

APPLICATION OF THE USED SOLVENT ELIMINATION (USE) PROGRAM TO THE ORDNANCE COMMUNITY*

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Summary

A DoD directive dated January 10, 1984, requested that the various services initiate a Used Solvent Elimination (USE) Program and eliminate the disposal of recyclable solvents as waste by October 1, 1986. As a result, the Ordnance Environmental Support Office (OESO) conducted a study to determine the USE Program's application to ordnance contaminated solvents and to compile tentative guidelines for the program's implementation within the ordnance community.

The Naval Ordnance Station was used as a vehicle for the project which included the following: inventories of (1) the types of solvents at NAVORDSTA, (2) possible contaminants in the solvents, (3) forms of recycling presently in use, as well as current disposal methods, and (4) the available distillation/evaporation equipment at NAVORDSTA; a literature and data search into the use of distillation methods; development of McCabe—Thiele diagrams for the solvents of interest; and bench-scale demonstrations of selected systems.

The data gathered during the study were evaluated in terms of technical, economic and safety considerations. The feasibility of the program's implementation as it applies to ordnance contaminated solvent was assessed.

Introduction

The Used Solvent Elimination Program is a new development in the Department of Defense's efforts to reduce the risks and costs of hazardous waste disposal. In general, its purpose is to establish better management procedures for used solvent with an aim toward totally eliminating disposal of solvents as waste.

Background

In the past decade, the disposal of hazardous waste has increasingly

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been the focus of media attention. We have heard a great deal about the mismanagement of hazardous material or hazardous waste. Though the laws and regulations for proper waste management have been developed over the past couple of decades, there is much that remains to be learned about past and present treatment, storage and disposal operations. The Resource Conservation and Recovery Act of 1976 (RCRA) was written to prevent the midnight dumping of hazardous waste and to create the cradle to grave responsibility for hazardous waste generators.

With the advent of the Comprehensive Environmental Response Compensation and Liabilities Act (CERCLA), or as it is better known, the Superfund, and its associated investigations of past disposal sites, we have begun to see some of the results of this cradle to grave philosophy. Hazardous waste generators are being held responsible for the cleanup of their own waste, sometimes at great expense.

The practice of landfilling hazardous wastes has recently come under close scrutiny. The rationale has become that all landfills eventually leak. With the recent passing of the 1984 Amendments to RCRA, much more stringent reins are to be placed on landfill disposal both in what is permitted in hazardous waste landfills and in the design criteria of the landfill itself, e.g., number of liners, etc.

Another disposal method of concern to the ordnance community is open burning. The Navy's Ordnance Environmental Support Office (OESO) was instrumental in obtaining an exception to the regulation prohibiting open burning. This was part of the RCRA interim status standards of 1980. It states in part: "Open burning of hazardous waste is prohibited except for the open burning and detonation of waste explosives. Waste explosives include waste which has the potential to detonate and bulk military propellants which cannot safely be disposed of through other modes of treatment" [1]. The DoD is currently working in concert with EPA on developing design criteria for explosive waste burning grounds based on the best available technology. This will likely result in amendments to the current exception.

We must therefore be aware of the perpetual risk of multimillion dollar cleanup costs associated with land disposal. Since waste organic solvents make up a large fraction of DoD's hazardous waste load, the *recycling* of solvents would greatly reduce these risks and costs of hazardous waste disposal.

With this in mind, in addition to reports indicating that much can be done in the area of solvent handling, the Assistant Secretary of Defense established a policy directing the services to avoid disposal of used solvents. The Navy program implementing this policy applies to all activities generating more than 400 gallons per year of any used organic solvent. A number of the major users of solvents must fully implement the program by October

1, 1986. These include the following activities:

CHNAVMA

NAVSHIPYD Portsmouth, NH	NAVAIREWORKFAC Norfolk, VA
NAVSHIPYD Philadelphia, PA	NAVAIREWORKFAC Cherry Pt, NC
NAVSHIPYD Portsmouth, VA	NAVAIREWORKFAC Jacksonville, FL
NAVSHIPYD Charleston, SC	NAVAIREWORKFAC Pensacola, FL
NAVSHIPYD Long Beach, CA	NAVAIREWORKFAC Alameda, CA
NAVSHIPYD Mare Island, CA	NAVAIREWORKFAC San Diego, CA
NAVSHIPYD Puget Sound, WA	NAVUSEAWARENGSTA Keyport, WA
NAVSHIPYD Pearl Harbor, HI	NAVWPNSUPPCEN Crane, IN
NAVORDSTA Louisville, KY	NAVAVIONICCEN Indianapolis, IN
PWC Norfolk, VA	NAVWPNSTA Yorktown, VA
PWC Pearl Harbor, HI	NAVAIRENGCEN Lakehurst, NJ

CINCPACFLT

NAVSHIPREPFAC Yokosuka, JA

CINCLANTFLT

NAS Jacksonville, FL
 NAS Cecil Field, FL

CNET

NAS Pensacola, FL

The remaining activities that generate more than 400 gallons per year are to comply by October 1, 1987. Activities that generate less than the applicable amount are encouraged to participate in the program as practical.

Only the following two exceptions to the USE Program apply:

“(a) Used organic solvent recycling byproducts, i.e., “still bottoms”.

(b) Where the “USE Plan” shows recycling or sale of the used solvent are not viable options, and such plan has been reviewed and approved by knowledgeable personnel of a flag officer command” [2].

OESO Study

In response to the above direction, a project was undertaken at the Naval Ordnance Station, Indian Head, Maryland, to determine the USE Program's application to ordnance contaminated solvents and to compile tentative guidelines for the program's implementation within the ordnance community.

The study included the following: inventories of (1) the types of solvents used at NOS, (2) possible contaminants in the solvents, (3) forms of recycling or disposal currently in use, and (4) the available distillation or evaporation equipment at NOS; a literature and data search into the use of

distillation methods; and bench-scale demonstrations of selected systems. Needless to say, the application of USE to explosive contaminated (EC) solvents, presents special problems associated with the hazards involved in handling sensitive material and the possibility of concentrating or entraining this material in the recovery equipment. Consequently, safety was of primary concern in this study. In addition, the data gathered were evaluated in terms of technical and economic considerations, and the feasibility of implementing the USE Program at ordnance activities was assessed.

From the information gathered in the various inventories, the following solvents were selected for bench-scale experiments. They are representative of those used in large quantities throughout the Ordnance Department at NAVORDSTA, Indian Head. Actual process wastes were used.

<i>Solvent</i>	<i>Group classification</i>	<i>Contaminants</i>
Trichloroethylene	Halogenated	sand, grit, oil, grease
Toluene	Hydrocarbon	RDX, aluminum, R-45, isocyanates
Toluene	Hydrocarbon	binders, aluminum, MAPO, AP
Acetone	Oxygenated	PEG, 2-NDPA, methylene chloride

Testing was accomplished by running separate samples of the selected solvents through a laboratory-scale packed bed distillation column and a rotary evaporator. The distillation column was chosen to represent a batch column. The evaporator is representative of the larger scale Luwa thin-film evaporator unit.

TABLE 1

Bench-scale solvent recovery results for the packed-bed distillation column

Solvent system	Contaminants	Feed conditions, wt. %		Distillate conditions, wt. %	
		solvent	explosive	solvent	explosive
Acetone/ methylene chloride	PEG, 2-NDPA	n.a.	- ^a	99.5	- ^a
Toluene	Binders, Al, Isocyanates, RDX	99.4	3×10^{-5}	99.5	5×10^{-7}
Toluene	Binders, Al, MAPO, AP	98.7	8×10^{-3}	98.9	9×10^{-4}
Trichloro- ethylene	Sand, grit, oils, grease	91.1	- ^a	91.5	- ^a

n.a. — not available

^a Does not apply.

