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Used Solvent Testing and Reclamation, Volume I: Cold-Cleaning Solvents

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Large amounts of waste solvent are generated each year at many Department of Defense (DOD) installations. Standard practice at these sites has been to discard spent solvents. However, increasingly stringent environmental regulations, coupled with the soaring cost of waste disposal and new solvent purchase, have led DOD to seek safe, cost-effective methods of managing waste solvent.

Some DOD installations are reclaiming used solvents rather than discarding them. Reclamation is feasible because the solvents usually do not break down chemically during the cleaning operations for which they are used. However, this type of recycling has seen limited success in the past due to the lack of scientific tests and criteria for judging a solvent as spent.

This study has evaluated tests for assessing the quality of used Stoddard solvent (a class primarily employed in cleaning). This work is the first phase of a project that will address several different types of solvent. From the findings, guidelines have been generated that will allow installation Directorates of Engineering and Housing to quickly assess a solvent's quality and determine if it should be reused or recycled. Reclamation techniques also have been reviewed, with advantages and drawbacks of several methods presented. Batch distillation appears to be the most promising alternative for installations in reclaiming used Stoddard solvent.

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FOREWORD

This work was performed for the U.S. Army Engineering and Housing Support Center (USAEHSC) under Project 4A162720A896, "Environmental Quality Technology;" Work Unit AO-032, "Treatment Technology for Hazardous Wastes." The USAEHSC Technical Monitor was Thomas Wash, CEHSC-FU-S. In addition, reimbursable funding was provided by the U.S. Air Force through a Military Interdepartmental Procurement Request.

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COL Carl O. Magnell is Commander and Director of USA-CERL, and Dr. L. R. Shaffer is Technical Director. COL Roy G. Kennington is the Commander of AFESC.



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USED SOLVENT TESTING AND RECLAMATION, VOLUME I: COLD-CLEANING SOLVENTS

1 INTRODUCTION

Background

Department of Defense (DOD) installations use large amounts of solvent each year in cleaning operations, which generates a huge volume of waste solvent. Much of this waste is or will be considered hazardous as stricter regulations are promulgated and enforced. Thus, proper handling and disposal practices are becoming of increasing concern to DOD. Coupled with these environmental issues is the rising cost of both waste disposal and new solvents. These concerns have prompted DOD to seek safe, cost-effective methods of managing waste solvent.

Solvents used at DOD installations can be classified into five groups based on chemical makeup and function: (1) vapor degreasers, (2) cold-dipping cleaners, (3) paint thinners, (4) paint strippers and carbon removers, and (5) precision cleaners. Most of these solvents are considered to provide one-time use; when they become contaminated, they are discarded. In these cases, disposal methods are mainly destructive, i.e., waste solvents are incinerated, evaporated, or dumped.

Some military facilities have initiated programs for reclaiming used solvents. This option is technically feasible because the solvents usually do not break down chemically during cleaning operations. Their role in cleaning is limited mainly to physical solubilization of waxes, greases, oils, and other contaminants. In fact, laboratory tests of major waste streams at installations have indicated that most solvents present could be recovered by recycling; the reclaimed material would generally be of suitable quality for effective reuse in cleaning.

A situation that has limited recycling is the lack of scientific tests and criteria for judging a solvent as spent (i.e., contaminated to the point that it is no longer effective for its intended purpose). Discarding a solvent before this point fails to maximize the material's life from an economic standpoint, whereas keeping it in service too long may result in use of an ineffective cleaner.

To make solvent recycling practical at installations, DOD needs criteria and simple test(s) for identifying spent solvents and/or indicating when the solvent should be discarded. These tests could have major impact on the environmental and cost issues facing DOD. Specifically, effective tests could:

1. Maximize solvent life for the most economical use of product; solvent cleaning operations would realize a savings through a reduction in new purchases.
2. Allow recycled solvent to be evaluated, preventing the use of inadequate quality materials in the cleaning process.

3. Minimize the amount of hazardous wastes generated, thus limiting the cost of handling and disposal. This benefit is especially important in light of the DOD Used Solvent Elimination (USE) program,¹ which bans the disposal of used solvent in landfills.

Purpose

The overall purpose of this work is to (1) establish criteria for identifying spent solvents and recommend simple tests to determine when solvents must be changed and (2) evaluate methods of reclaiming solvents as an alternative to disposal. Volume I addresses solvents used mainly in cold-cleaning operations (e.g., mineral spirits, PD-680). Volume II covers halogenated solvents used in vapor degreasing and metal cleaning/surface preparation.

Approach

This phase of the study involved the following steps:

1. Review the literature for methods of monitoring solvent quality.
2. Investigate physicochemical test methods.
3. Analyze Stoddard solvents (SS) and evaluate test results.
4. Rate the test methods and determine their practicality for use in the field.
5. Evaluate methods of reclaiming spent and partially spent solvent.
6. Study the economics of solvent reclamation.

7. Recommend test methods and reclamation strategies for use at military installations.

Mode of Technology Transfer

It is recommended that the test procedures be verified in the field and refined through a transfer medium such as the Facilities Engineering Applications Program (FEAP) program. When the tests are validated, they should be implemented at all military installations where solvents are used. The procedures would be incorporated into the appropriate technical manuals for implementation.

¹Memorandum from the Office of the Assistant Secretary of Defense, Director of Environmental Policy, "Used Solvent Elimination (USE) Program," Interim Guidance (February 1985).

2 SOLVENT PROPERTIES AND USE WITHIN DOD

Cleaning Mechanism

For background information, the literature was surveyed to learn about solvent chemistry and its role in the overall cleaning operation. To understand how a solvent works, it is first necessary to study the types of contaminants that require solvent cleaning. Solvent contaminants are generally a heterogeneous mixture of substances with different physical and chemical characteristics. They can be roughly grouped as:

1. Hydrocarbon oils, such as lubricating oils and greases, transmission oil, fuel oil, asphalt, and tar.
2. Paints and varnishes.
3. Soily material, such as clay and silt, cement, soot, and lampblack.

The first two categories are inert organic materials (liquids and semiliquids), whereas the third category consists mainly of insoluble inorganic materials which are, as a group, solids in various states of subdivision. However, the contaminants can occur as liquid, solid, or a combination of the two (e.g., soot in oily material).

Several phenomena contribute to adhesion of these contaminants to metal parts, all of which can be classified generically as: (1) mechanical entrapment onto/into the part; (2) bonding to the part by cohesion or wetting; and (3) bonding by chemical or adsorptional combination with the part material.

The first category, mechanical entrapment, is limited to solid soil or contaminants on the rough protuberances of a part or in crevices of the part structure.

The second mechanism of attachment is by cohesion or wetting. Here, the contaminant, if in liquid form, is held by wetting of the part surface; in the case of a liquid/solid mixture, the liquid acts as an adhesive between the solid particles and the part material by mutual wetting. The bond can be broken by an increase in the free energy of the liquid contaminant/part interface, substitution of a new interface that has lower free energy (by adding surfactants), or imparting of mechanical energy to the contaminant/part interface as by brushing or wiping action.

The third mechanism, chemical or adsorptional combination of the contaminants with the part material, is not generally observed in routine cleaning operations except in situations for which a part has been exposed to strong acids or alkalis. Thus, this report emphasizes the first two mechanisms.

Given these mechanisms, an effective cleaning operation can be divided into three steps:

1. Separation of contaminants from part material.
2. Dispersion and solubilization of contaminants in the solvent.
3. Stabilization of the dispersed contaminants.

In many situations, these steps are interdependent and the limits of each are not always defined clearly.

The known actions of solvents that characterize their ability to effect cleaning are: (1) wetting and spreading on both part and contaminant surfaces, (2) lowering the surface free energy of contaminant surfaces, (3) speeding movement of solid and liquid particles, and (4) solubilization. The degree of solubility of a solute in a solvent is known as the "solvent power" of the solvent. For a homologous series of hydrocarbons, the volume of a liquid solute (oil and grease) solubilized at constant temperature is generally inversely proportional to the molar volume of the solute. Thus, the degree of solubilization depends to a large extent on the chain length of a hydrocarbon solute. Greases of high molecular weight are sparingly soluble in SS. The situation is complicated by the fact that solvents such as SS and mineral spirits are themselves a mixture of aliphatic and aromatic hydrocarbons. Different groups or series of hydrocarbons in SS have different solubilities for oily and greasy contaminants.²

Although solubilization has been studied by many researchers, most of the literature relates to final equilibrium solubilization of oils by surfactants. Only a few studies are concerned with the mechanism and kinetics.³

Stabilization of insoluble materials means that solid and liquid contaminants are kept dispersed in the cleaning medium to minimize redeposition. (Most studies in this area have been limited to aqueous surfactants acting on soiled fabrics.) One method of decreasing redeposition is by subjecting a part to multiple dippings in different vats instead of one-time dipping in a single vat. In the first vat, contaminants are removed from the part up to a certain point in a short time. This vat thus provides preliminary cleaning; a complete cleaning consists of two or more of these short dippings in additional vats. The solvent can be cycled from vat to vat on a periodic basis counter to the flow of parts, i.e., solvent from a "cleaner" vat could be moved to a preceding vat where a lower degree of cleaning is required. Solvent from the first vat (preliminary cleaning) would be reclaimed or discarded after it is spent. The number of vats in the counterflow scheme need not be large--two or three would be enough for routine cleaning.

Another method of decreasing redeposition is to use filters that trap insoluble particulates. This option leaves the vat liquid essentially free of solids and insoluble mass.

²W. W. Niven, *Fundamentals of Detergency* (Reinhold, 1950); J. M. Rosen (Ed.), *Structure/Performance Relationships in Surfactants*, ACS Symposium Series 253 (American Chemical Society [ACS], 1984).

³J. M. Roser (Ed.), *Structure/Performance Relationships in Surfactants*, ACS Symposium Series 253 (ACS, 1984).

Solvent Characterization

Several characteristics are required of solvents to be used in the cold degreasing process.⁴ They must:

- Dissolve oils, grease, and other contaminants.
- Have a high vapor density relative to air and a low vapor pressure to minimize solvent losses.
- Be chemically stable under conditions of use.
- Be essentially noncorrosive to common construction materials.
- Have a boiling point and latent heat of vaporization low enough to permit the solvent to be separated easily from oil, grease, and other contaminants by simple distillation.
- Not form azeotropes with liquid contaminants or with other solvents.
- Remain nonexplosive and nonflammable under the operating conditions.

A typical solvent satisfying these properties is mineral spirits. This type of solvent is known by various trade names, e.g., SS, drycleaning solvent, PD-680, Varsol (Exxon), turpentine substitute, white spirit, and petroleum spirit. SS is used mainly in cold cleaning metal parts and equipment in vats. Its low evaporation rate and high flashpoint make it a widely used solvent for removing oils, greases, and dirt from metal. Table 1 lists the specifications of Types I and II SS as developed by the American Society for Testing and Materials (ASTM).⁵ The two types are distinguished primarily by their flashpoints, i.e., Type I solvent flashes at 100 °C whereas Type II flashes at 140 °C. Since these solvents are petroleum distillates, variations in solvent power between batches can be significant as reflected by Kauri-butanol values (between 29 and 45).

There is a broad distillation range for these solvents and the components are mainly alkane isomers between C₆ and C₁₆. They contain approximately 2 percent toluene and a maximum of 0.5 percent benzene. The toxic hazard rating for mineral spirits is considered to be slight to moderate.⁶

⁴Source Assessment: *Reclaiming of Waste Solvents, State of the Art*, EPA 600/2-78-004f (U.S. Environmental Protection Agency [USEPA], April 1978); *Source Assessment: Solvent Evaporation-Degreasing Operations*, EPA 600/2-79-019f (USEPA, August 1979).

⁵*Annual Book of ASTM Standards*, Vol 6.03, Section 6 (American Society for Testing and Materials [ASTM], 1983).

⁶A. L. Bunge, *Minimization of Waste Solvent: Factors Controlling the Time Between Solvent Changes*, USA-CERL Contract No. DACA 88-83-C-0012 (Colorado School of Mines, September 1984).

Table 1

Physical and Chemical Properties of Stoddard Solvent*

Property	Type I	Type II
Commercial reference	Stoddard	140°F Solvent
Appearance	Clear and free of suspended matter and undissolved water	
Flashpoint, min. °F (°C)	100 (38)	140 (60)
Distillation, °F (°C)		
Initial boiling pt., min.	300 (149)	350 (177)
50% recovered, max.	350 (177)	385 (196)
Dry point, max.	407 (208)	412 (211)
Kauri-butanol value:		
Min.	29	29
Max.	45	45
Color, max.	Water-white or not darker than +2	
Residue from distillation:		
Percent, max.	1.5	1.5
Acidity	Neutral	Neutral
Doctor test	Negative	Negative
Copper corrosion		
Max. rating	1	1
Odor	Characteristic, nonresidual	
Bromine no., max.	5.0	5.0
Apparent specific gravity (60°F/60°F):		
Min.	0.754	0.768
Max.	0.820	0.820

*Source: *Annual Book of ASTM Standards*, Vol 6.03 (ASTM, 1983). Used with permission.

Generation of Waste Stoddard Solvent

Some 485,000 cold cleaning operations in the United States use Stoddard-type solvents. The annual consumption of SS in degreasing operations amounts to more than 220,000 MT.⁷

In assessing SS usage within DOD, the military installations can be classified as large and small.⁸ Large bases include shipyards, air logistics centers, Army depots, and air rework facilities. Each installation in this category annually generates 500 drums (55 gal) of SS, and there are 29 such installations. Small installations are much more

⁷Source Assessment: *Reclaiming of Waste Solvents, State of the Art; Source Assessment: Solvent Evaporation-Degreasing Operations.*

⁸R. W. Bee and K. E. Kawaoka, *Evaluation of Disposal Concepts for Used Solvents at DOD Bases*, TOR-0083(3786)-01 (February 1983).

numerous (at least 124 bases) and are low-volume solvent consumers.⁹ Representative annual volumes for small bases are 150 drums of SS each. Table 2 lists the amount of spent solvent observed at some large and small DOD installations.

A pollution abatement study conducted by Lee et al. revealed that a large volume of solvents also is being used annually by five of the six Naval Air Rework Facilities (NARFs).¹⁰ Table 3 lists quantities used by each NARF.

Disposal Alternatives

The waste solvent generated at DOD installations is disposed of in four primary ways: incineration, fuel substitution, surface disposal, and sale. These practices were reviewed and are summarized below.

Incineration

Incineration is the burning of wastes with air in an incinerator. This disposal alternative is useful for a number of waste solvents including cold-dipping wastes. However, segregation of these wastes from chlorinated hydrocarbons, lead and other metals, and water contaminants is essential so that emissions from the incinerator satisfy U.S. Environmental Protection Agency (USEPA) and state regulations. Incineration is an attractive disposal method for wastes that contain a variety of hydrocarbon products that cannot be reclaimed readily. Incinerators have been used to dispose of a variety of oil and grease waste generated at refineries.¹¹ In some instances, effluent combustion gases from this burning are passed through heat exchangers to preheat process streams.

Fuel Substitution

Many DOD installations burn spent or waste solvents in boilers and other firing equipment. This option is preferable to incineration because the fuel energy of the waste solvent is used beneficially. However, the wastes have to be segregated such that no halogenated hydrocarbons can contaminate the waste streams.

Several industrial studies have shown that blending waste solvents with regular fuel causes no noticeable increase in burner maintenance costs (due to corrosion) or adverse air pollution effects.¹² The advantages to combustion are that liquid wastes are disposed of profitably and safely, resulting in conservation of solvent resources.

Surface Disposal

Heavy nonvolatile waste solvents have been used in the past as road oil for dust control. However, waste streams consisting primarily of SS would evaporate into the air or run off with rain, thus contaminating local water sources (e.g., streams and lakes).

⁹R. W. Bee and K. E. Kawaoka.

¹⁰H. J. Lee, I. H. Curtis, and W. C. Hallow, *A Pollution Abatement Concept, Reclamation of Naval Air Rework Facilities Waste Solvent, Phase I* (Naval Air Development Center, April 1978).

¹¹*Disposal/Recycle Management System Development for Air Force Waste Petroleum Oils and Lubricants*, AD779723 (U.S. Air Force, April 1974).

¹²*Disposal/Recycle Management System Development for Air Force Waste Petroleum Oils and Lubricants*.

Table 2
Spent Solvent Generation at Major DOD Bases*

Bases	Cleaning Bath Solvents (55-gal drums/yr)	All Solvents Total (55-gal drums/yr)
Seneca Army Depot, NY	140	180
Kelly AFB, TX	152	1134
Hill AFB, UT	455	2270
Tyndall AFB, FL	50	118
Jacksonville NAS, FL	60	2285
Davis Monthan AFB, AZ	190	227
Bergstrom AFB, TX	170	243
Corpus Christi Army Depot, TX	750	1025
Norfolk NARF, VA	540	1084
McClellan AFB, CA	90	935
Aunston Army Depot, AL**	660	1455

*Source: R. W. Bee and K. E. Kawaoka, *Evaluation of Disposal Concepts for Used Solvent at DOD Bases*, TOR 0083(3786)-01 (The Aerospace Corp., February 1983). Used with permission.

**Survey by the Chemical Engineering Dept., Auburn University.

Table 3
Spent Solvent Generated at Naval Air Rework Facilities*

Base	Stoddard Solvent Generation Rate (1000 gal/yr)	All Solvents (1000 gal/yr)
Alameda, CA	90.0	176
Norfolk, VA	24.0	78.1
North Island, CA	262.9	392.8
Pensacola, FL	57.2	209.9
Jacksonville, MI	7.7	106.4
Total	450.9	963.2

*Source: H. J. Lee, I. H. Custis, and W. C. Hallow, *A Pollution Abatement Concept, Reclamation of Naval Air Rework Facilities Waste Solvent, Phase I* (Naval Air Development Center, April 1978).

Another method of surface disposal is by contacting waste solvents with oil-consuming soil microorganisms under ambient conditions.¹³ Results using this method have been encouraging, except in cases of excessive rainfall which led to runoff of hydrocarbons into adjacent water sources.

Sanitary landfilling has been selectively used for disposal of petroleum-based wastes, usually in combination with other landfilled waste. Use of this mechanism for disposal of solvent wastes is still experimental.

Sale

The Defense Reutilization and Marketing Service (DRMS) is responsible for selling used solvent material. The sale option is profitable as well as an environmentally acceptable disposition practice, provided the buyers use appropriate reprocessing methods. The buyers' qualifications must be evaluated carefully because unscrupulous buyers have been known to improperly release the used materials into the environment, which could result in potential DOD liability. Used solvent material for sale must be segregated at the point of generation and labeled properly. Mineral spirit wastes have been sold at some installations for \$0.40/gal.*¹⁴

¹³H. Kobayashi and B. E. Rittman, "Microbial Removal of Hazardous Organic Compounds," *Environ. Sci. Technol.*, Vol 16, No. 3 (1982).

*Metric conversion chart is shown on p 64.

¹⁴R. W. Bee and K. E. Kawaoka; *Disposal/Recycle Management System Development for Air Force Waste Petroleum Oils and Lubricants*.

