic EPA media will be used to dilute the solvent and culture material in the test columns.

All test columns will be filled to a total final volume of 250 mL.

The solvent test columns will be filled accordingly:

- -225 mL of basic EPA media.
- -0.417 mL of most concentrated manufacturer's recommended mix of solvent (based on a 1:600 dilution, which is a typical IWTP dilution ratio at Tinker AFB)
- -25mL of culture column microorganisms

The phenol test column will be filled as follows:

- -200mL of basic EPA media.
- -25mL of a 1000 mg/L phenol solution (0.1000 g of phenol added to a 100 mL volumetric flask and filled to the mark with nanopure water).
- -25 mL of culture column microorganisms

COD's will be run according to HACH, Chemical procedures:

Filtered: 2 mL samples will be filtered using a syringe-filter system equipped with a 0.45 micron pore-size filter.

Unfiltered: 2 mL samples, collected from one column at the first and fifth hours of testing, will be measured for total COD.

ATP will be run according to the internal standard method of Turner Instruments, Inc.

Dry weights will be collected on the culture column and initial samples at the beginning and end of the test runs. 25 mL of material will be placed in a preweighed drying pan. The pan will be placed in a drying oven (103^{0}C) till dryness. The pan will be reweighed and the difference between the initial and final pan weights divided by the volume placed in the drying pan will give solid dry weights per unit volume.

COD's will be compared to a control phenol column run simultaneously during each test period.

Also, COD's will be compared to each other based upon solid dry weights, ATP, and relative phenol degradations.

ATP Procedure

Set ATP Photometer: 3 second delay, 10 second integration period

Reading Unknown (RU)

1. 50 uL sample in 8 X 50 mM polypropylene tube
2. Add 50 uL Releasing Agent, mix, and let stand 30 seconds
3. Add 50 uL HEPES buffer
4. Place in photometer
5. Inject 100 uL Luciferin-Luciferase (L&L)
6. Record full integral

Reading Internal Standard (RIS)

1. 50 uL sample in 8 X 50 mM polypropylene tube
2. Add 50 uL Releasing Agent, mix, and let stand 30 seconds
3. Add 50uL ATP Standard, 2.5-E-2uG/mL ATP
4. Place in Photometer
5. Inject 100 uL Luciferin-Luciferase (L&L)
6. Record full integral

Reading the Blank (RB)

1. 50 uL distilled water in 8 X 50mM polypropylene tube
2. Add 50 uL Releasing Agent, mix, and let stand 30 seconds
3. Add 50 uL HEPES buffer
4. Place in Photometer
5. Injects 100 uL Luciferin-Luciferase (L&L)
6. Record full integral

Reagents

Releasing Agent - purchased, ready-to-go from Turner Designs, Inc.
HEPES buffer - purchased, ready-to-go from Turner Designs, Inc.
ATP Standard - purchased as a concentrated, sterile liquid from Turner Designs, Inc., see the following page for preparation details
Luciferin-Luciferase - purchased as a sterile, dry powder (5.5 mL preparation volume) from Turner Designs, Inc., see the following page for preparation details

KEEP ALL REAGENTS REFRIGERATED AND COOLED
ATP STANDARD SHOULD BE FROZEN BETWEEN TESTING PERIODS
DISCARD ANY THAWED L&L FOLLOWING THE TEST PERIOD

Basic Calculations

1. ATP in sample (grams/mL) = $\frac{(RU - RB)}{(RIS - RU)}$ X ATP in standard* (g/mL)

2. Solids in sample (g/mL) = $\frac{\text{pan dry weight (final-initial, grams)}}{\text{volume of sample (mL)}}$

3. ATP per gram solids gram/gram = $\frac{\text{ATP in sample}}{\text{Solids in sample}}$

---

* 2.5×10^{-8} grams ATP/mL (Standard concentration currently prepared)

ATP Standards Preparation

1. Fill Dewar with liquid nitrogen.
2. Calibrate 100 micro-liter pipet (Eppendorf) to deliver 25 uL, by weight using the microbalance, 0.2500 g/10 deliveries.
4. Use a 10 mL volumetric pipet to deliver 10 mL of sterile HEPES buffer into five clean plastic tubes.
5. Pipet 25 uL of ATP Standard (5 mL bottle, blue label, liquid, Turner Designs) into each 10 mL tube.
6. Vortex mix each tube following the addition of the ATP standard.
7. Pipet 2 mL of the diluted standard into blue, snap cap tubes.
8. Place the 2 mL ATP standards in the liquid nitrogen.
9. Continue steps 5 thru 8 until of the 5 test tubes of HEPES buffer have been used.
10. Remove the prepared standards from the liquid nitrogen and place them in a labelled beaker (indicating the date of preparation and the people who prepared them) and place the beaker in the freezer.

Luciferin-Luciferase Preparation

1. Remove 5 or 6 bottles of L&L (green labels, Turner Designs) from the refrigerator.
2. Using a 10 mL syringe (calibrated to 0.2 mL volume), add 5.5 mL of sterile HEPES buffer to 3 of the bottles of L&L.
3. Using a 1 mL pipet, transfer 1 mL of the L&L into a blue, snap-cap, conical plastic tube.
4. Close the cap and place the tube in liquid nitrogen.
5. After all of the bottles have been made up, remove the prepared L&L tubes from the liquid nitrogen and place them in a labelled beaker (indicating the date of preparation and the people who prepared them) and place the beaker in the freezer.

COD Standard Preparation

Do not add dry chemical or strong acid/base to a dry volumetric; therefore, add approximately 10mL's of nanopure water to 3-100 mL volumetric flasks.

Mark one of the three volumetric flasks as number "1". This is the initial solution flask. Mark the other two flasks as "A" and "B". These will be the two standards, actually measured.

Initial Solution

Weigh out 9.800 g of ferrous ammonium sulfate (FAS).
Add this to the volumetric flask.
Using a 2 mL volumetric pipet, transfer 2 mL of concentrated sulfuric acid to the volumetric flask.
Bring the volume in the volumetric flask to about 3/4 total volume.
Swirl the flask until all of the FAS crystals have dissolved.
Bring the flask volume to the mark with nanopure water and seal with parafilm.
Invert the volumetric at least 13 times, allowing the neck to fill and empty completely each time (rotate the flask slightly each inversion also).

Standard Solution A

Using the Solution 1, fill a 10 mL volumetric pipet to just above the mark.
Empty the pipet into a large volume waste beaker.
Draw a second volume of a solution to the mark and transfer this volume to the volumetric labelled "A".
Fill the volumetric to the mark with nanopure water, seal with parafilm, and invert at least thirteen times (same as making the initial solution).
Rinse a small, clean, plastic weigh boat with this solution.
Discard the rinse into the waste beaker.
Fill the weigh boat again with this solution and transfer 2 mL of this solution to two separate COD analysis tubes.
Vortex the tubes and place them in the COD incubator.

