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Chlorinated Solvent Replacements Recycle/Recovery Review Report

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ABSTRACT

This report is a literature review of waste solvents recycle/recovery methods and shows the results of solvent separations using membrane and distillation technologies. The experimental solvent recovery methods were conducted on solvent replacements for chlorinated solvents at Montana State University. The literature review covers waste solvents separation using distillation, membranes decantation, filtration, carbon adsorption, solvent extraction, and other vapor-phase separation techniques. The results of this study identify solvent distillation methods as the most common separation technique. The alternative separation methods typically supplement distillation. The study shows the need for industries to identify waste solvent disposal methods and investigate the economics of waste solvent recycling as a possible waste reduction method.

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Chlorinated Solvent Replacements Recycle/Recovery Review Report

INTRODUCTION

The objective of this study is to review the literature for solvent recycle and recovery technologies in current use by industry, study the recovery of the nonchlorinated replacement solvents for chlorinated solvents using distillation and membrane separation techniques, and evaluate these processes and their economics. Solvent recycling has been practiced by a few industries for over 30 years. For example, dry cleaning has recycled solvent waste using distillation to remove the solvent from its impurities. The oil embargo of 1973, which caused a sharp increase in solvent costs, and the U.S. Congress passage of the Resource Conservation and Recovery Act (RCRA) regulations for waste disposal in the 1980s has made solvent recycling more economically feasible to many other solvent-using industries and government agencies.

These changes also brought about investigation into the methods of solvent recovery and development of the methods to meet the specific needs of industries and government agencies. This report includes a review of techniques of solvent recovery in current use.

The review covered in the distillation processes have been developed for site-specific needs and economic operation. Other innovative separation processes and predistillation techniques are part of the review. A brief review of the FY-91 studies is reported by Dan Hsu, in Appendix A. Also, the distillation and membrane research studies conducted at Montana State University (MSU) at Bozeman, Montana, are reported. These studies included the reports "Membrane Process for Solvent Recycle" by Dr. F. P. McCandless (see Appendix B), "Recovery of Waste Solvents by Rectification, Azeotropic and/or Extractive Distillation" by Dr. Lloyd Berg (see Appendix C), "Economic Analysis of 1 Plant Versus 5 Plants" by Charmin Peterson (see Appendix D), and "5 Plant to 1 Plant Paint Solvent Recovery of TURCO T-5668 Solvent" by Scott Waltari (see Appendix E). The distillation studies at MSU were conducted with the "new" solvents developed to replace the chlorinated solvents in current use. A study of defoaming agents was a part of the MSU distillation study, which is part of the text of this report.

BACKGROUND

Waste solvent recycle recovery processes, though practiced by some industries for more than 30 years, represent less than 12% of the total solvent waste generated in the United States in 1981.¹ Even though it is estimated that solvent recycle has increased at about 5% per year, less than 21% are being recovered currently. Almost 4.0 billion gallons of solvent waste, of which 1.6 billion gallons are classified as hazardous waste according the RCRA classification, were generated in this country this year (see Reference 1). These hazardous solvent wastes must be either recycled, destructively treated, replaced by nonhazardous solvents, or treated by removal of the hazardous constituents.

The United States has more than 450,000 cold cleaning operations using Stoddard-type solvents (petroleum distillates), 25,000 degreasing operations using halogenated solvents (mostly Freons), and an undetermined amount of metal finishing operations using isopropyl alcohol (IPA). These solvents and groups of solvents represent 23% of the solvents used in this country.² Other solvents used in industrial applications are listed in Table 1.

Table 1. Common solvents used in industry.^a

<u>Halogenated Solvents</u>	<u>Ketones</u>
Dichloromethane	Acetone
Carbontetrachloride	Methyl Ethyl Ketone
Chloroform	Methyl Isobutyl Ketone
Tetrachloroethylene	
1,1,1-Trichloroethane ^b	<u>Alcohols</u>
Freon ^b	Methanol
Trichloroethylene	Ethanol
Tetrachloroethane ^b	Isopropanol ^b
<u>Petroleum Solvents</u>	<u>Esters</u>
Kerosene C	n-Butyl Acetate
Aliphatic Naphtha	Ethyl Acetate
Stoddard ^b	
Toluene	
Xylene	

a. This table is only a partial list of solvents used in industry, but represents the solvents most commonly used.

b. Major Volume Solvents.

In 1978, over 80% of the solvent recovery operations were found in the following industries: solvent refining, polymer synthesis and applications, vegetable oil products manufacturing, metallurgical processes, pharmaceutical manufacturers, cleaning operations, and outside solvent recovery operations.³ Solvent refining operations were the major contributor to this effort by reclaiming 72% of the solvents recycled at that time. In 1984, Congress amended RCRA to restrict land disposal of many hazardous wastes. Most industrial organic solvents are classified hazardous by the RCRA criteria for hazardous materials. This restriction on landfill disposal of most solvent waste forced the industries to look for alternatives for hazardous waste disposal. These alternatives included recycle/recovery and chemical destruction methods (incineration, wet oxidation, etc.). Also, the Environmental Protection Agency's (EPA's) cradle-to-grave regulatory requirements for hazardous waste generators (lifetime responsibility for the generators) requires decisions concerning whether to treat hazardous materials onsite or face increased liability by sending the waste to an offsite treatment facility. This motivated many solvent users to consider onsite recycling processes. Good waste management practices require investigation into the economics of these processes. This report is, in part, a review of the separation technologies in current use for solvent recovery.

DISTILLATION, THEORY AND PROCESS

Congress enacted the RCRA legislation to deal with the increasing concern of hazardous waste treatment, storage, and disposal. The act deals with all types of waste, of which a large portion are organic solvents. In the past, solvent wastes were disposed of in landfills. This practice is no longer acceptable under RCRA regulation. Two alternatives to landfill disposal are incineration and reclamation. Currently, many industries are recycling their spent solvents due to the increasing costs of new solvents and the costs of spent solvent disposal. Distillation and other vapor phase separation techniques have been the most common methods of purifying the solvents for reclamation. Distillation process equipment has undergone more innovative development to meet a variety of industrial site-specific needs. This section discusses the distillation processes and equipment.

Typically, simple distillation is used in single solvent waste to evaporate and condense the solvent away from its impurities. Distillation uses a batch or continuous feed system in which the heat is applied external to the system or steam can be directly injected into the solvent waste to volatilize the solvent away from its impurities.⁴ Simple distillation is used, as stated before, for single solvents. It is also possible to separate two and three component solvent waste with simple distillation if the differences in vaporization temperatures of the solvents is great enough and azeotropes are not formed. For example, water (boiling point 100°C) and ethanol (boiling point 78.5°C) mixtures can be separated by this method. However, the ethanol purity will be something less than 95%, as the azeotrope formed between ethanol and water is 95% and 5%, respectively. To separate this azeotropic mixture requires adding an entrainer, such as benzene, to the mixture and using a fractional distillation column with pressure control (vacuum and pressure).

Typically, multi-component solvent waste requires a fractional distillation column. These columns have trays or packing to improve column vapor-liquid interface. Other column controls include the reflux rates, temperature control, pressure and vacuum control, packing/tray design, and column diameter and height. In addition, the distillation process may require two or more distillation column units.

Distillation unit selection is dependent on the solvent purity requirements. Industries using high purity solvents in their processes require a more complex distillation and pretreatment system. However, many industries using solvents for cleaning processes or using recovered solvents as a fuel supplement require the reclaimed solvents be less pure. In these industries, simple distillation of the solvent waste is adequate.

Because of the variety of industries considering solvent recycle in their hazardous waste reduction efforts, innovation in solvent reclamation methods have developed equipment and processes specific to their needs. Small distillation units for point source solvent recycling have been developed.⁵ Also, industries preferring onsite treatment, but whose reclamation needs do not justify the capital costs required in building a distillation unit, have the option of having a mobile distillation unit^{6,7} moved to their facilities for solvent recovery. Also, the mobile distillation unit is advantageous to a company having solvent use facilities that are not centrally located.

Although there are other methods of solvent recovery, such as thin-film rotary evaporators (vapor phase separation), solvent extraction, steam stripping, carbon adsorption, and super critical fluid extraction, these methods are generally used as a pretreatment to distillation.⁸

Because the distillation process is energy intensive, energy costs can be reduced using multi-effect or mechanical recompression, or an incinerator and waste heat recovery system in which the still bottoms are used in the incinerator.⁹ There are many other energy saving modifications for the distillation process and with increasing energy costs many more innovative energy reduction methods and apparatus will be developed.

ALTERNATE PROCESSES

The distillation processes, which include all the solvent recovery techniques based on liquid-gas phase separation, are the primary methods used for solvent recovery. However, other processes are effectively used to supplement distillation, generally as pretreatment steps in waste processing. Typically, the output streams of the alternate processes serve as feed stock for two or more other applications. For example, one product stream is used as fuel and a second is processed by distillation.¹⁰ Usually, this produces at least one out-put stream which is distilled. In certain circumstances, the output stream is sufficiently pure for direct re-use without further purification.¹¹ The alternate techniques include filtration, carbon adsorption, density separation (centrifuge and decantation), solvent extraction, and process systems designed for special applications (see Reference 1).

Filtration

Filtration is a pretreatment step used in virtually all solvent recovery processes to remove particulate matter. An example is the specialized ultrafilters used in conjunction with self-cleaning centrifuges to effectively process oil waste.¹²

Carbon Adsorption

Carbon adsorption is the principle process used to remove gaseous materials, mainly organic, from industrial ventilation and fume hood off-gas systems.^{11,13,14} In general, the process directs solvent laden air into beds of activated charcoal. The solvents are absorbed onto the activated charcoal until the charcoal becomes saturated with solvent. The charcoal is reactivated by a steam distillation process which removes the solvent from the charcoal. The solvent is usually recovered from the spent steam by density separation and/or distillation (see Reference 11).

Density Separation

Density separation includes two related processes, decantation and centrifuge, which use the density difference among the phases present in order to affect phase separation. The decantation process is usually applied to systems containing two (or more) phases, usually immiscible liquids such as oil and water which have a different density. The denser liquid settles to the bottom of the container while the less dense liquid floats on the top. The two phases are then separated by simple decantation.^{11,15,16} The two fractions usually receive additional processing (see Reference 16). Density separation using a centrifuge rather than simple gravity settling is more effective and faster in separating the immiscible phases of different densities, but is more expensive (see Reference 12).

Solvent Extraction

Solvent extraction includes those processes which use the addition of a suitable solvent to the system to dissolve the material to be recovered. The solvent is typically a solvent which is immiscible with the host liquid. The material to be recovered preferentially concentrates in the extraction solvent, which is then removed by some method such as decantation. The solvent is then processed, usually by distillation, to remove the material to be recycled and the solvent is reused.^{16,17}

The typical application of solvent recovery processes does not rely on a single method, but uses a combination of procedures to optimize the efficiency of each. This is illustrated by considering the B.E.S.T. process as an example (see Reference 16). The B.E.S.T. process is a solvent extraction system designed to treat oil-contaminated waste, but it uses several types of procedures to remove the oil. Triethylamine is used as the extraction solvent. At temperatures below 20°C the triethylamine is miscible with water and organic liquids, such as petroleum. Solid contaminants are separated using a density separation. At temperatures >20°C, the water and triethylamine are immiscible and the petroleum compounds are more soluble in the triethylamine phase. The two liquid phases are separated by gravity, i.e., decantation. The final step is solvent recovery from each of the two liquid streams. The water stream is cleaned to <50 ppm triethylamine/petroleum compounds by "conventional air stripping." The triethylamine is recovered from the petroleum compounds by distillation (see Reference 16).

ECONOMIC ASPECTS

The increasing costs of energy and raw materials have drawn attention to the use and/or recovery of solvent by-products from manufacturing processes, which were once considered not economically feasible to recover. However, in some industries the sale or reuse of recovered solvents contributes a significant amount to the profitability of their operations. The increasingly stringent federal, state, and local requirements controlling waste emissions and traditional waste disposal practices, e.g., in controlled landfills, have further increased the incentive for solvent recovery and reuse. For example, a study of six Naval Air Rework Facilities (NARF) indicates that 1,103,000 gallons of solvent are not being reclaimed. Reclaiming six of the solvents with the largest volumes represents 87% of the total solvent waste. To replace the major used solvents costs \$1,088,000. To reclaim these six solvents, allowing for a 20% loss in processing, saves the six NARF's \$870,000 in the cost for new solvents and the elimination of the disposal costs for these six solvents of \$757,000 per year (87% of the estimated costs of \$870,000 per year for solvent waste disposal). This does not take into account the capital and operational costs for reclamation process equipment. However, the reclamation costs at "out of house" recovery is approximately \$670,000 at an average cost of \$0.70 per gallon. This shows a savings of \$957,000 for reclaiming the six solvents.¹⁸

Many variables control the feasibility of solvent recovery and the type of system used. Clearly, important factors include regulatory requirements, equipment costs, personnel training costs, available treatment technologies, and waste properties such as composition, concentration, viscosity, vapor pressure, etc. Feasibility is also affected by recovery objectives. A possible objective is the reuse of the recovered solvent in the original application. It may be that the specifications of the recovered material do not meet the requirements of the original application. If so, then the recovered material may be sold or used for another application within the plant. Where direct solvent recovery is not economically feasible, the energy content of the waste may be recovered by incineration in industrial or specially-designed boilers. Each recovery application requires a detailed review to ensure that the system chosen is the most efficient available. Factors to be considered in an economic evaluation of a solvent recovery system include waste properties, treatment objectives, regulatory requirements, personnel training costs, and available treatment technologies.¹⁹⁻²²

ANALYTICAL

Even when the spent solvents are recovered, a great deal of waste can occur if the spent solvent is sent for recovery before it is fully used. To maximize the use of the original solvent, guidelines must be developed to determine when a solvent should be processed and recycled. These tests are relative and must be developed further for each different type of solvent application. In addition, there is no single analytical method which can be used to evaluate when a solvent is fully spent. A variety of analytical methods are more effective in evaluating a solvent condition allowing a more efficient use of the original solvent.