3 EVALUATION OF DETECTION METHODS

Literature Review

A literature survey indicates extensive use of SS as a cleaning agent in the dry-cleaning industry.¹⁵ Although there is a standard for new or virgin SS (ASTM D 484-71), no such specification is available for spent or contaminated solvents. However, some arbitrary criteria are used in various industries; for example, in the drycleaning industry, the transmittance of light through a sample of dirty solvent is the determining factor as to when to change the solvent.¹⁶ In other degreasing operations, the solvent color as well as the presence of dirt are taken into consideration for changing these agents.¹⁷

Various physical properties of solvents have been proposed to reflect the extent of contamination. These include boiling point, density, refractive index, color, and viscosity.¹⁸ However, these properties may not be truly indicative of a solvent's ability to remove grease and soil. In addition, variations in the values of these properties, as a function of solvent strength, may be small and thus require very accurate measurements. This factor could be a potential problem for a test that is to be performed at a field station, although simple modern instrumentation may facilitate such measurements.

Color is commonly used as a criterion to evaluate dirty solvents in the drycleaning industry.¹⁹ Generally, a clean solvent will allow a transmission of 90 percent visible radiation at 500 nm. However, after prolonged use, the transmittance drops to the vicinity of 50 percent (after filtration of solid residue), and the solvent is discarded for reclamation. The addition of aqueous hydrogen peroxide to dirty solvents rejuvenates them and allows reuse of vat solvents without distillation. It is speculated that a dual action occurs: (1) bleaching by the peroxide which decreases light absorption and (2) a physical effect on the suspended fine dirt by particles of aqueous hydrogen peroxide; these particles act as nuclei to which small dirt particles agglomerate to a size where they will filter out of the solvent.²⁰

¹⁵Source Assessment: *Reclaiming of Waste Solvents, State of the Art; Source Assessment: Solvent Evaporation-Degreasing Operations; Annual Book of ASTM Standards*; A. E. John, *Drycleaning* (Merrow Publishing Co., England, 1971); A. R. Martin and G. P. Fulton, *Drycleaning Technology and Theory* (Textile Book Publishers, 1958); E. R. Phillips, *Drycleaning* (National Institute of Drycleaning, Inc., 1961); C. B. Randall, *The Drycleaning Department* (National Association of Dyers and Cleaners, 1937); K. Johnson, *Drycleaning and Degreasing Chemicals and Processes* (Noyes Data Corp., 1973); I. Mellan, *Industrial Solvents Handbook* (Noyes Data Corp., 1977); T. H. Durrans, *Solvents*, 2nd ed. (Van Nostrand, 1931); I. Mellan, *Industrial Solvents* (Reinhold, 1950); L. Schefflan and M. B. Jacobs, *The Handbook of Solvents* (Van Nostrand, 1953); *International Fabricare Institute Bulletin T-447* (1969).

¹⁶K. Johnson; *International Fabricare Institute Bulletin; National Institute of Drycleaning Bulletin Service*, T-413 (1965); H. M. Castrantas, R. E. Keay, and D. G. MacKellar, *Treatment of Dry Cleaning Baths*, U. S. Patent 3,677,955 (July 1972).

¹⁷A. L. Bunge.

¹⁸A. L. Bunge; K. Johnson.

¹⁹K. Johnson.

²⁰W. W. Niven; K. Johnson; *National Institute of Drycleaning Bulletin Service*.

The viscosity of a solvent usually increases greatly when the solvent becomes contaminated with grease and/or oil. This change is due to a high intermolecular attraction between the solvent and the dissolved contaminants.

In thin-layer chromatography, a standard dye is "spotted" onto a glass microfiber sheet, and the sheet is then placed in the solvent sample. As the solvent moves up the plate by capillary action, the dye migrates at a rate characteristic of the sample's solvent power. The distance traveled by the dye is divided by the distance traveled by the solvent to obtain the R_f value of the dye. The R_f value has been shown to have direct correlation with solvency and solvent power.²¹

Another category of tests (compared with those based on physical parameters) rate solvent power in terms of chemical reactivity or degree of solubility of certain materials. These properties include acid number, aniline point, dimethyl sulfate value, Kauri-butanol value (KBV), and cellulose-nitrate solution value.²² KBV has been used traditionally in the drycleaning and varnish industries to represent solvent performance. Solvent KBV decreases with increased solvent contamination by grease, oil, or soil. A drawback to this test is that KBV reflects the solubility of Kauri resin in a solvent and possibly will not accurately represent the solvent's ability to dissolve compounds that have structures significantly different from those of Kauri resin.

Table 4 summarizes some current techniques for determining solvent quality.

Current Solvent Testing at Military Installations

To identify existing criteria for determining the change schedule of solvents at various DOD installations, a questionnaire was prepared and sent to 20 military facilities. However, responses were received from only three facilities. Of these three, Robins AFB, GA, does not have a cold-dipping operation that uses SS. SS is used only to clean grime and dirt from machinery parts. The Appendix presents the questionnaire in full along with responses.

Anniston Army Depot requires that all cleaned parts be tested by wiping with a clean white cloth. If there is no visible residue on the cloth, the part is considered to be clean. In addition, a laboratory centrifugation test is performed on the spent solvent. The solvent is changed when the amount of solids exceeds 2 percent.

Tyndall AFB, FL, sent responses from two operating departments. The EMS wheel and tire shop uses SS for removing carbon deposits, grease, and dirt from aircraft wheels and wheel bearings. The degree of cleanliness is determined through close inspection by experienced personnel. The 25th EMS AGE branch uses cold dipping to remove grease, dirt, etc., from parts prior to disassembly for repair or overhaul. The parts, as in the other department, must be very clean and the degree of cleanliness is determined by visual inspection.

²¹G. G. Esposito, Solvency Rating of Petroleum Solvents by Reverse Thin-Layer Chromatography, AD753336 (Aberdeen Proving Ground, 1972).

²²Annual Book of ASTM Standards; A. L. Bunge; International Fabricare Institute Bulletin.

Table 4

**Measurement Techniques for Determining Solvent Quality
as Reported in the Literature**

Method	Principle	Reference*
Electrical Conductivity (ASTM D 2624 & D 3114)	Measures the ability of a solution to carry an electric current. A metal part is cleaned with solvent and then dipped in a relatively more conductive liquid (e.g., ethyl alcohol). If the part is clean, the alcohol will not show a significant change in conductivity. Apparatus: conductivity meter and probe.	1 - 3
Ultraviolet Spectroscopy (ASTM D 1319)	Absorptivity of liquids at specified wavelength in the UV region is used to characterize petroleum products. Apparatus: UV spectrophotometer.	1 - 3
Fluorescent Indicator Adsorption (ASTM D 1319)	Sample is introduced into a glass adsorption column packed with activated silica gel. When the sample has been adsorbed on the gel, alcohol is added to desorb and force it down the column. The hydrocarbons are separated into aromatics, olefins, and saturates. A dye is added to the silica gel which illuminates the different zones under UV light. Apparatus: glass adsorption column.	4
Sediment Extraction (ASTM D 473)	Sample, contained in a refractory thimble, is extracted with hot toluene until the residue reaches constant mass. The mass of residue is reported as "sediment by extraction."	4
Thin-Layer Chromatography	Standard dye is spotted on a glass microfiber sheet and the edge of the sheet is placed into the solvent. After the solvent has migrated to the top of the sheet, the sheet is removed and dried. The ratio of the distances traveled by the dye and solvent is established and related to solvent power.	5,6
Density, Specific Gravity, or API Gravity (ASTM D 1298)	Sample is brought to a prescribed temperature. A hydrometer is placed into the sample container and allowed to come to equilibrium. The scale is read and converted to appropriate units. If a density meter or a specific gravity meter is used, the sample is brought within 5°C of ambient temperature after introduction into the meter oscillator and a digital readout is obtained. Apparatus: hydrometer or density meter.	4,7
Refractive Index	Measured by critical angle method with a refractometer. Refractive index is used to characterize hydrocarbons and their mixtures. Apparatus: refractometer, thermometer.	4,8

*References are listed in numerical order at the end of this table.

Table 4 (Cont'd)

Method	Principle	Reference
Acid Number	Determines the amount of fatty acid in a solvent. Defined as "mg of KOH to neutralize 1.28 mL of the solvent." Apparatus: buret, pipet, flask. Chemicals: KOH, methanol, phenolphthalein.	5,9,10
Color (Visible Absorbence)	Sample's light transmittance is observed between 450 and 600 nm. In drycleaning industry, if transmittance drops to near 50% after filtration, solvent is usually changed. Equipment: Visible spectrometer or colorimeter.	11,12
Kauri- Butanol Value (ASTM D 1133)	Gives an index number for ranking solvents. The basis of the test is that Kauri gum is very soluble in butanol but its solubility decreases as the butanol is diluted with a solvent that will not dissolve the resin. Apparatus: buret, flask, precision balance. Chemicals: Kauri-butanol solution.	6,7,9
Aniline Point (ASTM D 611)	Useful in characterizing pure hydrocarbons (HCs) and mixtures. Aromatic HCs exhibit the lowest, and paraffins the highest, values. Aniline point is most often used to estimate aromatic HC content of mixtures. Apparatus: aniline point apparatus, temperature bath, and thermometers. Reagents: aniline, CaSO_4 , n-heptane, and Na_2SO_4 .	9
Cellulose Nitrate Dilution Ratio for Active Solvents (ASTM D 1720)	Determines the volume ratio of HC diluent to active solvent required to cause precipitation in a solution of cellulose nitrate. By using a standard material for any two of the three components, the effect of different types of third component can be determined. Apparatus: titration buret and accessories. Reagents: n-butyl acetate, cellulose nitrate, and toluene.	9

¹Annual Book of ASTM Standards, Section 5, Vol 5.02 (1983).

²Annual Book of ASTM Standards, Section 5, Vol 5.03 (1983).

³H. H. Bauer, G. D. Christian, and J. E. O'Reilly, *Instrumental Analysis* (Allyn and Bacon, 1979).

⁴Annual Book of ASTM Standards, Section 5, Vol 5.01 (1983).

⁵National Institute of Drycleaning Bulletin Service, T-413 (1965).

⁶G. G. Esposito, *Solvency Rating of Petroleum Solvents by Reverse Thin-Layer Chromatography*, AD-753338 (Aberdeen Proving Ground, 1972).

⁷A. L. Bunge, *Minimization of Waste Solvent: Factors Controlling the Time Between Solvent Changes*, CERL Contract DACA 88-83-C-0012 (Colorado School of Mines, September 1984).

⁸Refractometer Manual, ABBE-56 (Bausch and Lomb Optical Co.).

⁹Annual Book of ASTM Standards, Section 6, Vol 6.03 (1983).

¹⁰A. R. Martin and G. P. Fulton, *Drycleaning Technology and Theory* (Textile Book Publishers, 1958).

¹¹K. Johnson, *Drycleaning and Degreasing Chemicals and Processes* (Noyes Data Corp., 1977).

¹²H. M. Castrantas, R. E. Keay, and D. G. MacKellar, *Treatment of Dry Cleaning Baths*, U. S. Patent 3,677,955 (July 1972).

Anniston Army Depot was visited to observe the cold-dipping facilities there. Cold-dipping operations are done to clean transmission parts of tanks and military vehicles. A typical vat contains 50 to 60 gal of solvent. The parts are immersed in the solvent for a period of time and, occasionally, a brush is used to dislodge grime and dirt.

Anniston personnel were questioned as to how the samples are collected for determining the amount of solid and water contamination. According to these individuals, a layer of sludge usually forms on the bottom of a vat if a filtering system is not used. The sludge can easily be removed using a paper filtering system.

Fort Benning, GA, uses a portable 1-micron paper filtering system at its weapons consolidation pool. This filtering system has saved about \$70,000 over just 6 months. In this operation, the solvent is mixed with an oil and other additives, and the mixture is used to wash weapons. This is a different type of cleaning operation than the others surveyed, but the savings are impressive and suggest that such filtering systems should be examined for use in similar applications.

Physicochemical Tests

To evaluate some of the physicochemical test methods, an experimental study was done using SS. The following properties were measured: (1) Kauri-butanol value, (2) viscosity, (3) specific gravity, (4) refractive index, (5) visible absorption, (6) electrical conductivity, and (7) thin-layer chromatography. These techniques were selected from the literature on the basis of reported scientific reliability and consistency, as well as relative ease of performing in field conditions. The background and procedures for these tests are described below.

Kauri-Butanol Value

As mentioned, the ASTM Kauri-butanol method is a convenient way to measure the relative power of solvents. This method includes an index for ranking solvents for their ability to dissolve other materials.^{2 3}

SS is a mixture of hydrocarbons distilled from petroleum. It can vary in composition, depending on the nature of the petroleum from which it was distilled. SS contains three classes of hydrocarbons: aliphatic (paraffins), alicyclic (naphthenes), and aromatics (benzene and its derivatives). The paraffinic hydrocarbons have the lowest solvent power and the aromatics have the highest. Therefore, the solvent power in terms of Kauri-butanol value (KBV) largely depends on the amount of aromatics present. This is because the Kauri resin is standardized against (1) toluene (an aromatic compound) which has an assigned value of 105 and (2) a mixture of 75 percent heptane and 25 percent toluene (an aliphatic-aromatic mix) which has an assigned value of 40. The basis for the test is that the Kauri resin becomes less soluble in "weaker" solvents such as aliphatic hydrocarbons. Therefore, the solvent being tested is added in small portions until the solution becomes cloudy due to precipitation of the resin. The greater the volume of solvent added to the Kauri-butanol (K-B) solution before it becomes cloudy, the higher the KBV. This simple test is widely accepted as a good measure of relative solvent power. The methodology is as follows.^{2 4}

^{2 3} *Annual Book of ASTM Standards; National Institute of Drycleaning Bulletin Service; G. G. Esposito.*

^{2 4} *Annual Book of ASTM Standards.*

Apparatus:

- Erlenmeyer flask, 250-mL.
- Buret, 50-mL (Figure 1).
- Print sample (a sheet of white paper with black 10-point print, No. 31 Bruce Old Style type).

Reagents:

- Standard K-B solution; a prepared solution was obtained from Chemical Service Lab, 5543 Dyer St., Dallas, TX 75206.
- Reagent-grade toluene.
- Reagent-grade heptane.

Procedure:

1. Weigh 20 g of standard K-B solution into a 250-mL Erlenmeyer flask.
2. Place the sheet of 10-point print under the flask.
3. Fill buret with solvent to be sampled.
4. Titrate into the flask until printed material becomes obscured or blurred but not to the point where the print becomes illegible.
5. Calculate the Kauri-butanol value using the following formula:

$$KBV = 65(C-B)/(A-B) + 40 \quad [Eq 1]$$

where:

A = mL of toluene required to titrate 20 g of K-B solution (should be around 105).

B = mL of 75 percent heptane/25 percent toluene blend needed to titrate 20 g of K-B solution (should be around 40).

C = mL of sample solvent needed to titrate 20 g of K-B solution.

Values of A and B can be obtained from standard titrations or from the supplier of the K-B solution.

Viscosity

Viscosity is the internal friction or resistance to flow that exists within a fluid, either liquid or gas. This property depends on the intermolecular attractive forces within the fluid. Viscosity is an extremely useful method for characterizing oils and solvents. Viscosities of "heavier" and "lighter" oils are significantly different, whereas their densities may differ very little.

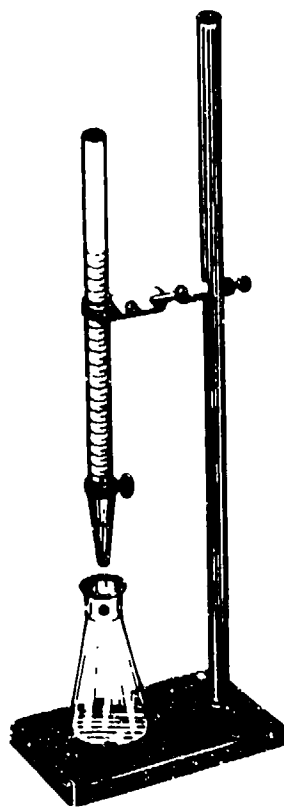


Figure 1. Kauri-butanol value apparatus.

A common unit of viscosity is the poise, which is equal to 1 gram per centimeter second (g/cm-sec), usually given in centipoise (cp). Viscosities in this work were measured using an Ostwald viscometer. This type of viscometer measures the flow rate of a fluid through a capillary tube in a gravity field. Newtonian behavior was assumed for all solvent mixtures. A Newtonian fluid is one that shows a linear relationship between the magnitude of the applied shear stress and the resulting rate of deformation. The viscosity (μ) of a given fluid is calculated using Equation 2:

$$\mu = k \times t \quad [\text{Eq 2}]$$

where t is the time required for a fixed volume of fluid to flow through the capillary and k is a constant obtained by measuring the time of a liquid that has a similar known viscosity.

Apparatus:

- Ostwald viscometer (Figure 2).
- Stopwatch.

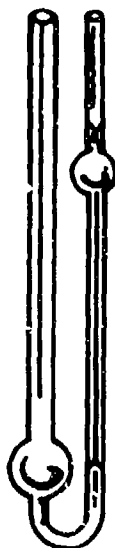


Figure 2. An Ostwald viscometer.

Procedure:²⁵

1. Wash the viscometer thoroughly and rinse with distilled water, making sure the instrument is clean and dry before taking readings.
2. Introduce distilled water and allow it to come to thermal equilibrium in a constant-temperature bath.
3. Draw liquid into upper bulb to marked line with a suction bulb.
4. Remove bulb and record time needed for level of water to pass between markings.
5. Repeat steps 3 and 4 until readings are fairly constant.
6. Clean and dry viscometer thoroughly.
7. Add an appropriate volume of the solvent to be tested into the viscometer.
8. Repeat steps 3 through 5.

Refractive Index

The refractive index of a liquid is the ratio of the velocity of light in a vacuum to the velocity of light in the liquid. This property can be used to identify a substance and determine its purity. Since the angle of refraction varies with the wavelength of light

²⁵G. J. Shugar, et al., *Chemical Technician's Ready Reference Handbook*, 2nd ed. (McGraw-Hill, 1981).

used, the measurement of refractive index requires that light of a known wavelength be used. However, a white light can be used if the refractive index of a reference liquid is measured in the same light.

Refractive index is commonly reported to four decimal places and, since it can easily be determined experimentally to a few parts in 10,000, it is a very accurate physical constant. Small amounts of impurities can have significant effects on the experimental value. Refractive indices in this study were determined using an Abbe refractometer.²⁶ This instrument compares the angles at which light from an effective point source passes through a test liquid and into a prism for which the refractive index is known.

