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SCALE-UP OF RECOVERY PROCESS FOR WASTE SOLVENTS

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Final Report

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SCALE-UP OF RECOVERY PROCESS FOR WASTE SOLVENTS

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Prepared by G. W. Bohnert and D. A. Carey

Recycling of spent cleaning solvents, 1,1,1 trichloroethane, trichloroethylene, and trichlorotrifluoroethane at KCP was evaluated. Gas chromatography was used to identify stabilization levels in virgin and recycled solvent. Segregation, pretreatment and distillation processes were defined. Existing distillation equipment was modified and a solvent drying process was added. Recycled solvent quality of several production lots is also presented.

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SUMMARY

This project was initiated to minimize hazardous material waste though recycling of spent cleaning solvents such as 1,1,1 trichloroethane (TCA), trichloroethylene (TCE) and trichlorotrifluoroethane (CFC 113).

Segregation procedures were established and special collection containers for each solvent were utilized to prevent cross contamination between solvents. Pretreatment prior to distillation was necessary to remove catalyst from solvent containing epoxy resin. Alcohol-contaminated TCE also required pretreatment prior to distillation.

Gas chromatography was used to determine stabilizer concentration in virgin and distilled solvent. Stabilizer additions were made to return distilled solvent to virgin stabilizer concentrations.

Modifications were made to existing distillation equipment to simplify the operation, to reduce solvent emission, to minimize cross contamination between recycle streams and to provide additional operating safeguards.

Solvent drying equipment, utilizing a regenerative 3 Å desiccant, was designed and built to reduce residual water levels to less than 5 ppm.

Recycled TCA, TCE, and CFC 113 met requirements defined by Federal Specification O-T-634, Mil-T-81533, and Mil-C-81302, Type II, respectively. In addition, requirements of KCD Material Standard 4702652, CFC 113/isopropyl alcohol blend, were met using recycled CFC 113.

Recycled solvents meeting test requirements were returned to WR stores for reuse. Nearly 24,000 lbs of TCE, 19,300 lbs. of TCA and 15,000 lbs. of combined CFC 113 and CFC 113/isopropyl blend have been returned to stores.

DISCUSSION

SCOPE AND PURPOSE

Allied-Signal Inc., Kansas City Division (KCD) formed a Hazardous Materials Minimization Committee (HMMC) to address the problems of KCD use and subsequent disposal of hazardous materials. As a part of that endeavor, this project was initiated to develop recovery techniques for chlorinated solvents and identify stabilization packages. It was expanded to also include chlorofluorohydrocarbons.

ACTIVITY

Background

Total halogenated solvent usage at KCP in CY1989 was 6.2×10^5 lb. Of this quantity, approximately 80% came from three solvents: 1,1,1 trichloroethane (TCA), 1,1,2 trichloroethylene (TCE), and trichlorotrifluoroethane (CFC 113). Generally, these solvents are used in vapor degreasing, spray booth, and other cold cleaning operations which remove oils, waxes, solder flux, and soils from parts.

Laws and regulations governing the use and disposal of halogenated solvents are strict and becoming more stringent. Increasing disposal cost coupled with solvent price increases and added excise tax have placed increased emphasis on recycling.

KCD is under increased pressure from federal, state, and local regulatory agencies to minimize/eliminate the use of halogenated cleaning solvents (Montreal Protocol, Clean Air Act, Kansas City Ozone Attainment Region, State of Missouri Regulation on New Sources of Air Toxics). Internal directives require reduced usage and conservation.

Recycling was investigated as a means of maximizing solvent efficiency. Recovery and reuse of spent solvent several times prior to disposal was desired.

A project entitled "Waste Solvent Recovery" was completed in 1987. This project was successful in the development of a distillation process on a laboratory scale for recovering used perchloroethylene, 1,1,2 trichloroethylene, and 1,1,1 trichloroethane. In addition, the stabilization packages for 1,1,1 trichloroethane and perchloroethylene were completely identified. However, only partial identification of 1,1,2 trichloroethylene stabilization package was established. As a follow-up to that project, this long-term project was initiated to scale-up the distillation process and determine a stabilization package for the recovered TCE. This project was later expanded to include CFC 113 recycling.