The solids or residue in each solvent sample were analyzed using liquid chromatographic techniques. Tables 1 and 2 summarize the results obtained from the analyses. The recovered toluene samples show that there was an extremely small amount of RDX and AP in the distillate (the percentages of AP and RDX shown in the tables are the percent of the total residue in that sample). The actual feed samples proved to be very complicated for liquid chromatographic analysis owing to the number of components present. However, based on the results in the first table, one could conclude that there is essentially no carry-over of the non-volatile hazardous components in the toluene samples studied.

TABLE 2

Bench-scale solvent recovery results for the rotary evaporator^a

Solvent system	Contaminants	Feed conditions, wt. %		Distillate conditions, wt. %	
		solvent	explosive	solvent	explosive
Acetone/ methylene chloride	PEG, 2NDPA	n.a.	- ^b	99.0	- ^b
Toluene	Binders, Al, Isocyanates RDX	95.4	3×10^{-5}	99.3	1.5×10^{-6}
Toluene	Binders, Al, MAPO, AP	98.7	8×10^{-3}	99.8	1.2×10^{-3}
Trichloro- ethylene	Sand, grit, oils, grease	91.1	- ^b	91.3	- ^b

n.a. not available

^a All runs at 70 mmHg.^b Does not apply.

Conclusions

The results of these tests show that many explosive contaminated solvents can be effectively recovered. It is important to note that the simple recovery methods employed in this study are effective for single component waste solvents from non-volatile contaminants. The increased complexity of fractionating solvents needs to be tested in more detail to determine appropriate processing conditions and equipment. However, much of this commingling of solvents can be avoided by proper waste solvent segregation procedures. Each type of solvent waste should have its own storage container adjacent to the process that produces it. These containers should be inspected and emptied regularly.

Since safety is a major concern, several factors should be considered when selecting proper equipment and methods for solvent recovery. These include: the maximum and minimum safe operating temperatures and

pressure, the maximum safe explosive concentrations, safe methods of EC solvent storage and transfer (i.e., types of containers, pumps, etc.), methods of decontamination and safe operating procedures.

Temperature limitations must be considered since excessive cooling of the EC solvent might result in the precipitation or sensitization of the explosive and excessive heating might cause explosive decomposition with a resultant fire or explosion [3].

The pressures should be chosen to minimize explosive entrainment in the purified solvent and boiling point temperatures.

Maximum safe solvated explosive concentrations are of utmost importance. Below this concentration, the explosive is desensitized and is considered much safer to work with than the otherwise sensitive material. This concentration will also determine the maximum amount of solvent that may be recovered. For example, suppose an EC solvent contains 2 wt.% of an explosive and the maximum safe concentration is 3 wt.%. Assuming all of the explosive remains in the residue, a mass balance on the system shows a maximum of 33% of the solvent can be recovered in the distillate. Once the safe concentration limits have been firmly established, a more accurate estimate of actual solvent recovery rates and their economic benefits can be forecast. Although little information on safe explosive content exists, certain limits have been tentatively established. An upper limit of 5 wt.% NG in organic solvents has been forwarded. However, this is an estimate and should only be used as a rough guide for continuing laboratory research to investigate actual limits. One source states that an emulsion composed of one-third NG and two-thirds water is incapable of being initiated. But for complete safety, a ratio of one-fourth NG (25%) to three-fourths water (75%) is recommended [4].

Due to the unknown hazards involved with handling EC solvents, careful consideration must be given to equipment types used in any reclamation scheme. All equipment must be compatible with the solvents and explosives for which it is intended. Methods of effective explosive and equipment decontamination must be determined to deal with accidental spills and to allow for equipment repair and reconditioning.

Another method of solvent recovery involves chemical treatment of the explosive followed by distillation or evaporation of the solvent. Methods for deactivating the explosive vary from case to case. Some reactions that will decompose nitric esters include: reduction with alkalies (e.g., NaOH, sodium borohydrate, etc.); acid hydrolysis (heated with iron and sulfuric acid); or destruction by bacterial oxidation [5]. All of these reactions will inactivate the explosives but they have several disadvantages, including solvent reaction or decomposition, and the production of a myriad of organic compounds. Owing to the difficulty of purifying the reaction mixture and the hazards introduced by the toxic reaction products or incomplete deactivation of the explosive, this method was not considered a viable one.