Procedure:²⁷

1. Unlock the hinged assembly and lower the bottom part of the prism.
2. Clean the upper and lower prisms with soft, nonabrasive, absorbent, lint-free cotton wetted with benzene. Rinse by wiping with petroleum ether and allow to dry.
3. Place a drop of solution of known refractive index (e.g., water) on the prism.
4. Record the temperature indicated by the thermometer next to the prism.
5. Set the scale to correspond with the known refractive index at the corresponding temperature.
6. Look through the eyepiece and turn the compensator knob until the colored, indistinct boundary seen between the light and dark fields becomes a sharp line.
7. Adjust the magnifier arm until the sharp line exactly intersects the midpoint of the crosshairs in the image (Figure 3).
8. Repeat steps 1 through 7 using the solvent to be tested.
9. Clean prisms and lock them together.

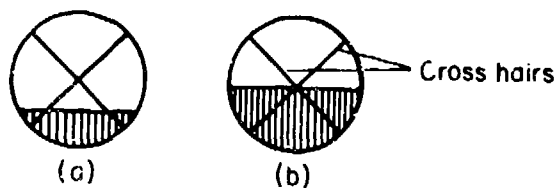


Figure 3. Adjusting the refractometer.

²⁶*Refractometer Manual*, ABBE-56 (Bausen and Lomb Optical Corp.).

²⁷*Refractometer Manual*.

Specific Gravity

Specific gravity is defined as the ratio of the density of a liquid to that of water at the same temperature. Density is a fundamental physical property of a substance denoting the mass of a substance per unit volume.

Specific gravity can be measured easily using a specific gravity meter, a hydrometer, or a pycnometer. Any of these devices can give very accurate results with little training or experience on the part of the tester. A hydrometer generally is not sensitive enough to detect the small specific gravity variations that occur when a solvent becomes contaminated.

In this study, specific gravity of SS was measured using two devices: (1) a pycnometer bottle, which holds a precise volume of liquid and is weighed on a balance, and (2) an electronic specific gravity meter (Mettler/Paar DMA35SG).²⁸ Both methods give accurate results, but the specific gravity meter is easier to use and requires no weighing. Specific gravity is very sensitive to changes in temperature because, as temperature increases, fluids have a tendency to expand, thus reducing the amount of mass in the same volume of fluid. The opposite effect occurs when a fluid is cooled.

Apparatus:

- Analytical precision balance.
- Pycnometer (Figure 4), or
- Electronic specific gravity meter.

Procedure:²⁹

1. Clean pycnometer thoroughly.
2. Dry pycnometer in an oven for 30 min.
3. Remove from oven and allow to cool.
4. Weigh pycnometer on a precision balance.
5. Repeat steps 2 through 4 until a constant weight is obtained.
6. Fill pycnometer completely with liquid.
7. Wipe cap with tissue and weigh pycnometer.

²⁸ *Mettler/Parr DMA 35 Density Meter* (Mettler Instrument Corp., 1986).

²⁹ G. J. Shugar, et al.

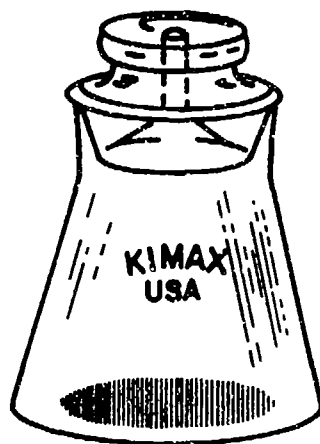


Figure 4. Pycnometer.

When using a specific gravity meter:³⁰

1. Turn on meter.
2. Fill bulb on meter, making sure no air bubbles are in the measuring tube as this will cause errors.
3. Record the temperature of the liquid as well as the specific gravity referenced to 20 °C.
4. Turn off meter.
5. Empty meter of all fluid and clean thoroughly.

Electrical Conductivity

According to Ohm's Law, the resistance of a conductor of length L and cross sectional area A is given by:

$$R = k \times (L/A) \quad [\text{Eq 3}]$$

where R is the resistance in ohms and k is the specific resistivity, an inherent property of the material being examined which is expressed in ohm-cm. In dealing with liquids, the reciprocal of k usually is measured; this value is called the "specific conductance" or "conductivity" and is expressed in $\text{ohm}^{-1}\text{cm}^{-1}$ or mhos/cm. Thus, from Equation 3, the conductivity is given by:

$$c = (L/A) \times (1/R) \quad [\text{Eq 4}]$$

³⁰Mettler/Parr DMA 35 Density Meter.

Electrical conductivity is generally measured using a conductance cell for which the factor L/A in Equation 4 can be determined by measuring the known conductance of a standard solution, usually potassium chloride in water. For a cell of given geometry, the factor L/A is called the "cell constant" and, once it has been determined, the conductance of unknown solutions can be determined by applying the same procedures.

The electrical conductivity of pure organic liquids is usually very small--on the order of 10^{-8} mhos/cm or less at 25 °C. Because electrical conductivity is a function of temperature, some attention must be given to controlling the liquid's temperature while determining this value.

Since the conductance of a solution is a function of concentration, it would be expected that the electrical conductivity of a solvent, e.g., new SS, would change as impurities are accumulated during usage. Thus, monitoring a solvent's conductivity might provide one method of indicating solvent bath contamination. During the course of solvent usage, the conductivity could increase or decrease, depending on the particular impurities being accumulated.

Apparatus:

Conductivity meter (YSI Model 32).

Probe (YSI #3402).

Procedure:

1. Clean probe thoroughly (Figure 5).
2. Measure temperature of solvent to be tested.
3. Set conductivity meter to conductivity setting.
4. Dip probe in solvent and set instrument to proper scale.
5. Allow about 5 min for probe to reach equilibrium.
6. Record conductivity.
7. Repeat until constant.

Visible Absorbance

Because there is usually a noticeable change in the color of a contaminated solvent, light absorbance is an obvious choice for a test method. The amount of light absorbed could indicate the amount of contamination of a solvent. This type of test is currently used in the drycleaning industry.³¹

³¹ K. Johnson; I. Mellan.

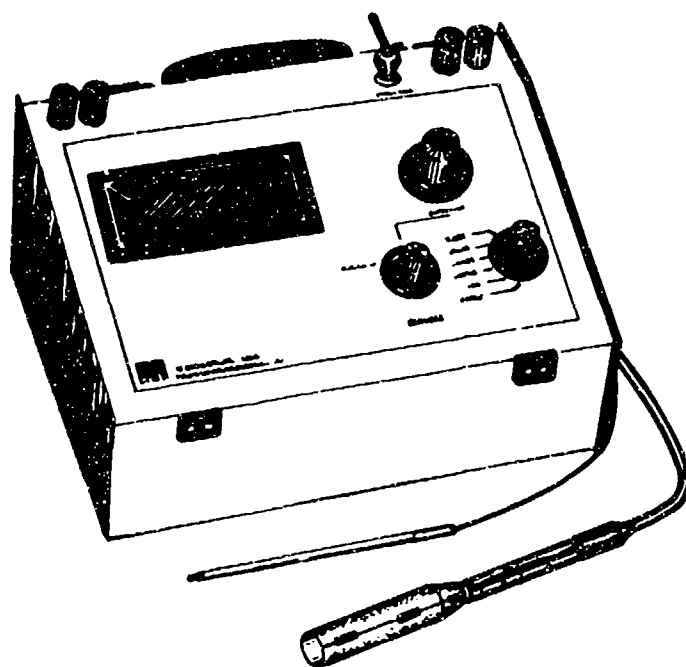


Figure 5. Conductivity meter with probe.

When an electromagnetic wave of a specific wavelength impinges upon a substance, the fraction of radiation absorbed will be a function of the concentration of the substance in the light path and the thickness of the sample. It has been found that increasing the concentration of the absorber has the same effect as a proportional increase in the radiation-absorbing path length. Therefore, the absorbance, A , is proportional to the concentration of absorbing solute:³²

$$A = a \times b \times C \quad [\text{Eq 5}]$$

where b is the sample path length (cm), a is specific absorptivity in $\text{g}^{-1}\text{-cm}^{-1}$, and C is the solvent concentration in g/L. This equation holds only for low concentrations. The derivation of Beer's law assumes the use of monochromatic light; however, if absorptivity is essentially constant over the instrumental bandwidth, Beer's law will be followed closely. Departure from Beer's law is most serious for wide slit widths and narrow absorption bands, and is less significant for broad bands and narrow slits. Therefore, the most significant measurements were made using a very narrow slit width of 0.02 mm and a broad band between 400 and 600 nm.

³²H. H. Bauer, G. D. Christian, and J. E. O'Reilly; H. H. Willard, L. L. Merritt, Jr., and J. A. Dean, *Instrumental Methods of Analysis*, 5th ed. (D. Van Nostrand, 1974).

Apparatus:

- UV/visible spectrophotometer (Gilford 250).
- Cuvette.

Procedure:

1. Turn on instrument and allow a 30-min warmup.
2. Clean and dry cuvette, making sure that all smudges are wiped off and there are no scratches on any surfaces in the light path.
3. Fill cuvette with sample and place in the spectrometer.
4. Set slit width and take reading.

Thin-Layer Chromatography

Chromatography, in general, is a separation technique based on the fact that a substance has different affinities for each of two phases--stationary and mobile. The relative distribution of a substance between the two phases is known as the distribution coefficient, K . The fact that different substances have different distribution coefficients makes it possible to separate them by chromatography. Two substances, A and B, with unequal distribution coefficients K_A and K_B will spend different periods of time in mobile and stationary phases. Movement of the mobile phase leads to a separation. For example, if $K_A > K_B$, then A spends more time in the mobile phase and thus travels faster than substance B.³³

In classic thin-layer chromatography (TLC), a mixture to be separated (in this case, a mixture of dyes) would be deposited at a starting point on a plate or paper and the mobile phase (solvent) would be allowed to travel up the plate/paper by capillary action. Because of differences in distribution coefficients, the substances (dyes) in the mixture separate. The distances traveled by substances A and B, and the solvent (mobile phase), respectively, would then be recorded. Separation efficiency is presented as R_f (response factor) values, where R_f is the ratio of the distance traveled by a substance being separated to that of the solvent (mobile phase).

The ability of a solvent to keep a substance in solution can be termed its "solvent power" with respect to that substance. By visualizing a solvent as the mobile phase in TLC, it is clear that a solvent with higher solvent power should produce higher K_A and R_f values than a solvent with lower solvent power. TLC has been used to rank the solvent power of various petroleum solvents.³⁴

Apparatus:

- TLC glass microfiber paper.
- Dyes (Brilliant Blue and Disperse Yellow 9).

³³G. G. Esposito; H. H. Bauer, G. D. Christian, and J. E. O'Reilly; H. H. Willard, L. L. Merritt, Jr., and J. A. Dean.

³⁴G. G. Esposito.

Procedure:

1. Activate paper by heating it in an oven for 30 min.
2. Cut paper into strips that will fit into TLC jar.
3. Place a mark across paper approximately 2 cm from the bottom.
4. Pour solvent to be tested into jar to a level of about 1 cm.
5. Spot dye(s) on paper at the 2-cm mark.
6. Place paper into jar so that it remains vertical. The dye spots should be approximately 1 cm above the liquid.
7. Cover the jar so that the liquid and vapor can come to equilibrium.
8. When the solvent (mobile) phase nears the top of the strip, remove strip from bottle and mark solvent front (Figure 6).
9. Allow strip to dry.
10. Measure the distance traveled by the dyes from the starting line to the middle of the dye spot. Measure the distance traveled by the solvent front. The ratio of the distance traveled by the dye to that of the solvent is the R_f value.

Stoddard Solvent Analysis and Test Results

Samples of new and spent SS were obtained in 5-gal containers from Anniston Army Depot, AL. From these samples, new samples were prepared (test series 1) using different proportions of new and spent solvents (0, 25, 50, 75, and 100 percent by volume of spent solvent). The properties measured for this set of samples were Kauri-butanol value, viscosity, specific gravity, refractive index, and visible absorption.

An arrangement was made with the quality control officer at Anniston Army Depot to obtain solvent samples from a vat at various time intervals prior to failure and removal of the solvent. The physicochemical properties measured for this series of time-study samples (test series two) provide the transient properties profile of the solvent. Nine periodic samples were received, including some taken the day the solvent was charged and the day it was discarded. The solvent usage life was 22 days. It was learned that when SS is charged to a vat (50 to 60 gal), 2 gal of motor lubricating oil are added to minimize drying of hands and other dermatological effects on the workers.

The new and spent SS samples were analyzed by gas chromatography (GC), and some of the many components present in these solvents were identified (see **Cleaning Mechanisms** above). Again, the physicochemical properties measured were:

- Kauri-butanol value.
- Viscosity.
- Refractive index.

- Specific gravity.
- Electrical conductivity.
- Visible absorbence.
- Thin-layer chromatographic profile.

The results of these measurements are described for two sets of conditions: (1) test series 1, i.e., laboratory simulation of solvent contamination by mixing various proportions of new and spent solvent (0, 25, 50, 75, and 100 percent by volume of spent solvent), and (2) test series 2, i.e., authentic time-study series samples.

Gas Chromatographic Analysis of Stoddard Solvent

An attempt was made to identify the primary constituents of SS using GC. The equipment used for this analysis was a Varian model 3700 gas chromatograph. All n-alkane constituents were identified. Figure 7 shows a typical chromatogram of new SS. This chromatogram contains many peaks; the four major n-alkane components were identified as decane, undecane, dodecane, and tridecane. The n-alkanes generally are higher boiling compounds than their respective isomers. This is true because n-alkanes have the greater hydrogen bonding due to lower steric hindrance of the molecules. Since most isomers of an alkane have lower boiling points than the n-alkane isomer, the series of peaks eluted prior to each n-alkane peak is speculated to be those of the branched isomers.

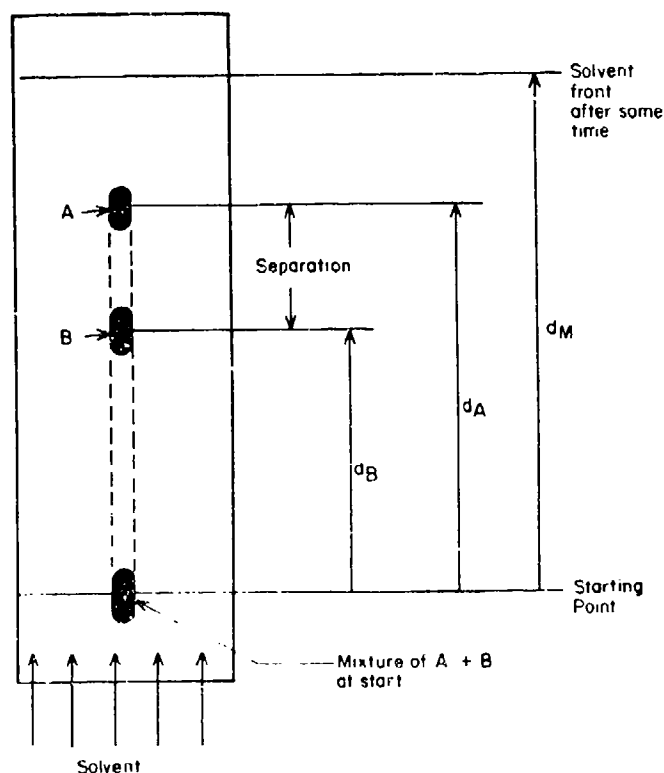


Figure 6. Mechanism of thin-layer chromatography.

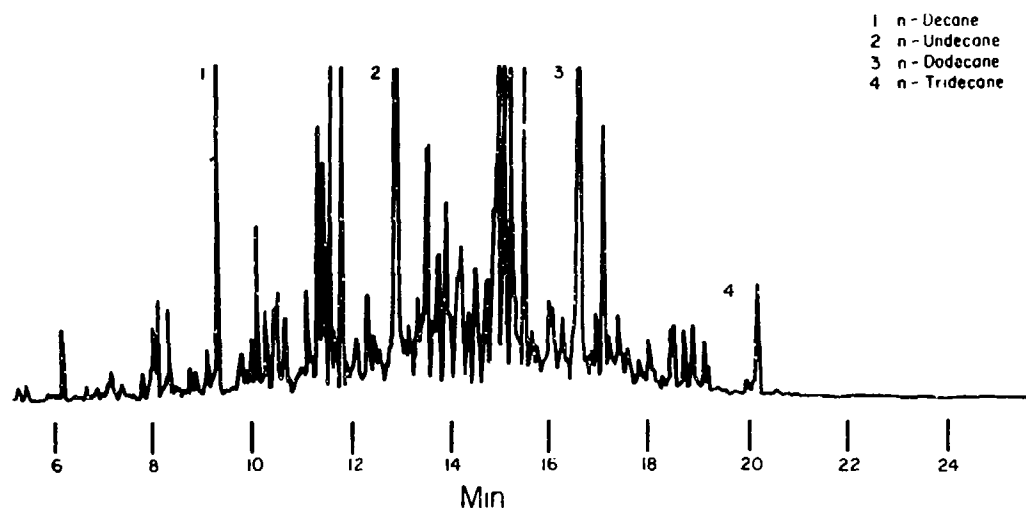


Figure 7. New Stoddard solvent chromatogram. DB-5 Fused Silica Capillary Column, 30 m x 0.25 mm (ID), column temperature 2 min at 60 °C, then raised to 220 °C at 4 °C/min and held 7 min. Detection and injection temperature: 300 °C. Sample: 0.05 μ L of new Stoddard solvents; split ratio: 200:1.

Figure 8 shows a chromatogram of spent SS. The chromatograms of new and spent solvent show no significant differences either in terms of new peaks or in concentrations of existing peaks.

The time-study samples also were analyzed by GC to obtain information on contaminants. Hexane was used as an internal standard to determine the concentrations of n-alkanes in the time-series and new solvent samples. There was a significant difference in n-alkane concentrations between the two sets of samples: the concentrations of decane and tridecane increased by 20 percent and dodecane concentrations decreased by 20 percent in the time-study samples compared with those in the new SS. The concentration of undecane remained practically unchanged.

The change in concentration can be attributed to the common practice of adding lubricating oil to new SS. The hydrocarbon composition of a typical crankcase lubricant consists mainly of saturated compounds having roughly a 2:1 ratio between naphthenes and paraffins (linear and branched-chain).³⁵ The paraffins present constitute about 25 percent by weight of the oil and consist of low-volatile compounds ($C_{11}+$). A lubricating oil also normally contains an additive package that may comprise 20 percent of the oil by weight.

There was no significant change in n-alkane concentrations within the time-study samples analyzed, i.e., between the first day's sample (new Stoddard plus oil) and the other eight samples.

³⁵Disposal/Recycle Management System Development for Air Force Petroleum Oils and Lubricants.