Standard Solution B

Using Solution 1, fill a 25 mL volumetric pipet to just above the mark.
Empty the pipet into a large volume waste beaker.
Draw a second volume of a solution to the mark and transfer this volume to the volumetric labelled "B".
Fill the volumetric to the mark with nanopure water, seal with parafilm, and invert at least 13 times (same as making the initial solution).
Rinse a small, clean, plastic weigh boat with this solution.
Discard the rinse into the waste beaker.
Fill the weigh boat again with this solution and transfer 2 mL of this solution to two separate COD analysis tubes.
Vortex the tubes and place them in the COD incubator.

NOTES:

When you are through with the solutions prepared for COD analysis:

a. Discard remaining solutions into the waste solution beaker.
b. Add an equal amount of water to dilute the acidic solution.
c. Neutralize and discard this solution (it is only an iron precipitate).
d. Wash the outside of the volumetric flasks with soap and hot water
e. Rinse the volumetric flasks (fill & dump) three times with tap water, three times with a 5% HNO_3 acid solution, three times with deionized water, and three times with nanopure water.
f. Invert the volumetric flasks on a drying rack and allow them to air dry.
g. Rinse the volumetric pipets (fill & dump) three times in the 5% HNO_3 solution, three times with deionized water, and place them on the drying rack.

Note: Check the volumetric pipets for completely wetted surfaces. If droplets form on the inside of the glass bulb repeat step "G".

ADAPTED ASTM 8-DAY TEST PROTOCOL

(The reverse of this page is blank.)

STANDARD ASTM TEST METHOD for
BIODEGRADABILITY OF ALKYLBENZENE SULFONATES
(Designation: D 2667-82)

Presumptive Test

In the presumptive test, microorganisms are inoculated into a flask that contains a chemically defined microbial growth medium (basal medium) and the surfactant to be tested. Aeration is accomplished by continuous shaking of the flask. Following two adaptive transfers, biodegradation is determined by measuring the reduction in surfactant content during the test period.

PROTOCOL

1. Addition of Surfactant to Basal Medium

Add 30 mg/L test material to the flasks containing basal medium. If surfactant stock solutions are used, stability during storage must be confirmed.

Use one flask for each surfactant being tested

One control flask for dodecene-1 derived LAS, additional controls if desired (see Note 1)

One blank flask containing all basal medium components but with no surfactant.

Note 1: A reference LAS sample that meets the standards of biodegradability of both the presumptive and confirming tests is available through the Environmental Protection Agency. This sample is a composite of several commercially available products, believed to be typical (from a biodegradability standpoint) of LAS surfactants in commercial use. It is suggested that a control test should be conducted using this material, whenever surfactant biodegradability determinations are undertaken.

As a control on the culture and test conditions used, the total run is invalid if the result with dodecene-1 derived linear alkyl sulfonate is less than 97.5% removal as measured by MBAS loss.

Failure to repeatedly attain prescribed minimum biodegradation values for the surfactant control (dodecene-1 LAS) indicates that conditions are unfavorable for normal microbial activity or that an analytical problem exists. Such problems should be investigated by an experienced microbiologist or an analytical chemist.

2. Inoculation

Inoculate the flasks with the microbial culture. Use the same culture for all flasks including control and blank. Use 1mL of inoculum for each 100 mL of basal medium in the flask.

3. Incubation

Place flasks containing basal medium, surfactant, and inoculum on a shaking machine that will produce acceptable aeration and mixing for biodegradation. Maintain the temperature of the flak contents at 25 ± 3°C.

4. Adaptation (acclimation)

Prior to beginning the biodegradation test, make two 72 hour acclimation transfers from previously inoculated flasks, following the procedures as outlined above and illustrated below.

5. Analysis

To follow the course of biodegradation, remove 25mL samples from the shake flasks for analysis. The samples are collected using sterile techniques to minimize contamination of the test solutions. Samples will be collected during the adaptation period and daily during the 8-day presumptive test. The samples will be divided as follows:

2 - 2 mL samples; COD analysis (1500 mg/L COD vials)
2 - 1 mL samples; TOC analysis (glass tube)
1 - 1 mL sample; ATP analysis (direct analysis of solution)
remaining material for GC or other analysis

Note: All TOC and GC samples must be preserved if not analyzed immediately. The recommended preservation is refrigeration and 100 uL of mercuric chloride per 10 mL of sample.

Samples must be taken during the 8 day test at zero time (immediately after inoculation and mixing of the flask contents) and on each day (at the same time of day) until the end of the 8 day test. Samples at zero time of the two adaptive transfers are desirable to ensure proper initial concentration. Unless analyses are run immediately the addition of 1mL of formaldehyde/100 mL of sample should be used for preservation for any sample. When preservative is used, add to all samples including blank.

Since the analytical result from the blank sample is used to correct the results from the other flasks, use the same sample size (or dilution factor) for the blank as is used for the other samples.

REAGENTS AND MATERIALS

Water

Either distilled or deionized water may be used in the test. It must be free of bacteriostatic material. Water derived from steam condensate in many cases will contain amines which are inhibitory to microbial growth.

Basal Medium

The composition of the basal medium is as follows:

NH_4Cl	3.0	g
K_2HPO_4	1.0	"
$MgSO_4 \cdot 7H_2O$	0.25	"
KCl	0.25	"
$FeSO_4 \cdot 7H_2O$	0.002	"
Yeast Extract	0.30	"
Water	1.0	liter

The basal medium may be prepared by dissolving the dry ingredients in the water, or by adding 10X stock solutions of the salts. The 10X stock solutions may be prepared in 500 mL volumetric flasks in the following manner:

Stock Solution I.

KCl	1.25	g
NH_4Cl	15.00	g
Nanopure Water	500	mL

Stock Solution II.

K_2HPO_4	5.00	g
Nanopure Water	500	mL

Stock Solution III.

$MgSO_4 \cdot 7H_2O$	1.25	g
$FeSO_4 \cdot 7H_2O$	0.01	g
Nanopure Water	500	mL

Note: The stock solutions are originally made up in 500 mL volumetric flasks and then transferred to 1 liter, brown bottles which are then refrigerated to reduce the chance of microbial growth. If cloudiness occurs in the stock solution bottles, these solutions should be properly disposed, the bottles cleaned, and new solutions prepared.

