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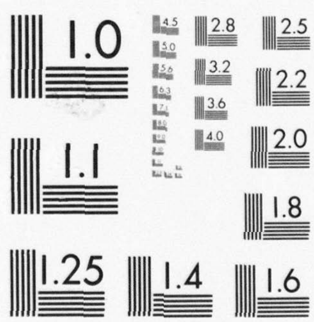

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(14) REPORT NO. NADC-79278-60

(6) SUBSTITUTION AND MINIMIZATION OF SOLVENT CLEANERS USED AT THE NAVAL AIR REWORK FACILITIES

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(11) 5 MARCH 1980

(12) 18

(16) F57572

(17) ZF57572401

(9) PHASE REPORT.

AIRTASK NO. A340-0000/001B/6F57-572-401
Work Unit No. VQ301

APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED

Prepared for
NAVAL MATERIAL COMMAND
Department of the Navy
Washington, D.C. 20361

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NADC-79278-60	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Substitution and Minimization of Solvent Cleaners Used at the Naval Air Rework Facilities		5. TYPE OF REPORT & PERIOD COVERED 6. PERFORMING ORG. REPORT NUMBER NADC-79278-60
7. AUTHOR(s) H. J. Lee		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Air Development Center Aircraft and Crew Systems Technology Directorate Warminster, Pennsylvania 18974		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE 5 March 1980 13. NUMBER OF PAGES 15
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Pollution Abatement, Solvent Substitution
Solvent Minimization, Solvent Cleaners

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Solvents used by the Navy for various applications are many and diverse. In keeping with the objective of pollution abatement a study was made to substitute for and minimize the number of hazardous and toxic solvents for cleaning operations used at Navy facilities. The impact of waste solvents on the environment can be lessened by eliminating those solvents that perform the same functions and by minimizing the number of different types of solvents.

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INTRODUCTION

Solvents used by the Navy for various applications are many and diverse. Data obtained from the Naval Air Rework Facilities (NAVAIREWORKFACS) surveyed (five of six responded) for the types and quantities of solvents used indicated that over 800,000 gallons of individual solvents are being used annually (Table 1 and reference (a)). These solvents range from materials that have no flash points such as halogenated hydrocarbons, and solvents with flash points such as hydrocarbons, alcohols, esters, ketones, and aromatics (Table 2).

In keeping with the objective of pollution abatement, a study was made under reference (b) to minimize the number of hazardous and toxic solvents and solvents mixtures for cleaning operations used at Navy facilities. The bulk of these solvents are used for cleaning, degreasing, and carbon removing operations and after use the waste solvents are either dumped into the environment, sold to industrial reclaimers or disposed of for a fee. Some in-house reclamation is sporadically practiced. Some of the useable and waste solvents are lost through spillage, washdown, evaporation, or by discarding.

The impact of waste solvents on the environment can be lessened by eliminating those solvents that perform the same functions and by minimizing the number of different types of solvents used. This approach can be accomplished by determining which solvents can be substituted for by non or less pollutive and non or less toxic ones. The selection of a recommended solvent of comparable or superior performance would be based on the effectiveness for the intended application, probable impact of the solvents on the environment and on the worker.

It is to be noted that this approach at the present stage cannot be applied to those solvents or solvent mixtures that are used as diluents for paint and lacquer systems since the solvent type and solvent mixture ratios are critical to the end product for each particular coating system. Any modification that would cause an imbalance to the total system would negate the effectiveness of the original formulation.

The implementation of such a program as set forth in this report would have a decided impact on the easing of the energy crisis through the realization of energy conservation meeting of national energy requirements and reducing the dependence on imported oil.

By substitution and minimization, the demand and drain on petrochemicals would be lessened and the many environmental problems caused by petrochemical products would be eased.

APPROACH

A study on the types and volumes of solvents used by the military services, specifically those used at the NAVAIREWORKFACS (excluding paint and lacquer diluents) was made. Studies of each solvent and component of solvent mixtures were also conducted to determine;

1. Pollutive, hazardous, or toxic nature, if any and degree

2. Adverse effect on the environment

3. Degree of volatility

4. Ease of reclamation

Especially investigated was the reduction in the number of different types of solvents performing the same or equivalent functions and those solvents that could be substituted for pollutive, hazardous or toxic ones. This latter approach was made from considerations of solvency or dissolving power, kauri butanol value, aniline point, boiling point, flash point and hazardous and toxicity ratings as established by the American Conference of Government Industrial Hygienists. The solvents with their properties are listed in Table 2.