Identification of Stabilizers

Three are three known suppliers of TCE and TCA. These supplier's materials were analyzed in an effort to completely identify a suitable stabilizer package and also to determine the amount needed to be added to used TCA and TCE, so that they could be returned to the level of virgin materials. Mass spectrometry (MS) and gas chromatography (GC) were used to evaluate them.

All the additives used as stabilizers in one vendor's that were detectable by GC were identified: 1,2 butylene oxide; cyclohexene oxide; para-tert-butyl phenol and 1-propanol. The additives used by the other two were ethyl acetate and 1,2 butylene oxide. As previously reported, one TCA material contains 1,4 dioxane; nitromethane; and 1,2 butylene oxide. Another uses 1,3 dioxolane instead of 1,4 dioxane, but the other part of the stabilizer package remains the same.

A method was also developed to determine the amount of known additives in TCE and TCA. The procedure used is as follows.

1) An accurate weight of approximately 0.250 g of o-xylene, which is the internal standard, was added to 50 g of TCE.

2) The TCE was then divided into five individual samples which were weighed separately. To four of the samples, various amounts (0.5 to 0.10 wt.%) of 1,2 butylene oxide were added to obtain different weight ratios of 1,2 butylene oxide/o-xylene between samples.

3) All five samples were run under identical conditions on the GC using a CP Wax 52 CB capillary column. Then peak area ratios of 1,2 butylene oxide to o-xylene for all samples were determined from the GC data. The peak area ratio for the sample without any 1,2 butylene oxide addition was subtracted from each of the other samples.

4) A linear graph was constructed using peak area ratios versus ratios of the samples. From the graph, the weight ratio of 1,2 butylene oxide/o-xylene in the original sample was determined.

5) The actual weight of 1,2 butylene oxide in the original sample is determined from the weight ratio and the amount of xylene in that sample.

This procedure was repeated for each of the other known additives in TCE and TCA. The only exception was the amount of para-tert-butyl phenol in TCE which was too low to measure (<20 ppm). The results using this procedure are shown in Tables 1 and 2. As shown, TCA contains a higher percent of stabilizers. Discussion with the suppliers of TCA and TCE indicated that TCA is more susceptible to degradation, thus, a higher level of stabilizers is needed.

Segregation of Solvents

Vapor Degreasers

To successfully reclaim used solvent, a segregation system was implemented to avoid cross-contamination with other cleaning solvents. Dirty solvent (TCA, TCE or CFC 113) is pumped into 55-gallon drums labeled only for that particular product. Once sufficient quantities (300 gallons) are collected, a distillation run is made. The collection drums are reusable and are drawn from stockpile as needed. This operation has proven effective in handling spent solvent from departments with large vapor degreasers.

Cold Cleaning

A similar segregation procedure was established to collect spent solvents from various KCD cold cleaning operations. That is, five-gallon containers were labeled and distributed to Multiwire Cables, Electrical Assembly, Hybrid Microcircuit Assembly, Miniature Electromechanical Assembly, and Light Machining. These departments were determined to have acceptable spent solvent as determined by laboratory evaluation. The five-gallon containers are dumped and stored.

Pretreatment for Contaminated Solvents

Analysis of spent TCE collected from Hybrid Microcircuit and Miniature Electromechanical Assembly indicated that isopropy alcohol (IPA) contamination was present. Typical level of contamination ranged from 0.8% to 10.0% by weight. A batch distillation of this material did not yield distillate meeting acceptable requirements. Therefore, a process to remove the alcohol was necessary prior to distillation.