The yeast extract should be added in dry form immediately before use; or alternatively, solutions containing yeast extract must be sterilized and maintained sterile if held more that 8 hours before beginning the test. The basal medium shall be dispensed into one of the following standard Erlenmeyer flasks:

500 mL
1000 mL
1500 mL
1 L
2 L
4 L

Note 2: The 1-L and 2-L flasks are best suited for a gyratory shaker and the 4-L flask for a reciprocating shaker.

The flasks shall be stoppered with cotton plugs or the equivalent to reduce contamination and evaporation.

Microbial Culture

The microbial inoculum may be obtained from any of the following sources:

Natural sources (soil, water, sewage, activated sludge, etc.)
Laboratory cultures (activated sludge, river die-away, etc.)

If desired, the culture may be maintained as a shake flask culture by weekly transfers in the basal medium plus 30 mg/L dodecene-1 derived linear alkyl sulfonate. For each weekly transfer use 1mL of 7-day culture for each 100 mL of fresh medium.

PILOT-SCALE BIOLOGICAL ACCLIMATION PROTOCOL

(The reverse of this page is blank.)

Pilot-Scale Biological Acclimation Procedures

During the pilot test for biodegradable solvents the pilot plant was run in a manner similar to that of previous programs (Reference 2). There were a few exceptions in operation of the pilot. Metal bearing sludge from the industrial waste plant's (IWTP) solids contact clarifier (SCC) was not used to seed the pilot scale SCC due to instability of the sludge (i.e. floating due to biological activity and/or oil and grease content). A sludge depth greater than sixteen inches was achieved by adding hexavalent chromium (Cr^{6+}) to the industrial wastewater feeding the pilot plant. The Cr^{6+} was added in the form of sodium dichromate, at a concentration range of 5 - 8 mg/L Cr^{6+}. Actuators were installed on the SCC and final clarifier (FC) sludge return systems. The actuators allowed for automated control of solids. Sludge from the FC was wasted continuously in previous programs. With the adductor in place the wasting will be done intermittently. Previously SCC sludge was wasted by manually turning valves. An adductor in place decreased the chance for operator error.

The pilot plant was run at a flow rate of 3.5 gallons per minute (gpm) during the biodegradation testing. The effluent from the SCC was pumped from the SCC outlet to the activated sludge basin. In previous operations, the SCC effluent was gravity fed into the AS basin.

Flow rates throughout the plant were tested using graduated containers and stop watches. Flows were determined every sampling period for the AS system influent, nutrient feed, return activated sludge (RAS), and polymer feed. Nutrient feed was used during baseline testing when phenol concentrations coming through the plant were not high enough to maintain the biological system. The flow rate of the plant influent, at the E-tank, was checked at random times throughout the testing period to determine whether the flow was accurate.

In the biodegradable solvents testing period, parameters were measured to determine the solids inventory, nutrient ratios, total metals and biological activity.

Solids determinations were done to determine solids removal efficiency of the plant and to have an idea of the solids contained in the biological system. Samples that were tested to determine suspended solids were activated sludge (AS) influent, AS basin, RAS, and FC effluent. A 10 mL aliquot of each sample was dispensed into preweighed ceramic crucibles. The sample containing crucibles were placed in a drying oven set at 103°C. The samples were allowed to evaporate and dry for a period of at least six hours. After the samples were dry they were cooled in a desiccator and weighed. From the difference between the dry weight and the crucible the mixed liquor suspended solids in the AS system was determined. Solids contained in the RAS and waste activated sludge (WAS) were determined from the RAS sample and suspended solids in the influent and effluent were determined from the AS influent and FC effluent, respectively.

Volatile suspended solids were determined for the AS and the RAS by igniting the dried and weighed samples at 550°C in a muffle furnace. The value obtained gives an idea of the organic matter present in the activated sludge and return.

Samples from the AS were microscopically examined, as needed, to determine what microorganisms were present in the system. Microbial content of the AS is a good indicator of sludge health.

From the results of the above analyses other important parameters important in biological plant operation, such as, sludge age, sludge volume index (SVI) and mean cell residence time (MCRT) can be determined.

Nutrient profiles through the plant were followed using various waste water testing kits obtained from Hach chemical corporation. Chemicals being tested were ammonia-nitrogen (NH_4-N), nitrate-nitrogen (NO_3-N), phosphorus, chemical oxygen demand (COD) and phenol.

Methods found in the Hach manual of tests procedures were used to perform the following analyses. Concentrations of substances found in the samples were determined using a Hach DR/3000 spectrophotometer. Tests were done on samples from the E-tank, SCC, FC and the nutrient feed.

During the 3-D Supreme and Exxate 1000 solvent runs the E-tank, SCC and FC samples were not filtered because it was thought that both soluble and insoluble fractions of the waste stream were needed for the above analyses. After it had been determined that the soluble fraction was the parameter of interest, the samples for the Fremont 776 biodegradation run were filtered through a grade G4 Fisher brand glass fiber filter, with a pore retention of 1.2 μm, a common filter for water and wastewater analysis.

Samples tested for NH_4-N, NO_3-N and phosphorus were diluted 1/5 to stay within maximum sensitivity limits of the test methods used. NH_4-N was determine using the Nessler Method for ammonia from Hach. NO_3-N was determined by the cadmium reduction method from Hach. Phosphorus was determined by the amino acid method for orthophosphate.

Phenol concentrations were determined using the 4-aminoantipyrine method from Hach. E-tank, SCC and FC samples were diluted 1/300, the nutrient feed was diluted 1/30,000. Through testing it was found that pentene stabilized chloroform could not be used, because of a cloudy chloroform layer forming after the extraction took place.

The COD concentration of the samples was determined by the reactor digestion method from Hach. The colorimetric determination was used in this testing. Samples for analysis were not diluted, except for the nutrient feed which was diluted 1/100. High-range (0-1,500 mg/L) vials were used.

Methods used to follow the solvents tested through the pilot plant were two indirect methods, COD, total organic carbon (TOC) analysis and one direct method, gas chromatography (GC).

The COD method from above was used in determining if there was any increase in COD concentrations, above values obtained in the baseline testing.

TOC samples were prepared by adding 100 microliters of 2500 ppm $HgCl_2$ to 10 mL of sample. Samples from the E-tank, SCC and FC were refrigerated until being run on a TOC analyzer from OIC Model 524 direct injection module (DIM) with a model 3300 infrared gas analyzer. This analyzer used the combustion-infrared method for carbon determination. The sample was injected into a heated reaction chamber packed with the oxidative catalyst copper sulfate. Sample sizes of 50 µL were injected into the analyzer. Two standards were used in the TOC determination a 1000 mg/L carbon standard and a 100 mg/L carbon standard. The 1000 mg/L standard was prepared by adding 1.068 g of potassium biphthalate to 500 mL of distilled water. The 100 mg/L standard was made by diluting the 1000 mg/L standard 1/10. The standards were also injected into the DIM unit in 50 µL aliquots. The concentration of the samples was then determined using linear regression, comparing sample readings to the standard curve.