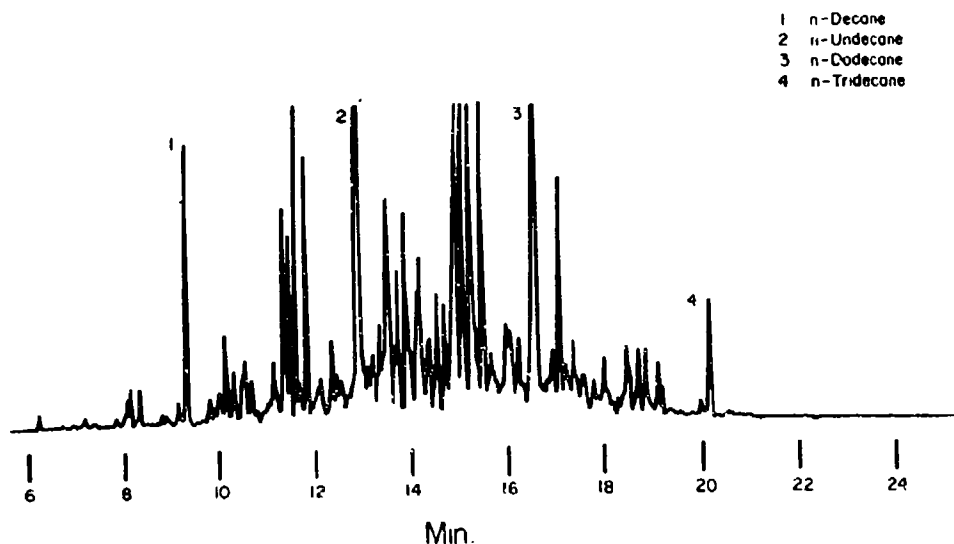


Figure 8. Spent Stoddard solvent chromatogram. DB-5 Fused Silica Capillary Column, 30 m x 0.25 mm (ID), column temperature 2 min at 60 °C, then raised to 220 °C at 4 °C/min and held 7 min. Detection and injection temperature: 300 °C. Sample: 0.05 μ L of spent Stoddard solvent (SS#1); split ratio: 200:1.

The n-alkanes and their respective isomers are responsible for the cleaning action of SS; hence, their apparent nondepletion in the cleaning operation indicates that spent SS could be restored to the specifications of new solvent by simple distillation, without requiring further reprocessing or makeup of lost crucial cleaning component.

Figure 9 shows the variation in solvent KBV for the simulated samples (test series 1). The KBV decreases linearly as the solvent becomes more contaminated. However, the magnitude of the decrease is not great enough to cause a significant decline in solvent power on the overall KBV scale. This finding indicates that the spent solvent is still potent provided it is decolorized. The ASTM standard on new SS specifies a KBV between 29 and 45. The new solvent from Anniston Army Depot has a KBV of 27.5, which is slightly lower than the minimum allowable value specified by ASTM.

Figure 10 shows the variation in KBV of the solvent for the time-study samples. The KBVs show no decrease for the first three samples that cover a 13-day period (one intermediate sample was not measured), then decrease by 0.8 percent and hold steady for the three subsequent samples (9 days), and finally decrease by another 0.8 percent to a value of 26.3 when the solvent was changed. Overall, the decrease in KBV is about 1.5 percent within the time period for which the samples were taken (22 days). The KBV for the first sample (day zero in Figure 10) is 2.9 percent below that of the new solvent due to the addition of lubricating oil. This factor accounts for 66 percent of the decrease that was observed in KBV over the total 22-day sampling period.

The relatively small overall change observed in KBV for the two sets of samples leads to two apparent conclusions:

1. The test is not sensitive enough to be effective for predicting solvent change. However, if a recycling facility exists, this test may serve as a quality control criterion for the reclaimed solvent.

2. The spent solvent does not lose its cleaning ability significantly, and removal of color and particulates will essentially rejuvenate it.

Viscosity

The variation in SS viscosity with increasing contamination (test series 1) is shown in Figure 11. The viscosity of the spent solvent increases by 37 percent over that of new solvent. The increase in viscosity varies quadratically with the percentage of spent solvent added (Figure 11). The significant change is not surprising because it is well known that intermolecular interactions between solute (i.e., the contaminants) and solvent increase as more contaminants are dissolved in the solvent, causing an increase in solvent viscosity.

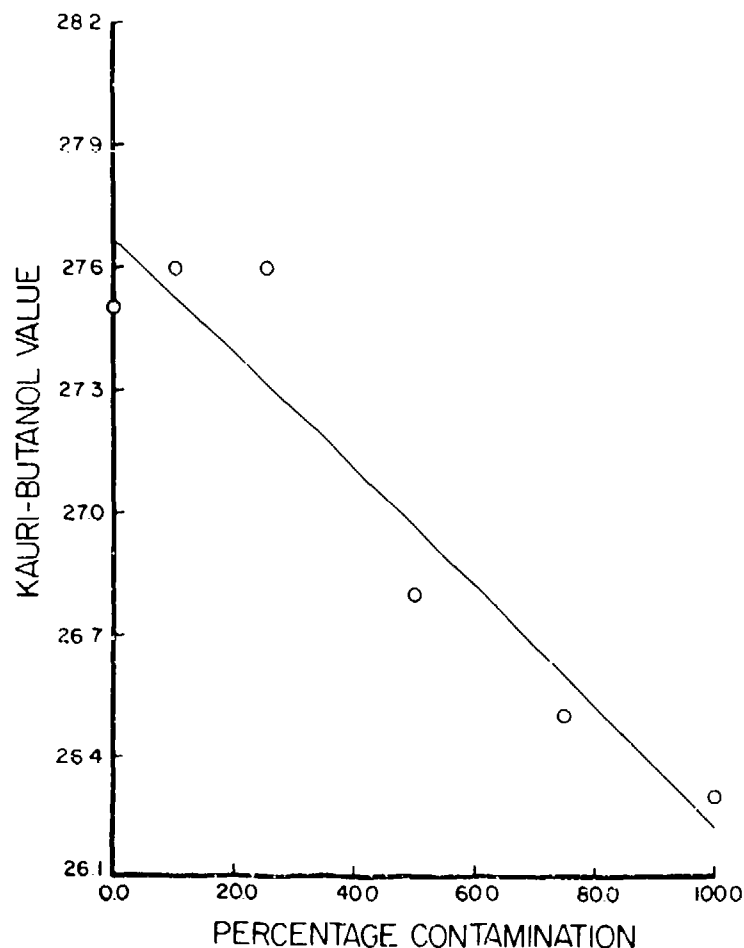


Figure 9. Variation in Kauri-butanol value of Stoddard solvent with contamination.

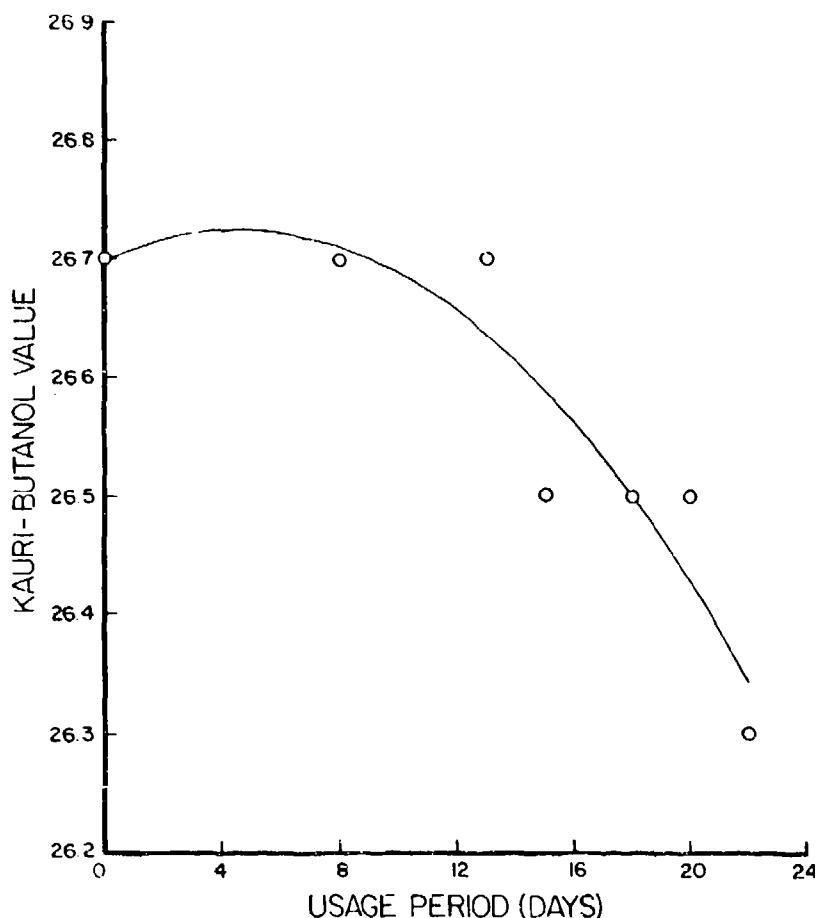


Figure 10. Variation in Kauri-butanol value of Stoddard solvent with usage time.

Figure 12 shows the viscosity variation of SS in response to increasing usage (time-series samples). The first sample shows an increase of about 20 percent over that of the new solvent (see Figure 11), primarily due to the addition of motor oil. The range of increase in viscosity is 14 percent for the entire usage period (22 days), which amounted to an increase of more than 35 percent over that of new solvent. As observed for the KBV measurements, the initial addition of motor oil contributes to more than 60 percent of the total increase observed in viscosity above that of the new solvent.

On the basis of these results, viscosity appears to be a fairly sensitive property. An important factor that must be taken into consideration while measuring viscosity is the effect of temperature. Care was taken so that all measurements were made at the same temperature (usually 20 °C). A small decrease in ambient temperature may cause a significant increase in viscosity and yield erroneous conclusions about the solvent condition. This situation can be remedied in one of two ways: (1) provide a constant temperature bath for immersion of the viscometer or (2) construct several nomograms for viscosity so that the measurements can be corrected to the same temperature. Another factor that must be considered in interpreting changes in a solvent's viscosity is the amount and size of particulates in spent solvent. The presence of particles larger than the diameter of the capillary in an Ostwald viscometer will interfere with liquid flow

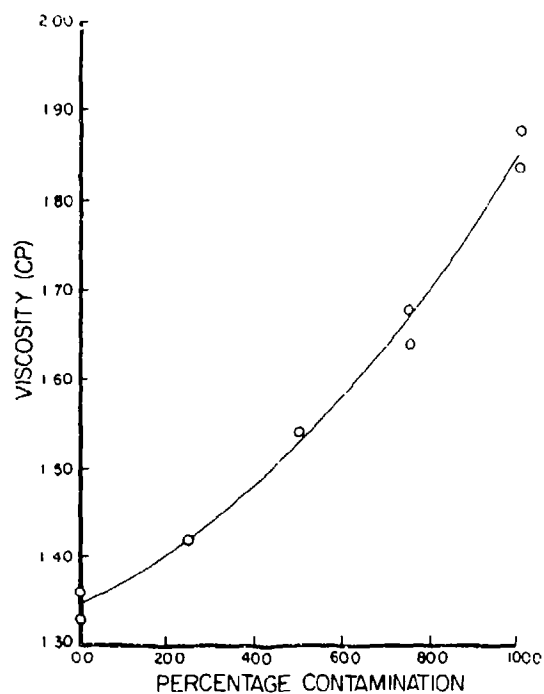


Figure 11. Variation in viscosity of Stoddard solvent with contamination.

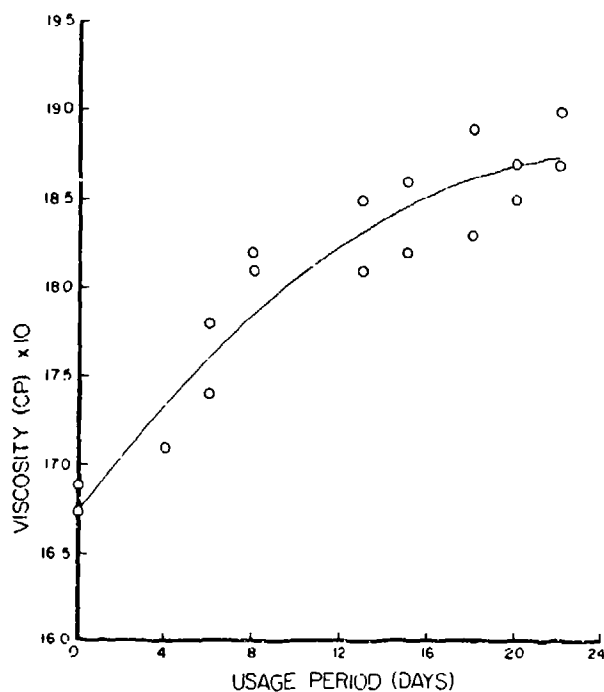


Figure 12. Variation in viscosity of Stoddard solvent with usage time.

through the capillary. For this reason, a spent solvent may have to be filtered prior to measuring its viscosity.

Refractive Index

Refractive index was measured using a Bausch and Lomb (Model ABBE-56) refractometer.³⁶ The refractive index of water was measured as 1.3309 at 30 °C, which compares with a literature value of 1.3319.³⁷

Figure 13 shows the variation in refractive index of SS with increasing contamination (test series 1). The measurements were made at two temperatures--22 and 31 °C. The two isotherms indicate that refractive index increases almost linearly with increasing contamination and decreases with an increase in solvent temperature.

The refractive index profile of SS (Figure 14) with usage time for the time-series samples (test series 2) indicates a fairly significant increase. However, refractive index measurements of contaminated halogenated solvents did not yield the degree of sensitivity seen in past studies with SS at Auburn University. The sensitivity of a solvent's refractive index thus may be contaminant-specific or solvent-specific. As a result, refractive index as an indicator of solvent contamination is promising for monitoring the SS contamination, but it may not be very effective with other types of solvents.

Specific Gravity

The variation in specific gravity for test series 1 is shown in Figure 15 as a function of volumetric percentage addition of contaminated solvent. The presence of dirt and other impurities generally increases the specific gravity of SS. The range of increase seen was about 1.7 percent.

Specific gravity was measured by filling a pycnometer with solvent, followed by weighing on an analytical balance and then repeating the procedure with water. A specific gravity meter was also used to compare and supplement the pycnometer procedure.

Figures 16 and 17, respectively, show the results obtained using a pycnometer and specific gravity meter. The reproducibility of the specific gravity meter measurements was within 0.001, whereas that using a pycnometer and analytical balance was around 0.002. The solvent in the pycnometer evaporates to some extent, thus contributing to a lesser accuracy and reproducibility than can be observed with the specific gravity meter. The specific gravity meter contains an oscillator which is filled with sample and then excited electromagnetically. The period of oscillation is a function of sample density. The density reading is automatically compared with the density of water (a value stored in a microprocessor within the meter), thus producing the specific gravity of the sample. In addition, the densities are evaluated at a set temperature by the meter--usually 20 °C--thus circumventing the need for a temperature control system.³⁸

³⁶ *Refractometer Manual*; G. J. Shugar, et al.

³⁷ *Handbook of Chemistry and Physics*, 57th ed. (CRC Press, 1976).

³⁸ *Mettler/Paar DMA 35 Density Meter*.

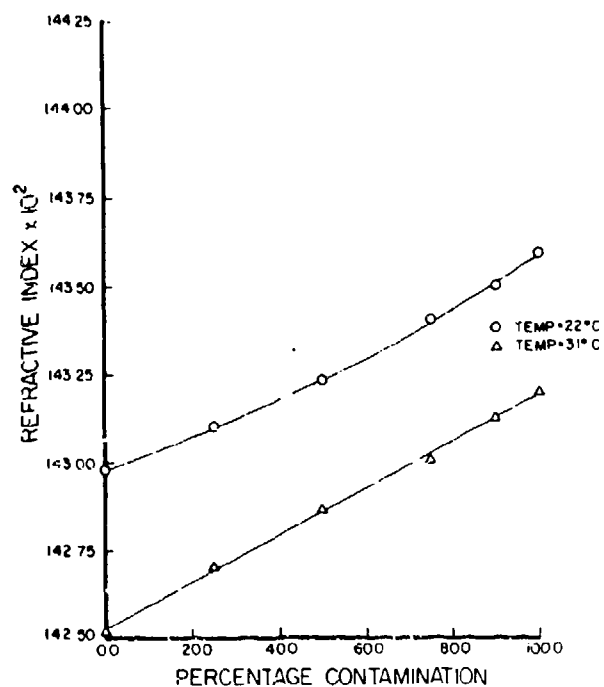


Figure 13. Variation in refractive index of Stoddard solvent with contamination.

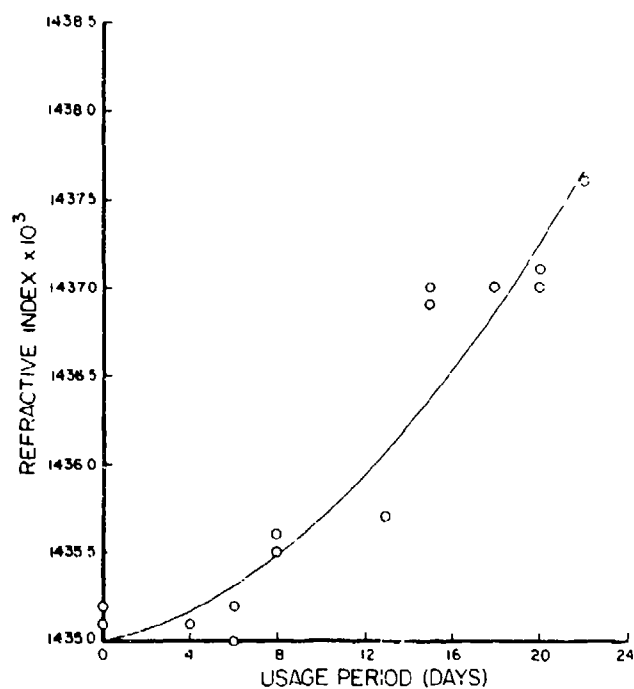


Figure 14. Variation in refractive index of Stoddard solvent with usage time.

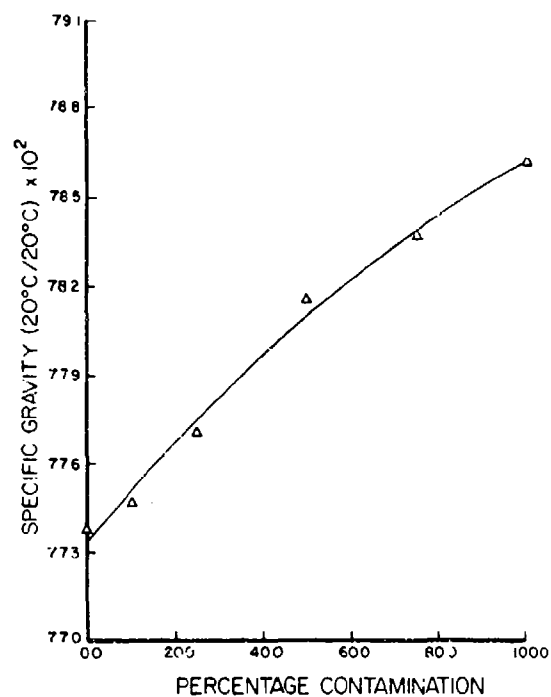


Figure 15. Variation in specific gravity of Stoddard solvent with contamination.