A water extraction process was developed to remove the un desirable IPA. This process involves the addition of 20 weight percent DI water to the contaminated solvent. The mixture is agitated to extract the alcohol into aqueous phase. The batch is allowed to settle for 30 min. and then decanted. The alcohol-free solvent is drawn from the bottom of the mixing vessel and the alcohol/water phase is properly discarded. This extraction process has proven to be a viable technique to remove unwanted alcohol.

Table 1. Amount of Additives Used to Stabilize TCE

Supplier	1,2-Butylene Oxide Weight Percent	N-Propanol	Ethyl Acetate Oxide	Cyclohexene
One	0.48	—	0.053	—
Two	0.52 ---		0.03	—
*Three	032	0.137	--	0.033

*Stabilizer package used for KCD recovered solvent.

Table 2. Amount of Additives Used to Stabilize TCA

Vendor	1,4 Dioxane Weight Percent	1,2 Butylene Oxide	Nitromethane	1,3 Dioxide
One	---	1.45	0.3	2.45
Two	3.17	0.45	0.35	---

Solvent Still Modification

Extensive modifications were made to an existing solvent still. They include the following:

1. Conversion of the still to a gravity drain batch system eliminated the need for level controls and transfer pumps. An earlier revision converted the still from direct steam sparge to an immersion heat exchanger eliminating the need for a coalescing tank, a second level control, and a transfer pump.

2. A cooling water flow switch was interlocked with the steam supply to prevent start up without cooling water flow to the condenser.

3. A manual throttling valve and pressure gage was added to regulate steam pressure to the heat exchange tube bundle.

4. Drain valves were added at low points in piping to eliminate cross contamination from hold-up.

5. Four stainless steel portable storage tanks of approximately 300 gal each have replaced a single 5,000-gal fixed-in-place tank used for clean distillate storage. The smaller tanks are better suited for the quantities presently being recovered. These designated tanks allow different solvents to be recycled without product cross contamination. In addition, the tanks are easily weighed (using the truck scale) and transported for stabilizer addition and subsequent packaging.

6. The still has been equipped with a Teflon coated carbon epoxy rupture disc which replaced a leaking stainless steel disc.

7. Improved temperature monitoring is now possible with the addition of two thermocouples. Digital readout of overhead vapor and bottom temperatures to 0.1°C has greatly improved the operation.

8. A manifold was added to direct distillate to a clean storage tank or waste container.

9. Trench containment for solvent spills has been added at the entrance of the solvent still room.

These modifications have simplified operation, reduced solvent emissions, minimized cross contamination between recycle streams, and provided additional operational safeguards.

Distillation Process

Spent solvents are collected, stored, and processed in batch sizes ranging from 200 to 350 gal using a modified still (Figure 1). Solvents collected from cold cleaning operations require pretreatment to remove specific contaminants. Prior to loading the still, the feed lines, condenser, and still are drained to avoid cross-contamination.

The temperature of the solvent is continuously monitored during the distillation process. During heatup, the condenser distillate is diverted to a waste drum. Upon reaching the desired boiling temperature, the distillate is switched to a