There are seven different measurements that have been explored as possible characterization tests for spent solvents (see References 2 and 23). These measurements include:

- Kauri-Butanol Values
- Viscosity
- Refractive Index
- Density
- Electrical Conductivity
- Visible Absorbance Spectroscopy
- Thin Layer Chromatography.

Each of these processes was evaluated based upon sensitivity and reliability, reproducibility, ease of operation, operator training, equipment costs, and maintenance costs. Based upon these criteria, five processes were selected as the best available tests. Each of these tests is discussed.

Viscosity

This measurement is easily made in the laboratory and is reproducible, requires minimal training for the technician, equipment costs are under \$500, and the annual maintenance costs are minimal. The only drawback with this test is that it is temperature dependent. Therefore, close attention is necessary to ensure that all samples are tested at the same temperature for an accurate measurement.

Refractive Index

This measurement is easily reproducible in the laboratory, is easy to operate, requires minimal operator training, and has a low annual maintenance cost. The only drawback with this process is that it is not sensitive to halogenated material in the spent solvents. It is sensitive for most all other solvents.

Density

This measurement is easily reproducible in the laboratory, is easy to operate, requires minimal operator training, and has low annual maintenance cost. It does require close attention to volume and weight measurements.

Electrical Conductivity

This measurement is easily reproducible in the laboratory, is easy to operate, and requires minimal operator training. The drawback with this measurement is high maintenance on the conductivity probe which requires frequent replacement.

Visible Absorbance Spectroscopy

This measurement is very sensitive and reliable, is easily reproduced in the laboratory, requires minimal technician training, and has minimal annual maintenance costs. Of all the processes this is the best single measurement. An optical probe colorimeter can be dipped directly into the solvent vat to give an instantaneous readout.

A set of guidelines have been developed in which all of the discussed measurements are used collectively to determine whether or not a solvent is spent (see Reference 23).

- Measure the absorbance with an optical probe colorimeter or a hand-held spectrometer placed directly into a vat or container to obtain an instantaneous readout of visible absorbance (at 500nm). Assign a rating (0 to 2) based on Table 2.
- Measure the density using an electronic meter or pycnometer. Assign a rating (0 to 3) based on Table 2.
- Measure the viscosity using an Ostwald viscometer. Assign a rating (0 to 2) based on Table 2.
- Measure the electrical conductivity with a conductivity meter. Assign a range (0 to 1) based on Table 2.
- Sum the individual rating in steps 1 through 4 to obtain an overall rating for the solvent.
- If the cutoff rating is greater than or equal to six, the solvent can be considered spent and is a candidate for reclamation. Solvents with a rating of less than six should be kept in service.

As stated, the values in Table 2 are guidelines developed for one specific solvent recovery process. Values must be determined for each individual process.

Table 2. Test criteria for used solvents (see Reference 23).

Rating	Absorbance (500 nm)	Density 17°C)	Viscosity cp (18°C)	Conductivity nmbo (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	-	-	-

EXPERIMENTAL DISTILLATION STUDY

Distillation studies of replacement solvents for chlorinated solvents were conducted at Montana State University, Bozeman, Montana, by the Chemical Engineering Department. Thirteen solvents were studied in FY-92. These solvents were selected from the Chlorinated Solvent Replacement Program for their performance as solvents and minimum corrosion effects. It was assumed that the solvents be used in clean up after a paint stripping operation. To simulate this, the solvents refluxed in paint chips were obtained from a paint stripping facility at Kelly Air Force Base, San Antonio, Texas. Also, it was assumed that the solvents would be used in metal cleaning processes where grease, oil, and wax would be part of the residual material on the metal surfaces. To simulate this, two solvents, Orange-Sol De-Solv-It and EXXON EXXATE 1000, were loaded with wax (Petrolite BE SQUARE 175) to simulate the effect of metal cleaning on the solvents. In the wax-loaded solvents a problem arose with foaming in the distillation column. This resulted in a study of defoaming agents. Twenty nine defoaming agents were obtained from 11 vendors. The results of the study are discussed in the following section. Also the distillation study and results are shown in Appendix F.

DEFOAMING AGENT STUDY

During the distillation study, some of the solvents caused foaming in the distillation column. This was especially true in the solvents loaded with wax. This initiated a study of defoaming agents. Table 3 lists the defoaming agents used in the study.

Of the 29 defoaming agents studied, only one (Dow Corning 7 Additive) worked in the distillation of the wax-loaded solvents Exxate 1000 and Orange-Sol De-Solv-It. Three defoaming agents worked in the distillation of the solvent Exxate-1000. They were Dow Corning 7 Additive, WITCO BB 3295, and Henkel Dehydran 1628.

Table 3. Defoaming agents investigated by MSU.^a

Air Products Surfynol DF-1100	Henkel Dehydran 1628
" " DF-58	" " 1208
" " XF-B4152	" " 1293
Witco BB 3295	" " 1513
" BB 3056A	" ARA-7219
" BB 7762	" Perenol S-43
EXXON COREXIT 362	" " E-2
" Surflo AF 2436	" " E-3
Surflo AF 8574	
" " AF 7669	Union Carbide SAG 47
PPG MAZU DF-200-EX	" "SAG 1000
" MACOL 5100	BASF Pluronic L-31
" MAZTREAT 246	" " 25 R-2
AKZO Propomeen T-25	Hercules Defoamer 831
Genesee Polymers DB-12	Dow Corning 7 Additive

a. Personal correspondence from L. Berg, Montana State University, to R. E. McAtee, EG&G Idaho, Inc., June 21, 1992.

SOLVENT DISTILLATION PROCEDURES AND RESULTS²⁴

1. Prepare a mixture of 450 grams of the solvent and 50 grams of paint chips. Stir this mixture at the solvent manufacture's suggested operating temperature for approximately 48 hours.
2. For the samples refluxed in paint chips, use a 11.0 μM filter in the prefiltering step and a 0.7 μM filter as the final filter. After filtering, if the solvent is in two phases, separate by decantation before distillation.
3. Do not filter the wax-loaded samples.
4. Rectify liquid samples in batch mode in rectification column. Have 8, 15, and 30 theoretical plate helices packed columns available. Record and plot data as temperature of overhead vs. percent of charge distilled. This will indicate the quality and boiling point of each constituent.
5. Repeat rectification and collect samples of the pure material as they come off. Check purity on the Alltech RSL 300 gas chromatograph and Spectra-Physics Chrom-Jet integrator.
6. Knowing the several compounds in the mixture, determine the relative volatility in the other type vapor-liquid equilibrium still between each adjacent pair.
7. On the adjacent pairs from #5, if the relative volatility is above 1.4, demonstrate separation in the rectification column of known theoretical plates to determine precisely the true relative volatility.
8. Identify from all the samples received which can be separated by straight rectification and which will require more intensive separation methods, such as azeotropic or extractive distillation.

The solvents used in the above distillation study by Montana State University are listed in Table 4.

Table 4. Chlorinated solvent replacement.

<u>Manufacture</u>	<u>Solvent</u>
Ambion Corp	Hotstrip
Specialty Prod.	SP-828
Orange-Sol	De-Solv-It
Petroferm Corp.	Bioact VS-5
Colloid Prod.	RBD SEMI
Harry Miller Corp.	Citriterge 8910
Exxon	Exxate 1000
Arco Chemical Co.	Acrosolv-TMP
Vista	LPA-210
Boeing	MOK
	MOK 2437
GAF	Ship Shape
	n-methylpyrrolidene

CONCLUSION

This report is a review of the literature on current and past solvent recycling efforts by industry in this country. It shows that only about 20% of the solvent waste is being recycled. Several articles discuss the economics of recycling and how specific industrial processes have greatly reduced their hazardous waste output and their costs for new solvents. Even when the recycled solvents are of a purity that cannot be reused in the original applications, it is marketable to other industries or can be used as a fuel substitute. In general, recycling solvents reduces the amount and cost of solvent waste disposal.

This study shows that the distillation process is still the primary solvent recycling method. Because it is energy intensive, there has been much effort to reduce the energy requirements through innovative design and pretreatment. Analytical methods have been studied to determine the life cycle of a solvent so it can be used to maximum efficiency. These innovations contribute to the reduction of solvent waste.

The distillation study at Montana State University has shown that many of the replacement solvents for chlorinated solvents can be recovered for reuse. The percentage of recovery of these solvents is comparable to that of other solvent distillation processes. Finally, the data collected in this study will be entered into the Solvent Handbook.

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Appendix A

Solvent Recycle/Recovery Subtask
FY-91 Summary Report

**CHLORINATED SOLVENT SUBSTITUTION PROGRAM
SOLVENT RECYCLE/RECOVERY SUBTASK
SUMMARY OF FY-91 INVESTIGATION**

D. Hsu

December 1991

SUMMARY

Distillation and membrane separations tests on recovering non-chlorinated solvents that meet the performance efficiency and corrosion criteria were conducted in the laboratory in FY-91. The results, summarized in this report, show that distillation could be both technically and economically feasible. Membrane separations technology, on the other hand, does not appear promising. As a result, study of distillation is recommended to be continued, but that of membrane separations discontinued.

INTRODUCTION

As an outgrowth of the Department of Energy (DOE) Chlorinated Solvent Substitution Program, the Solvent Recycle/Recovery Subtask was initiated two years ago in FY-90. The goal was to develop substitute solvent recycle/recovery process(es) so that the use of fresh solvents can be reduced and the generation of spent solvents that need to be disposed can be minimized. Specific objectives of the subtask were: (a) to identify and test available technologies to recover and recycle substitute solvents used in production and maintenance operations and (b) to identify emerging technologies promising for recovering and recycling spent substitute solvents.

Candidate substitute solvents that pass the test criteria, such as paint stripping performance efficiency and corrosion test, examined in separate subtasks under the Chlorinated Solvent Substitution Program, are studied in the solvent recycle/recovery subtask. The first phase of this subtask, conducted in FY-90, consisted of a literature search of solvent recovery technologies and a preliminary distillation study. In the distillation study, fresh substitute solvents were distilled. The results of the Phase I study have been previously reported.¹

As a result of the Phase I literature search, distillation and membrane separations technology were identified to be promising for further investigation. Accordingly, the effort in FY-91 was focused on these two technologies. Laboratory tests using these technologies to recover spent substitute solvents was subcontracted to and conducted at the Department of Chemical Engineering, Montana State University. Professors Lloyd Berg and F. Phil McCandless were responsible for conducting, respectively, the distillation and membrane separations tests.

SCOPE OF INVESTIGATION

The scope of investigation for FY-91 for distillation included examining spent and fresh solvents to determine which method should be recommended for solvent recovery application. Possible distillation methods include precision rectification and azeotropic and extractive distillation.

For membrane separations technology, microfiltration, ultrafiltration (UF), and nanofiltration were to be examined to determine the feasibility of using these processes for solvent recovery.

Fresh, spent, and recovered solvents would be analyzed by high pressure liquid chromatography (HPLC) to compare their characteristics. A HPLC system was to be acquired in FY-91 for the analyses.

A total of 15 solvents, including 10 paint stripping solvents and 5 biodegradable cleaning solvents, were originally planned to be tested¹. For various reasons, including candidate substitute solvent not truly commercially available, containing highly toxic ingredients, being aqueous, and showing intolerable corrosion characteristics upon further testing, through the course of the study, the number of solvents was reduced to 9.

RESULTS AND DISCUSSION

The results of the distillation and membrane separations studies are contained in the two reports, prepared, respectively, by Professors Berg and McCandless, attached to this summary report. Because of the difficulties incurred in obtaining true spent solvents, tests were conducted on simulated spent solvents. For paint strippers, paint chips obtained from a solid CO₂ blasting paint removing demonstration project were dissolved in fresh solvents to generate simulated spent solvents. For biodegradable cleaners, wax was dissolved in fresh solvents to generate simulated spent solvents.

Distillation

Distillation tests show that it is generally feasible to recover the substitute solvents by distillation. For single-component paint strippers, the recovery procedure is relatively simple—a single-temperature distillation/precision rectification will achieve recovery of the solvents. For multi-component paint strippers, distillation/precision rectification at multiple temperatures is needed. For either single- or multi-component paint strippers, vacuum distillation may be required, depending on the thermal stability of the solvent components.

Although not specified in the scope of work, a couple of sample economic analyses, one of a single-component solvent and the other of a multi-component solvent, were conducted and presented in Berg's report. It shows that, with a hypothetical plant size of 30,000 gal/year, distillation recovery of solvents used for paint stripping would have a payback period of about three months. For a three-component paint stripper, the same plant size would result in a payback period of approximately 13.5 years. However, if one large facility is used to process the same three-component solvent from five 30,000 gal/year

operations (e.g., a centrally located solvent recovery plant to process spent solvents from five Air Force Logistic Centers), the payback time would be approximately 7 months.