GC samples were prepared in the same manner as the TOC samples, and stored in the refrigerator until run through the GC instrument. The samples were run on a Perkin-Elmer Sigma 2000/2100 series gas chromatographer, equipped with an on-column injection port and a flame ionization detector (FID). Data was collected on a Perkin-Elmer LCI-100 Laboratory Computing Integrator.

Each solvent required a different run program. The column used for all of the testing was a Supelco 30 m SPB-5 0.5 µm ID fused silica capillary column. For 3-D Supreme the injector temperature was held at 280°C and the FID was at 300°C. The temperature program started at 65°C and was held there for 3 minutes. After 3 minutes the oven temperature was ramped to 120°C at a rate of 10°C per minute. At 120°C the oven temperature was ramped at 30°C per minute to 300°C, the data stopped at 8 minutes and the temperature program was recycled. Helium was the carrier gas and was set at a flow rate of 25, as measured by an internal instrumental flow gauge. The column head pressure was 20 psi. The integrator was set at an attenuation of 8. Fremont 776 was run in the manner described above but the run time was 12.8 minutes.

The Exxate 1000 was run as described above except with the following changes to the temperature program. The oven temperature was started at 80°C and was held for 4 minutes. After 4 minutes the temperature was ramped to 150°C at 7.5°C per minute, then recycled. The program was run for 12 minutes.

GC samples were prepared by adding 2 mL of sample to a 3 mL sample container. The solvent was extracted from the sample by adding 1 mL of methylene chloride to the sample. The sample was then mixed vigorously and the layers were allowed to separate. 0.2 L of the methylene chloride layer was injected into the instrument.

Biological activity throughout the activated sludge system was monitored using adenosine triphosphate (ATP) determinations. The activated sludge samples were diluted 1/10 for use in the ATP testing. A blank was run with each sample to determine baseline illumination in each sample from the reagents used. For each blank and sample there were two readings, one with an internal standard and one without internal standard. The internal standard contained 2.5×10^{-8} mg/L ATP. In each blank there was 50 µL of distilled water, 50 µL of ATP Releasing Agent (Turner Designs), and 50 µL of Hepes buffer (Turner Designs), for samples without internal standard , or 50 µL of ATP standard for samples with internal standard. The prepared sample was placed in a Turner Designs Model TD-20e luminometer, where it was incubated at room temperature for approximately 15 seconds. After the incubation period 100 µL of Luciferin/Luciferase (L and L) was injected. A full scale reading was taken and logged. Each sample contained 50 µL of diluted activated sludge, 50 µL of ATP Releasing Agent, and 50 µL of Hepes buffer or ATP standard, depending on whether the sample was the internal standard or not. The sample was incubated, the L and L injected and the interval read.

Solvents being tested in the biodegradable solvents program have been shown to cause the flotation of the metal bearing sludge in the SCC. Prior to being tested in the pilot plant each solvent was run through a series of jar tests to determine the effect of ferric chloride ($FeCl_3$) on sludge flotation. Six 1-liter beakers were filled with industrial wastewater. The beakers were mixed with a Phipps and Bird multiple stirrer apparatus. To each beaker solvent was added at a 1/600 dilution of the concentration used for cleaning. Exxate 1000 and Orange-Sol were not soluble in water. The solutions were mixed into an emulsion by mixing in a blender for 30 to 60 seconds. During each jar test period chromium was added to each jar in amounts that would give a final concentration of Cr^{6+} that would be the same as that found in the pilot plant. To each beaker enough sodium sulfide was added to give the stoichiometric amount of 2 mg/L S^{2-} per 1 mg/L Cr^{6+}. The solutions were then mixed at 70 rpm for 5 minutes. Next, enough ferrous sulfate was added to each beaker to give the stoichiometric equilibrium of 1.5 mg/L Fe^{2+} per 1 mg/L Cr^{6+} and the solutions were mixed for 5 minutes at 70 rpm. At this point 20 mg/L of cationic polymer Betz 1195 and $FeCl_3$ concentrations of 0 - 150 mg/L (for the water soluble solvents, 3-D Supreme and Fremont 776) was added to the beakers. Beaker 1 had no $FeCl_3$ added, this would be the control. The second beaker contained 25 mg/L $FeCl_3$. To the rest of the beakers up to beaker five, $FeCl_3$ was added in increasing increments of 25 mg/L $FeCl_3$. Between beakers 5 and 6 there is an increase of 50 mg/L $FeCl_3$ giving a final concentration of 150 mg/L. For non water soluble solvents (Exxate 1000 and Orange-Sol) a concentration range of 100 to 500 mg/L $FeCl_3$ was used. After polymer and $FeCl_3$ additions the solutions were mixed for five minutes with a reduced stirring rate of 45 rpm. After the five minutes 0.5 mg/L of anionic polymer Betz 1120 was added to each beaker and mixed for 2 minutes at 45 rpm. The mixing paddles were then removed from the beakers and the sludge formed was allowed to settle for 30 minutes. The sludge settling characteristics and pH of the final solutions were then noted and logged.

Filtered samples from the E-tank, SCC and FC samples were analyzed for total chromium (Cr), iron (Fe) and zinc (Zn). Samples were stored at 4°C with 1.0% nitric acid if not analyzed immediately. The samples were run on a Zeeman spectrAA model 400 atomic absorption (AA) spectrophotometer. All elements were run with an air/acetylene gas mixture. Cr was run with an oxidizing flame. The rest of the metals (Fe and Zn) were run with a reducing flame. The samples were aspirated into the mixing chamber manually. Metal concentrations of the samples were determined by comparison to standard curves. All of the AA grade standards were obtained from Fisher Scientific.

APPENDIX F

PHASE II CORROSION DATA

The ASTM method F 483-77 was followed for precleaning and postcleaning of the test coupons. After cleaning and weighing, three coupons of the same metal were hung from a nylon lid and immersed in a beaker of the solvent to be tested. For the mixing tests, a nylon-coated stir bar was placed in a constant temperature bath. For ultrasonic tests, the beakers of each metal and the solvent were placed in an ultrasound full of water at a constant temperature and wattage. Conditions for each test are listed with the corresponding data. The descriptions were obtained with a microscope and the naked eye.

Corrosion tests were run for Fremont 776 and a low-foam version of 3D Supreme during full-scale testing. These data are also included.

(The reverse of this page is blank.)

3D SUPREME RUN 9-5-89 02:30 through 9-12-89 04:00
Conditions: 1:3 diln, ultrasound at 300 W, 77 F, 169.5 hrs.