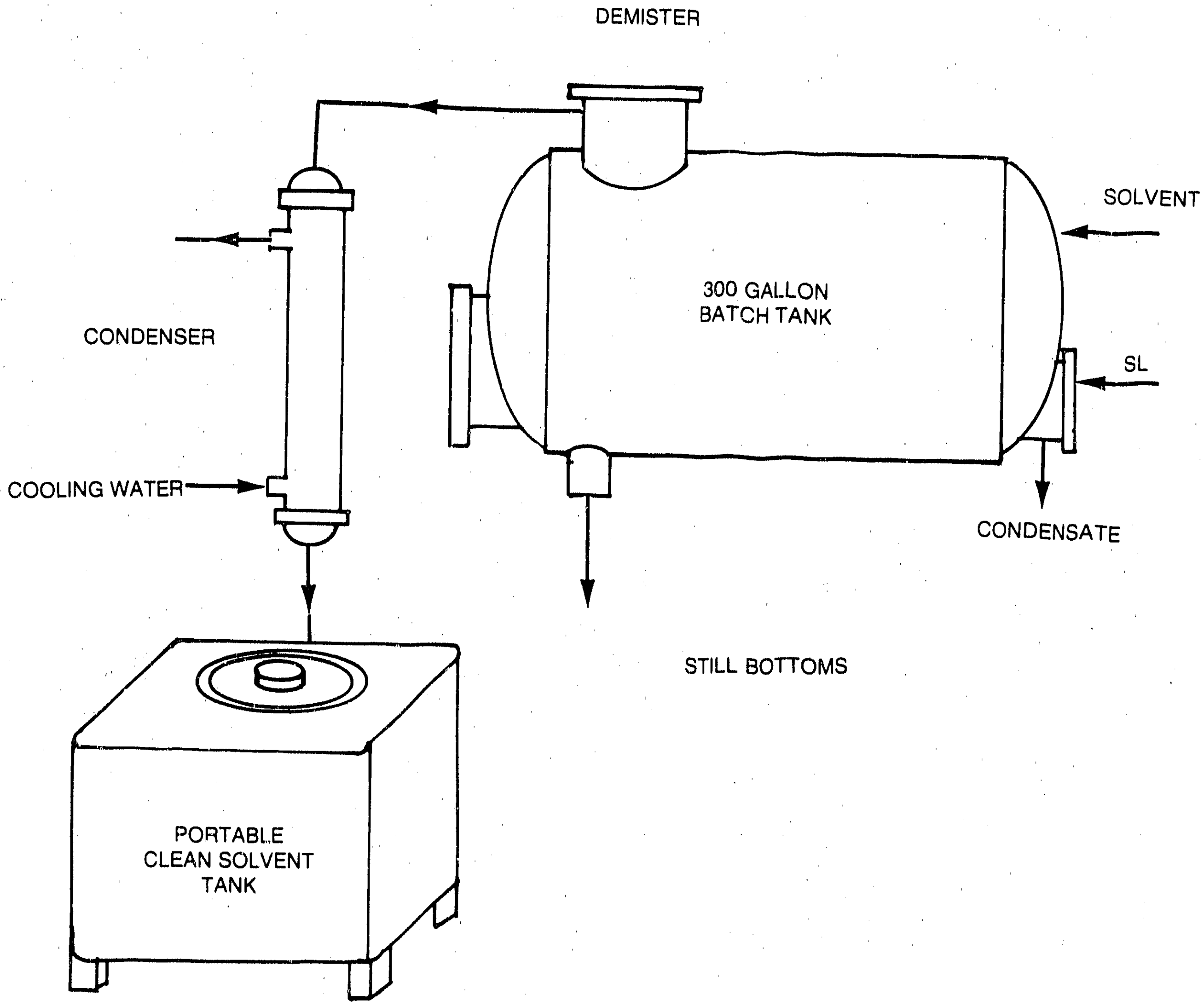

Figure 1. Modified Still

clean bulk storage tank. This process is continued until the clean bulk storage tank is full or until all available spent solvent is processed. The clean distillate is dried using the process described in the following section.

Drying Operation

In order to meet moisture requirements, (100 ppm for TCA and TCE, 10 ppm for CFC 113) it was necessary for each solvent to be dried. A recirculating desiccant drying system was designed and built. The drying system consists of a recirculating pump, a desiccant bed, and necessary connecting piping (Figure 2).

The desiccant (3 Å molecular sieve) is held in a 1 micron polypropylene filter bag within a stainless steel filter assembly (Figure 3).

During drying, wet solvent is pumped from the storage tanks though the desiccant bed and returned to the top of the storage tank continuously. Depending on initial moisture level, drying time varies between 24 and 48 h. A sample is taken after 24 h and tested. If the moisture content is above the specified level, the desiccant bed is changed and the drying process is continued. The wet desiccant is regenerated for reuse.