It should be noted, however, that the economic analyses presented in Berg's report were preliminary in nature. In-depth analyses will be required to further identify the economic feasibility of recovering substitute paint strippers by distillation.

Distillation recovery of biodegradable cleaners is not as straightforward. Tests show that foaming would be a problem and an antifoaming agent would be necessary to break the foam in the distillation column. An appropriate antifoaming agent is being sought at the present time.

Membrane Separations

Preliminary membrane separations tests show that, using a membrane made of material compatible with the solvent, UF can remove contaminants in the spent solvent. However, two problems appear to exist that will need to be solved before a practical membrane process can be developed for solvent recovery application. First, current commercial membranes are designed primarily for aqueous system applications. A commercial membrane for organic solvent application is yet to be developed. Second, for one membrane (made of cellulose acetate) that is compatible with several substitute solvents tested, the system pressure required to obtain measurable flux was excessive (over 600 psi versus typical UF pressures of less than 100 psi).

HPLC Analysis

HPLC analysis of fresh, spent, and recovered substitute solvents was planned to be conducted to verify the integrity of the recovered solvents. Unfortunately, because of a series of unexpected analytical difficulties, ranging from setting up of the HPLC system to getting the system to function properly (involving selecting proper system parameters), no usable results have been generated as of the time of the report. Work is still ongoing in trying to produce the planned analyses.

CONCLUSIONS

Since the work is still ongoing, only tentative conclusions can be made:

- Both distillation and membrane technologies are technically feasible for recovering substitute solvents after they have become spent
- Because of the excessive system pressure required and because of the challenging task of finding appropriate membranes for use, membrane technology does not appear promising for substitute solvent recycle/recovery at present
- Limited preliminary economic analyses show distillation to be promising for substitute solvent recycle/recovery application; the payback period for investment appears favorable

- The characteristics of recovered substitute solvents are yet to be determined, pending completion of the HPLC analyses.

RECOMMENDATIONS

Based on the results obtained thus far, the following recommendations are made:

1. Complete HPLC analysis of fresh, spent, and recovered substitute solvents to verify the integrity of the recovered solvents.
2. Continue searching for an appropriate antifoaming agent for use in distillation recovery of biodegradable cleaners.
3. Discontinue laboratory testing of solvent recycle/recovery by membrane separations.
4. Expand/Refine the economic analysis initiated by Dr. Berg; conduct, to the extent practical, in-depth analysis to better define the economic feasibility of distillation recovery of substitute solvents. If the results are favorable, a pilot plant test program should be considered.

REFERENCES

1. Paffhausen, M. W., D. L. Smith, and S. N. Ugaki, "Solvent Recycle/Recovery Phase I Final Report," EGG-WTD-9297, September 1990.

Appendix B

Membrane Process for Solvent Recycle

Chlorinated Solvent Substitution Program
Recycle/Recovery Subtask

MEMBRANE PROCESS FOR SOLVENT RECYCLE

FINAL REPORT
CONSULTING AGREEMENT NO. C90-103140, MOD. 1
F. P. McCANDLESS
DEPT. OF CHEMICAL ENGINEERING
MONTANA STATE UNIVERSITY
BOZEMAN, MT 59717

SUMMARY

Microparticle filtration followed by ultrafiltration was investigated as a process to recover and recycle non-chlorinated solvents used for paint stripping operations. Spent solvents were simulated by digesting paint chips with hot solvents. These chips were obtained from airplane surfaces by blasting with solid CO₂. From about 47 to 80 percent of the paint solids were recovered by MF through filters that reject particles greater than 11 μ M, while another 0.1 to 1.0 percent was recovered with 0.7 μ M filters. UF through teflon membranes with 0.02 μ M pores resulted in no further paint solids rejection. UF tests of solvents containing no aprotic/highly polar solvents (i.e. 2-(β -butoxyethoxy)ethanol, benzyl alcohol, glycol phenylethers) were carried out with a cellulose acetate - 10,000 MWCO membrane using the filtrate from the 0.7 μ M filters as feed. From about 38 to 90 percent of the dissolved paint "solids" was rejected in these tests. Membrane flux varied from 0.04 to 0.2 CC/HR CM² with Δ P between 650 and 750 psi. Commercially available UF Membranes were not found that are compatible with the aprotic/polar solvents such as N-methylpyrrolidone and ethanolamine.

Based on the successful UF tests with the alcohol/ether based solvents, it is concluded that MF followed by UF is a feasible process for solvent recovery/recycle. However, the practical application of these processes for most commercially available solvents awaits the development of suitable solvent compatible UF membranes.

INTRODUCTION AND BACKGROUND

Chlorinated solvents are being phased out because they are environmentally objectionable, and costly to dispose of. As a result, the CHLORINATED SOLVENT SUBSTITUTION PROGRAM was initiated to find suitable substitutes for chlorinated solvents used for paint stripping, degreasing, and metal cleaning operations; and to develop process to recover and recycle the used non-chlorinated solvents. The recycle/recovery research is aimed at restoring used solvents to their pure and/or usable forms. Both distillation and membrane processes are being considered for solvent recycle. This particular subtask is concerned only with membrane processes that might be used for solvent recovery.

The objective of this research was to determine if present Microfiltration (MF) and/or Ultrafiltration (UF) processes can be applied to solvent recycle. The objective was to find suitable MF and UF membranes that will reject particulate matter as well as dissolved "large molecule" contaminants and pass the solvents. The key membrane properties are pore size, porosity, and membrane composition. The pore must be small enough to prevent contaminants from passing, but large enough for solvent molecules to freely pass. Porosity must be high enough so that a reasonable permeate flux can be obtained. The membrane material must be chemically inert to the solvent/contaminant species.

The processes are roughly characterized by pore size and/or the size of solute or particulate species that will be rejected as shown below:

<u>PROCESS</u>	<u>MEMBRANE PORE SIZE</u>	<u>SMALLEST SPECIES REJECTED</u>
MF	0.1 - 10 μ M	paint pigments, bacteria, red blood cells
UF	0.001 - 0.1 μ M	virus, protein molecules 1000 - 100,000 MW

Many proprietary processes and materials are used to manufacture these membranes. Only commercially available membranes were considered for this investigation. However, based on inquiries to both domestic and foreign manufacturers, very few UF membranes are being made that OP, compatible with the solvents being tested.

MATERIALS

Paint stripping, degreasing, and metal cleaning tests of non-chlorinated solvents are being carried out elsewhere as different subtasks. Paint loaded solvents from paint stripping operations were simulated for the membrane tests by contacting paint chips with the candidate solvents in a stirred flask fitted with a water cooled condenser. The paint chips were obtained by INEL from a company specializing in paint removal by "blasting" the painted surface with solid CO₂. The various solvents were loaded with paint chips as shown in table 1. Heating of the solvent-paint chip mix was continued with constant agitation for 48 hours.

TABLE 1. SOLVENT LOADING WITH PAINT CHIPS

Number	Solvent	Temperature (°F)	Solvent Amount (gram)	Water Amount (gram)	Paint Chips (gram)
1	Fine organics FO 606	ambient	900	--	100
2	Frederick Gumm Clepo Environstrip 222	180	450	450	100
X 3	Exxon Exxate 1000	140	900	--	100
X 4	BioTek no. 140 Saf Solv	150	900	--	100
X 5	Patclin #126	180	900	--	100
6	Turco T5668 w/ seal	150	900	--	100
7	Rochester Midland PSS 600	150	900	--	100
8	McGean Rohco CEE BEE A 245 w/ seal	240	900	--	100
9	GAF m-Pyrol	150	900	--	100
X 10	Orange Sol De-Solv-it	140	900	--	100
11	McGean Rohco CEE BEE A477 w/seal	180	900	--	100

-- = NO WATER

X = ELIMINATED FROM CONSIDERATION AFTER PROJECT STARTED

The composition of the solvents are given in table 2:

TABLE 2. COMPOSITION OF SOLVENTS

<u>SOLVENTS</u>	<u>APPROXIMATE SOLVENT COMPOSITION</u>
FINE ORGANICS FO 606	ETHANOL AMINE 30%, ETHYLATED NONYL PHENOL 6%, N-METHYLPYRROLIDONE 50%, WATER 14%. 20% MINERAL OIL SEAL
FREDERICK GUMM CLEPO ENVIRONSTRIP 222	DODECYL BENZENE SULFONIC ACID 25%, ETHYLENE GLYCOL PHENYL ETHER 65% DIETHYLENE GLYCOL PHENYL ETHER 10%
PATCLIN #126	WATER 20%, 2(B-BUTOXETHOXY)ETHANOL 50%, ALKANE SULFONIC ACID 30%
TURCO T5668 W/SEAL	POTASSIUM HYDROXIDE 5%, MONOETHANOL AMINE 30%, N-METHYLPYRROLIDONE 45%, HYDROTREATED NAPHTHENIC DISTILLATE 15%, N-BUTYL and N-ETHYL-P-TOLUENE SULFONAMIDE 5%. WITH 20% MINERAL OIL SEAL
ROCHESTER MIDLAND PSS 600	N-METHYLPYRROLIDONE 100%
McGEAN ROHCO CEE BEE A 245 W/SEAL	BENZYL ALCOHOL 94% UNKNOWN 6% WITH 20% MINERAL OIL SEAL
GAF M PYROL	N-METHYLPYRROLIDONE 100%
McGEAN ROHCO CEE BEE A 477 W/SEAL	ETHANOLAMINE 100%. WITH 20% MINERAL OIL SEAL

NOTE: Compositions based on distillations carried out at MSU together with data presented by the solvent manufacturer on material safety data sheets - constituents have been confirmed, percentages are approximate.

MICROPARTICLE FILTRATION

Loaded solvents were first filtered through Whatman #1 filter paper (11 μ M retention), then through Whatman GF/F microfiber filter discs (0.7 μ M retention) to remove particulate matter. In general the loaded solvents were very viscous and difficult to filter; requiring several hours in a conventional filter flask with house vacuum on the flask. Residual solvent was evaporated from the particulate matter by

placing the solids filter paper in an oven overnight at 150°C. The fraction of solids recovered by microparticle filtration is shown in table 3.

**TABLE 3. PERCENT OF PAINT
SOLIDS RECOVERED BY MICROPARTICLE FILTRATION**

<u>SOLVENTS</u>	WT. PERCENT OF PAINT SOLIDS RETAINED ON FILTER	
	<u>11µM</u>	<u>0.7µM</u>
FINE ORGANICS FO 606	-	-
FRED GUMM CLEPO	78.7	0.06
PATCLIN # 126	51.0	0.39
TURCO T5668	47.4	0.35
ROCHESTER MIDLAND PSS 600	51.9	0.96
McGEAN ROHCO A-245	58.6	1.03
GAF M-PYROL	51.9	0.96
McGEAN ROHCO A-477	63.2	0.72

UF MEMBRANES AND TESTS

In an effort to identify commercially available membranes suitable for the solvent recycle process, inquiries were made to 22 membrane manufactureres(10 USA, 4 Japan, 8 European). These companies are listed in the appendix. Most of the companies never replied, and those that did indicated that none of their membranes were compatible with the paint stripping solvents.

In addition, most of the catalogs from chemical and laboratory supply companies were pursued to see if membranes could be supplied through these vendors.

These efforts resulted in 6 membranes to try as listed in Table 4.

TABLE 4. UF MEMBRANES: SOURCE AND CHARACTERISTICS

<u>SOURCE</u>	<u>MEMBRANE CHARACTERISTICS</u>
GOODFELLOW CORPORATION MALVERN, PA	PTFE .02 μ PORES x 0.085MM thick PTFE .02 μ PORES x 0.225mm thick (backed with 0.15mm POLYPROPYLENE FABRIC)
SPECTRUM HOUSTON TEXAS	MOLECULAR POR TYPE C CELLULOSE ACETATE DISC MEMBRANE, 10,000 MWCO
MEMBRANE DEVELOPMENT SPECIALISTS ESCONDIDO, CALIFORNIA	EXPERIMENTAL MEMBRANES DESIGNATED VX, N-25, K-50 COMPOSITION AND PORE SIZE UNKNOWN.

UF TESTS

The UF test apparatus is shown schematically in Figure 1. It consists of a metering pump (MILROYAL CONTROLLED VOLUME PUMP, MODEL A-1), membrane test cell, back pressure regulator together with appropriate feed and product reservoirs. The test cell provides support for the thin membrane, and separates the system into feed and product (permeate) regions. The cell body consists of two stainless steel flanges which are held together by a large compassion nut. A porous stainless steel disc fits snugly into a cavity machined into the low pressure side and provides the necessary support for the membrane, while allowing flow of the permeate out of the cell. Two o-rings, one in either half of the cell are placed in machined grooves to provide the necessary seals from the atmosphere, and between the feed and permeate side of the membrane. The high pressure half of the cell includes a feed inlet, a cavity for flow past the membrane surface, and a reject outlet. The low pressure half consists of the porous support disc, and the permeate outlet. Exposed membrane area is 17 cm².

Back pressure is maintained on the feed side of the test cell with a grove, "MITY MITE" back pressure regulator.