COUPON	CORROSION RATE	DESCRIPTION
AL1100 #34	78.7	Lt. gray discoloration, heavy corrosion, .08-.14mm deep.
AL1100 #35	61.8	Heavy corrosion, .04-.16mm deep, ave. depth .04mm, lt. gray discol.
AL1100 #87	54.4	Heavy corrosion, .04-.16mm deep, ave depth .04mm, lt. gray discol.
N200 #30	0.71	Heavy oxidation, beginnings of pits but with no depth.
N200 #64	0.47	Heavy oxidation, approx. 26 pits. .060-.080 mm deep.
N200 #84	0.85	Heavy oxidation, approx. 30 pits ave. depth .040 mm.
SS410 #4	0.4	Approx. 12 pits, .08 mm deep, localized with black discol., lt. oxidation.
SS410 #5	0.37	No pits, lt. oxidation.
SS410 #6	0.56	No pits, lt. oxidation.
C1020 #95	0.55	Lt. oxidation, 10 pits, .08mm deep. pits localized with black discol.
C1020 #96	0.63	15 pits, .16 mm deep, pits are localized with black discoloration.
C1020 #97	0.56	Lt. oxidation, 13 pits, .12mm deep. pits localized with black discol.
CDA110 #107	0.15	Orange discol., too many pits to count, .04-.12mm, ave. .08mm deep.
CDA110 #108	0.2	Orange discol., too many pits to count, .08-.16mm, ave depth .08mm.
CDA110 #109	0.35	Orange discol., too many pits to count, .04-.14mm, ave depth .08mm.
IX750 #25	0.14	No pits, lt. oxidation, orange discol.
IX750 #26	0.13	No pits, lt. oxidation.
IX750 #27	0	No pits.

C4340 #40	0.48	Hole rusted, 12 pits, .08mm deep. pits localized with black discol.
C4340 #41	0.41	Lt. oxidation, 8 pits, .12mm deep. pits localized with black discol.
C4340 #42	0.29	Lt. oxidation, 36 pits, .08mm deep. pits localized with black discol.
AL7075 #14	1.34	Lt. oxi., beginnings of pits w/o depth. 36 pits, .04-.12mm, localized.
AL7075 #79	1.47	Beginnings of pits with no depth.
AL7075 #80	0.72	Lt. oxidation, beginnings of pits with no depth.
TI-2 #1	0.77	No pits, heavy oxi., orange discol.
TI-2 #17	0.69	No pits, heavy oxi., orange discol.
TI-2 #18	0.8	No pits, heavy oxidation.
MAG #58	584	Coupon is oblong due to severe corrosion, remaining surface severely pitted, .08-.16mm, ave depth .10mm.
MAG #59	727	Half of coupon gone due to severe corrosion, remaining surface severely pitted, .10-.26mm, ave depth .14mm.
MAG #60	412	Rounded corners due to severe corrosion, surface severely pitted, .04-.14mm, ave .08mm, white discol.
AL2024 #102	0.94	No pits, heavy oxidation.
AL2024 #103	0.31	No pits, lt. oxidation.
AL2024 #104	0.52	No pits, heavy oxidation.
WASP #67	-0.03	No pits, orange discoloration.
WASP #68	0.04	No pits.
WASP #97	0.08	No pits.
S310 #4	0.14	Scattered corrosion at a uniform depth of .001 mm. Rust spots.
S310 #40	0.12	Scattered corrosion at a uniform depth of .001mm. Approx. 254 pits, at .002 mm deep. Lt. oxidation
S310 #84	0.15	Scattered corrosion at a uniform depth of .001mm. Lt. oxidation.
MK500 #72	0.28	Orange discoloration, approx. 8 pits .12 mm deep, localized with black discol.
MK500 #73	0.22	Approx. 24 pits, .10 mm deep, localized with black discoloration.
MK500 #74	0.28	Approx. 15 pits, .080mm deep, localized with black discoloration.
CDA443 #74	0.29	Uniform corrosion at .10mm deep, black discoloration, lt. oxi.
CDA443 #75	0.24	Uniform corrosion at .14mm deep, black discoloration, heavy oxi.
CDA443 #77	0.23	Uniform corrosion at .12mm deep, black & orange discoloration.

	A	B	C
1			CHEMICAL LABORATORY SERVICES
2	AMBER		1321 E. SOUTH TEMPLE #4
3	SCHULZ		SALT LAKE CITY, UT 84102
4			(801) 364-9303
5			
6	3D SUPREME 8120 LF	RUN:	18-APR-90 16:30 through 26-APR-90 15:00
7	CONDITIONS:	190.5 hrs.,	diluted 1:3 with water, 140 F.
8			
9		CORROSION	
10	COUPON	RATE	DESCRIPTION
11		(- is gain)	
12	AL1100 #11	-0.24	No pits, patchy brown and blue discoloration.
13	AL1100 #12	-0.17	No pits, patchy brown discoloration.
14			
15	SS310 #46	-0.04	No pits.
16	SS310 #47	0.02	No pits.
17			
18	C1020 #103	0.06	No pits, light oxidation.
19	C1020 #104	0.02	No pits, light oxidation.
20			
21	IX750 #9	-0.12	No pits, patchy white film.
22	IX750 #10	-0.02	No pits, patchy white film.
23			
24	C4340 #19	0.01	No pits.
25	C4340 #20	0.00	No pits.
26			
27	TI-2 #37	-0.01	No pits, patchy brown discoloration.
28	TI-2 #38	-0.08	No pits, patchy brown discoloration.
29			
30	AL7075 #99	-0.07	No pits.
31	AL7075 #100	-0.05	No pits.
32			
33	CDA443 #91	1.16	Shiny, uniform corrosion of surface, .030mm deep,
34			heavy black discoloration over coupon.
35	CDA443 #92	1.23	Shiny, uniform corrosion over surface, .035mm deep
36			heavy black discoloration over coupon.
37			
38	SS410 #11	0.00	No pits.
39	SS410 #12	0.03	No pits.
40			
41	MK500 #52	0.15	No pits.
42	MK500 #53	-0.04	No pits.
43			
44	CDA110 #36	1.55	Dull, uniform corrosion over surface, .010mm deep,
45			brown and orange discoloration over coupon.
46	CDA110 #37	1.74	Dull, uniform corrosion over surface, .012mm deep,
47			red, orange, yellow, & pink discoloration over coupon.