Stabilization of Recovered Solvent

The use of TCA and TCE in vapor degreasing equipment gradually depletes the stabilizers in virgin material. Distillation further depletes stabilizer levels. The stabilizers prevent formation of degradation by-products (acids) which may corrode parts being cleaned. Because of this gradual depletion of stabilizers, addition is necessary to ensure that recovery solvent exhibits the same margin of protection against corrosion as virgin material.

Stabilizers used include butylene oxide, cyclohexene oxide, 1-propanol and nitromethane. Each stabilizer performs a certain function. Nitromethane and 1-propanol protect white metals by preventing formation of oxides on the surface. Butylene oxide is an acid acceptor reacting with any acid component which might be introduced into the cleaning equipment or generated from solvent breakdown. Cyclohexene oxide performs the same function as butylene oxide; however, because cyclohexene oxide has a higher boiling point, a larger percentage remains in the boil pump. This compares to butylene oxide which concentrates in the vapor phase.

Stabilizer levels in distilled solvent prior to re-stablization vary depending on cleaning use and virgin solvent manufacturer. Each recycled lot is tested for stabilizers after distillation. Additions are made to bring the distillate to the desired levels. Typical stabilizer values after distillation are given in Table 3. Target stabilizer levels are listed in Table 4. Two stabilizer packages are possible for TCA depending on