All candidate UF membranes were tested for solvent compatibility by placing fresh solvent on the membrane surface and visually observing any membrane deterioration. Solvents containing ethanolamine and/or N-methylpyrrolidone dissolved the cellulose acetate membrane as well as the membrane coating on the MDS K-50 and VX membranes. The solvent compatible membranes were

FIGURE 1. MEMBRANE TESTING CONFIGURATION

tested by mounting the membrane in the test cell and circulating feed (filtrate from the 0.7 μ M microparticle filtration) through the cell under pressure, back to the feed reservoir

Dissolved solids in the feed, permeate, and fresh solvent were determined by simple evaporation. A weighed amount of solvent was placed in ceramic evaporation dishes and the solvent evaporated from the solids by placing the dishes in an oven maintained at 150°C overnight. In some cases the fresh solvent contained considerable dissolved solids (i.e. potassium hydroxide), or material that produces solids on decomposition (dodecyl-benzene sulfonic acid).

The results of the UF tests are presented in Table 5.

TABLE 5. RESULTS OF UF TESTS FOR DISSOLVED

PAINT SOLIDS REJECTION

A. 0.02 μ M PORE TEFLON MEMBRANE (RESULTS WERE SIMILAR FOR BOTH MEMBRANES)

<u>SOLVENTS/CONDITIONS</u>		<u>WT% SOLIDS</u>		<u>PERMEATE</u>	<u>WT% PAINT SOLIDS REJECTED</u>	<u>FLUX CC/HRCM²</u>
		<u>FRESH SOLVENT</u>	<u>UF FEED</u>			
FINE ORGANIC	600 psi	3.7	10.2	10.1	----	0.22
FRED GUMM	50 psi	17.9	14.7	14.9	----	2.76
TURCO 5668	35 psi	6.9	10.2	10.8	----	1.62

B. 10,000MWCO SPECTRUM TYPE C (CELLULOSE ACETATE)

<u>SOLVENTS/CONDITIONS</u>		<u>WT% SOLIDS</u>		<u>PERMEATE</u>	<u>WT% PAINT SOLIDS REJECTED</u>	<u>AVERAGE FLUX CC/HRCM²</u>
		<u>FRESH SOLVENT</u>	<u>UF FEED</u>			
FRED GUMM 222	750 psi					
FRESH SOLVENT		21.0	21.0	18.5	---	0.02
PAINT LOADED SOLVENT		17.7	15.2	13.0	---	0.05
PATCLIN #126	685 psi	1.6	9.3	5.1	37.7	0.16
				4.0	51.7	0.07
				3.2	61.7	0.06
				3.9	52.9	0.05
McGEAN ROHCO A-245						
FRESH SOLVENT		1.91	1.91	1.40		0.07
PAINT LOADED SOLVENT		1.91	4.45	1.65	90.5	0.04
	650 psi					

C. N-25 MEMBRANE DEVELOPMENT SPECIALIST EXPERIMENTAL MEMBRANE

TURCO T566;	350 psi	6.9	10.6	10.3	8.0	0.90
McGEAN ROHCO A-245		2.0	4.8	4.6	9.0	0.60
	350 psi					

- NOTES: (1) FRED GUMM SOLVENT IS NOT A HOMOGENEOUS MIXTURE,
 (2) CALCULATIONS FOR PATCLIN SOLVENT ASSUMES THAT SOLIDS IN FRESH SOLVENT
 ARE NOT REJECTED BY MEMBRANE

DISCUSSION

From about 47 to 80 percent of paint solids in the loaded solvents was recovered by microparticle filtration through filters that reject 11 μ M and greater particles; while an additional 0.1 to 1.0 percent was rejected by the 0.7 μ M filter. Evaporative analysis of the filtrate from the 0.7 μ M filtration showed that the used solvents contained from about 4 to 15 wt. percent "solids" depending on solvent. These compositions are generally consistent with the amount of paint chips recovered by microparticle filtration; that is from about 20 to 50 percent of the weight of the paint chips is dissolved in the solvents.

In general the solvents loaded with paint chips were very viscous and difficult to filter through the Whatman #1 paper, requiring several hours using 11 cm diameter filters and house vacuum. Filtration rate was greatly increased by frequent changing of the filter paper. No judgement was made as to the degree of filtration difficulty among the solvents, however.

Ultrafiltration through either 0.02 μ M teflon membrane resulted in no apparent dissolved paint solids rejection. UF with aprotic/highly polar solvents such as those containing ethanolamine and/or N-methylphrrolidone could not be carried out with membranes other than the teflon films since other solvent compatible membranes apparently do not exist. Inquiries were made of 22 domestic and foreign companies who manufacture UF membranes with no indication that UF membranes with suitable pore characteristics are now manufactured from materials that are compatible with these solvents.

UF tests with alcohol and ether based solvents (2-(β -butoxyethoxy)ethanol, benzyl alcohol, glycol phenyl ethers) using a SPECTRUM TYPE C (cellulose acetate) membrane characterized as having pores with 10,000 MWCO confirmed the technical feasibility of using UF for solvent recovery from paint loaded solvents. This membrane rejected over 90 percent of the dissolved paint solids from the McGean Rohco A-254 solvent, from about 38 to 62 percent from the PATCLIN #126 solvent, and a significant but undetermined amount from the FRED. GUMM 222 solvent. This membrane also rejected 27 percent of the solids from fresh McGean Rohco A-245 Solvent and 24 percent of the solid from fresh Fred. Gumm solvent. Paint solids rejection from the GUMM solvent could not be determined because the fresh solvent contains more "solids" than the permeate. It was later discovered that this solvent is not a homogeneous mixture, which accounts for the difficulty in analysis. However, in all cases a high (650-750psi) pressure was required to obtain a measurable permeation rate.

Although these tests confirmed the technical feasibility of recycle paint solvents by UF, the practical application would require membrane system engineered for this use. These membranes would require much higher porosity than the laboratory films used in this study. Indeed, better membranes that might be applied to the alcohol/ester solvents probably now exist. For example, we obtained literature from DOW/DANMARK separation systems that indicates they manufacture polyvinylidene fluoride UF membranes with pore characteristics between 100,000 and 6,000 MWCO. Dow claims water flux through these membranes in the range of 200-500 L/M²HR with maximum operating pressure between 10 and 15 bar. These membranes could probably be applied to the alcohol/ether based solvents but attempts to obtain membrane samples for testing have been unsuccessful to date.

Application of UF to recycle of solvents such as N-methylpyrrolidone and ethanolamine awaits development of membranes from materials that are compatible with those solvents.

APPENDIX A

LIST OF COMPANIES CONTACTED FOR UF MEMBRANES

OSMONICS
5951 CLEARWATER DRIVE
MINNETONKA, MINNESOTA 55343

ABCOR, INC.
850 MAIN STREET
WILMINGTON, MA 01887

AMICON CORP
21 HARTWHEEL AVENUE
LEXINGTON, MA 02173

DESALINATION SYSTEMS, INC
1107 WEST MISSION AVENUE
ESCONDIDO, CA 92025

DORR-OLIVER
77 HAVEMEYER LANE
STANFORD, CT 06904

MILLIPORE CORP
ASHBY ROAD
BEDFORD, MA 01730

NUCLEPORE CORP
7035 COMMERCE CIRCLE
PLEASANTON, CA 94566

ROMICON INC.
100 CUMMINGS PARK
WOBBURN, MA 01801

DOW CHEMICAL
SEPARATION SYSTEMS
100 LARKIN CENTER
MIDLAND, MICHIGAN 48674

MEMBRANE DEVELOPMENT SPECIALISTS
1313 SIMPSON WAY, SUITE E
ESCONDIDO, CA 92025

ASAHI GLASS CORP
2-1-2, MARUMOCHI
CHYODA-KU, TOKYO
JAPAN

NITTO ELECTRIC INDUSTRIAL CO., LTD
1-1-2, SHIMOHOZUMI, IBARAKI
OSAKA
JAPAN

DAICEL CHEMICAL INDUSTRIES, LTD
8-1, 3-CHOME, KASUMIGASEKI
CHLYODA-KU, TOKYO 100
JAPAN

TEIJIN, LTD.
MEMBRANE PROJECT
1-1, UCHISAIWAI-CHO 2-CHOME
CHLYODA-KU, TOKYO 100
JAPAN

PATTERSON CANDY INTERNATIONAL, LTD
LAVERSTOKE MILL
WHITCHURCH, HAMPSHIRE RG287NR
ENGLAND

RHONE-POULENC
SPECIALITES CHIMIQUES
18, AVENUE d'ALSACE
92400 COURBEVOIE
FRANCE

SOCIETE DE FABRICATION
d'ELEMENTS CATALYTIQUES
BP33
84500 BOLLENE
FRANCE

WAFILIN
P.O. BOX 5
7770 AA HARDENBERG
THE NETHERLANDS

D.D.S. INC.
P.O. BOX 149
4900 NAKSKOV
DENMARK

BERGHOF GmbH.
P.O. BOX 1523
7400 TUBINGEN 1
WEST GERMANY

KALLE
POSTFACH 3540
620 WIESBADEN 1
WEST GERMANY

SATORIUS GmbH.
POSTFACH 19
3400 GOTTINGEN
WEST GERMANY

APPENDIX B

MICROFILTRATION/ULTRAFILTRATION OF WAX LOADED SOLVENTS

SUMMARY

Microfiltration through a 0.7 μ m filter followed by ultrafiltration through a 10,000 MWCO Membrane was investigated as a means of removing wax from loaded solvents. Spent Cleaning solvents were simulated by dissolving wax in ORANGE - Sol DE-SOLV-IT and EXXON EXXATE 1000. About 40 percent of the wax is removed by MF. The UF Membrane was swollen by the ORANGE-SOL solvent and made it impremiable. About 5 percent of the wax in the EXXON solvent UF feed was removed by UF.

MF/UF TESTS

Two additional solvents were loaded with wax to simulate waste solvents used in cleaning operations. PETROLITE BE SQUARE[®] 175 wax was dissolved in ORANGE-SOL DE-SOLV-IT and EXXON EXXATE 1000 solvents with loading levels of 50 and 10 g/l respectively. At this loading level the wax was rapidly and completely dissolved in hot (140^o F) solvent, resulting in clear solutions. Both solvents became cloudy as wax crystals precipitated as the loaded solvent's cooled to room temperature. This material was then filtered through the 0.7 μ m glass microparticle filters with the filtrate being used as feed to the UF (SPECTRUM TYPE C 10,000 MWCO) system. This was the only UF membrane available that appeared to be compatible with these solvents.

Quantative analysis for wax concentration in the various feed and product stream was accomplished by evaporation at 100^oC. Blank determination on the wax showed no loss of wax under evaporation conditions. The result's of the tests are presented below:

RESULTS:

Solvent compositions as reported by the manufacturer:

ORANGE-SOL DE-SOLV-IT: Mixture of orange oil and technical grade menial oil.

EXXON EXXATE 1000: Mixture of C₉-C₁₁ branched oxo-alcohol esters of acetic acid.

<u>SOLVENT</u>	<u>WT. PERCENT WAX</u>			<u>UF PERMEATE</u>	<u>% REJECTION FROM 0.7μm FILTRATE BY UF</u>
	<u>LOADED SOLVENT</u>	<u>FILTRATE FROM 0.7μm</u>	<u>% OF LOADED WAX RETAINED ON 0.7μm</u>		
ORANGE.SOL DE-SOLV-IT	5.94%	4.71	41.0	---	---
EXXON EXXATE	1.15%	0.67	46.0	0.64	6.3

FLUX of EXXON EXXATE THROUGH UF MEMBRANE: 0.63 CC/HR CM² Δ P MEMBRANE = 750 PSI

DISCUSSION:

The wax from the loaded ORANGE-SOL solvent was very difficult to filter through the 0.7 μ M filter because the large amount of precipitated wax rapidly "blinded" the filters. The small amount of wax that precipitated from the EXXON Solvent was easily filtered. Forty and forty two percent of the loaded wax was removed from the two loaded solvents by the 0.7 μ M filter.

No permeate was obtained during the UF test of the ORANGE-SOL solvent after about 7 hours at 750 psi. When the membrane was removed from the test cell it showed considerable swelling.

A reasonable flux was obtained during UF of the EXXON solvent, but soluble wax rejection was low with only about 5 percent of the wax in the UF feed being rejected.

From these results it is concluded that UF through 10,000 MWCO cellulose acetate membrane is not practical for removal of wax from wax loaded solvents.

Appendix C

Recovery of Waste Solvents by Rectification, Azeotropic and/or Extractive Distillation

RECOVERY OF WASTE SOLVENTS BY RECTIFICATION, AZEOTROPIC AND/OR EXTRACTIVE DISTILLATION

By Lloyd Berg, Chemical Engr. Dept., Montana State University,
Bozeman, Montana.

The objective of the Solvent Recycle/Recovery Task of the DOE Chlorinated Solvent Substitution Program is to minimize hazardous wastes by identifying recycle/recovery techniques for the proposed substitute solvents.

Solvents are utilized for cleaning, stripping and various other maintenance operations of aircraft parts and equipment. After use, many of the solvents can be recovered and reused. However, several of the solvents currently in use are chlorinated and emit volatile organic compounds, which are toxic to the environment and to operating personnel. Wastes generated from these solvents are regulated by the U.S. Environmental Protection Agency, and soon use and manufacture of the solvents may be restricted.