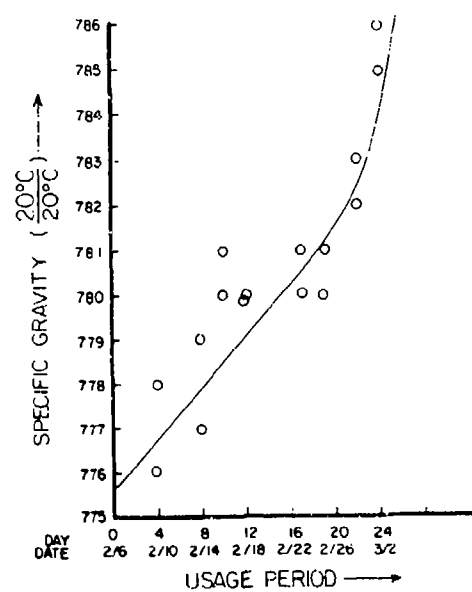


Figure 16. Variation in specific gravity of Stoddard solvent with usage time using a pycnometer.

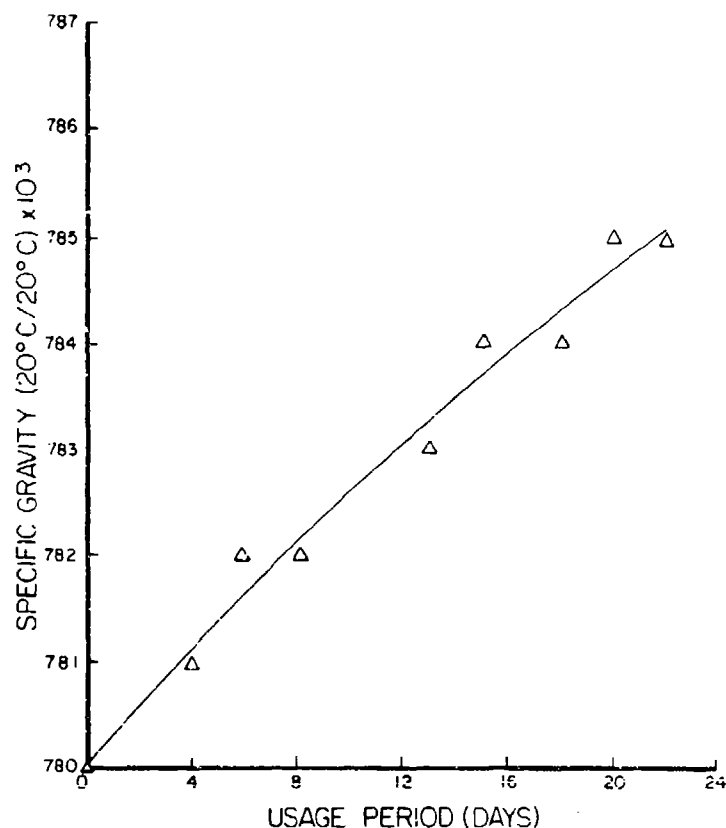


Figure 17. Variation in specific gravity of Stoddard solvent with usage time using a specific gravity meter.

Apparently, specific gravity is not as sensitive an indicator of solvent quality as is viscosity. However, using a specific gravity meter as a measuring tool makes specific gravity a quick, fairly reliable way to monitor solvent quality.

Electrical Conductivity

Figure 18 shows electrical conductivity measurements of SS as a function of simulated contamination (test series 1). The test is easy to conduct and shows good sensitivity to contamination. The conductivity of spent SS decreases by 17.3 percent with respect to new solvent.

Figure 19 shows the conductivity profile of the time-series (test series 2) samples. In these results, the conductivity also decreases with usage time, i.e., with increasing contamination. The addition of motor oil significantly changes the conductivity of the first sample of the time-series samples (day zero in Figure 19) compared with that of new solvent (35 percent). Thereafter, the variation between the first sample and the final sample of the time-study samples is only about 5 percent. This finding shows that the addition of motor oil has a major effect on this property.

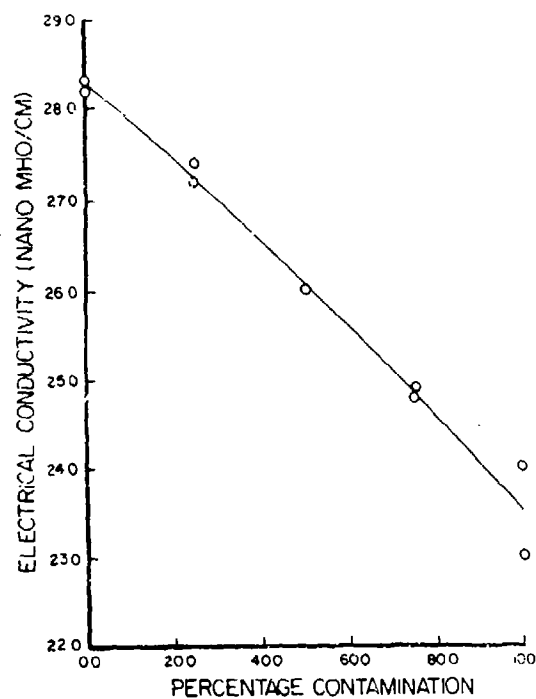


Figure 18. Variation in electrical conductivity of Stoddard solvent with contamination.

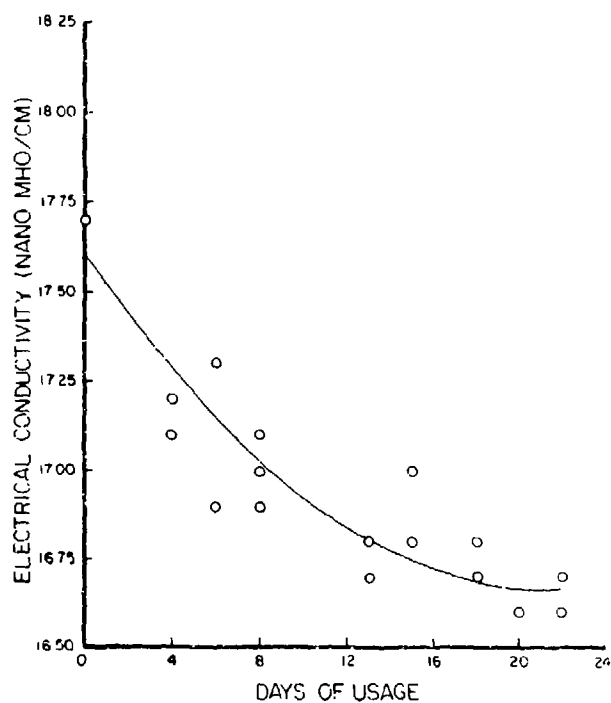


Figure 19. Variation in electrical conductivity of Stoddard solvent with usage time.

The effect of contamination was also studied by adding motor lubricating oil to new SS in different proportions. Figure 20 shows the variation in conductivity of SS after addition of oil. The conductivity initially decreases sharply with increasing oil concentration until about a 20 percent (v/v) oil concentration is reached. The conductivity keeps decreasing at a much slower rate until the curve shows a minimum at roughly a 50 percent (v/v) oil concentration. It then increases with further oil additions for concentrations of oil above 50 percent. As the concentration of oil approaches 100 percent (pure motor oil), the conductivity value approaches that of pure motor oil (which is slightly higher than the conductivity value for new SS). Figure 20 indicates that the conductivity variation for SS is more pronounced at low concentrations of contaminant, and is relatively insensitive at higher contaminant concentrations. It should be mentioned that the high concentrations of oil which cause a reversal in the conductivity slope (Figure 20) are never reached in practical cleaning operations.

Conductivity is a simple, quick test to measure solvent quality. The sensitivity of this test to solvent contamination is also very significant. The only disadvantage of this property as an indicator of solvent quality is the extra care required to clean and maintain the conductivity probe in good condition. The probe may require replatinizing annually if used extensively. This test also requires some form of temperature control because conductivity is highly dependent on temperature.

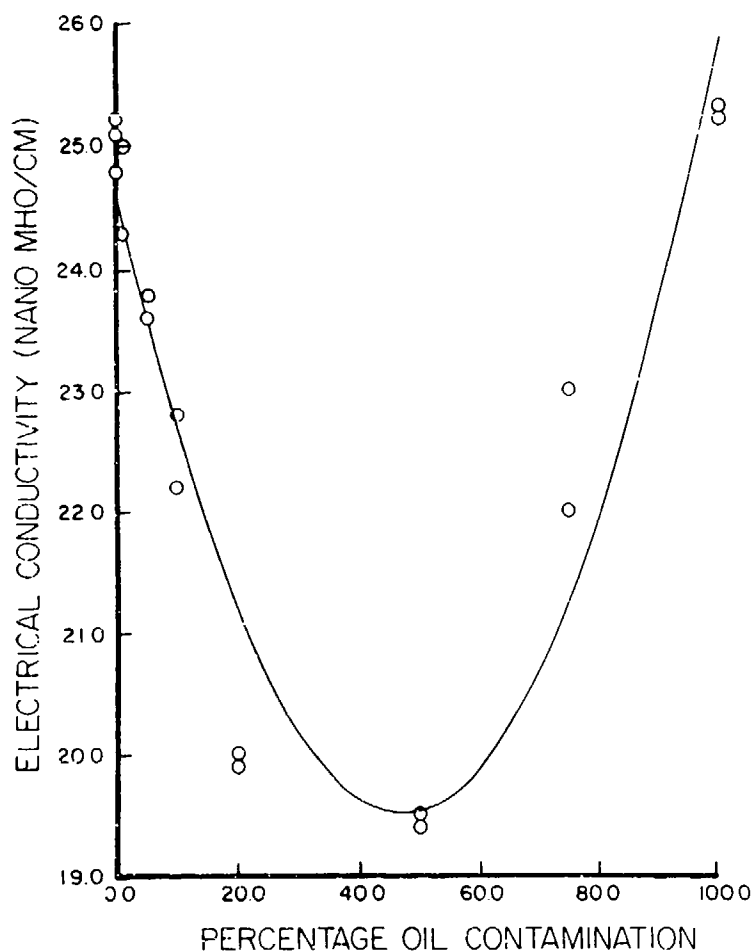


Figure 20. Variation in electrical conductivity of Stoddard solvent with oil contamination.

Visible Absorbance Spectroscopy

The new and spent solvents were first analyzed over almost the entire range of ultraviolet (UV) and visible radiation wavelength spectra (180 to 700 nm). A major peak was observed at 300 nm. However, most spectroscopy studies on SS have been performed between 400 and 600 nm.³⁹ Accordingly, the investigation was limited to this range of visible radiation.

The visible absorbences of new and various proportions of spent solvent (test series 1) are shown in Figures 21 and 22. The absorbences of new and mixtures containing 25, 50, 75, and 100 percent spent solvent were measured at 400, 450, 500, and 600 nm. In Figure 21, the absorbance was measured at a constant slit width for each of the four wavelengths (the slit width was set to a value at which the new solvent showed zero absorbance for each wavelength). All four curves in Figure 21 followed Beer's law except for a small positive deviation at higher concentrations of contaminants (>75 percent). This deviation from Beer's law may be due to intermolecular attraction between the solvent and its contaminants. In general, solvent absorbance increases with contamination and, as the wavelength decreases, the sensitivity (slope) of the plot increases.

Figure 22 shows the absorbance of constant composition spent solvent at different wavelengths. The variation in absorbance with the addition of various proportions of spent solvent is significant. Typically, a new solvent has a transmittance ranging from 91 percent at 450 nm to 99.1 percent at 600 nm.⁴⁰ In the spectroscopic analyses, new solvent had a transmittance ranging from 80 percent at 500 nm to 90 percent between 500 and 600 nm. The spent solvent shows a transmittance of 0.1 percent at 450 nm and about 35 percent at 600 nm. Absorbances at other concentrations between new and spent solvent are also shown in Figure 22; the increase observed in absorbance with increasing contamination is significant.

The time-study samples (time series 2) were also analyzed, and the absorbance profile is illustrated in Figure 23. The discoloration with use, as reflected by increased absorbance, increases almost linearly with usage time. The sensitivity of visible spectroscopy of SS increases with decreasing wavelength.

Visible light absorbance appears to be a reliable, consistent indicator of solvent performance. Absorbance can be measured quickly, and the necessary analytical instrumentation is fairly rugged and requires no special maintenance. For example, a dipping optical probe colorimeter is available that can be dipped directly into a vat or container to obtain an instantaneous readout.

Thin-Layer Chromatography (TLC)

Various dyes were tested to determine those most effective and sensitive for measuring the solvent power of SS. Brilliant Oil Blue BMS (Fischer) and Disperse Yellow 9 (Aldrich cat# 21225-3) worked the best on silica-impregnated glass microfiber sheets. The R_f values of these two dyes are shown in Table 5 for various solvents. Brilliant Oil Blue BMS separates into at least four color components; of these, there are fast-moving violet and blue-1 colors that can be used to characterize solvents of low aromaticity.

³⁹K. Johnson; I. Mellan; *International Fabricare Institute Bulletin T-447*; *National Institute of Drycleaning Bulletin Service*, T-413.

⁴⁰K. Johnson.

Disperse Yellow 9 adsorbs strongly onto the microfiber sheet, and only solvents with a high aromatic content can transport this dye. Benzene and its mixtures with new and spent SS proved to be very effective in moving both dyes. Aliphatic solvents, such as pure heptane, had no effect on the dyes, and their low KBVs verify that they are poor solvents.

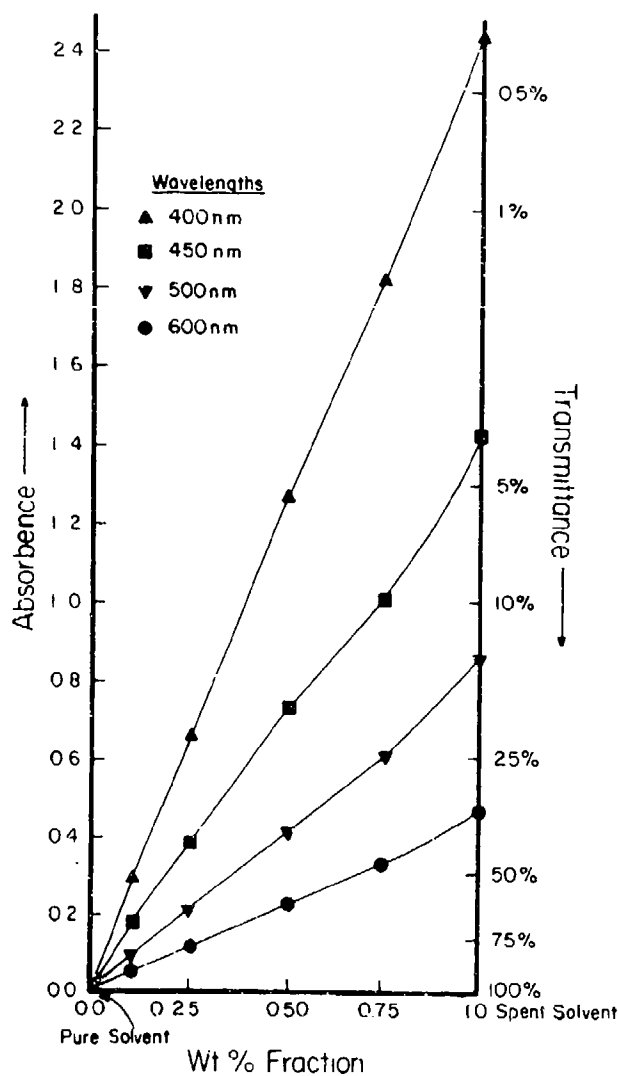


Figure 21. Absorbance of contaminated Stoddard solvent as a function of wavelength.

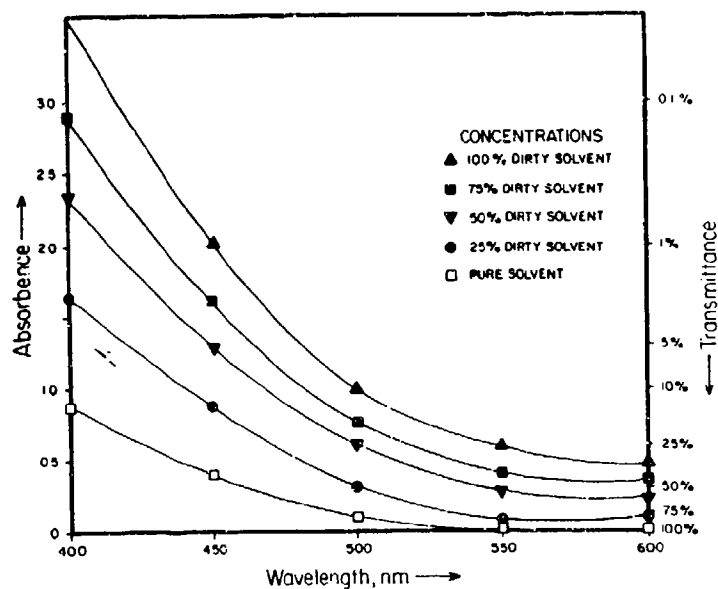


Figure 22. Absorbance of contaminated Stoddard solvent as a function of volumetric concentration.

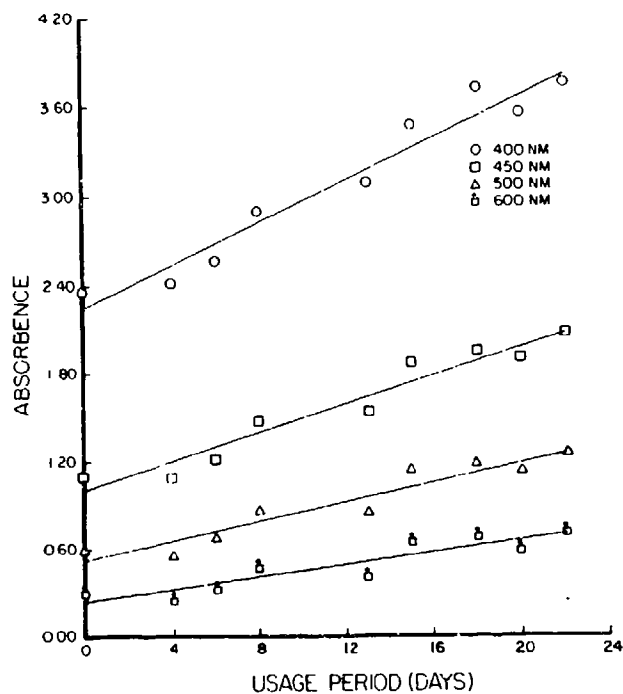


Figure 23. Variation in visible absorbance of Stoddard solvent with usage time.

Table 5
R_f Values of Different Dyes on Microfiber Paper

Solvent	Brilliant Oil Blue BMS				Disperse Yellow-9	K-B*
	Violet	Blue-1	Blue-2	Blue-3		
Heptane	>0.0	>0.0	>0.0	>0.0	>0.0	17.1
Benzene	0.96	0.84	0.66	0.46	0.53	107.0
25% New Stoddard Solvent 75% Benzene (% Vol.)	0.93	0.73	0.56	0.30	0.23	87.2
25% Spent Stoddard Solvent, 75% Benzene (% Vol.)	0.90	0.71	0.51	0.24	0.23	87.2
New Stoddard Solvent	0.11	0.05	0.04	**	>0.0	27.6
Spent Stoddard Solvent	0.30	0.22	0.12	0.06	0.06	26.3
Spent Stoddard Solvent Distillate	0.13	0.09	0.06	**	>0.0	27.7
Spent Stoddard Solvent Bottoms	***	0.44	0.27	0.16	0.11	-

*Some K-B values are from literature; mixture K-B values were computed in proportion to the volume fraction of the pure components.