	A	B	C
48			
49	MAG #71	2.29	Severe corrosion in middle of bottom edge only, area
50			7 by 3mm, white powder in area, brown discoloration
51	MAG #72	0.96	Severe corrosion left side of bottom edge only, area
52			11by 2mm, white powder in area, brown discoloratio
53			
54	AL2024 #31	-0.09	No pits.
55	AL2024 #32	-0.16	No pits.
56			
57	N200 #60	-0.03	No pits.
58	N200 #109	0.04	No pits.
59			
60	WASP #86	0.00	No pits.
61	WASP #87	-0.01	No pits.
62			
63			
64			

BIOTEK SAFETY SOLV RUN 8-23-89 18:00 through 8-31-89 23:00
Conditions: concentrated, ultrasound at 300 W, 120 F, 197 hrs.

COUPON	CORROSION RATE a minus sign is a wt. gain	DESCRIPTION
CDA110 #19	0.79	Approx. 36 pits, .002-.012 mm deep. Heavy oxidation.
CDA110 #41	0.86	Lt. oxidation, blue discoloration Beginnings of pits with no depth.
CDA110 #83	0.73	Lt. oxidation, blue discoloration. No pits.
AL1100 #4	0.11	Uniform corrosion, .004 mm deep. Lt. oxidation.
AL1100 #5	0.07	Uniform corrosion, first layer .004 mm deep second layer .006 mm deep.
AL1100 #6	0.16	Uniform corrosion, .004 mm deep. Lt. oxidation.
C1020 #7	-0.02	Widespread uniform corrosion, .002mm deep Lt. oxidation.
C1020 #8	-0.04	Uniform corrosion, .002mm deep. Lt. oxidation.
C1020 #9	0.05	Uniform corrosion, .001mm deep. Lt. oxidation.
C4340 #43	0.05	No pits, blue & brown discol. Lt. oxidation.
C4340 #44	-0.02	No pits, brown discoloration.
C4340 #45	0	No pits, lt. oxidation, brown, pink, & blue discoloration.
CDA443 #78	0.16	No pits, orange & blue discol.
CDA443 #79	0.09	No pits, orange discoloration.
CDA443 #80	0.09	No pits, blue & orange discoloration.
TI-2 #78	0.04	No pits. Lt. oxidation.
TI-2 #79	0	No pits. Lt. oxidation.
TI-2 #80	0.03	No pits. Lt. oxidation.
IX750 #77	-0.007	Lt. oxidation-upper edge, No pits.
IX750 #78	0.007	No pits.
IX750 #79	0.02	No pits. Blue & orange discoloration.
WASP #81	-0.03	No pits.
WASP #82	0.03	No pits.
WASP #83	0.02	No pits.

MK500 #69	0.05	Lt. oxidation, brown discoloration. No pits.
MK500 #70	0.05	Lt. oxidation, brown discol., No pits.
MK500 #71	-0.007	Lt. oxidation, brown discol. no pits.
AL2024 #105	-0.02	No pits. Lt. oxidation.
AL2024 #106	0.02	No pits.
AL2024 #107	0.07	No pits.
AL7075 #57	0.07	Lt. oxidation. Approx. 12 pits, .004-.008 mm deep.
AL7075 #58	0	No pits. Lt. oxidation.
AL7075 #59	0.07	No pits. Lt. oxidation.
S310 #13	-0.03	Lt. oxidation. Approx. 56 pits .002-.004 mm deep, near top.
S310 #14	-0.06	Lt. oxidation. Approx. 45 pits, .002mm deep, near top edge.
S310 #15	0	Lt. oxidation. No pits.
MAG #51	0.43	Blue & gray circles of discoloration. Beginnings of pits with no depth. Orange discoloration.
MAG #52	0.29	Heavy oxidation, gray & brown discol. beginnings of pits with no depth.
MAG #53	0.46	Heavy oxidation, gray & brown discol. Beginnings of pits with no depth.
SS410 #1	0.02	No pits.
SS410 #2	0.008	No pits.
SS410 #3	0.05	No pits, brown discoloration.
N200 #85	0.17	No pits.
N200 #86	0.06	No pits.
N200 #87	0.13	No pits.

CALLA RUN 10-2-89 04:30 through 10-11-89 03:00
Conditions: 1:1 diln., ultrasound at 300 W, 120 F, 214.5 hrs.

COUPON	CORROSION RATE a minus sign is a wt. gain	DESCRIPTION
C1020 #71	0.03	No pits, lt. oxi., brown & blue spots.
C1020 #72	0.01	Lt. oxi., 16 pits .084 mm deep, blue and brown spots.
C1020 #73	0	No pits, orange and brown spots.
MK500 #63	0.03	No pits.
MK500 #64	-0.02	No pits.
MK500 #65	0.007	No pits.
IX750 #21	0.06	No pits, blue discoloration.
IX750 #41	-0.04	No pits.
IX750 #54	0	No pits.
AL2024 #82	0.02	No pits.
AL2024 #83	-0.08	No pits.
AL2024 #84	-0.02	No pits.
N200 #57	0.04	No pits.
N200 #58	0.05	No pits.
N200 #59	0.03	No pits.
TI-2 #21	0.05	No pits, lt. oxidation.
TI-2 #46	0.04	No pits, light oxidation.
TI-2 #47	0.08	No pits, light oxidation.
C4340 #30	0.01	No pits, brown & blue spots, lt. oxidation.
C4340 #37	0	No pits, brown discoloration.
C4340 #38	0.02	No pits, brown discol., lt. oxi.
SS410 #13	0.01	No pits, light oxidation.
SS410 #46	0.01	No pits.
SS410 #47	-0.01	No pits.

AL1100 #58	2.89	257 pits, .08-.12mm, ave depth .10mm.
AL1100 #59	2.24	196 pits, .04-.12mm, ave depth .08mm.
AL1100 #60	0.42	231 pits, .02-.08mm, ave depth .06mm.
AL7075 #101	-0.06	No pits.
AL7075 #102	-0.02	No pits, lt. oxidation.
AL7075 #103	-0.02	No pits.
WASP #61	-0.05	No pits, brown & blue discoloration. light oxidation.
WASP #62	-0.09	No pits, pink,blue & green, discol.
WASP #63	-0.07	No pits, brown discoloration.
S310 #19	-0.03	No pits, brown & blue discoloration.\
S310 #20	-0.03	No pits, brown discol., lt. oxi.
S310 #21	-0.02	No pits, lt. oxidation.
MAG #38	39	Too many pits to count, .08-.22mm, ave depth .10mm, gray discoloration.
MAG #39	40.8	Too many pits to count, .08-.48mm, ave depth .14mm, gray discoloration.
MAG #40	102.1	Too many pits to count, bottom fifth of coupon corroded away, .10-.50mm, ave depth .12mm, gray discoloration.
CDA110 #76	0.94	Heavy oxi., 37 pits, .08-.20mm, ave depth .15mm orange discoloration.
CDA110 #77	0.95	Heavy oxi., 42 pits, .01-.08mm, ave .04mm, green & orange discol.
CDA110 #78	0.83	Heavy oxi., 29 pits, .025-.08mm, ave .04mm, brown & orange discol.
CDA443 #68	0.09	No pits, top 1/4 discol. pink & blue
CDA443 #69	0.06	No pits, pink, blue & green discol.
CDA443 #70	0.04	No pits, pink, blue & green discol.