The first phase of the program was to examine by distillation the potential solvents as designated by INEL. The following solvents were received and tested. They are listed in Table 1. All contained the chemical compounds that the manufacturer claimed. The distillation plots for the new and unused solvents are in Appendix 1.

Table 1 - Solvents Received

<u>Company</u>	<u>Product Designation</u>	<u>Compound(s)</u>
EXXON	Exxate-1000	Nonyl acetate, Undecyl acetate
Orange-Sol	De-Solv-It	Mineral oil, Orange ester
3D	3d Supreme	Dipropylene glycol methyl ether, water
Chemical Solvents	SP-800	N-Methyl pyrrolidinone, Tetrahydrofurfuryl alc. Diethanolamine
FineOrganics	FO-606	N-Methyl pyrrolidinone, Ethanolamine, Water
Frederick Gumm	Clepo 222	Ethylene glycol phenyl ether
GAF	M-Pyrol	N-Methyl pyrrolidinone
Patclin	Hot Strip 126	2-Butoxyethoxyethanol, Water
McGean-Rohco	C B A-245	Benzyl alcohol
McGean-Rohco	C B A-477	Ethanol amine

Table 1 - Continued

Rochester Midland	PSS-600	N-Methyl pyrrolidinone
Turco	T-5668	N-Methyl pyrrolidinone, Ethanolamine
Bio-Tek	Saf-Solv-140	Cetyl acetate, Octadecyl acetate, Decyl acetate

The second phase of the program was to simulate the solvents in the condition that they would be in after being used in paint stripping. This was done by heating and stirring a mixture of the solvent and the paint chips for 48 hours. The temperature and amount of solvent, water and paint chips are listed in Table 2. EXXON Exxate 1000, BioTek-140 and Orange Sol De-Solv-It were eliminated from this test program.

-Table 2 Solvent Loading With Paint Chips

NUMBER	Solvent	Temperature (°F)	Solvent Amount (gram)	Water Amount (gram)	Paint Chips (gram)
1	Fine Organics FO 606	ambient	900	--	100
2	Frederick Gum Clapo Envirostrip 222	180	450	450	100
X 3	Exxon Exxate 1000	140	900	--	100
X 4	BioTek no. 140 Saf solv	150	900	--	100
5	Patellin #126	180	900	--	100
6	Turco T5668 w/ seal	150	900	--	100
7	Rochester Midland PSS 600	150	900	--	100
8	McGean Rhoco CEE BEE A 243 w/ seal	240	900	--	100
9	GAF m-Pyrol	150	900	--	100
X 10	Orange Sol De-Solv-It	140	900	--	100
11	McGean Rhoco CEE BEE A477 w/ seal	180	900	--	100

-- = no water

The results with the paint chips were as follows:

This is a report on our run with Fine Organics 606W/Seal. It comprises:

<u>Compound</u>	<u>Percent</u>	<u>Boiling Point</u>
Ethanolamine	25	170°C.
Ethylated Nonyl Phenol	5	168 @ 5 mm.
N-Methyl pyrrolidone	45	202
Mineral Oil	15	150 - 300
Water	10	100

A mixture containing 450 grams of FO 606W/Seal and 45 grams of paint chips was stirred at 25°C. for 48 hours. The product was filtered. The paint chips remained on the filter; the filtrate formed two liquid layers. The lower layer boiled at 180 - 200°C. and had an $n_D = 1.465$. The upper layer boiled at 260 - 270°C. and had an $n_D = 1.473$.

The distillation proceeded with a constantly rising boiling point with two plateaus, one at 180 - 200°C. and the other at 260 - 270°C.

Procedure for Recovering Fine Organics FO 606W/Seal After Use as a Paint Remover.

Assuming that the 48 hrs. at 25°C. agitation with the paint chips gives the same results as the actual paint removal, the procedure for recovery is as follows:

1. Filter out the paint chips.
2. Allow the liquid to settle into two layers.
3. Separate the two layers by decantation.
4. Distill off the upper layer at 180 - 200°C. getting a mixture of ethanolamine and similar boiling hydrocarbons.
5. Distill off the lower layer at 260 - 270°C. getting a mixture of N-methyl pyrrolidone and similar boiling hydrocarbons.
6. Distill off the residue from the above distillations at 168°C and 5 mm. Hg getting ethylated nonyl phenol.
7. These three distillations will all contain a similar boiling hydrocarbon fraction. If pure ethanolamine and N-methyl pyrrolidone are desired, an azeotropic or extractive distillation process will have to be developed. None is now in existence.

This is a report on our run with F. Gumm's Clepo Env. #222. A mixture containing 225 gms. #222, 225 gms. water and 50 gms. paint chips was stirred at 80°C. for 48 hours. The product was cooled to room temperature and filtered. A sample of the paint chips removed is enclosed. The final product separated into two layers, one water, the other phenyl ethers. Samples of these two layers are enclosed to show you the quality (or lack of it) and are marked "crude". The phenyl ethers were distilled in an ordinary distilling flask. Some water is present in this layer and comes off as a two-phase azeotrope at 95°C. The ethylene glycol phenyl ether then boils off at about 270°C. and the diethylene glycol phenyl ether boils off at above 300°C. with decomposition. These will have to be recovered by vacuum rectification. Samples of these two fractions are enclosed.

Procedure for Recovering F. Gumm's Clepo Env #222.

Assuming that the 48 hrs. at 80°C. agitation with the paint chips gives the same results as the actual paint removal, the procedure for recovery is as follows:

1. Filter out the paint chips.
2. Allow the liquid filtrate to settle into two layers, water layer on top.
3. Decant, discard water layer.
4. Distill the organic layer. The dodecyl benzene sulfonic acid will cause some of the water to dissolve in the phenyl ethers. The first distillation will yield the ethylene glycol phenyl ether - water azeotrope boiling at about 95°C.
5. Separate the distillate from No. 4 by decantation discarding the water and recovering the ethylene glycol phenyl ether.
6. Rectify under reduced pressure the remaining organic material. Rectification at 1 Atm. pressure will cause thermal decomposition of the diethylene glycol phenyl ether because it boils above 300°C.
7. The bottoms from No. 6 will contain the decomposed dodecyl benzene sulfonic acid and any other solids. These go to a landfill.

Note: F. Gumm's Clepo Env. #222 consists of: 22% dodecyl benzene sulfonic acid, 56.7% ethylene glycol phenyl ether, 6.3% diethylene glycol phenyl ether.

This is a report on our run with Patclin #126 Solvent. It comprises:

<u>Compound</u>	<u>Percent</u>	<u>Boiling Point</u>
Water ^s	27	100°C.
Alkane Sulfonic Acid	8	95°C @ 1 mm.
2-Butoxyethoxy ethanol	65	115°C. @ 1 mm.

A mixture containing 450 grams of Patclin #126 and 50 grams of paint chips was stirred at 82°C. for 48 hours. The product was filtered. The paint chips remained on the filter.

The distillation proceeded with water removal at 100°C. and then distillation at 1 mm. Hg to remove the alkane sulfonic acid and the 2-butoxyethoxy ethanol.

Procedure For Recovering Patclin #126 After Use as a Paint Remover.

Assuming that the 48 hours at 82°C. agitation with the paint chips gives the same results as the actual paint removal, the procedure for recovery is as follows:

1. Filter out the paint chips.
2. Distill the liquid phase at 1 Atm. to get the water.
3. Distill the liquid phase at 1 mm.Hg to get off the 2-butoxyethoxy ethanol at 105 - 115°C.

This is a report on our run with TURCO T-5668 Solvent. It comprises:

<u>Compounds</u>	<u>Percent</u>	<u>Boiling Point</u>
Ethanolamine , B.P. = 170°C. :	22	65-75 @ 1 mm.
N-Methyl pyrrolidone , B. P. = 202°C.	60	75-85 @ 1 mm.
Hydrogenated Naphthenes	10	> 170 @ 1 mm. Hg.
KOH	2	

A mixture containing 450 grams of TURCO T-5668 and 50 grams of paint chips was stirred at 66°C. for 48 hours. The product was filtered. The paint chips remained on the filter.

The distillation proceeded with ethanolamine removal at 65-75°C. at 1 mm Hg followed by the N-Methyl pyrrolidone at 75 - 85°C. at 1 mm. Hg. The hydrogenated naphthenes and the KOH remained in the residue.

Procedure For Recovering TURCO T-5668 Solvent After Use As A Paint Remover

Assuming that the 48 hours at 66°C. agitation with the paint chips gives the same results as the actual paint removal, the procedure for recovery is as follows:

1. Filter out the paint chips.
2. Rectify the liquid phase in column containing at least 23 theoretical plates. Take off ethanolamine at 170°C. and 99% purity. Relative volatility is about 1.5 which requires 23 T.P. to get 99% purity.
3. When ethanolamine is exhausted, continue rectification to get the N-methyl-1-pyrrolidone at 202°C. and 99% purity.
4. Withdraw hydrogenated naphthenes for use as recycle. All impurities will wind up in naphthene fraction which will have to be redistilled eventually.

This is a report on our run with Rochester Midland PSS 600 Solvent. It comprises 100% N-methylpyrrolidone.

A mixture containing 450 grams of R-M PSS 600 and 50 grams of paint chips was stirred at 66°C. for 48 hours. The product was filtered. The paint chips remained on the filter.

The distillation proceeded with the removal of the N-methyl pyrrolidone at 73°C. at 1 mm. Hg.

Procedure For Recovering Rochester Midland PSS 600 After Use As A Paint Remover.

Assuming that the 48 hours at 66°C. agitation with the paint chips gives the same results as the actual paint removal, the procedure for recovery is as follows:

1. Filter out the paint chips.
2. Distill the liquid phase at 1 mm. Hg to get the N-methyl pyrrolidone at 73°C.

This is a report on our run with McGeon-Rohco CEE BEE A-245 Solvent.
It comprises:

<u>Compounds</u>	<u>Percent</u>	<u>Boiling Point</u>
Benzyl alcohol	94	93-98°C. @ 1 mm.
Unknown	6	-

A mixture containing 450 grams of CEE BEE A-245 and 50 grams of paint chips was stirred at 116°C. for 48 hours. The product was filtered. The paint chips remained on the filter.

The distillation proceeded with the removal of the benzyl alcohol at 93-98°C. at 1 mm. Hg. A small amount of residue accumulated in the stillpot.

Procedure For Recovering CEE BEE A-245 After Use As A Paint Remover.

Assuming that 48 hours at 116°C. agitation with the paint chips gives the same results as the actual paint removal, the procedure for recovery is as follows:

1. Filter out the chips.
2. Distill the liquid phase at 1 mm. Hg. to get the benzyl alcohol at 93 -98°C.
3. Discard the residue.

This is a report on our run with GAF m-Pyrol Solvent. It comprises N-methyl pyrrolidone.

A mixture containing 450 grams of GAF m-Pyrol and 50 grams of paint chips was stirred at 66°C. for 48 hours. The product was filtered. The paint chips remained on the filter.

The distillation proceeded with the removal of the N-methyl pyrrolidone at 73 - 76°C. @ 1 mm. Hg. $n_D = 1.420$ (pure is 1.580 at 20°C)

Procedure For Recovering GAF m-Pyrol After Use As A Paint Remover.

Assuming that the 48 hours at 66°C. agitation with the paint chips gives the same results as the actual paint removal, the procedure for recovery is as follows:

1. Filter out the paint chips.
- 2 Distill the liquid phase at 1 mm. Hg to get the N-methyl pyrrolidone

This is a report on our run with McGeon-Rohco CEE BEE A-477 Solvent. It comprises:

<u>Compounds</u>	<u>Suppliers Analysis %</u>	<u>Our Analysis %</u>	<u>Boiling Point</u>
Ethanolamine	50	65	65-72°C @ 1 mm. Hg
Mineral Oil	50	35	170°C. & higher @ 1 mm. Hg.

A mixture containing 450 grams of CEE BEE A-477 and 50 grams of paint chips was stirred at 82°C. for 48 hours. The product was filtered. The paint chips remained on the filter.

The filtrate formed two liquid layers which were decanted. The lower layer, the ethanolamine, distilled off at 65-72°C. The upper layer, the mineral oil, was separately distilled at >170°C. @ 1 mm. Hg. The purity of the ethanolamine obtained in this one theoretical plate distilling flask was 99%. The n_D was 1.458; pure ethanolamine is 1.454.

Procedure For Recovering CEE BEE A-477 After Use As A Paint Remover.

Assuming that 48 hours at 82°C. agitation with the paint chips gives the same results as the actual paint removal, the procedure for recovery is as follows:

1. Filter out the chips.
2. Decant the two immiscible liquid layers that form.
3. Distill the lower layer at 65-72°C. at 1 mm. Hg getting at least 98% of the ethanolamine in 99% purity. Discard the residue, less than 5%.
4. Distill the upper layer at 170°C. and greater at 1 mm Hg to recover the mineral oil (hydrocarbon) layer. Discard the residue; less than 5%.

An economic evaluation of the process to recover and recycle the used solvents was done. The GAF M-Pyrol study represents a single compound solvent and the TURCO T-5668 is a study for a multi-component mixture.

The following is an economic evaluation for the recovery of GAF Corp. M-PYROL spent solvent.