Also, contractors are available that will provide many types of services for solvent recovery. One will inventory a station's waste solvent, set up a segregation plan and prepare a plan for implementation of the USE Program. Some contractors will recycle EC solvent wastes. One such contractor currently recycles NG contaminated Elba Solvent from the Naval Ordnance Station, Indian Head, using a thin-film evaporator. Although contracting out solvent recovery will require the least amount of capital investment and labor costs, it will realize the smallest net savings due to the off-setting costs for solvent purchase.

Economic evaluation

An economic evaluation of the USE Program is difficult because actual solvent recovery rates and equipment costs are uncertain. Table 3 shows current and anticipated waste solvent generation rates and expected savings for 100% recycle of these solvents. These values are calculated in terms of present worth and do not reflect solvent price changes. A more realistic evaluation is for a 50% recovery rate with an annual increase in solvent costs of 5% [6]. This evaluation yields a savings of \$97,000 for FY84, \$135,000 for FY85 and \$218,000 for FY86. Table 4 shows the yearly gross savings, the estimated operating expenses and the yearly net savings that can be expected by implementing the USE Program at NAVORDSTA, Indian Head.

For the ordnance community as a whole, the USE Program should be economically beneficial by off-setting the costs of solvent purchase and disposal.

TABLE 3

Anticipated savings for ordnance waste solvent reclamation at NAVORDSTA, IH

Solvent	Waste generated, gallon/year			100% recycle savings 1984 dollars		
	Current	9/85-9/86	9/86 on	Current	9/85-9/86	9/86 on
Acetone	45,944	17,800	26,250	107,968	41,828	61,688
Ethanol	32,536	47,080	56,590	42,622	61,676	74,132
Ethanol, 200 Pf	825	825	825	2,714	2,714	2,714
Ether	14,500	14,500	14,500	18,560	18,560	18,560
Ethyl acetate	1,600	37,590	72,450	4,928	115,777	223,149
Heptane	1,200	1,200	1,200	9,252	9,252	9,252
Toluene	1,715	1,715	1,715	2,984	2,984	2,984
Triacetin	207	207	207	1,658	1,658	1,658
Trichloro-ethane	415	415	415	1,444	1,444	1,444
Trichloro-ethylene	670	670	670	2,157	2,157	2,157
Total	100,000	122,000	175,000	194,300	258,000	398,000

All volumes and savings reflect the amount consumed and do not account for losses due to spills, evaporation or entrainment in the products. Also, all future values are anticipated and may not reflect actual usage.

TABLE 4

Approximate net savings to be realized by implementing USE at NAVORDSTA, IH

Time period	Yearly gross savings, \$	Yearly operating expenses, \$	Yearly net savings, \$
FY 84	97,000	79,000	18,000
FY 85	135,000	83,000	52,000
FY 86	218,000	87,000	131,000

Recommendations

In summary, the study concluded that waste solvents, including those contaminated with some types of explosives, can be recovered and recovered economically. We recommend that more research into the hazards involved with recycling explosive contaminated solvents, especially with nitric esters, be conducted. An accurate risk assessment should be accomplished for each solvent waste to determine if the recycling can be done safely prior to implementing the USE Program. Also, on-line waste segregation and proper solvent storage procedures will greatly benefit the implementation of the USE Program.

References

- 1 U.S. Code of Federal Regulations, 40 CFR 265.382, EPA, 1980.
- 2 Navy Used Solvent Elimination (USE) Program, CNM 1tr 5090 04H2/40639, January 9, 1985.
- 3 Army Material Command Pamphlet 706-177, Properties of Explosives of Military Interest, Engineering Design Handbook — Explosive Series, March, 1967.
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- 5 Hazardous Waste Regulatory Guide, J.J. Keller and Assoc., Neenah, WI, 1983.
- 6 P. Mraz, Chem. Process., 47(10) (1984) 40, 41.