EXTENDED CORROSION TESTING   JULY-OCTOBER 1989

EXXATE 1000   RUN 7-11-89 16:15 through 7-18-89 16:15
Conditions: concentrated, 120 F, mixed with stir bar, 168 hours
A minus sign shows a wt. gain

COUPON	CORROSION RATE	DESCRIPTION
C1020 #28	0	7 main areas of corrosion .04mm deep also 9 pits .032mm deep, oxidation.
C1020 #29	0.009	15 pits .034mm deep, lt. oxidation.
C1020 #30	0.68	12 pits .022mm deep, lt. oxidation.
C4340 #48	0.08	No pits, lt. oxidation.
C4340 #49	0.04	14 pits .004mm deep, lt. etching.
C4340 #50	0.009	No pits, lt. oxidation.
SS410 #48	0.04	No pits, lt. oxidation.
SS410 #49	0.15	No pits, rusted near circle.
SS410 #50	0.03	No pits, lt. oxidation.
S310 #10	-0.03	9 pits .06mm deep.
S310 #11	0.009	No pits.
S310 #12	0	No pits, black oxidation.

EXXATE 1000 conc., 120 F, mixed with stir bar, 185 hours
RUN 7-18-89 16:30 through 7-26-89 10:45

CDA110 #67	0.03	No pits, blue discoloration.
CDA110 #90	-0.01	No pits, blue & orange discol.
CDA110 #94	0.02	No pits, blue & orange discol.
CDA443 #114	0.008	No pits, lt. oxidation.
CDA443 #115	0	No pits, lt. oxidation & etching.
CDA443 #116	-0.03	No pits, lt. oxidation.
N200 #12	0.11	No pits, lt. oxidation.
N200 #19	0.03	No pits.
N200 #20	0.01	No pits.
AL1100 #10	0.07	Widespread corrosion .04mm deep.
AL1100 #19	0.07	Widespread corrosion .052-.06mm deep.
AL1100 #20	0.1	Widespread corrosion .02-.048mm deep

EXXATE 1000 conc., 120 F, mixed with stir bar, 168 hours
RUN 7-19-89 10:45 through 7-26-89 10:45

MAG #75	-0.67	Heavy, widespread oxidation.
MAG #76	-1.01	Widespread oxidation, no pits.
MAG #77	-0.46	Heavy coat of oxidation, no pits.
WASP #104	0.03	No pits.
WASP #105	0.03	No pits.
WASP #106	0.009	No pits.

EXXATE 1000 conc., 120 F, mixed with stir bar, 188.33 hours
RUN 8-7-89 11:20 through 8-15-89 08:40
A MINUS SIGN IS A WT. GAIN

AL2024 #108	-0.02	No pits.
AL2024 #109	-0.05	No pits.
AL2024 #110	-0.07	No pits.
IX750 #28	-0.02	No pits.
IX750 #29	0.02	No pits.
IX750 #30	-0.02	No pits.
TI-2 #71	-0.04	No pits.
TI-2 #72	0.01	77 pits .002mm, front-center.
TI-2 #73	0.04	No pits, lt. oxidation.
AL7075 #54	-0.02	No pits, area of orange discol.
AL7075 #55	-0.05	No pits, lt. oxidation.
AL7075 #56	-0.05	No pits.
MK500 #66	0	No pits, areas of orange oxidation.
MK500 #67	0.03	No pits, lt. oxidation.
MK500 #68	0.04	No pits, lt. oxidation.

EXXATE 1000 RUN 8-16-89 09:35 through 8-23-89 1500
Conditions: concentrated, ultrasound at 600 W, 140 F, 173.5 hrs.

COUPON	CORROSION RATE a minus sign is a wt. gain	DESCRIPTION
C1020 #1	0.11	Uniform corrosion all over with no depth. Beginnings of pits with no depth. Lt. oxidation. Orange discoloration.
C1020 #2	-0.04	No pits. Uniform corrosion, no depth.
C1020 #3	-0.18	Uniform corrosion, .004 mm deep. No pits. Rust spots scattered.
AL1100 #7	0.08	Uniform corrosion .012-.016 mm deep. Lt. oxidation.
AL1100 #8	0.16	Uniform corrosion .018-.040 mm deep. Lt. oxidation.
AL1100 #9	0.23	Uniform corrosion .020-.042 mm deep. Lt. oxidation.

SS410 #7	0.2	No pits. Lt. oxidation.
SS410 #8	-0.25	No pits.
SS410 #9	-0.28	No pits. Lt. oxidation.
MAG #73	0.28	Heavy oxidation, black & brown discol. Beginnings of pits with no depth.
MAG #74	0.2	No pits. Heavy oxidation, black & orange discoloration.
MAG #100	0.57	Heavy oxidation. Orange & brown discol. Beginnings of pits with no depth.
N200 #1	0.06	Widespread corrosion .01mm deep.
N200 #2	0.19	No pits, blue discoloration.
N200 #3	0.17	Widespread corrosion .008mm deep.
C4340 #39	0.02	Lt. oxidation. Orange discoloration. Beginnings of pits with no depth.
C4340 #46	0.13	Lt. oxidation. Orange discoloration. Beginnings of pits with no depth.
C4340 #47	0.03	No pits. Lt. oxidation. Orange discol.
CDA443 #71	0.09	No pits.
CDA443 #72	0.07	No pits, lt. oxidation.
CDA443 #117	0.06	No pits, brown discoloration.
WASP #107	0.05	No pits.
WASP #108	0.03	No pits.
WASP #109	0.02	No pits.
S310 #16	0	Uniform corrosion but with no depth.
S310 #17	0.01	Corrosion front-center no depth.
S310 #18	0.01	Corrosion front-bottom no depth.

EXXATE 1000 RUN 9-15-89 02:00 through 9-23-89 02:00
concentrated, ultrasound at 600 W, 140 F, 192 hrs.