M-PYROL is N-methyl pyrrolidone, B.P. = 202°C., Density = 1.026

30,000 gal/yr. x 8.337 #/gal. x 1.026 = 257,000 #/yr.

257,000 #/yr x 1/365 x 1/24 = 293/hr x 125% oversize = 37 #/hr.

Allowable vapor velocity = 1.0 ft/sec.

37 #/hr x 1/0.2 #/ft³ x 1/ 3600 sec/hr = 0.15 ft³/sec.

Running 30,000 gal/month: 0.15 ft³/sec x 12 = 1.8 ft³/sec.

1.8 ft³/sec / 1 ft./sec. = 1.8 ft², which = 18" column diameter

Assuming 99% purity of overhead & bottoms, rel. vol. = 2, 13 theor.plate

257,000 #/mo. x 1/30 x 1/24 = 360 3/hr x 125% = 450 #/hr.

450 #/hr x 250 Btu/# = 112,500 Btu/hr to condense

450 #/hr x (202-30) x 1.8 x 0.5 = 70,000 Btu/hr to cool

112,500 + 70,000 = 200,000 Btu/hr in condenser

200,000 x 1/120 x 1/150 = 11 ft²

70,000 x 1/200 x 1/50 = 7 ft²

Richard Rall, Koch Engr. Co., Wichita, KS. estimated the column & condensers as follows:

Columns, pumps, column internals, reflux tank, heat exchangers

& controls

\$100,000

Bidding, designs & simulation

100,000

Assembling

50,000

Putting on skids

20,000

Storage tanks

15,000

Piping & Electrical installation

80,000

Contingency

65,000

-Total Investment

\$450,000

Annual Expenses

Operating Labor: \$40/hr x 2 people x 168 hr/mo x 5 mos. = \$67,000

Supervision: \$50/hr x 42 hr/mo. x 5 mos. 10,500

Maintenance & Repairs 15,000

Steam Cost: 200,000 Btu/hr x 168 hr/wk x 20 wk/yr x \$3.50/ million Btu 2,350

Sludge Recovery & Disposal

100,000

Moving Expenses	50,000
Depreciation - 10% per year	45,000
Property taxes @ 3%	<u>13,500</u>
Total Expenses	\$303,350

Revenue: \$2,185,000
 Total Expenses 303,350
 Net Income, \$1,881,650
 before Income tax

This is an economic evaluation of the recovery of TURCO T-5668 solvent which comprises 22% ethanol amine, 60% N-methyl pyrrolidinone and 10% hydrogenated naphthenes.

The recovery procedure is as follows:

1. Filter out the paint chips.
2. Rectify the liquid phase in a batch column. Distill off the ethanolamine at 170°C. and 99% purity.
3. Put midfraction, ethanolamine and M-Pyrol in storage tank for recycle.
4. Distill off the M- Pyrol at 202°C.
5. Put midfraction, M-Pyrol and naphthenes in storage tank for recycle.
6. Distill off naphthenes at 170°C and reduced pressure.
7. Empty stillpot, send to waste.
8. Refill stillpot with new charge plus both midfraction recycle streams from previous run.

Batch operation and midfraction recovery about 50% more time. Batch operation requires extra charge capacity for recycle fraction.

INVESTMENT

Column, pumps, column internals, reflux tank, heat exchangers & controls	\$100,000
Bidding, designs & simulation	100,000
Assembling	50,000
Putting on skids	20,000
Storage tanks	30,000
Piping & electrical installation	80,000
Contingency	<u>65,000</u>
Total Investment	\$465,000

Annual Expenses - Five sources, 150,000 gallons per year

Operating Labor: \$40/hr x 2 people x 24hr/day x 240 days	= \$460,800
Supervision: \$50/hr x 42 hr/mo x 8 mos	16,800
Maintenance & Repairs	15,000
Steam Cost: 200,000 Btu/hr x 168 hr/wk x 32 wk/yr x \$3.50 M	3,760
Sludge Recovery & Disposal	100,000
Moving Expense	50,000
Depreciation - 10% per year	46,500
Property Taxes @ 3%	<u>14,000</u>
TOTAL EXPENSES	\$706,860

Revenue:

Ethanolamine: 150,000 gal x 8.55 x 22% x \$0.59	\$166,500
M-Pyrol: 150,000 gal x 8.55 x 60% x \$1.70	1,308,150
Hydrogenated Naphthenes: 150,000 x 8.55 x 10% x \$0.20	<u>25,650</u>
TOTAL REVENUE	\$1,500,300

Net Income: \$1,500,300 - \$706,860 = \$793,440

Return on Investment: \$793,440 / \$465,000 = 171%

Payout Time: 7 months

Annual Expenses: Operating one plant, 1.5 months, 30,000 gallons

Operating Labor: \$40/hr x 2 people x 24hr/d x 45 days	\$86,400
Supervision: \$50/hr x 10 hr/wk x 6 weeks	3,000
Maintenance & Repairs	15,000
Steam Cost: 200,00 Btu/hr x 168 hr/wk x 6wk/mo x \$3.50/M	700
Sludge Recovery & Disposal	100,000
Depreciation - 10% per yr	46,500
Property taxes @ 3%	<u>14,000</u>
Total Expenses	\$265,600

Revenue:

Ethanolamine: 30,000 gal x 8.55 x 22% x \$0.59/lb	\$33,300
M-Pyrol: 30,000 gal x 8.55 x 60% x \$1.70/lb	261,630
Hydrogenated Naphthenes; 30,000 gal x 8.55 x 10% x \$0.20/lb	<u>5,130</u>
Total Revenue	\$300,060

Net Income: \$300,060 - \$265,600 = \$34,460

Return on Investment: \$34,460 / \$465,000 = 7.4%

Payout Time: 13.5 years

SOLVENT & WAX RECOVERY

Two solvents were mixed with Petrolite BE SQUARE #175 Amber wax as follows:

EXXATE 1000 - 10 gm wax/liter

Orange Sol De-Solv-It - 50 gm wax/liter

Both solvent-wax mixtures foamed when distilled. The following anti-foaming agents were investigated:

EXXON Corexit 362

" Surflo AF 2436

" " AF 7669

" " AF 8574

PPG MAZ TREAT 246

" MAZU DF 200 SX

" MACOL 5100

Genesee DB 12

Union Carbide SAG 47

" " SAG 1000

None of the above anti-foaming agents were effective in reducing the foaming.

Lloyd Berg

APPENIX 1 - Distillation Results, New Solvents (unused)

CHLORINATED SOLVENT SUBSTITUTION PROGRAM

TEST CONDITIONS:

CONDITION

Vacuum, 24.5 inches, 8 theor. plates

Solvent Name 600ml Error 1.50

Distillation Procedure Simple Batch X Extractive _____ Azeotropic _____

Recovered Component, Critical Temperature and % Moles from GC Analysis

Normal Acetic	101	°C	69	%
Undersat. Acetic	103	°C	33.5	%
		°C		%
		°C		%
		°C		%

- Residue 17.5%

Remarks:

Time of Day

Duration of Experiment

Test Date

Test Performed By

(hr.-min.-sec.)

1990

TEST CONDITIONS:

CONDITION: 8 T.P. Helices packed
column. 500 ml. charged

Solvent Name Orange-Sol Co., De-Solve-It

Distillation Procedure Simple Batch X Extractive _____ Azeotropic _____

Recovered Component, Critical Temperature and % Moles from GC Analysis

Orange Oil - esters	50 °C	10 %
Mineral Oil - hydrocarbons	90-120 °C	90 %
	°C	%
	°C	%
	°C	%

Remarks:

Time of Day

Duration of Experiment

Test Date

Test Performed By

(hr.-min.-sec.)

Sent 23

1990

Ernest Young

DATA ACCUMULATION SHEET

CHLORINATED SOLVENT SUBSTITUTION PROGRAM

SOLVENT RECYCLE/RECOVERY TASK

TEST CONDITIONS:

Parameter: 1 mm Hg.

CONDITION: 8 T.P. helices packed
column, 700 ml.

Solvent Name 3-D Supreme

Distillation Procedure Simple Batch X Extractive _____ Azeotropic _____

Recovered Component, Critical Temperature and % Moles from GC Analysis

<u>Water</u>	<u>30 °C</u>	<u>86</u> %
_____	_____ °C	_____ %
_____	_____ °C	_____ %
_____	_____ °C	_____ %
_____	_____ °C	_____ %
_____	_____ °C	_____ %

Residue 14%

Remarks: Residue boils at very high temperature

Time of Day _____
Duration of Experiment _____
Test Date _____
Test Performed By _____

Sept 10, 1990
William Yang

TEST CONDITIONS:

CONDITION: 8 T.P. helices packed
column, 400 ml. charge

Distillation Procedure Simple Batch x Extractive Azeotropic

Water	30 °C	4 %
N-Methyl pyrrolidone	73 °C	34 %
Tetrahydro furfuryl alcohol	76 °C	6 %
Diethanolamine	141 °C	25 %
	°C	%

Remarks: The stillpot temperature exceeded 260°C. @ 1 mm Hg at end of run.

, 1990

C-20

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DATA ACCUMULATION SHEET

CHLORINATED SOLVENT SUBSTITUTION PROGRAM

SOLVENT RECYCLE/RECOVERY TASK

TEST CONDITIONS:

Parameter: 1 mm. Hg

CONDITION: 8 T.P. helices packed
column, 500 ml. charged

Solvent Name Fine Organics, FO-606

Distillation Procedure Simple Batch X Extractive Azeotropic

Recovered Component, Critical Temperature and % Moles from GC Analysis

<u>Water</u>	<u>25 °C</u>	<u>8 %</u>
<u>Ethanolamine</u>	<u>64 °C</u>	<u>24 %</u>
<u>N-Methyl pyrrolidone</u>	<u>72 °C</u>	<u>45 %</u>
<u> </u>	<u>°C</u>	<u>%</u>
<u> </u>	<u>°C</u>	<u>%</u>

Remarks: Decomposition took place after 385 ml. had been removed from
the 500 ml. charge-

Time of Day

Duration of Experiment

Test Date

Test Performed By

 (hr.-min.-sec.)
 Sept. 30, 1990

DATA ACCUMULATION SHEET
 CHLORINATED SOLVENT SUBSTITUTION PROGRAM
 SOLVENT RECYCLE/RECOVERY TASK

TEST CONDITIONS:

Parameter CONDITION
1 mm Hg 1. Loading with paint chips
Solvent Name GAF m-Pyrol & Simple Distillation
Distillation Procedure Simple Batch X Extractive _____ Azeotropic _____

Recovered Component, Critical Temperature and % Moles from GC Analysis

<u>N-Methyl pyrrolidone</u>	<u>73-76°C</u> °C	<u>110 ml</u> <u>91.7%</u>
_____	_____ °C	_____ %
_____	_____ °C	_____ %
_____	_____ °C	_____ %
_____	_____ °C	_____ %

Remarks:

Time of Day _____
 Duration of Experiment _____ (hr.-min.-sec.)
 Test Date Sept 15, 1991, 1990
 Test Performed By _____

DATA ACCUMULATION SHEET

CHLORINATED SOLVENT SUBSTITUTION PROGRAM

SOLVENT RECYCLE/RECOVERY TASK

TEST CONDITIONS:

Parameter CONDITION

640 mm Hg , 8 1/2 core plates

Solvent Name GAF M-Purrol 500ml New material

Distillation Procedure Simple Batch X Extractive _____ Azeotropic _____

Recovered Component, Critical Temperature and % Moles from GC Analysis

<u>n-Heptane</u>	<u>194</u>	<u>°C</u>	<u>62</u>	<u>%</u>
_____	_____	<u>°C</u>	_____	<u>%</u>
_____	_____	<u>°C</u>	_____	<u>%</u>
_____	_____	<u>°C</u>	_____	<u>%</u>
_____	_____	<u>°C</u>	_____	<u>%</u>

Residue 38 %

Remarks:

Time of Day

Duration of Experiment

Test Date

Test Performed By

_____ (hr.-min.-sec.)

_____ , 1990

James J. [Signature]

DATA ACCUMULATION SHEET

CHLORINATED SOLVENT SUBSTITUTION PROGRAM

SOLVENT RECYCLE/RECOVERY TASK

TEST CONDITIONS:

Parameter

CONDITION

1 mm Hg

1. LOADING WITH PAINT CHIPS
2. SIMPLE DISTILLATION

Solvent Name

PATCLIN

Distillation Procedure Simple Batch X Extractive _____ Azeotropic _____

Recovered Component, Critical Temperature and % Moles from GC Analysis

<u>H₂O</u>	<u>30 - 35 °C</u>	<u>25ml</u>	<u>21 %</u>
<u>2 - Butoxyethoxy-</u>	<u>90 - 95 °C</u>	<u>10ml</u>	<u>8.3 %</u>
<u>2 - ethanol</u>	<u>95 - 115 °C</u>	<u>42ml</u>	<u>35 %</u>
	<u>°C</u>		<u>%</u>
	<u>°C</u>		<u>%</u>

Remarks: 1. severely bumping over, so stuff recovered is black liquid

2. The amount of stuff loading was 120 ml

Time of Day

Aug 29, 1991

Duration of Experiment

(hr.-min.-sec.)