RESULTS AND DISCUSSIONS

A study of all the types and volumes of solvents used in cleaning operations by the military indicates a total volume of approximately 800,000 gallons used by the five NAVAIREWORKFACS surveyed. The types include hydrocarbons, alcohols, esters, ketones, aromatic and halogenated solvents. Table 1 lists individual solvents and quantities used by each NAVAIREWORKFAC. The quantities listed therein exclude those volumes of solvents found in solvent mixtures. Solvent mixtures are not considered because:

1. Solvent mixtures, in general, are used as thinners and diluents and to suggest changes in constituents and ratios would constitute a separate study since any changes may reduce the effectiveness of the original formulation.

2. The total volume of different types of solvent mixtures is relatively small compared to individual solvents - about 20% of the total.

3. Effects of solvent mixture ratios on solvency power, toxicity, and hazardousness are beyond the scope of this study.

Specific applications for individual solvents were obtained through a survey of local process specifications obtained from two NAVAIREWORKFACS, Alameda and North Island. These local process specifications in many instances include an alternative solvent. The existence of the alternative facilitates the substitution and the minimization of the solvent type. Where one is totally hazardous or toxic and the other not, the latter naturally is recommended for use. If both are undesirable, a safe or safer substitute is recommended where possible. The lesser of two dangerous solvents is selected if no substitute is available or known to exist.

Specifications on individual solvents were also surveyed as to their intended uses. Many serve several applications including cleaning. While these surveys are not all inclusive they do indicate the major solvents being used at the NAVAIREWORKFACS.

RECOMMENDATIONS AND DISCUSSIONS

In order to take full advantage of a comprehensive substitution program, it is recommended that materials currently being used be considered for replacement as follows:

1. It is recommended that Varsol PD-680 (Stoddard Solvent), a general purpose cleaning solvent for the removal of oil, grease, and preservation compounds, be substituted for toluene and xylene where these latter solvents are used for cleaning applications stated above and where the retention of a solvent residue on the cleaned surface is not undesirable.

The advantages of this substitution are:

a. Varsol or Stoddard Solvent (TLV = 100 ppm)[1] from a health hazard standpoint is less toxic in use than toluene (TLV = 100 ppm) and xylene (TLV = 100 ppm). Although these solvents have equal threshold limit values, Varsol (Stoddard Solvent) has an appreciable higher boiling point and flash point than both toluene and xylene; its vapor pressure is considerably lower than both. Thus, concentrations, in air, of the former comparable to those of the latter two for the same cleaning operation would not be encountered.

b. It is not as highly flammable at room temperature.

c. It costs considerably less per unit volume (52-55% less).

d. More commercial reclaimers exist for the recovery of Varsol.

e. By this substitution the problems of solvent segregation, a prerequisite for more efficient solvent recovery and costs are reduced.

2. It is also recommended that the use of trichloroethylene (TLV = 100 ppm) be discontinued as a cleaning agent. In its stead, 1,1,1-trichloroethane (methyl chloroform) (TLV = 350 ppm) should be used because trichloroethylene[2] is:

a. A potential carcinogen[2]

b. Three and a half times more toxic.[1]

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1. Threshold Limit Value - The time weighed average concentration considered safe for a continuous exposure over a normal workday. American Conference of Governmental Industrial Hygienists 1977.
2. National Cancer Institute, 21 Mar 1975

Since both types of solvents are highly volatile with low residue properties, are non-flammable and have good solvency power, the advantages derived by substituting 1,1,1-trichloroethane for trichloroethylene far outweighs any disadvantages that may exist by the substitution.

3. Acetone (TLV = 1000 ppm) should be used in place of MEK (methyl ethyl ketone) (TLV = 200 ppm) whenever possible as it is:

a. 1/5 as toxic as MEK.

b. 32% less costly.

However, acetone has the disadvantage of a lower flash point.

Reference should be made to the NIOSH[1] report of 10 October 1974 which states that serious consideration be given to the discontinuance of MEK pending determination of safe levels.