COUPON	CORROSION RATE a minus sign is a wt. gain	DESCRIPTION
AL7075 #76	0.14	No pits.
AL7075 #77	0.05	No pits.
AL7075 #78	0.07	No pits.
TI-2 #19	0.11	No pits. Scattered rust spots but no depth, in center. Lt. oxidation.
TI-2 #20	0.16	No pits. Lt. oxidation.
TI-2 #77	0.06	No pits. Lt. oxidation.
MK500 #113	0.06	No pits. Lt. oxidation.
MK500 #114	0.05	No pits.
MK500 #115	0.05	Three pits, ave. depth .004 mm.
CDA110 #71	0.56	Purple, red, blue discoloration. Approx. 475 pits, .002-.006 mm deep.
CDA110 #72	0.5	Purple and red discoloration. Heavy oxidation. 360 pits, ave. .002 mm deep
CDA110 #73	0.46	Purple, red, blue discoloration. Heavy oxidation. Beginnings of pits all over but no depth obvious.
AL2024 #17	0.07	Lt. oxidation, no pits.
AL2024 #56	0.09	No pits. Lt. oxidation.
AL2024 #101	0.07	No pits. Lt. oxidation. Blue discoloration.
IX750 #22	0.01	No pits.
IX750 #23	0.03	No pits.
IX750 #24	0.01	No pits.

Fremont 776 DOD Solvents

RUN 8/7/90 16:15 THROUGH 8/14/90 16:15
Conditions: 140 F, 168 hrs, concentration of 6 oz per gallon.

Metal	Corrosion Rate	Description
AL2024 #47	0.11	No pits.
AL2024 #48	0.05	No pits.
AL2024 #49	0.08	No pits.
SS310 #3	0	No pits.
SS310 #6	0	No pits.
SS310 #50	0	No pits.
C1020 #107	0.04	Slight orange discoloration, no pits
C1020 #108	0.02	Slight orange discoloration, no pits
C1020 #109	0.02	Slight orange discoloration, no pits
C4340 #16	0.03	No pits.
C4340 #31	0	No pits.
C4340 #32	0.01	No pits.
N200 #6	0.01	Slight brown discoloration, no pits.
N200 #8	0.03	Slight brown discoloration, no pits.
N200 #9	0	Slight brown discoloration, no pits.
CDA110 #23	0	Brown discol., white powder, no pits
CDA110 #24	0	Brown discol., white powder, no pits
CDA110 #25	0	Brown discol., white powder, no pits
TI2 #51	0.06	Slight brown discoloration, no pits.
TI2 #69	0.06	Slight brown discoloration, no pits.
TI2 #70	0.03	No pits.
CDA443 #59	0.31	Uniform corrosion .10mm deep, heavy black oxidation over entire coupon.
CDA443 #67	0.4	Uniform corrosion .12mm deep, heavy black oxidation over entire coupon.
SS410 #43	0	No pits.
SS410 #44	0	No pits.
SS410 #45	0	No pits.
AL1100 #5	0	No pits.
AL1100 #6	0.03	No pits.

AL1100 #7	0.05	No pits.
MAG #63	0	Heavy, brown scale over all, no pits
MAG #64	0	Heavy, brown scale over all, no pits
MAG #65	0	Heavy, brown scale over all, no pits
MK500 #56	0	No pits.
MK500 #57	0.01	Slight brown discoloration, no pits.
MK500 #58	0.02	Slight brown discoloration, no pits.
AL7075 #44	0.13	Slight brown discoloration, no pits.
AL7075 #45	0.1	No pits.
AL7075 #46	0.13	No pits.
IX750 #18	0	No pits.
IX750 #19	0	No pits.
IX750 #20	0.01	No pits.
WASP #72	0.01	No pits.
WASP #77	0.01	No pits.
WASP #78	0.01	No pits.

DESOLVIT ORANGE-SOL RUN 9-25-89 02:00 through 10-2-89 02:00
Conditions: concentrated, ultrasound at 600 W, 140 F, 168 hrs.

COUPON	CORROSION RATE a minus sign is a wt. gain	DESCRIPTION
CDA443 #73	0.04	No pits, blue & pink discol.
CDA443 #76	0.03	No pits, blue, pink, yellow, green & purple discoloration.
CDA443 #90	0.05	No pits, blue, pink, yellow, green & purple discoloration.
SS410 #16	0.06	No pits.
SS410 #17	0.06	No pits.
SS410 #18	-0.01	No pits.
AL1100 #36	0.4	Beginnings of pits with no depth, heavy oxidation.
AL1100 #37	0.32	Beginnings of pits with no depth, heavy oxidation.
AL1100 #38	0.27	Beginnings of pits with no depth, heavy oxidation.
WASP #89	-0.02	No pits, lt. oxidation.
WASP #90	0	No pits, lt. oxidation.
WASP #110	0	No pits, lt. oxidation.
AL7075 #60	0.05	No pits, lt. oxidation.
AL7075 #74	0.05	No pits, lt. oxidation.
AL7075 #75	0.03	No pits, lt. oxidation.
MAG #55	2.18	Gray coating, pink & yellow discol.
MAG #56	1.51	Gray coating, pink & blue discol.
MAG #57	2.35	Gray coating, pink & blue discol.

AL2024 #18	-0.37	No pits, Lt. oxi., yellow discol.
AL2024 #19	0.05	No pits, lt. oxidation.
AL2024 #20	0.18	No pits, lt. oxidation.
IX750 #66	-0.02	No pits.
IX750 #67	-0.03	No pits.
IX750 #80	-0.02	No pits.
C4340 #34	4.93	No pits, heavy oxi., dull surface. orange discoloration.
C4340 #35	4.37	No pits, heavy oxi., dull surface brown discoloration.
C4340 #36	4.42	No pits, heavy oxi., dull surface, brown discoloration.
CDA110 #79	0.53	No pits, pink, blue & green discol.
CDA110 #80	0.38	No pits, lt. oxi., orange discol.
CDA110 #110	0.32	No pits, lt. oxidation.
N200 #50	0.58	No pits, heavy oxidation, orange discoloration.
N200 #99	0.32	No pits, heavy oxidation, blue & orange discoloration.
N200 #100	0.8	Beginnings of pits with no depth, heavy oxidation.
S310 #1	-0.08	No pits, yellow coating, lt. oxi.
S310 #2	-0.04	No pits, yellow coating along top.
S310 #3	-0.09	No pits, lt. oxidation.
MK500 #35	0.51	No pits, brown & blue discoloration.
MK500 #85	0.08	No pits, brown & blue & pink discol.
MK500 #112	0	No pits, lt. etching, brown, blue, pink, purple & green discoloration.
C1020 #91	3.15	No pits, heavy oxidation.
C1020 #92	3.39	No pits, heavy oxidation.
C1020 #93	2.68	No pits, heavy oxidation.
TI-2 #74	0.03	No pits, lt. oxidation.
TI-2 #75	0.05	No pits, lt. oxidation.
TI-2 #76	0	No pits, lt. oxidation.