Test Date

, 1990

Test Performed By

DATA ACCUMULATION SHEET

CHLORINATED SOLVENT SUBSTITUTION PROGRAM

SOLVENT RECYCLE/RECOVERY TASK

TEST CONDITIONS:

Parameter

CONDITION

1 mm Hg

1. Loading with Paintchips
2. Simple Distillation

Solvent Name

CEE BEE A-205

Distillation Procedure

Simple Batch

X

Extractive

Azeotropic

Recovered Component, Critical Temperature and % Moles from GC Analysis

Benzyl alcohol + Unknown

93 ~ 98

°C

93.3%

°C

%

°C

%

°C

%

°C

%

Remarks:

Time of Day

Duration of Experiment

Test Date

Test Performed By

Sept. 12 1991

(hr.-min.-sec.)

, 1990

DATA ACCUMULATION SHEET

CHLORINATED SOLVENT SUBSTITUTION PROGRAM

SOLVENT RECYCLE/RECOVERY TASK

TEST CONDITIONS:

Parameter

CONDITION

640 mm Hg, 8 Theor plates

Solvent Name Cee Bee #245 640 ml

Distillation Procedure Simple Batch X Extractive _____ Azeotropic _____

Recovered Component, Critical Temperature and % Moles from GC Analysis

<u>Unknown</u>	<u>173</u>	<u>°C</u>	<u>15.6</u>	<u>%</u>
<u>-05 Benzyl Alcohol</u>	<u>179</u>	<u>°C</u>	<u>36.9</u>	<u>%</u>
_____	_____	<u>°C</u>	_____	<u>%</u>
_____	_____	<u>°C</u>	_____	<u>%</u>
_____	_____	<u>°C</u>	_____	<u>%</u>

Residue

Remarks: It seems that the decomposition of the solvent took place. It needs to be distilled under vacuum pressure

Time of Day _____

Duration of Experiment _____

Test Date _____

Test Performed By _____

(hr.-min.-sec.)
, 1990

DATA ACCUMULATION SHEET

CHLORINATED SOLVENT SUBSTITUTION PROGRAM

SOLVENT RECYCLE/RECOVERY TASK

TEST CONDITIONS:

Parameter

CONDITION

640 mm Hg

8 Theor. plates.

Solvent Name

Cee Bee B 477 (400 ml)

Distillation Procedure Simple Batch X Extractive _____ Azeotropic _____

Recovered Component, Critical Temperature and % Moles from GC Analysis

<u>Ethanolamine</u>	<u>163</u>	<u>°C</u>	<u>50</u>	<u>%</u>
<u>unknown</u>	<u>187</u>	<u>°C</u>	<u>16.3</u>	<u>%</u>
_____	_____	°C	_____	%
_____	_____	°C	_____	%
_____	_____	°C	_____	%

Residue 33.7 %

Remarks:

Time of Day

Duration of Experiment

Test Date

Test Performed By

 _____ (hr.-min.-sec.)
Aug 19, 1990
2.0000

DATA ACCUMULATION SHEET
 CHLORINATED SOLVENT SUBSTITUTION PROGRAM
 SOLVENT RECYCLE/RECOVERY TASK

TEST CONDITIONS:

Parameter CONDITION

Vacuum, 24.5 inches

Solvent Name PCS 600 400 ml

Distillation Procedure Simple Batch X Extractive Azeotropic

Recovered Component, Critical Temperature and % Moles from GC Analysis

<u>N-Methylpyrrolidone</u>	(Uncorrected) 77 °C	80	%
	@ 24.5" vacuum °C		
	°C		%
	°C		%
	°C		%
	°C		%

Residue 20%

Remarks: The boiling point of N-methylpyrrolidone is 78°C

Time of Day _____
 Duration of Experiment _____
 Test Date _____
 Test Performed By _____

 _____ (hr.-min.-sec.)
Aug 24, 1990
J. J. [Signature]

CHLORINATED SOLVENT SUBSTITUTION PROGRAM

TEST CONDITIONS:

Vacuum 24.5 inches, & theor plates

Distillation Procedure Simple Batch X Extractive _____ Azeotropic _____

171	Ethanolamine	(uncorrected) 165	°C	44	%
202	N-Methylpyrrolidone	(uncorrected) 72	°C	26.3	%
			°C		%
			°C		%
			°C		%

Residue 29.75

Remarks:

Time of Day _____
Duration of Experiment _____ (hr.-min.-sec.)
Test Date June 5, 1990
Test Performed By J. J. G. G.

DATA ACCUMULATION SHEET
 CHLORINATED SOLVENT SUBSTITUTION PROGRAM
 SOLVENT RECYCLE/RECOVERY TASK

TEST CONDITIONS:

Parameter CONDITION
Vacuum Dist. 24.5 inches 8 theor. plates
Solvent Name H 140 Saf-Sol (Bio-Tek) 400ml
Distillation Procedure Simple Batch X Extractive _____ Azeotropic _____

Recovered Component, Critical Temperature and % Moles from GC Analysis

<u>Cetyl Acetate</u>	<u>1.00 (uncorrected) °C</u>	} @ <u>24.5"</u> Vacuum	<u>30</u> %
<u>Octadecyl Acetate</u>	<u>104 (uncorrected) °C</u>		<u>30</u> %
<u>Decyl Acetate</u>	<u>125 (uncorrected) °C</u>		<u>15</u> %
_____	_____ °C		_____ %
_____	_____ °C		_____ %

Residue 25 %

Remarks:

Time of Day _____
 Duration of Experiment _____
 Test Date _____
 Test Performed By _____

 _____ (hr.-min.-sec.)
Sept. 2, 1990
J. J. J.

Appendix 2 - Distillation Results, Used Solvents

CHLORINATED SOLVENT SUBSTITUTION PROGRAM

TEST CONDITIONS:

CONDITION: 8 T.P. helices packed
column, 500 ml. charged

Solvent Name Fine Organics, FO-606

Distillation Procedure Simple Batch X Extractive Azeotropic

Recovered Component, Critical Temperature and % Moles from GC Analysis

Water	25 °C	8 %
Ethanolamine	64 °C	24 %
N-Methyl pyrrolidone	72 °C	45 %
	°C	%
	°C	%

Remarks: Decomposition took place after 385 ml. had been removed from the 500 ml. charge-

_____ (hr.-min.-sec.)
 _____, Sept. 30, 1990
William G. Lang

Figure 3.

DATA ACCUMULATION SHEET
CHLORINATED SOLVENT SUBSTITUTION
SOLVENT RECYCLE/RECOVERY

DISTILLATION

Solvent Name CLEO ENVIROSTRIP 222

Solvent Soil _____

Distillation Procedure: Simple Batch X Extractive _____ Azeotropic _____

Test Conditions:

ParameterCondition

1 mm Hg pressure

8 theoretical plate
helices packed column

Recovered Component

Critical Temperature(°C)

% Moles

<u>unknown</u>	<u>38°C</u>	<u>22%</u>
<u>Ethylene Glycol phenyl ether</u>	<u>42°C</u>	<u>15.4%</u>
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

REMARKS: Analysis by GC unless otherwise noted;

Sample from 5 ml distillate to 81 ml distillate

Refractive Index: 1.4255 ~ 1.443

Sample from 100 ml ~ 187 ml

Refractive Index: 1.5125 - 1.536

After 187 ml of distillate, overhead temperature decreased,
decomposition took place.Date and Time of Test: 6-14-91Test Performed by: Zunin Yang

DATA ACCUMULATION SHEET

CHLORINATED SOLVENT SUBSTITUTION PROGRAM

SOLVENT RECYCLE/RECOVERY TASK

TEST CONDITIONS:

Parameter

CONDITION

1 mm Hg

1. LOADING WITH PAINT CHIPS
2. SIMPLE DISTILLATION

Solvent Name

PATCLIN

Distillation Procedure Simple Batch X Extractive _____ Azeotropic _____

Recovered Component, Critical Temperature and % Moles from GC Analysis

<u>H₂O</u>	<u>30 - 35 °C</u>	<u>25ml</u>	<u>21 %</u>
<u>2 - Butoxyethoxy-</u>	<u>90 - 95 °C</u>	<u>10ml</u>	<u>8.3 %</u>
<u>2 - ethanol</u>	<u>95 - 115 °C</u>	<u>42ml</u>	<u>35 %</u>
_____	_____ °C	_____	_____ %
_____	_____ °C	_____	_____ %

Remarks: 1. Severely bumping over, no stuff recovered is black liquid

2. The amount of stuff loading was 120 ml

Time of Day

Duration of Experiment

Test Date

Test Performed By

Aug 29, 1991

(hr.-min.-sec.)
_____, 1990

DATA ACCUMULATION SHEET

CHLORINATED SOLVENT SUBSTITUTION PROGRAM

SOLVENT RECYCLE/RECOVERY TASK

TEST CONDITIONS:

<u>Parameter</u>	<u>CONDITION</u>
1 mm Hg	1. LOADING WITH PAINT CHIPS
Solvent Name	2. SIMPLE DISTILLATION
<u>TURCO T-5668</u>	

Distillation Procedure Simple Batch X Extractive _____ Azeotropic _____

Recovered Component, Critical Temperature and % Moles from GC Analysis

<u>Ethanolamine</u>	<u>65 - 75</u>	<u>°C</u>	<u>33 ml</u>	<u>22 %</u>
<u>N-Methyl pyrrolidone</u>	<u>75 - 85</u>	<u>°C</u>	<u>9 ml</u>	<u>60 %</u>
_____	_____	<u>°C</u>	_____	<u>%</u>
_____	_____	<u>°C</u>	_____	<u>%</u>
_____	_____	<u>°C</u>	_____	<u>%</u>

Remarks:

150 ml of lower layer from solvent loading with paint chips was charged in the still.

Time of Day	<u>Sept. 6, 1991</u>
Duration of Experiment	_____ (hr.-min.-sec.)
Test Date	_____, 1990
Test Performed By	_____

DATA ACCUMULATION SHEET

CHLORINATED SOLVENT SUBSTITUTION PROGRAM

SOLVENT RECYCLE/RECOVERY TASK

TEST CONDITIONS:

Parameter

CONDITION

1 mm Hg

1. LOADING WITH PAINTCHIPS

Solvent Name

PSS 600

2. SIMPLE DISTILLATION

Distillation Procedure Simple Batch Y Extractive _____ Azeotropic _____

Recovered Component, Critical Temperature and % Moles from GC Analysis

<u>N-Methyl pyrrolidone</u>	<u>73</u>	°C	<u>125 ml</u>	<u>46</u>	%
_____	_____	°C	_____	_____	%
_____	_____	°C	_____	_____	%
_____	_____	°C	_____	_____	%
_____	_____	°C	_____	_____	%

Remarks:

It seems to be a pure compound

Time of Day

Duration of Experiment

Test Date

Test Performed By

Sept 10, 1991

(hr.-min.-sec.)

_____, 1990

DATA ACCUMULATION SHEET

CHLORINATED SOLVENT SUBSTITUTION PROGRAM

SOLVENT RECYCLE/RECOVERY TASK

TEST CONDITIONS:

Parameter

CONDITION

1 mm Hg

1. Loading with Paintchips
2. Simple Distillation

Solvent Name

CEE BEE A-205

Distillation Procedure

Simple Batch X

Extractive _____

Azeotropic _____

Recovered Component, Critical Temperature and % Moles from GC Analysis

Benzyl alcohol + Unknown

93 ~ 98

°C

93.3%

°C

%

°C

%

°C

%

°C

%

Remarks:

Time of Day

Duration of Experiment

Test Date

Test Performed By

Sept. 12, 1991

(hr.-min.-sec.)

, 1990

DATA ACCUMULATION SHEET

CHLORINATED SOLVENT SUBSTITUTION PROGRAM

SOLVENT RECYCLE/RECOVERY TASK

TEST CONDITIONS:

Parameter

CONDITION

1 mm Hg

1. Loading with paint chips

Solvent Name

GAF m-Pyrol & Simple Distillation

Distillation Procedure Simple Batch X Extractive _____ Azeotropic _____

Recovered Component, Critical Temperature and % Moles from GC Analysis

N-Methyl pyrrolidone

73-76°C °C

110 ml 91.7%

°C

%

°C

%

°C

%

°C

%

Remarks:

Time of Day

Duration of Experiment

Test Date

Test Performed By

Sept. 15, 1991

(hr.-min.-sec.)

Sept 15, 1991

, 1990

Appendix D

**Economic Analysis of
1 Plant Versus 5 Plants**

RECOVERY OF M-PYROL SPENT SOLVENT

ECONOMIC ANALYSIS OF 1 PLANT VERSUS 5 PLANTS

WRITTEN BY: CHARMIN PETERSEN

MAY 5, 1992

SPENT SOLVENT $\xrightarrow{\text{SIMPLE DISTILLATION}}$ M-PYROL + CONTAMINANTS

The purpose of this project was to discuss the economics of recovering M-PYROL from the spent paint solvent. The process was designed by Dr. Berg for this particular solvent. The spent solvent is produced at five Air Force Bases around the country (from Delaware to Texas). Each base contaminates approximately 30,000 gal. of solvent a year. The scope of this study is to determine if it is more economical to build one plant at Tinker Air Force Base in Oklahoma and have the over four bases ship their spent solvent for recovery or if each base should build its own plant to recover the solvent they contaminate. The spent solvent is free since it is contaminated and unusable. After recovery of the M-PYROL it is sold as the product.