**This color did not separate distinctly from the dye source spot.

***The color of the solvent overshadowed the faint violet color of the dye.

Both dyes yielded better R_f values with spent SS than with new SS. This finding implies that the new SS becomes contaminated with aromatics during the cleaning operation. To determine the nature of the contaminating aromatics, the spent solvent was distilled and TLC analyses were conducted separately on the distillate and on the bottoms. The R_f values of the dyes with the distillate were identical to those of new SS. The R_f results for the bottoms were significantly better than those with distillate, new SS, and spent SS. This result indicates that the contaminants are heavy aromatics and cannot be distilled easily. This property is beneficial from the standpoint of solvent recycling.

Table 6 shows the R_f value of the dyes for the first and final samples of the time-study series. The final sample shows a small increase in the R_f values for the violet, blue-1, and blue-2 segments of the blue dye relative to the first sample. The R_f value of the yellow dye, however, is higher for the final sample by 40 percent over that of the first sample. This finding suggests that the contaminants contain aromatics, since the yellow dye moves well only in aromatics. However, the KBV for this sample shows no increase above that of the new solvent, which implies that the concentration of aromatic contaminants is very small.

R_f value determination requires an eye estimate of the height the dye travels. This method may lead to erroneous conclusions in cases for which there are minor differences in samples' solvent power. Overall, TLC provides an effective way to compare solvents with significant differences in solvent power, and also to roughly indicate the degree of solvent aromaticity.

Tables 5 and 6 show the KBVs for various solvents. There is a good correlation between R_f values and KBVs. The concept of applying TLC in quantitative determination of solvent power is simple and innovative, and can be used to supplement an established method such as the KBV test.

Rating the Test Methods

Results of the property tests were analyzed and quantified to obtain a relative rating of the methods. Table 7 shows how the test methods were rated. The criteria used for the rating were: sensitivity and reliability; reproducibility; ease of operation; operator training requirements; equipment costs, and maintenance cost.

Table 6
R_f Values of Different Dyes in the Time-Study Series

Solvent	Brilliant Oil Blue BMS				Disperse Yellow-9	K-B
	Violet	Blue-1	Blue-2	Blue-3		
SS #2 (2/6/86)	0.40	0.27	0.18	0.09	0.06	26.7
SS #2 (2/28/86)	0.42	0.32	0.19	0.09	0.10	26.3

Table 7
Rating of Test Methods

	Column 2	Column 3	Column 4	Column 5	Column 6	Column 7	
Method	Sensitivity and Reliability	Reproducibility	Ease of Operation	Operator Training	Equipment Cost	Maintenance Cost (Annual)	Rating**
	A* (=4, Maximum) B (=3, Good) C (=2, Fair) D (=1, Minimum)	A* (=4, Excellent) through D (=1, Poor)	A* (=4, Excellent) through D (=1, Poor)	A* (=4, Minimum) through D (=1, Extensive)	A* < \$500 \$ 500 < B < \$1200 \$1200 < C < \$2900	A* < \$50 \$200 < B < 50 \$500 < C	
Visible Absorbance	A	A	A	A	C	A	3.8
Density	B	A	A	A	B	A	3.5
Viscosity	B	A	B	A	A	A	3.5
Electrical Conductivity	B	A	A	A	B	B	3.4
Refractive Index	C	A	A	A	C	A	3.0
Kauri-Butanol Value Test	C	A	B	B	A	B	2.8
Thin-Layer Chromatography	C	B	B	B	A	B	2.7

*A=4, B=3, C=2, D=1 Point.

**Rating = 1/10 (4 x Column 2 + 2 x Column 3 + Column 4 + Column 5 + Column 6 + Column 7).

Sensitivity and Reliability

These criteria evaluate the magnitude of change in a property with different levels of solvent contamination. The sensitivity of a method can be correlated as:

$$\%S = [(P_i - P_t) / P_i] \times 100 \quad [\text{Eq 6}]$$

where %S is percentage sensitivity, P_i is the property value of the first sample (test series 2), and P_t is the property of the "t"th sample.

Figure 24 is a plot of percentage sensitivity versus usage days for the time-study samples. Visible absorption has a sensitivity of 60 percent between the first and final samples. It is followed by viscosity, conductivity, and density with percentage sensitivities of 13.5, 6.2, and 1.2, respectively. KBV and refractive index methods have relatively lower percentage sensitivities of 0.2 and 0.1, respectively. TLC is not shown in Figure 24 because of the uncertainty involved in measuring R_f values. The levels of grading for each criterion rated were A, B, C, and D, or numerically, 4, 3, 2, and 1 points, respectively.

On the basis of sensitivity studies, visible absorbance was assigned an A ranking, followed by a B ranking for viscosity, conductivity, and density, and a C for KBV and refractive index.

Reproducibility

This factor accounts for the consistency of a method to repeatedly report the same values of a property when tested more than once. All methods showed good reproducibility.

Ease of Operation

This criterion rates the tests according to convenience, that is, the time required to prepare reagents (if necessary) and perform the tests. Visible absorbance, refractive index, specific gravity (by specific gravity meter), and conductivity measurements can be performed rapidly and no reagent preparations are required. One drawback of the viscosity test is that the sample may have to be filtered prior to testing because large particles suspended in the solvent could clog the viscometer's capillary and impede the flow of solvent. KBV measurement requires preparation and weighing of Kauri-butanol solution followed by titration with SS. To perform TLC using glass microfiber paper, a preheating stage is required, and dye solutions have to be prepared prior to use. Consequently, viscosity, KBV, and TLC were ranked lower than the other tests for this criterion.

Operator Training

This criterion rates the preparation and training required by the operator to perform the tests satisfactorily. All test methods in this study are fairly simple and do not require substantial operator training. However, KBV and TLC require relatively more preparation and training as well as operator judgment.

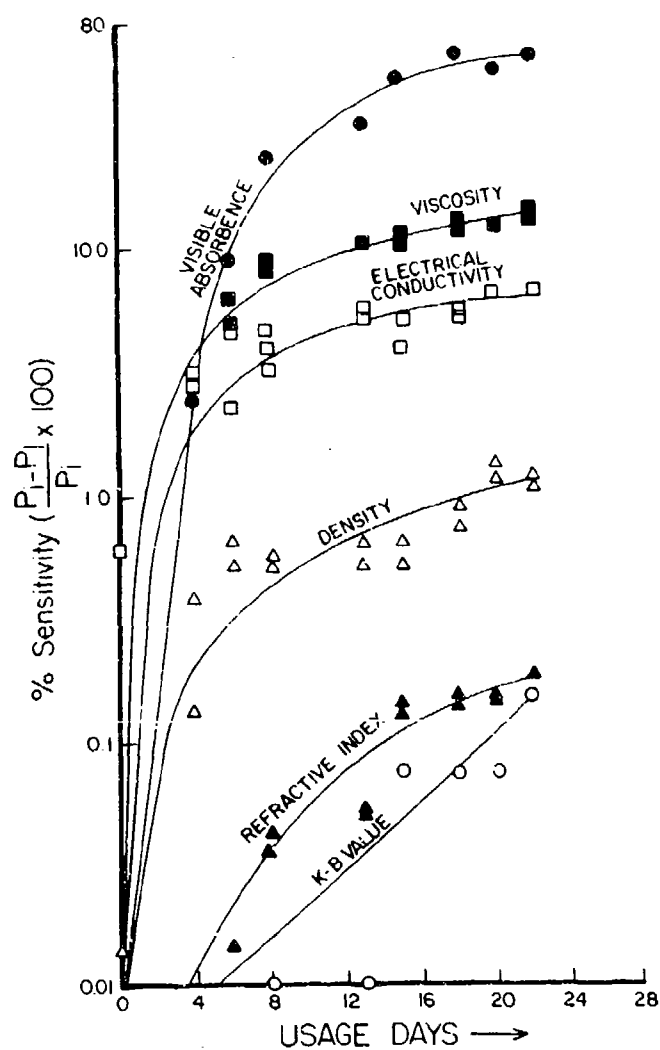


Figure 24. Sensitivity of measurement techniques.

Equipment Cost

This factor is based on the capital cost of the apparatus required for performing each test. Tests requiring equipment that costs \$500 or less were ranked A, those costing higher than \$500 but less than \$1200 were ranked B, and those with a cost higher than \$1200 but less than \$2000 were ranked C. The costs were obtained either from equipment suppliers' catalogs or direct vendor quotes.⁴¹

⁴¹Fisher Scientific Catalog (1985); Thomas Scientific Catalog (1986-87); Brinkmann Instruments Co.

The viscosity apparatus consists of an Ostwald viscometer and a stopwatch; the KBV apparatus is basically a buret and an Erlenmeyer flask. These setups cost less than \$100 each and were ranked A.

A specific gravity meter and an electrical conductivity meter with the probe cost around \$1200 and \$1000, respectively, and were ranked B in this category. Refractometers and spectrometers/in-situ dipping probe colorimeters cost about \$2000 each; these tests were ranked C.

Maintenance Cost

An annual operating cost was estimated for each test method, taking into account the cost of chemicals, probes, and/or supplies necessary to conduct a test at least once a week. Maintenance cost for test equipment such as the viscometer, refractometer, spectrometer, and specific gravity meter involve buying routine cleaning supplies, and should not exceed \$50. Consequently, these methods were ranked A.

In contrast, KBV and conductivity methods as well as TLC analysis require chemical and material supplies costing about \$300 annually for each, in addition to routine cleaning supplies. The KBV measurement requires periodic supplies of Kauri-butanol solution. TLC analysis requires glass microfiber paper, dyes, and chloroform. Conductivity probes may have to be replaced annually or require a platinizing kit to replenish the platinum in a used probe.

The overall rating was determined by a formula shown in Table 7. Since sensitivity and reproducibility of a test are of prime importance, they were assigned weights of 4 and 2, respectively. Visible absorbance was rated as the best method, followed by density, viscosity, and electrical conductivity. Refractive index, KBV, and TLC were useful in specific conditions but did not satisfy all criteria of the rating.

Evaluating Batches of Spent Solvent

An important aspect of this study was to establish consistency of the test methods for random batches of spent solvent. To achieve this end, four batches of spent solvent, taken at different times, were obtained from Anniston Army Depot. The first sample (SS#1) was received in October 1985. The second set of samples was obtained in January 1986 and consisted of two samples (TSS#2 and BSS#2) taken from the same vat and at the same time but at different depths. TSS#2 was skimmed off the top of the vat, whereas BSS#2 was taken from the bottom of the vat. The time-series samples (SS#3) were taken in February 1986.

Table 8 shows the variation in physicochemical properties between TSS#2 and BSS#2 samples. The BSS#2 sample contained more particulate matter than did TSS#2. Hence, a significant variation in properties of the two samples would indicate that the amount of particulates affects the properties substantially. However, no significant variation was observed in physicochemical properties except in the absorbences at 500 and 600 nm. The significant variations in absorbences at these two wavelengths could mean that there was some stratification within the contaminated solvent. Occasional stirring may eliminate this problem.

The maximum variation in physicochemical properties among the three spent SS samples is shown in Table 9, and indicates good consistency among the three samples.

Table 8**Physicochemical Tests on Spent Stoddard Solvent Batch 2**

Test	Top Spent Batch 2 (TSS#2)	Bottom Spent Batch 2 (BSS#2)	Variation in Batch 2 (%)
Refractive index (22°C)	1.4373	1.4375	0.014
Electrical conductivity, micromho (23°C)	0.0230	0.0230	0.000
Specific gravity (17°C/17°C)	0.7860	0.7870	0.127
Viscosity, cp (18°C)	2.1000	2.2200	5.410
Kauri- butanol value	25.200	25.400	0.790
Visible absorbance:			
400 nm	4.000	4.000	0.000
500 nm	1.850	3.050	39.30
600 nm	1.210	1.540	21.40

Table 9**Physicochemical Tests on New and Spent Stoddard Solvent**

Test	New	Spent Batch 1 (SS#1)	Spent Batch 2 (SS#2)	Spent Batch 3 (SS#3)	Maximum Variation (%)
Refractive index (22°C)	1.4298	1.4360 (31°C)	1.4374	1.4376	0.11
Electrical conductivity, micromho/cm (23°C)	0.028	0.024	0.023	0.017	29.20
Specific gravity (17°C/17°C)	0.774	0.785	0.787	0.785	0.25
Viscosity, cp (18°C)	1.350	2.200	2.160	1.880	14.50
Kauri- butanol value	27.600	25.300	25.300	26.500	4.50
Visible absorbance:					
400 nm	1.010	3.370	4.000	3.770	15.80
500 nm	0.170	0.950	2.450	1.230	61.30
600 nm	0.000	0.440	0.380	0.690	44.90

The value shown for SS#2 is the average of experimental values for TSS#2 and BSS#2. The conductivity of the spent solvents showed the greatest variation (29.2 percent), whereas specific gravity values were remarkably close (0.25 percent) among the three samples.

The absorbance at 400 nm indicates a difference of 15.8 percent between SS#2 and SS#1 samples. This result may be due to greater particulate matter in SS#2 than SS#1. The observed difference in absorbance becomes insignificant considering the fact that, for absorbances greater than or equal to 3, the transmittance is negligible.

SS#3 had significantly lower viscosity and conductivity than the other spent samples. This lower viscosity indicates that it was less contaminated than the other samples. On the other hand, the lower conductivity would signify that it was more contaminated than the other samples. These deductions show that relying on just one test method may allow misleading conclusions, resulting in premature removal of solvent or, in some cases, unsatisfactory cleaning.

SS is a mixture of many compounds and there is substantial variation in the properties of new solvent from batch to batch. Thus, it is best to convert the property measurements into nondimensional quantities so that the rating criteria are independent of batch variations.

Table 10 shows the reconstruction of Table 9 into respective nondimensional properties for some of the test methods. The nondimensional quantities for the spent solvent are obtained by the following relationship:

$$NDP = | C_m - C_o | / s \quad [Eq 7]$$

where NDP is the nondimensional property under study, C_m is the measured property value of spent solvent, C_o is the measured property value of new solvent, and s is the estimated measurement error of a test method.

This relationship of NDP is arbitrary and can be changed to fit the requirements of a particular situation. For example, C_o could be substituted for s to obtain NDP. This NDP, as defined above, conceptually represents the magnitude of change in a measured parameter from the new solvent value to the spent solvent value relative to the measurement error of a method. (The average of the three solvent batches also is shown in Table 10). If the average NDP is taken as the cutoff point to change a solvent, it can be observed that only SS#2 satisfied the cutoff points of visible absorbance, viscosity, and specific gravity. The electrical conductivity cutoff point was exceeded only by the SS#3 sample. Sample SS#1 did not meet the cutoff limits of any of the tests.

Discussion of Findings

From the results of the physicochemical test methods, the following conclusions are proposed:

1. At present, DOD uses inadequate, empirical field tests for solvent management. No standard test(s) is being used for predicting the need to change solvent. Development of a test(s) will lead to optimal solvent usage without compromising cleaning performance.

Table 10**Nondimensional Property Data on Spent Stoddard Solvent**

Test	Estimated Measurement Error	Spent Batch 1 (SS#1)	Spent Batch 2 (SS#2)	Spent Batch 3 (SS#3)	Average
Electrical conductivity (nanomho/cm)	0.300	13.3	16.0	36.7	22.0
Specific gravity	0.001	11.0	12.5	11.0	11.5
Viscosity (cp)	0.020	42.5	40.5	26.5	36.5
Visible absorbance: 400 nm	0.010	235.2	299.0	275.2	269.8

2. Laboratory tests show that some physical, chemical, and electrical properties of SS can be used successfully as criteria to identify spent solvents. Visible absorbance was rated as the best criterion among the methods evaluated. Specific gravity, viscosity, and electrical conductivity were also determined to be effective criteria. Kauri-butanol value, TLC, and refractive index methods did not satisfy all of the requirements for reliable criteria, but they are useful in specific situations.

3. These criteria were tested over several batches of spent solvent and were found to be consistent. However, the identification of spent solvent is most accurate when at least two or more criteria are used; reliance on a single criterion may occasionally lead to erroneous conclusions, resulting in either premature removal of solvent or unsatisfactory cleaning performance through prolonged use.

4 RECLAMATION AND REPROCESSING TECHNIQUES

Most solvents identified in large quantity in waste streams at military installations can be recycled using reclamation equipment, e.g., filtration or distillation units. Reclamation by filtration is mostly limited to transmitter and electrical equipment coolants (e.g., FC-77, DC-200, and 25E-F15 coolants). The filters consist of 0.1-micron synthetic fibers.^{4 2}

The other recycling technique, which is the most prevalent, is distillation to separate volatile solvent materials from less volatile contaminants. There are two major distillation methods used in reclaiming solvents: simple flash distillation and fractional distillation. The particular method used depends on the types and amounts of solvent and contaminants, and the specifications set for the reclaimed solvent. In most situations, solvent separation can be effected by simple distillation, with no enrichment trays or packing required. Proper segregation of the various solvents is necessary to reclaim the material by simple flash distillation. Fractional distillation in which the column has an enrichment tray or packing section is used when either solvent purity specifications are stringent or segregation of used solvents is not practiced properly.

This study is limited to a general discussion of simple distillation reclamation, with a more detailed look at batch distillation. DOD has identified batch distillation as one of the most promising processes for solvent recycling on military installations.

Methodology

A pure liquid boils when its vapor pressure equals the ambient pressure. In the case of a mixture, the total mixture vapor pressure must equal the ambient pressure to allow boiling. A pure component boils at a specific temperature, at a given pressure, known as the boiling point (BP). For example, at 1 atm pressure, water boils at 100 °C. A multi-component mixture boils within a temperature range, depending on its composition.

A liquid's BP decreases as the applied pressure decreases. Figure 25 shows the behavior of several halogenated solvents. As an example, methylene chloride boils at 40 °C at atmospheric pressure (760 mm mercury). However, if the ambient pressure is reduced to 400 mm of mercury by applying vacuum, the boiling point of methylene chloride is lowered to 25 °C. This property can be advantageous for high-BP solvents (e.g., SS) if the solvent decomposes, flashes, or ignites above a certain temperature. By knowing the solvent's flashpoint, distillation can be performed at a temperature lower than that value, which ensures safety. The BP can be lowered by using vacuum or by adding an azeotropic component such as water. When water is added to an immiscible solvent, two distinct liquid phases form. The added vapor pressure of water causes the liquid to boil at a lower temperature than if only solvent were present. The significance of codistillation with water or steam is that the solvent can be reclaimed at a temperature lower than its normal BP as illustrated in Table 11. The most common method of codistillation is to add live steam to the charge in the distillation chamber.