4. For those applications where toluene and xylene must be used and the absence of a residue is absolutely essential to the performance of the part cleaned, toluene (TLV = 100 ppm) should be substituted for xylene (TLV = 100 ppm) as it is:

a. Less toxic; although both have the same TLV rating. It has a less potent effect on the skin and occurrence of serious dermatitis is comparatively less likely from direct contact with liquid or vapor.

b. 7% less costly.

However, it has the disadvantage of having:

a. A slightly lower flash point than xylene.

b. Its solvency power as a degreaser is less than that of xylene.

In addition, recommendations for the use of specific solvents in the local process specifications used by Alameda and North Island NAVAIREWORKFACS are tabulated in Table 3. The inclusion of an alternative solvent in the specification facilitates the substitution and minimization of the solvent type. Where one is totally hazardous or toxic and the other not, the latter naturally is recommended for use. If both are undesirable, a safe or safer substitute is recommended where possible. The lesser of two dangerous solvents is selected if no substitute is available or thought to exist.

From a standpoint of economics some savings are realized by substitution and minimization. Table 4 lists prices of the solvents which, are current (October 1979). Since more data is necessary to determine the actual volumes of solvents that can be substituted for, assumptions of 10% and 50% substitutions were made to calculate some concept of the economics.

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1. National Institute for Occupational Safety and Health

From Table 5 which lists results of these cost calculations, it is observed that any savings realized is insignificant. Therefore, it is recommended that the economics of these materials be one of the lesser parameters used in selecting a substitute.

The impact of waste solvents on the environment can be lessened not only by eliminating those solvents that perform the same functions and minimizing the number of different types of solvents, but also by segregating the waste solvents according to their type and nature such as flash point and boiling point to simplify its reclamation or disposal. In addition, halogenated waste solvents should be separated from other solvents because of their reactivity and corrosiveness. Drum storing of unknown solvents is dangerous and the solvents are difficult to dispose of.

As an important extension to the substitution and minimization program, it is further recommended that future studies be directed toward the cancelling out of U. S. government specifications for individual solvents and solvent mixtures capable of serving a similar application to other specifications. The cancellation mechanisms would be achieved by utilizing aniline point[1] and solubility parameter[2] values as the criteria in determining solvent power efficiency of solvents for specific cleaning operations.

Considering oils and greases, which constitute a major part of the "dirt" encountered in cleaning operations at the NAVAIREWORKFACS, the matching or degree of matching of aniline point values for the cleaning solvent and of the "dirt" would facilitate selection of the suitable solvent for the cleaning operation to the exclusion of less efficient ones.

The use of solubility parameters, the thermodynamic method for predicting solubilities, is also a very valuable tool. To predict solubility, the solubility parameters of the solvent and solute are compared; both will be soluble if they have approximately the same solubility parameters. For solid solutes in liquid solvents, if the solubility parameter of the solvent is known, the solubility parameter of the solute can be determined. Solubility parameters can be calculated from many properties of the solvent and of the "dirt"; energy of vaporization, surface tension and viscosity. In the case of grease "dirt" the apparent viscosity property would suffice but if not, the solubility parameter can be calculated from the base stock.

In view of the above considerations, it is further recommended that solvent specifications and specifications for materials, which after usage, would end up as "dirt" (such as a grease or oil), on a part that requires cleaning by solvent action, contain aniline point and/or solubility parameter values for those materials.

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1. Mellan "Handbook of Solvents Vol I, Reinhold Publishing Corp., NY
2. West & Astle - "CRC Handbook of Chemistry and Physics" 59th Edition CRC Press Inc.

In summary, it is recommended that:

1. Varsol PD-680 (Stoddard Solvent) be substituted for toluene and xylene to remove oil, grease and preservation compounds where the retention of a solvent residue on the cleaned surface is not undesirable.

2. Trichloroethylene be discontinued as a cleaning agent and 1,1,1-trichloroethane be used in its stead.

3. Acetone should be used in place of methyl ethyl ketone whenever possible.

4. For those applications where toluene and xylene must be used and the absence of a residue is absolutely essential to the performance of the part cleaned that toluene be substituted for xylene.

5. Substitution of specific solvents in the local process specifications described in Table 3 be made.

6. Waste solvents be segregated according to their type and nature to facilitate reclamation or disposal.

7. Halogenated waste solvents should be separated from other solvents.

8. The practice of drum storing unknown solvents be stopped.

9. Future studies be directed toward the cancelling out of government specifications for individual solvents and solvent mixtures capable of serving a similar application to other specifications.