The separation of M-PYROL solvent from its paint contaminants is relatively simple. It has a boiling point of 202°C and the boiling point of the paint contaminants is much higher. The relative volatility of the mixture is 2, which allows for simple distillation. Assuming a 99% purity of overhead and bottoms, 13 theoretical plates are required. This amounts to 18 actual plates assuming an efficiency of 75%.

For a product capacity of 257,000 pounds per month of M-PYROL, a spent solvent feed of the same amount is required. The spent solvent costs nothing. M-PYROL is sold as product at \$1.59 per pound. The difference between the two options is basically the cost of shipping the spent solvents to one plant. Either option will require the same size plant, therefore capital investment will be identical. Option A will require that the plant be run for five months per year to recover a total of 150,000 gallons of solvent; while option B will only run for one month out of the year to recover only the 30,000 gallons of the solvent used at that base. Option A provides a net profit of

\$987,000 per year while option B yields a \$182,000 profit per year. Option A gives a rate of return on investment of 230% and a payout time of only 5.2 months. Option B produces only a 42% rate of return on investment and has a payout time of 2.4 years. Obviously, option A is the better plan as it will pay for itself faster.

SUMMARY AND COMPARISONS OF CALCULATIONS

	OPTION A	OPTION B
	1 plant <u>run 5 months</u>	1 plant per site <u>run 1 month</u>
MONTHLY CAPACITY	257,000 lb/mo	257,000 lb/mo
TOTAL REVENUE	\$ 2,043,000/yr	\$407,000/yr
CAPITAL COST		
TOTAL	\$430,000	\$430,000
10% DEPRECIATION	\$ 43,000/yr	\$ 43,000/yr
3% PROPERTY TAX	\$ 12,900/yr	\$ 12,900/yr
OPERATING COST	\$ 513,900/yr	\$ 79,400/yr
GROSS PROFIT	\$ 1,473,200/yr	\$ 271,700/yr
NET PROFIT (33% INCOME TAX)	\$ 987,000/yr	\$ 182,000/yr
RATE OF RETURN ON INVESTMENT	230%	42%
PAYOUT TIME	5.2 months	2.4 years

CAPITAL COST

Columns, pumps, column internals, reflux tank, heat exchangers & controls	\$100,000
Bidding, designs & simulation	\$100,000
Assembling	\$50,000
Putting on skids	\$20,000
Storage tanks	\$15,000
Piping & Electrical installation	\$80,000
Contigency	\$65,000
TOTAL INVESTMENT	\$430,000

OPERATING COST

	OPTION A 1 plant <u>run 5 months</u>	OPTION B 1 plant per site <u>run 1 month</u>
OPERATING LABOR	\$336,000/yr	\$53,800/yr
SUPERVISION	\$10,500/yr	\$2,100/yr
MAINTENANCE & REPAIRS	\$15,000/yr	\$3,000/yr
STEAM COST	\$2,350/yr	\$470/yr
SLUDGE RECOVERY & DISPOSAL	\$100,000/yr	\$20,000/yr
MOVING EXPENSES	\$50,000/yr	0
TOTAL OPERATING COST	<u>\$513,900/yr</u>	<u>\$79,400/yr</u>

ECONOMIC CALCULATIONS

Plant Capacity $\Rightarrow$ 257,000 lb/month M-PYROL produced

Prices $\Rightarrow$ spent solvent $\emptyset$

M-PYROL \$1.59/lb.

• (A) One plant (spent solvents shipped from other sites)

(B) Plant at each site (analysis for one plant)

*TOTAL REVENUE

(A) M-PYROL

$$\frac{257,000 \text{ lb}}{\text{mo.}} \times \frac{\$1.59}{\text{lb}} \times \frac{12 \text{ mo.}}{\text{yr.}} = \$2,043,000/\text{yr.}$$

(B) M-PYROL

$$\frac{257,000 \text{ lb}}{\text{mo.}} \times \frac{\$1.59}{\text{lb}} \times \frac{1 \text{ mo.}}{\text{yr.}} = \$407,000/\text{yr.}$$

*FEED COST

(A) & (B)

$\emptyset$

* CAPITAL COST

(A) & (B) for one plant (estimated by Richard Ball,
Koch Engr. Co., Wichita, KS & Dr. Berg)

Columns, pumps, column internals,
reflux tank, heat exchangers, & controls \$100,000

Bidding, designs & simulation 100,000

Assembling 50,000

Putting on skids 20,000

Storage tanks 15,000

Piping & Electrical Installation 80,000

Contingency 65,000

Total Investment \$430,000

* DEPRECIATION

(A) & (B) 10% per year

$$\frac{0.1}{\text{yr.}} \mid \$430,000 =$$

\$43,000/yr.

* PROPERTY TAX

(A) & (B) 3% per year

$$\frac{0.03}{\text{yr.}} \mid \$430,000 =$$

\$12,900/yr.

* OPERATING COST

(A) - running 5 months per year

Operating Labor:

$$\frac{\$40}{\text{hr}} \left| \frac{2 \text{ people}}{\text{hr}} \right| \frac{168 \text{ hr}}{\text{wk}} \left| \frac{4 \text{ wk}}{\text{mo}} \right| \frac{5 \text{ mo}}{\text{yr}} = \$336,000/\text{yr}$$

Supervision:

$$\frac{\$50}{\text{hr}} \left| \frac{42 \text{ hr}}{\text{mo.}} \right| \frac{5 \text{ mo.}}{\text{yr.}} = \$10,500/\text{yr.}$$

Maintenance & Repairs:

$$\frac{\$3000}{\text{mo}} \left| \frac{5 \text{ mo}}{\text{yr}} \right| = \$15,000/\text{yr.}$$

Steam Cost:

$$\frac{\$3.50}{1 \times 10^6 \text{ Btu}} \left| \frac{200,000 \text{ Btu}}{\text{hr}} \right| \frac{168 \text{ hr}}{\text{wk}} \left| \frac{4 \text{ wk}}{\text{mo}} \right| \frac{5 \text{ mo}}{\text{yr}} = \$2,350/\text{yr.}$$

Sludge Recovery & Disposal

$$\frac{\$20,000}{\text{mo.}} \left| \frac{5 \text{ mo.}}{\text{yr}} \right| = \$100,000/\text{yr.}$$

Moving Expenses

$$\underline{\$50,000/\text{yr.}}$$

Total Operating Costs

$$\underline{\$513,900/\text{yr}}$$

(B) - running 1 month per year

Operating Labor:

$$\frac{\$40}{\text{hr}} \left| \frac{2 \text{ people}}{\text{hr}} \right| \frac{168 \text{ hr}}{\text{wk}} \left| \frac{4 \text{ wk}}{\text{mo}} \right| \frac{1 \text{ mo}}{\text{yr}} = \$53,800/\text{yr}$$

Supervision:

$$\frac{\$50}{\text{hr}} \left| \frac{42 \text{ hr}}{\text{mo}} \right| \frac{1 \text{ mo}}{\text{yr}} = \$2100/\text{yr}$$

Maintenance & Repairs:

$$\frac{\$3000}{\text{mo}} \left| \frac{1 \text{ mo}}{\text{yr}} \right| = \$3000/\text{yr}$$

* OPERATING COSTS (cont.)

(B) (cont.)

Steam Cost:

$$\frac{\$3,500}{1 \times 10^6 \text{ Btu}} \times \frac{200,000 \text{ Btu}}{\text{hr}} \times \frac{168 \text{ hr}}{\text{wk}} \times \frac{4 \text{ wk}}{\text{mo}} \times \frac{1 \text{ mo}}{\text{yr}} = \$470/\text{yr}$$

Sludge Recovery & Disposal

$$\frac{\$20,000}{\text{mo.}} \times \frac{1 \text{ mo.}}{\text{yr.}} = \underline{\$20,000/\text{yr}}$$

Total Operating Costs

$$\underline{\$79,400/\text{yr}}$$

* GROSS PROFIT

GP = Revenue - Feed - Depreciation - Tax - Operating

$$(A) 2,043,000 - 0 - 43,000 - 12,900 - 513,900 = \$1,473,200/\text{yr}$$

$$(B) 407,000 - 0 - 43,000 - 12,900 - 79,400 = \$271,700/\text{yr}$$

* NET PROFIT

33% Income Tax

Net Profit = 0.67 x Gross Product

$$(A) \frac{0.67}{\text{yr}} \times \$1,473,200 = \$987,000/\text{yr}$$

$$(B) \frac{0.67}{\text{yr}} \times 271,700 = \$182,000/\text{yr}$$

* RATE OF RETURN ON INVESTMENT

$$RROI = \frac{\text{Net profit}}{\text{Capital Cost}} \times 100$$

$$(A) \frac{\$987,000}{\$430,000} \times 100 = 230\%$$

$$(B) \frac{\$182,000}{\$430,000} \times 100 = 42\%$$

* PAYOUT TIME

$$PT = \frac{\text{Capital Cost}}{\text{Net profit}}$$

$$(A) \frac{\$430,000}{\$987,000/\text{yr}} = 0.44 \text{ yr} = 5.2 \text{ mo.}$$

$$(B) \frac{\$430,000}{\$182,000/\text{yr}} = 2.4 \text{ yr}$$

Appendix E

5 Plant to 1 Plant Paint Solvent Recovery of TURCO T-5668 Solvent

Chemical Process Industries

Final Project

5 plant to 1 plant
Paint Solvent Recovery of
TURCO T-5668 solvent

Written by:

Scott Waltari

Due to the increasing taboo against chlorinated solvents, the government has decided to limit the use of said solvents in paint removal at their major air force bases. One possible solvent considered to replace the chlorinated solvents is TURCO T-5668. This solvent consists of 22% ethanol amine, 60% N-methyl pyrrolidinone(M-Pyrol), and 10% hydrogenated naphthenes.

The solvent will be recovered by using a continuous distillation process. The recovery procedure is as follows:

1. Filter out the paint chips.
2. Rectify the liquid phase in a batch column. Distill off the ethanolamine at 170°C and 99% purity.
3. Put midfraction, ethanolamine and M-Pyrol in storage tank for recycle.
4. Distill off the M-Pyrol at 202°C.
5. Put midfraction, M-Pyrol and naphthenes in storage tank for recycle.
6. Distill off naphthenes at 170°C and reduced pressure.
7. Empty stillpot, send to waste.
8. Refill stillpot with new charge plus both midfraction recycle streams from previous run.

Batch operation and midfraction recovery takes about 50% more time.

Two plant styles are being considered for use in the paint recovery. One style consists of 5 bases sending their used solvent to one central location where one plant will recover all of the solvent. The other style consists of 1 plant at each base which will treat the used solvent of only one base. Plants involved with each style will be the same size, only the operation time will change.

The initial investment for a plant that can handle a capacity of 30,000 gallons of solvent per month totals about \$465,000. This investment is the same for both styles. Table 1 gives a breakdown of the expenses.

Table 1, INVESTMENT

Column, pumps, column internals, reflux tank, heat exchangers, & controls	\$100,000
Bidding, designs, & simulation	100,000
Assembling	50,000
Putting on skids	20,000
Storage tanks	30,000
Piping & electrical installation	80,000
Contingency	65,000
TOTAL INVESTMENT	\$465,000

Annual expenses for each style will change due to varying operation times. Operating time for 1 central plant will be approximately 5 months where as the operating time for 5 plants will be approximately 1 month. Table 2 gives a breakdown of the annual expenses for each style.

Table 2, EXPENSES

	1 Plant	5 Plants
Operating Labor: \$40/hr*2 people	\$460,800	\$86,400
Supervision: \$50/hr*42 hr/mo	16,800	3,200
Maintenance & Repairs	15,000	3,000
Steam Cost: 200,000 BTU/hr*\$3.50 M	3,760	820
Sludge Recovery & Disposal	100,000	20,000
Moving Expense	50,000	0
Depreciation: 10% per year	46,500	46,500
Property Taxes @ 3%	14,000	14,000
TOTAL EXPENSES	\$706,860	\$173,920

Revenue for the project will be made by reselling the recovered paint solvent at market prices. Cost of raw materials is considered zero due to its status as waste. The revenue generated

from the solvent is found in Table 3. Also included in Table 3 are net income, return on investment, and payout time.

Table 3, REVENUE

Ethanolamine: \$5.0445/gal	\$166,500	\$33,300
M-Pyrol: \$14.535/gal	1,308,150	244,700
Hydrogenated Naphthenes: \$1.71/gal	25,650	5,130
TOTAL REVENUE	\$1,500,300	\$283,130
NET INCOME	\$793,400	\$109,210
Return on Investment: Income/Invest	171%	23%
Payout Time: 1 year/Return of Invest	7 mo	4.3 yrs

Overall both projects appear to be quite feasible. The most economical process would be to ship the solvent to one centralized location and process it there. If fees for shipping waste rise enormously, the 5 plant method would become more feasible. The 5 plant method would also become more feasible if the plant was scaled down.

Appendix F

Solvent Components Boiling Temperatures

Solvent Components Boiling Temperatures

TEMPERATURES IN DEGREES CENTIGRADE AT 1 mm Hg

(*Indicates temperatures taken at 620 mm Hg)

(Percentages indicate % moles from GC analysis)

END

**DATE
FILMED**

2 / 24 / 93