The three basic functions of batch distillation are evaporation, enrichment, and collection. Figure 26 outlines these three functions on a typical commercial distillation unit.

^{4 2}J. B. Systems, LaGrange, GA.

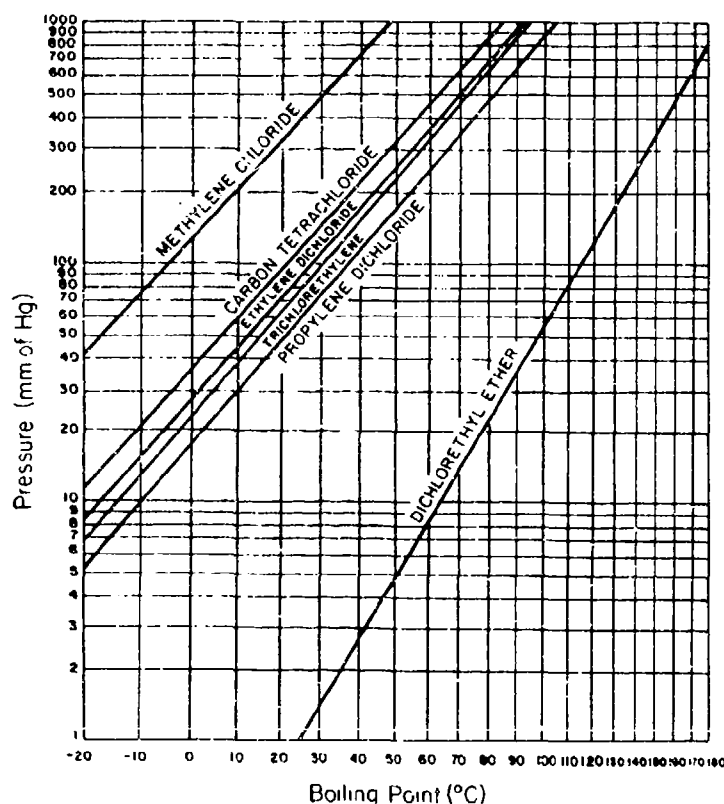


Figure 25. Boiling point variation with pressure for various chlorinated solvents.
(Source: I. Mellan, *Industrial Solvents*, 2nd ed. [Reinhold, 1950]. Used with permission.)

In simple batch distillation, spent solvent is first charged to a vessel. The liquid charge is boiled and the vapors are condensed and collected as purified solvent. The contaminants are left behind in the vessel.

The particular unit shown in Figure 26 uses live steam injection to evaporate the solvent. Another codistillation method is to use an electric heat source and add water to the charge. The liquid distillate is pumped to a gravity separator to remove the water, and the clean solvent is sent to storage.

Evaporation

The important factors in the evaporation stage of distillation are:

- The rate of evaporation is determined primarily by the rate at which heat is supplied to the distillation vessel.
- At very high temperatures, the solvent could degrade. Reducing the pressure within the system lowers the boiling point. Also, equipment limitations may prevent the use of extremely high temperatures.

Table 11

**Comparison Between Normal Boiling Points of Different Solvents and
Codistillation Boiling Point With Water***

Solvent	Boiling Point (°F)		Solvent Phase: Water Phase Ratio
	Atmospheric	Codistillation	
Hexane	157	142.9	25.3:1
Heptane	209	174.8	9.87:1
Stoddard	308-316	204	0.9:1
Benzene	176	157	10.24:1
Toluene	232	185	3.95:1
Xylene	261-318	202.1	1.5:1
Trichloro- ethylene	189	163.8	9:1
Tetrachloro- ethylene	249	189.7	3.4:1
1,1,1-Tri- chloroethane	166	149	15.8:1
Methylene chloride	104	101.2	61.5:1
Freon TF	117.6	112	9.5:1
Freon 112	199	166	8.5:1
MIBK	241	190.2	4.1:1

*Source: DCI International, Indianapolis, IN. Used with permission.

Two ways of lowering the boiling point are: (1) operate under a vacuum, i.e., use vacuum distillation, or (2) use a mass transfer medium. For example:

- Use codistillation with an insoluble lower BP material such as water. In this case, an azeotropic mixture will boil at a lower temperature than pure solvent.
- Pass a stripping vapor such as steam through the solvent. The steam heats the solvent, raising the vapor pressure while mass transfer occurs from the solvent to the water vapor phase.

Enrichment

As seen from the typical commercial distillation unit, the enrichment section usually plays a very small part in solvent reclamation. The enrichment section in this commercial distillation unit consists of a mist impinger.

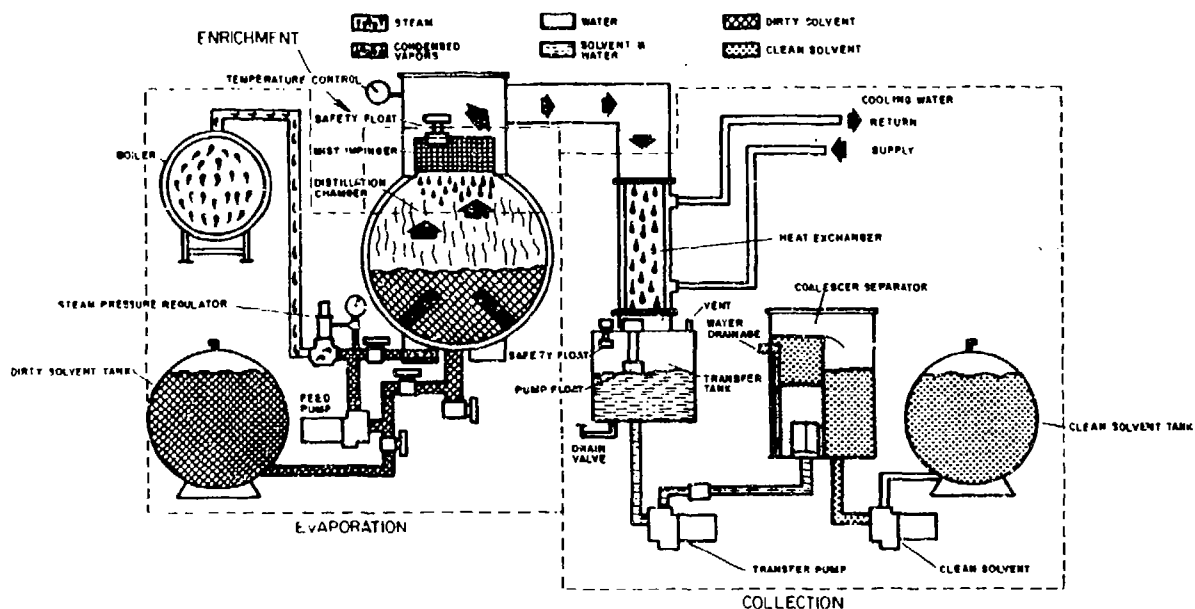


Figure 26. A typical commercial bath distillation unit. (Based on the Dyna I System, Live Steam Injection Model, DCI Corp.)

Condensation and Collection

The condenser is the main piece of equipment within the collection section (see Figure 26). In the condenser, the solvent vapors are cooled either by air, water, or refrigerant, and are condensed to a liquid. It may be necessary to separate the two immiscible liquid phases collected (e.g., water and solvent) by gravity settling and decanting.

Problems in Batch Distillation Operations

Several notable problems are involved in batch distillation. First, thermal degradation can be caused by poor heat transfer within the distillation chamber. The bottom of the chamber is usually hotter than the middle or top section. A very high bottom temperature could cause chemical breakdown of the solvent which may hinder its cleaning performance. Another major problem often encountered in batch distillation is solvent purity. Impurities in the recovered solvent or a loss of inhibitors during solvent recovery could hinder the overall effectiveness of the reclaimed solvent. Inhibitors or new solvent may have to be added to the recovered material to make it effective.

Solvent Characterization

Table 12 classifies solvents in terms of type and major process uses. For typical DOD applications, batch distillation is most attractive when the same unit is used to reclaim multiple solvents. The major solvents (excluding SS) that are recoverable by distillation are described below.

Table 12
Solvent Application on DOD Bases*

Operation Category	Solvent Type
Vapor degreasing	<u>Halogenated</u> 1,1,1-Trichloroethylene Tetrachloroethane Trichloroethylene
Cold-dipping vats	<u>Mineral Spirits</u> Stoddard Solvent PD-680
Paint and carbon removal	Methylene chloride with additives** (phenol, ethanol, petronate HL, water, toluene, paraffin, sodium chroma.e, methyl cellulose)
Paint thinners	Methyl ethyl ketone Toluene xylene
Metal preparation and precision cleaning	Alcohols Freons

*Source: R. W. Bee and K. E. Kawaoka, *Evaluation of Disposal Concepts for Used Solvents at DOD Bases*, TOR-0083(3786)-01 (The Aerospace Corp., February 1983).
Used with permission.

**Additives list was obtained from Robins AFB, GA.

Vapor Degreasers

Vapor degreasing of metal parts is done using chlorinated solvents. Because of EPA regulations, 1,1,1-trichloroethane is gradually replacing trichloroethylene and tetrachloroethylene at many DOD installations. This compound is less toxic than most halogenated solvents.

Paint Thinners

Paint thinner compounds include toluene, xylene, methyl ethyl ketone, and alcohols. The three major applications of paint thinners are to: (1) thin paint and coatings before application, (2) clean surfaces prior to painting and, (3) clean paint application equipment. The first two areas have wastes from which little or no solvent can be reclaimed; besides, thinners used in these areas require tightly controlled formulation. The third area produces a waste stream that yields a significant amount of solvent(s) which can be reclaimed. Solvent formulation for this application is not very stringent.

Thinners are generally mixtures of several solvents. Thus, it is not practical to use batch distillation to isolate each solvent unless several passes are made.

Paint Strippers and Carbon Removers

Paint strippers and carbon removers consist mainly of methylene chloride mixed with additives. The spent solvent has high disposal costs because it contains phenols and salts. Manufacturers of those strippers generally have a take-back policy because of their reprocessing capability. Material reformulation is required to reuse the solvent as a stripper.

Precision Cleaners

The typical cleaning solvents are ketones and esters, which are used for cleaning surfaces prior to painting. Freons are used to clean electrical parts and appliances, and for leak detection.

Batch Distillation Unit Design

Consultation with various solvent reclaimers and reclamation equipment manufacturers yielded a set of five criteria that should be considered to obtain the properly sized unit for individual operation:

1. Types of solvents to be reclaimed.
2. Types of contaminants in solvent.
3. Amount of solvent.
4. Utilities available.
5. Cycle times of solvents.

Since most installations must recycle more than one solvent, this information must be considered for all solvents. The type of solvent and contaminants must be specified to ensure proper selection of construction materials and waste-handling design.

The utilities available determine the heat source for the evaporation section. Most industrial batch distillation units are manufactured for steam heating but are convertible to natural gas or electricity.

Residence time of the solvents reclaimed is critical to proper sizing of batch units. The manager must consider the time required to reclaim each solvent used as well as the order of reclamation. Table 13 summarizes distillation equipment sizes. For large-scale operations, such as the 50 to 125 gal/hr range, continuous operation is applied.

Batch distillation requires little operator time. Most attention is required at the beginning and end of each cycle, with occasional monitoring during the cycle. Two methods used to determine the end of the cycle are temperature setpoint and cycle time. For a temperature setpoint system, once a certain temperature is reached, the operation is stopped. For the cycle-time method, a set amount of time is allowed to pass and the distillation is terminated.

Table 13
Typical Commercial Solvent Distillation Equipment*

Item	Size		
	Small	Medium	Large
Flow rate (gal/hr)	15	15-50	50-100
Operation type	Batch	Batch or continuous	Continuous
Solvents reclaimed	Paint thinners, chlorinated solvents	All solvents	All solvents
Attention required	Automated shut-down at end of batch	Automated, requires operator attention at end of batch	Automated with occasional operator checks
Cost (1987 dollars)	3,000-5,000	30,000-60,000	60,000-100,000

*Source: R. W. Bee and K. E. Kawaoka, *Evaluation of Disposal Concepts for Used Solvents at DOD Bases*, TOR-6083(3786)-01 (The Aerospace Corp., February 1983). Used with permission.

Solvent distillation equipment ranges in size from small, independent units (0.5 to 15 gal/hr) to large units capable of processing 100 gal/hr or more (Table 13). The small units are generally available in both atmospheric and vacuum distillation modes. These systems are self-contained and require only electrical and cooling water supply connections. The large units require more extensive support facilities (e.g., a boiler). The units are modular and may have an operating lifetime of 20 years or more if maintained properly. The operating costs include labor, utilities, and maintenance material.

Operator time is required only when loading and unloading charges (in the case of batch distillation) and occasional monitoring. Because the types of solvents recycled are relatively constant, operation of the units is fairly easy and requires only a few weeks of operator training.

Utilities expenses consist of electricity and cooling water costs. The electricity cost is a function of solvent type and the degree of contamination in the used material stream, whereas cooling water requirements are consistent for all solvent types.

Table 14 shows distillation equipment costs obtained from two manufacturers. The sizes are based on the amount of product collected per hour. The DCI unit includes the still and separation equipment. When choosing a system, the installation must consider the parameters that will allow maximum flexibility (e.g., Robins AFB has a vacuum system to handle SS even though Freon, another solvent reclaimed, needs no vacuum). To optimize the reclamation of multiple solvents in a single unit, the order of reclamation also must be considered.

If a large inventory is not available, the solvent order may have to be staggered so that all solvents are reclaimed according to their rate of generation. In this case, proper

coordination between the waste generation schedule, reclamation schedule, and the usage schedule is essential. Optimization techniques, e.g., linear programming, may be useful in this regard.

Experimental Reclamation of Spent Solvent

Reclamation studies on spent SS consisted of investigating decolorizing and filtration methods along with batch distillation using bench-scale and pilot units. Before proceeding with any one recycling technique, the concentration of chlorides in spent solvent samples was determined. This step is important because, if a substantial amount of chlorides is present in the spent solvent, it may carry over in recycled solvent and could pose potential health hazards to workers upon reuse in open vats.

Chloride Analysis

The ASTM standard test method requires combustion of the sample in a Schoniger combustion flask followed by a potentiometric titration. This method was attempted but found to be time-consuming and relatively insensitive to low chloride concentrations. Combustion of the oil sample in a Parr Bomb, followed by an Argentometric titration, was then tried and found more suitable.⁴³ A small sample of waste oil in a Parr Bomb with 10 mL of $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ solution was charged to 24 atm with oxygen and ignited. The bomb was next allowed to sit for 10 min and was then quantitatively rinsed with deionized water to a volume of 100 mL. Potassium chromate indicator solution (1 mL) was then added and the solution adjusted to a pH range of 7 to 10. The solution was then titrated with 0.0141N silver nitrate solution until a distinct color change took place. The results correlate well with the Beilstein test.⁴⁴ The chloride test results indicate that samples of spent solvent (SS#1) contain about 1000 ppm of total chloride. This concentration is well below the 4000-ppm level set by EPA for hazardous wastes.

Table 14
Typical Distillation Equipment Costs

Manufacturer	Size (gal/hr)	Cost (\$)	Additional Costs for Vacuum Systems (\$)
DCI*	100	42,600	7,690
500	63,100	11,200	
1000	77,800	15,700	
Gardner**	50	50,000	Included
100	70,000	Included	
200	103,000	Included	
500	133,500	Included	

*Data obtained from DCI Corp., 5752 W. 79th St., Indianapolis, IN.

**Data obtained from Gardner Machinery Corp., 700 N. Summit, Charlotte, NC.

⁴³Evaluation of Chlorine Determination in Waste Oils, Contract No. 68-01-7075 (USEPA, 1968).

⁴⁴Development of a Field Test for Monitoring Organic Halides in Waste Fuels, Contract No. 68-01-7075 (Auburn University, 1968).

Decolorization and Filtration

An effort was made to isolate the contaminants by contacting the spent solvent with various oxidizing reagents. Sulfuric acid, hydrogen peroxide, and sodium thiosulfate produced a turbid emulsion (Table 15). Sodium hypochlorite and activated charcoal treatments resulted in some improvement in color. A proprietary type of clay^{4,5} produced the most significant improvement in the color of the spent solvent.

Figure 27 shows the effects of the successful reagents in terms of visible absorbance spectroscopic analysis. The curves with the highest and lowest absorbances are those of spent and new SS, respectively. The intermediate curves represent the degree of color improvement by contacting with some of the reagents listed in Table 15. Sodium-hypochlorite-treated solvent was rejuvenated to an absorbance level of 25 percent spent solvent.

Solvent treated with activated charcoal showed little or no change in the 400 to 450 nm range, but improved significantly in the 500 to 600 nm range. Viscosity measurement of the charcoal-treated solvent showed no appreciable difference relative to the spent solvent (1.82 cp). Spent solvent treated with clay showed absorbance characteristics similar to that of new solvent. The solvent treated with clay which was used previously also showed a significant color improvement. Both clay and charcoal adsorbents can be contained in filter cartridges.

An important factor in determining the economic feasibility of clay filtering is how to safely dispose of what could be a voluminous amount of spent clay. Therefore, reclamation through clay filtration versus distillation would depend on the amount of solvent used at the installation.

Table 15

Regeneration Techniques Used To Reclaim Spent Solvent

Sodium Hypochlorite (6%) Reagents	Significant Change Effect
Absorbing Agents:	
Sulfuric acid	Turbid solvent
Hydrogen peroxide (30%)	Turbid solvent
Sodium thiosulfate	Turbid solvent
Sodium hypochlorite (6%)	Color improvement
Adsorbing Agents:	
Activated charcoal	Color improvement
Clay (china clay)	No change
Clay (Intusorial earth)	No change
Clay (proprietary)*	Significant change

*Data obtained from J. B. Systems, LaGrange, GA.

^{4,5}J. B. Systems, LaGrange, GA.

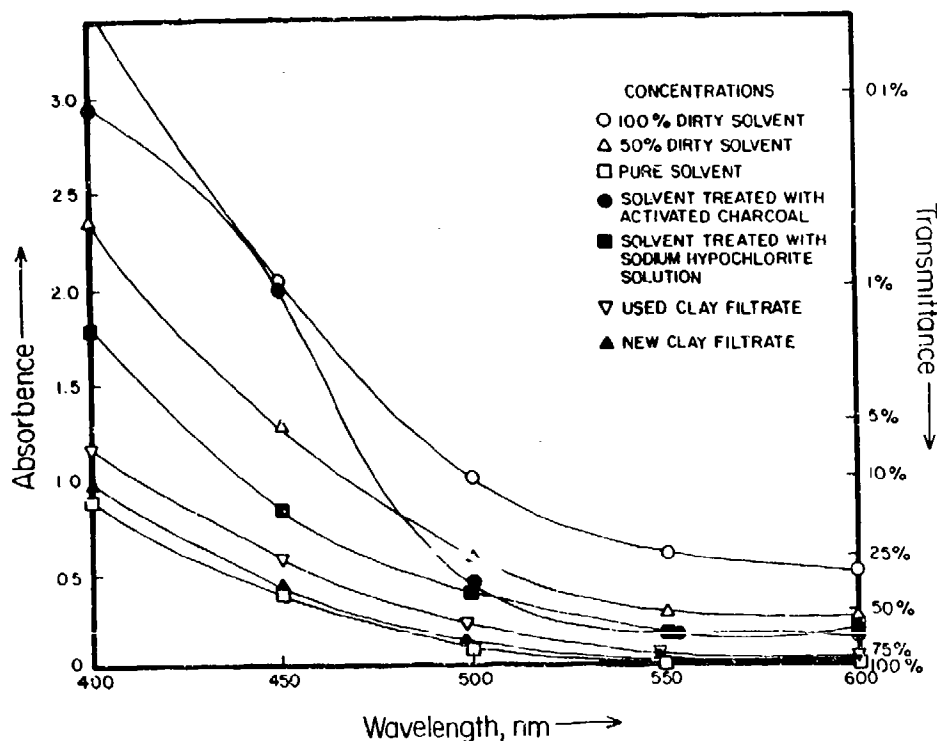


Figure 27. Absorbance of contaminated solvent treated with bleaching agents.