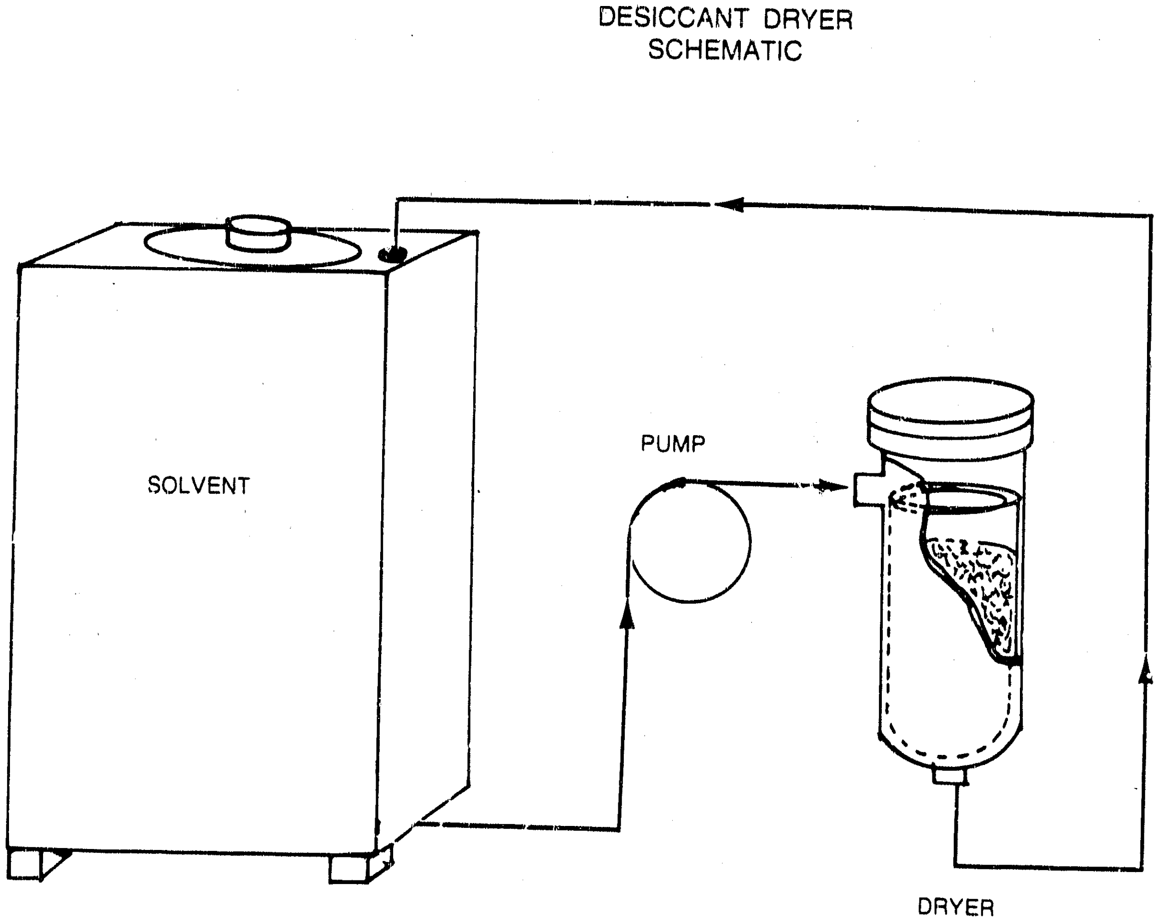

Figure 2. Drying System

distillate test results which best match the desired levels. Stabilizers are blended into the distillate using impeller agitation blanketed by nitrogen to exclude moisture.

Total stabilizer level in TCA amounts to 3.5 percent by weight compared to 0.5 percent for TCE. Because TCA is more susceptible to degradation, the higher stabilizer level is required.

Recycled Solvent Quality and Testing

Recovered solvents were tested to all applicable requirements as if they were virgin material supplied to KCD by outside suppliers. Testing was conducted by the Analytical Science Department and the Materials Engineering Laboratory.