10. Government specifications for all solvents, solvent systems, and materials that eventually would have to be removed from equipment by solvent action contain aniline point and/or solubility parameter values for those substances.

11. Solubility parameter values for solvents, oils and greases used at the NAVAIREWORKFACS be determined and noted in the specifications for these materials.

REFERENCES

(a) NAVAIRDEVCEN Report No. 78028-60 "A Pollution Abatement Concept, Reclamation of Naval Air Rework Facilities Waste Solvent, Phase I, 5 Apr 1978

(b) AIRTASK A340/0000/001B/6F57-572-401 Work Unit VQ301, Pollution Control in Aircraft Materials

TABLE 1. SOLVENTS USED INDIVIDUALLY BY NARFS
(THOUSANDS OF GALLONS PER YEAR)

	Alameda	Norfolk	North Island	Pensacola	Jax	Total
Halogenated Solvents						
Dichloromethane						
(Methylene Chloride)	2.5	7.4	-	3.0	3.0	15.9
1,1,1-Trichloroethane	24.2	4.4	48.0	31.0	7.4	115.0
Freon TF	9.9	25.5	9.7	10.6	-	55.7
Trichloroethylene	-	-	-	7.3	60.0	67.3
Ketones						
Acetone	7.8	-	-	-	-	7.8
Methyl Ethyl Ketone	18.2	1.9	40.0	18.0	-	78.2
Alcohols						
Methyl	-	-	-	-	-	-
Ethyl	-	-	-	-	-	-
Isopropyl	-	0.1	-	-	-	0.1
Petroleum Solvents						
Kerosene C	-	-	-	-	-	-
Aliphatic Naphtha	-	-	-	1.1	-	1.1
Stoddard	90.0	-	246.0	56.6	7.7	400.3
Toluene (Toluol)	2.6	4.4	-	3.6	-	10.6
Xylene	0.2	-	-	0.9	-	1.1
Esters						
Ethyl Acetate	20.0	5.3	-	-	-	25.3
TOTALS	175.4	49.0	343.7	132.2	78.1	778.4

TABLE 2. SOLVENTS USED BY THE NARFS

Solvents	Boiling Point (760 mm) °C	Boiling Point (760 mm) °F	Government Specification	Threshold Limit Values (ppm)	Flash Point (Closed Cup) °C	Flash Point (Closed Cup) °F	KB Value	Solubility Parameter	Aniline Point
Alcohols									
Methyl	64.9	149	O-M-232	200	12	54	---	11.5	---
Ethyl	78.5	173.3	O-A-396	---	---	---	---	12.7	---
Isopropyl	82.4	180.3	TT-I-735	400	11.7	53	---	11.5	---
Halogenated									
Dichloromethane (Methylene Chloride)	40	104	MIL-D-6998	200	Non Flammable		136	9.5	---
1,1,1-Trichloroethane (Methyl Chloroform)	74.1	165.2	OT-620 MIL-T-81533 Vapor Degrease	350	None		---	---	---
1,1,2-Trichloro-1,2,2 Tri-fluoroethane (Freon TF)	47.7	117.6	MIL-C-81302	1000	---	---	31	7.2	---
Trichloroethylene	87	188.6	O-T-634b	100	None		130	9.2	---
Chlorinated Hydrocarbon	---	---	---	---	---	---	---	---	---
Ketones									
Acetone	56.2	133.2	O-A-51-F	1000	0	-18	---	10.0	---
MEK	79.6	175.3	TT-M-261	200	20	-6.66	---	9.3	---

TABLE 2. SOLVENTS USED BY THE NARFS
(Continued)

Solvents	Boiling Point (760 mm) °C	°F	Government Specification	Threshold** Limit Values (ppm)	Flash Point (Closed Cup) °C	°F	KB Value	Solubility* Parameter	Aniline Point
Hydrocarbon Petroleum	---	---	---	---	---	---	---	---	---
Aliphatic Aromatic									
Kerosene	---	---	VV-K-211 VV-K-220	---	46.1	115	29.5	---	---
Aliphatic Naphtha	85-143	185-290	TT-N-95	260	---	35	38.5	7.5	125
Stoddard	154.4-191.3	310°-388	PD-680 Type I	100	40.5	105	34.0	---	126
Toluene	110.6	231	TT-T-548	100	4.44	40	94-105	8.9	8.8
Xylene (Mixed Isomer)	135-155	275-311	TT-X-916	100	27	63	94-98	8.8	10.4
Mineral Spirits	130-171	266-340	TT-T-291E	---	38-51.5	100-125	37-39	---	143-145
Esters									
Ethyl Acetate	77.1	170.8	TT-E-751	400	26	-3.33	---	8.1	---