Batch Distillation

Distillation of spent SS was studied experimentally on a bench scale and in pilot units. The boiling range of SS Type II is between 350 and 412 °F. The bench-scale distillation unit was connected to a vacuum pump capable of producing less than 1 mm mercury absolute pressure. This pressure reduced the boiling range to 100 to 200 °F and approximately 90 percent of the solvent was recovered with ease. The reclaimed solvent was colorless and was analyzed using GC. The chromatogram was very similar to that of new solvent, with no significant new peaks or changes in concentration of major compounds detected. The distillation residue, or bottoms, was also analyzed. Many heavy compounds (beginning with dodecane and continuing to those substantially heavier than hexadecane) were observed in minute concentrations. A TLC analysis of the bottoms showed that R_f values of the dyes in bottoms were significantly higher than those with distillate, new, and spent SS (Table 5). This finding indicates that the residue probably contains high-BP aromatics and/or polar species.

The Auburn Waste Oil Reprocessing Laboratory of Auburn University has access to a 15-gal batch distillation unit for fractionation studies. This pilot-scale unit was used to reclaim spent SS. Since the boiling range of SS is between 350 and 412 °F (Type II), water was added to the solvent to generate an azeotropic mixture that has a boiling point

substantially lower than that of the solvent alone (see Table 11). The azeotropic mixture containing the solvent and water vapor can be separated from impurities in the mixture, which do not form part of the azeotropic mixture. The water/solvent vapor is condensed and the water layer is separated by gravity.

Approximately 5 gal of spent solvent were charged into the still and 90 percent of the solvent was reclaimed. The reclaimed solvent was tested for quality and its comparison with new solvent is shown in Table 16. The properties evaluated were KBV, refractive index, viscosity, visible absorbance, electrical conductivity, and specific gravity. The properties of spent solvent show a significant difference compared with new and reclaimed SS. The properties of new and reclaimed solvent are remarkably close, thus indicating that the solvent loses no vital cleaning component during either reclamation or previous usage.

For SS, the visible absorbance, viscosity, electrical conductivity, and specific gravity appear to give the best indication of when to remove solvent from a vat, and also can be used to perform quality control checks of recycled solvent. For trichloroethylene and other halogenated solvents, absorbance, electrical conductivity, and acid acceptance value give the best measure of solvent contamination and quality after recycling.

Reclamation Economics

Robins AFB has reclaimed various spent solvents for several years. Table 17 shows the annual savings. These data indicate that Robins AFB is consistently saving up to \$0.5 million annually through solvent reclamation.

Table 16
Physicochemical Tests on New, Reclaimed, and Spent
Stoddard Solvent Samples

Test	New	Reclaimed by Distillation	Spent
Kauri-butanol value	26.5000	27.1000	25.3000
Refractive index	1.4394	1.4396	1.4375
Viscosity (cp, 20°C)	1.3500	1.3600	1.8000
Visible absorbance:			
400 nm	1.2900	1.3000	3.7900
500 nm	0.2800	0.3100	1.3300
600 nm	0.0300	0.0000	0.9900
Electrical conductivity (nmhos/cm)	22.0000	21.9000	14.8000
Specific gravity (26°C/26°C)	0.7740	0.7690	0.7860

Table 17
Material Savings Trend at Robins AFB by Reclamation*

Item	Fiscal Year			
	1982	1983	1984	1985
Material reclaimed** (gal)	5060	13,860	20,587	14,418
Material savings (\$K)	256.7	404.1	490.3	384.4
Cost avoidance (drums turn-in)	7.6	20.8	30.6	21.6
Gross savings (\$K)	264.3	424.9	520.9	406.0
Reclamation costs (\$K)	3.3	5.7	7.7	5.9
Total net savings (\$K)	261.0	419.2	513.2	400.1

*Source: Robins AFB, Warner-Robins, GA.

**Solvents reclaimed were FC77, Freon 113, trichloroethylene, and isopropyl alcohol.

A literature survey on solvent reclamation at other DOD bases indicates that annual cost savings are already significant at installations that reclaim solvent; thus, the savings could be substantial if this practice were applied to all DOD installations. Table 18 summarizes the potential cost savings (annual) for military bases.⁴⁶ Lee et al. have estimated the potential savings if most of the solvents used at NARFs were reclaimed.⁴⁷ These savings are shown in Table 19, and range from \$0.35/gal for Stoddard to \$8.40/gal for Freon TF. The potential savings for the Navy amount to \$1.1 million by reclamation of spent solvents at the NARFs.

A rough estimate of distillation costs by Bee and Kawaoka shows that about \$0.50/gal of solvent is incurred for a 50-gal/hr distillation unit.⁴⁸ The cost of new SS is around \$1.80 to \$2/gal.⁴⁹ Thus, the potential savings is fourfold in the case of Stoddard, and even more for halogenated solvents.

⁴⁶R. W. Bee and K. E. Kawaoka.

⁴⁷H. J. Lee, I. H. Curtis, and W. C. Hallow.

⁴⁸R. W. Bee and K. E. Kawaoka.

⁴⁹Chemical Market Reporter (October 1986).

Table 18

Annual Cost Savings for Large and Small Bases (\$K)*

Solvent	Cost Avoidance per Base		Savings	
	New Material	Disposal	Each Base	All Bases
<u>Large Bases (29)</u>				
Trichloro-ethylene	74.250	36.000	110.250	3200
Stoddard solvent	39.000	9.900	49.500	1400
Paint stripper**	0	40.425	40.425	1200
Paint thinner	41.940	7.555	49.995	1400
Freon	28.512	3.037	31.549	500
Subtotal	183.702	96.917	231.719	7700
<u>Small Bases (124)</u>				
Stoddard solvent	11.880	3.000	14.880	1900
Paint thinner	5.130	1.000	6.130	700
Subtotal	17.010	4.000	21.010	2600

*Source: R. W. Bee and K. E. Kawaoka, *Evaluation of Disposal Concepts for Used Solvents at DOD Bases*, TOR-0083(3786)-01 (The Aerospace Corp., February 1983). Used with permission.

**Manufacturer take-back option.

Table 19

Summary of Reclamation Economics for Solvents Used at NARFs*

Location	Savings in Stoddard (\$K)	Savings in Six Most Used Solvents (\$K)
Alameda, CA	28.3	192.2
Norfolk, VA	7.5	194.2
North Island, CA	85.5	278.5
Pensacola, FL	18.0	297.5
Jacksonville, MI	2.4	126.7
Total	141.7	1087.0

*Source: H. J. Lee, I. H. Custis, and W. C. Hallow, *A Pollution Abatement Concept, Reclamation of Naval Air Rework Facilities Waste Solvent, Phase I* (Naval Air Development Center, April 1978).

5 TESTING AND RECLAMATION GUIDELINES

In implementing a used solvent management program, the installation DEH must be aware of the solvent types, quality and quantity of waste solvents, segregation practices, current disposal practices, and feasibility of on-/off-site recycling/disposal options. This report has discussed in detail the variety of possible testing procedures to determine the quality of Stoddard-type waste solvents and their reclamation by batch disposal. Two additional documents are available which describe the wide variety of other solvents used at DOD installations and explain management strategies.⁵⁰

Based on the test methods evaluated in this report, some general guidelines can be recommended for testing and reclaiming used solvents. These recommendations are summarized below.

Testing Used Solvents

Subject solvent samples to the following tests:

1. Measure the absorbence with an optical probe colorimeter or a hand-held spectrometer placed directly into a vat or container to obtain an instantaneous readout of visible absorbence (at 500 nm). Assign a rating value (0 to 4) based on Table 20.
2. Measure the specific gravity using an electronic specific gravity meter or pycnometer as described in Chapter 3. Assign a rating (0 to 3) based on Table 20.
3. Measure the viscosity using an Ostwald viscometer according to the procedure described in Chapter 3. Assign a rating (0 to 2) based on Table 20.
4. Measure the electrical conductivity with a conductivity meter and assign a rating (0 or 1) based on Table 20.
5. Sum the individual ratings in steps 1 through 4 above to obtain an overall rating for the solvent.
6. If the overall rating is greater than or equal to 6, the solvent can be considered spent and is a candidate for reclamation. Solvents with a rating of less than 6 should be reused.

The cutoff values presented in Table 20 are suggested based on the results of spent solvent tested in this work. They should be modified as further experience is gained with measurements at an installation.

⁵⁰B. A. Donohue and M. B. Carmer, *Solvent "Cradle-to-Grave" Management Guidelines for Use at Army Installations*, Technical Report N-168/ADA137063 (USA-CERL, November 1983); *Used Oil and Solvent Recycling Guide* (Robert H. Salvesan Associates, 1985).

Table 29
Test Criteria for Used Solvents

Rating	Tests			
	Absorbance (500 nm)	Specific Gravity (17 °C)	Viscosity, cp (18 °C)	Conductivity, nmho (23 °C)
0	< 0.6	< 0.773	< 1.35	< 22.5
1	0.6 - 0.8	0.773 - 0.779	1.35 - 1.85	> 22.5
2	0.8 - 1.0	0.779 - 0.785	> 1.85	
3	1.0 - 1.2	> 0.785		
4	> 1.2			

Reclamation

Onsite distillation is considered the most promising process for reclamation of spent solvents. It has been shown to be cost-effective, easy to implement, and easy to operate.⁵¹ The following procedures are recommended:

1. Locate solvents for reclamation.
2. Determine the quality and quantity of waste solvents.
3. Select and install suitable equipment and facilities for reclamation.
4. Provide shop and departmental segregation facilities and mandate handling procedures to assure minimum contamination of wastes with undesirable materials. Color coding may be useful.
5. Place the distillation apparatus into operation.
6. Test the reclaimed solvent according to procedures outlined previously, and categorize and store them for reuse.

⁵¹Higgins (1985).

6 CONCLUSIONS AND RECOMMENDATIONS

This study is investigating methods of testing used cleaning solvents to determine the point at which they should be reclaimed or discarded. To be successful at military installations, these tests would have to be accurate, consistent, and simple to perform in the field. This work also is examining methods of reclaiming spent solvents in an effort to reduce the amount of this material that must be destroyed. By recycling solvents, installations could save money on new material and disposal charges while ensuring that the amount of potentially hazardous waste solvent entering the environment complies with future regulations, which are expected to be stringent.

Phase I of this work focused on Stoddard solvents. The literature was surveyed to identify properties of these solvents and their current use at DOD facilities. The most common solvents used within DOD are vapor degreasers, cold-dipping cleaners, paint thinners, paint strippers and carbon removers, and precision cleaners.

Another literature survey generated a list of physicochemical tests with potential application at military installations. The methods were assessed, compared, and rated in terms of sensitivity and reliability; reproducibility; equipment cost; and maintenance cost. For most military cleaning operations, the methods showing the most promise in judging solvent quality, in order of decreasing preference, are: visible absorbance, viscosity, conductivity, density, Kauri-butanol value, and refractive index. Besides providing a meter for changing solvents, these tests could be used to monitor the quality of reclaimed product.

Solvent reclamation by filtration and/or distillation was investigated to determine the feasibility of using these techniques at installations. Based on the track records of these methods as reported in the literature, bench- and pilot-scale studies were conducted using spent solvents obtained from Anniston Army Depot. The results indicated that the cleaning properties of these solvents are not lost during either use or reclamation; thus, it would be technically feasible to reclaim these materials throughout DOD. In addition, these methods are economically attractive. Most solvents can be reclaimed using batch distillation, with the most cost-effective system handling distillation of multiple solvents in one unit. Simple units are available which may be able to reclaim up to 98 percent of the solvent. The payback period for such systems can be less than 2 years.

In some cases, filtration to trap particulates from the spent solvent is an effective method of reclamation. The filter material usually is some type of clay. It must be recognized, however, that the process generates waste clay and thus would be practical only for installations using small amounts of solvent.

Based on an evaluation of the testing and reclamation techniques available for Stoddard solvents, guidelines were developed for use in an installation waste solvent management program. A simple numerical rating system has been proposed to allow quick assessment of the solvent and determination of reuse versus recycle.

These findings suggest that substantial savings could be realized if solvents were reclaimed at all DOD installations that conduct regular cleaning operations with these chemicals. In addition, less waste solvent would be targeted for disposal, with the dual effect of lowering disposal/handling costs and resolving environmental issues. On this basis, it is recommended that all DOD installations which generate waste solvent explore the possibility of implementing batch distillation and/or filtration to reclaim spent solvents.

METRIC CONVERSION CHART

1 atm = 1.013 bar

1 gal = 3.78 L

1 in. = 25.4 mm

1 oz = 28.35 g

$^{\circ}\text{F} = (^{\circ}\text{C} \times 1.8) + 32$

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APPENDIX:

QUESTIONNAIRE USED IN SURVEYING THE FIELD AND RESPONSES

Questions

1. Does your facility use Stoddard solvent, PD-680, or mineral spirits? For what? How much? Where is it obtained? Describe the equipment and operating procedures.
2. How do you classify your cleaning operation? Do you require maximal, intermediate, or minimal cleaning?
3. How "clean" do your parts have to be? How is the degree of cleanness determined?
4. How can you tell if the solvent is doing its job?
5. Does (4) above involve any tests? What are the testing procedures? What are the details of the test? Are any written procedures available?
6. How long do you use your solvent? Does the time vary from one operation to another? For the same operation, does the time vary from season to season?
7. How often is the solvent changed? What determines the time for a change? Any makeup added? Are any other chemicals added?
8. Would better tests on when to change solvents be of any use to you? Do you have any problems involving solvent operations? Would increasing the time of solvent use before recycle be helpful?
9. What is done with spent solvent? Is it recycled?
10. What is the nature of the residue (i.e., mainly dirt, oil)?
11. When collecting samples for 2 percent weight test, where in reference to the height of the tank are the samples taken?
12. What is the size of the vats?
13. How deep is the residue at the bottom of the vats?
14. Is the cleaning operation stage-wise or a one-vat job?
15. Is the color of the spent solvent always the same from vat to vat and month to month?

Responses*

Anniston Army Depot

1. Anniston Army Depot buys PD-680 in bulk. The solvent is received in 2400-gal tankers and stored in underground tanks. It is then distributed as needed by a gasoline-type pump system. No information is readily available on where it is obtained. The basic operating procedure is to clean mechanical parts manually in a solvent rinse vat.
2. Parts require minimal cleaning under normal conditions.
3. Parts have to be clean enough to pass a wiping test with a clean white rag.
4. Solvent is ineffective if it leaves a residue or an oil film after drying. An increase in drying time may also be used to decide when to change the solvent.
5. QA inspectors regularly perform a contamination test on samples of solvent by centrifuging. If the solvent contains more than 2 percent solids, it is discarded.
6. The length of time a solvent is used depends on the parts to be cleaned and their condition.
7. Solvent is changed at least once a month and no makeup solvent or performance-improving chemicals are added to spent solvent to extend the usage period.
8. An increase in duration of solvent use is desirable.
9. Spent solvent is used as a fuel along with coal.
10. Residue left on the parts and detected as a result of the wiping test is a combination of dirt and oil.
11. Samples for the monthly test of 2 percent solids are collected by men in the shops. These samples are taken while the parts are being cleaned and are said to be fairly uniform.
12. The vats are approximately 3 ft wide, 4 ft long, and 3 ft deep.
13. There is a residue of varying depth at the bottom of some of the vats. Many of the vats are equipped with filters and do not build up any significant amount of residue.
14. The cleaning operation is a one-vat job, i.e., no stage-wise cleaning is performed.
15. The color variation of spent solvent is significant from shop to shop and month to month.

*Numbered responses correspond with numbered questions in the previous section.

325th EMS Wheel and Tire Shop (Tyndall AFB, FL)

1. PD-680 (Stoddard solvent). Used for removal of carbon deposits, grease, and dirt from aircraft wheels and wheel bearings. 700 gal. PD-680 is obtained through normal USAF supply channels. Two each degreaser vats, one used strictly for cleaning aircraft wheel bearings and the other strictly for aircraft wheels. The bearing vat is set in an agitating mode and bearings are cleaned for 30 min. The wheel vat is used for soaking. Soft plastic brushes are used to remove deposits from wheels after the wheels have soaked for at least 5 min.
2. Maximal cleaning.
3. Extremely clean. Through close inspection and experience.
4. The time period it takes to remove hardened deposits from aircraft wheels.
5. No.
6. Varies. Yes. Yes.
7. Depends on how dirty solvent is. Composition of PD-680 is broken down through prolonged use and, consequently, it takes longer to clean aircraft wheels and bearings. No. No.
8. Yes. No. Yes.
9. Disposition through USAF supply channels. Unknown.
10. Nature of residue is mostly dirt and grease.
11. Unknown.
12. 500-gal wheel vat and 200-gal bearing vat.
13. For changing, 1 to 2 in.
14. It is a one-vat job.
15. No. It varies from time to time; depends on how extensively used and length of time involved.

325th EMS Age Branch (Tyndall AFB, FL)

1. PD-680 (Stoddard solvent). Used for removal of grease, dirt, etc., from AGE components prior to disassembly for repair or overhaul. Also used for cleaning internal parts after a component has been dismantled and for equipment wheel bearings prior to repacking. We use an average of 50 gal per month. PD-680 is obtained through normal USAF channels. We use a degreaser vat for all cleaning operations requiring the use of solvent. Cleaning time is contingent on condition of item being cleaned, but normally takes 10 to 30 min per job. Brushes are used to help remove unusually severe deposits.
2. Maximal.

3. Very clean. Through close visual inspection.
4. By the time required for cleaning operations.
5. No.
6. It varies depending on frequency of use. Yes. Yes.
7. It varies depending on how quickly it becomes dirty or diluted. Time for change is based on how dirty it becomes. No. No.
8. Yes. No. Yes.
9. Disposal through USAF supply channels. Unknown.
10. Dirt and grease.
11. Tests not done.
12. 40 gal.
13. Approximately 0.5 to 1 in. when replaced.
14. One vat.
15. No.

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