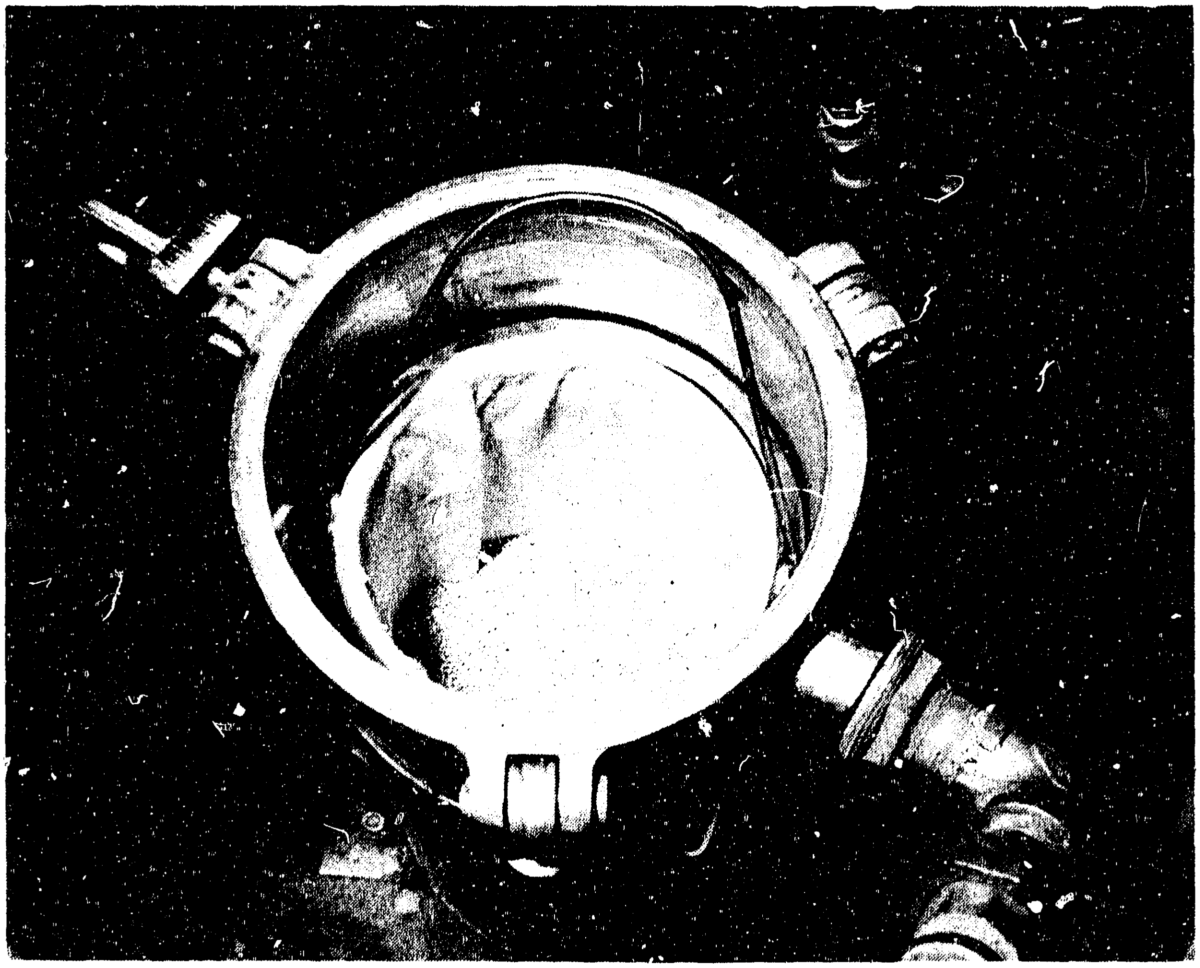

Figure 3. Filter Assembly

Standards which define requirements for each solvent are listed below:

Solvent	Requirements
TCE	FS O-T-634, Type II
TCA	MC MIL-T-81533
CFC 113	MS MIL-C-81302, Type II
CFC 113/IPA	Table 4 (Appendix)

FS = Federal Specification, MS = Military Specification

Table 3. Stabilizer Levels After Distillation

Stabilizer	Weight Percent
TCA	
Nitromethane	0.26 - 0.54
Butylene Oxide	0.26 - 1.59
1,4 Dioxane	0.92 - 2.79
TCE	
TCE Butylene Oxide	0.06 - 0.29
1 Propanol	0.02 - 0.15
Cyclohexene Oxide	0.009 - 0.028

Table 4. Target Stabilizer Levels

Stabilizer	Weight Percent
TCE	
Butylene Oxide	0.32
1-Propanol	0.137
Cyclohexene Oxide	0.033
TCA	
Nitromethane	0.51 or 0.34
Butylene Oxide	1.89 or 0.45
1-4 Dioxane	0.93 or 2.45
CFC 113/IPA Blend	
Nitromethane	0.3

Quality requirements defined by the above standards/ specifications for TCA, TCE, CFC 113, and CFC 113/IPA are listed in the Appendix. For comparison, actual test data for all recycled lots are also shown.

As shown, the test data non-volatile residue and residual water content are well within the specification requirements. In many instances, these values are below virgin material.

ACCOMPLISHMENTS

1) Gas chromatography was used successfully to identify stabilizer concentrations in virgin and distilled solvent.

2) Solvent drying equipment, utilizing a regenerative 3 Å desiccant, was designed and built to reduce residual water in distilled solvent to less than 5 ppm.

3) Nearly 24,000 lb of TCE, 19,300 lb of TCA, and 15,000 lb of CFC 113 and CFC 113/isopropyl alcohol blend were returned to stores for reuse.

4) Existing distillation equipment was modified to produce acceptable solvents.

FUTURE WORK

This project is complete and no future work is planned. Recycling of cleaning solvents will continue on a routine basis.