* CRC Handbook of Chemistry and Physics - 59th Edition 1978-1979

** American Conference of Governmental Industrial Hygienists 1977

TABLE 3. RECOMMENDATIONS FOR SOLVENT SUBSTITUTION

Local Process Specification	NARF	Solvents Currently Used	Substitute Solvents Recommended	Reason for Recommendation*
01-1-0030	Alameda	Ethyl Acetate, Methyl Ethyl Ketone	Ethyl Acetate	Ethyl acetate is ½ times as toxic as methyl ethyl ketone
04-2-0160	Alameda	Trichloroethylene, 1,1,1-Trichloroethane MIL-C-81302	Do not use trichloroethylene	Trichloroethylene is a potential carcinogen.
175	North Island	Methanol	Isopropanol	Isopropanol is not toxic and a moderate fire hazard. Methanol is extremely flammable and a moderate health hazard. It is dangerous and can be absorbed through the skin.
382	North Island	Lacquer thinner, Methyl Ethyl Ketone, Solvent Naphtha	Aliphatic Naphtha	Of the 3, naphtha is considered the least toxic. If possible, acetone should be considered.
600 Appendix B-1	North Island	Acetone, Methyl Ethyl Ketone	Acetone	Acetone is 5 times less toxic than methyl ethyl ketone and is less expensive.
600 Appendix F-2	North Island	Methylene Chloride, Trichloroethane, Methyl Ethyl Ketone	Methylene Chloride or Trichloroethane	Methyl ethyl ketone is more toxic.

TABLE 3. RECOMMENDATIONS FOR SOLVENT SUBSTITUTION (Continued)

Local Process Specification	NARF	Solvents Currently Used	Substitute Solvents Recommended	Reason for Recommendation*
600 Appendix H-1	North Island	Toluene, Low Boiling Ketone	Acetone	Acetone is ten times less toxic than toluene and less expensive.
601	North Island	Toluene, Acetone, Methyl Ethyl Ketone	Acetone	Acetone is five times less toxic than methyl ethyl ketone and ten times less toxic than toluene. It is also less expensive than both.
602	North Island	Toluene, Methyl Ethyl Ketone	Acetone	Acetone is five times less toxic than methyl ethyl ketone and ten times less toxic than toluene. It is also less expensive than both.

1 - Dangerous Properties of Industrial Materials - SAX - 4th Edition

2 - National Institute for Occupational Safety and Health - Report of 10 Oct 1974

3 - American Conference of Governmental Industrial Hygienists

TABLE 4. PRICES OF SOLVENTS PER 55 GALLON DRUM LOTS*

Halogenated Solvents	
Dichloromethane (Methylene Chloride)	$208.37
1,1,1-Trichloroethane	$208.10
Freon TF	$420.78
Trichloroethylene	$161.84
Ketones	
Acetone	$ 91.04
Methyl Ethyl Ketone (MEK)	$133.55
Alchohols	
Methanol	$ 71.78
Ethanol	$134.91
Isopropanol	$105.20
Petroleum Solvents	
Kerosene C	NA
Aliphatic Naphtha	$ 86.99
Stoddard	$ 52.99
Toluene (Toluol)	$110.25
Xylene	$118.56
Esters	
Ethyl Acetate	$139.59

*Prices as of October 1979

TABLE 5. SOLVENT SUBSTITUTION

	Substitute	Price/55 Gals (Dollars)	Price/Gal (Dollars)	Total Volume Used by NARFS per Annum (Gals)	Total Savings Realized with 10% Substitution (Dollars)	Total Savings Realized with 50% Substitution (Dollars)
Toluene		110.25	2.00	10,600	1102.40	5512.00
Xylene		118.56	2.15	1,100	130.90	654.50
	Varsol PD-680	53.00	.96			
MEK		133.55	2.43	78,200	6099.60	30,498
	Acetone	91.04	1.65			
Xylene		118.56	2.15	1,100	16.50	82.50
	Toluene	110.25	2.00			

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