Appendix

QUALITY REQUIREMENTS

Table 1. Recycled 1,1,1 Trichloroethane Test Results

Property	Requirement	Lot Number					
	MIL-T-81533	880608	880629	880907	881208	890308	890616
Non-volatile Residue, % Wt., Max.	0.001	0.001	0.001	0.0001	0.0001	0.0001	0.0002
Specific Gravity, 25°/25°C	1.300-1.327	1.317	1.317	1.307	1.315	1.311	1.3160
APHA Color, Max.	15	<5	<5	<5	<5 <	5	<5
Appearance	Free from Suspended Matter and Sediment	Pass	Pass	Pass	Pass	Pass	Pass
1,1,1 Trichloroethane Content % Wt., Min.	93.0	93.1	95.9	93.0	94.2	96.4	95.4
Water Content	100 ppm	92	62	43	75	46	40
Acidity (as HC1)							
As received (% Wt.), Max.	0.001	0.0002	0.001	0.0003	0.0006	0.0004	0.00082
After 48-Hour Accelerated Oxidation, Max.	0.020	0.0007	0.001	0.0005	0.001	*	*
Free Halogen	None	None	None	None	None	None	None
Metal Corrosion	No Visual Corrosion	None	None	None	None	*	*
Distillation Range							
Initial Boiling Point, Min.	70°C (158°F)	73.1	73.1	73.9	73.8	74.0	74.0
Dry Point	88°C (190°F)	78.2	78.5	85.7	80.6		82.0
Acid Acceptance As % Wt. as NaOH, Min	0.10	0.19	0.11	0.012	0.10	0.11	0.18
Residue Soluble in CC1H4 % by weight as iso-octane, Max.	0.0005	<0.0005	<0.0005	<0.0005	<0.005	*	*

Test Deleted from Acceptance requirements

Table 2. Recycled Trichloroethylene Test Results

Property	Requirement	Lot Number						
		881118	890214	890303	890406	890407	890613	89080
Specific Gravity	1.450-1.460	1.459	1.453	1.456	1.458	1.456	1.453	1.456
Distillation Range								
Initial Boiling Point, Minimum	86.0°C	86.2	86.3	86.1	86	86.4	86	86.1
95% Distilled, Maximum	87.5°C	86.9	87.3	87.0	86	87.3	87.2	87.5
Dry Point Maximum	90.0°C	87.8	87.6	88.8	87.4	89.1	87.8	89.7
Acidity (as HC1), Wt.% Maximum	0.001	0.0003	0.0005	0.0006	0.0006	0.0004	0.0005	0.0001
Alkalinity (as NaOH), Wt.%	0.015	0.00	0.00	0.00	0.00	0.000	0.00	0.00
Water, ppm, maximum	100	94	7	7	21	32	48	39
Appearance	Clear and Free of Suspended Matter	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Color APHA Scale	15	<10	<5	5	<5	<5	<5	<5
Non-Volatile Residue, Wt.%	0.010	0.001	0.0014	0.0044	0.0004	0.004	0.0002	0.0022
Acid Acceptance (as NaOH), Wt.% Minimum	0.160	0.302	0.185	0.185	0.19	0.18	0.215	0.176

Table 3. Recycled Trichlorotrifluoroethane Test Results

Property	Requirements MIL-C-81302D	Lot Number 880907	890929	900105
Boiling Point (at Standard Barometric Pressure)	47.6 ± 0.3	47.5	47.5	47.5
Chemical Purity Trichlorotrifluoroethane %Minimum (by weight)	99.8	99.85	99.97	99.97
Balance of Product	Other Halogenated Solvents			
Moisture Content Parts Per Million (ppm) Maximum	10	6	5	9.5
Chloride ion, ppm Maximum (by weight)	0.1	0.06	0.021	0.029
Acid Number Milligrams KoH per gram of sample, maximum	0.003	0	0.00027	0.00027
Residue, ppm Maximum (by	2	1	0.03	1.3

Table 4. Trichlorotrifluoroethane/Isopropyl Alcohol Blend Made From Recycled Trichlorotrifluoroethane

PROPERTY	Requirement	Lot Number			
		90803	890809	890831	890905
Composition:	Percent by Weight				
Trichlorotrifluoroethane	63 minimum	64.7	64.7	64.9	65.1
Isopropyl Alcohol	35.0 ± 1.0	34.8	34.8	34.7	34.5
Nitromethane	0.3 ± 0.1	0.29	0.30	0.31	0.31

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