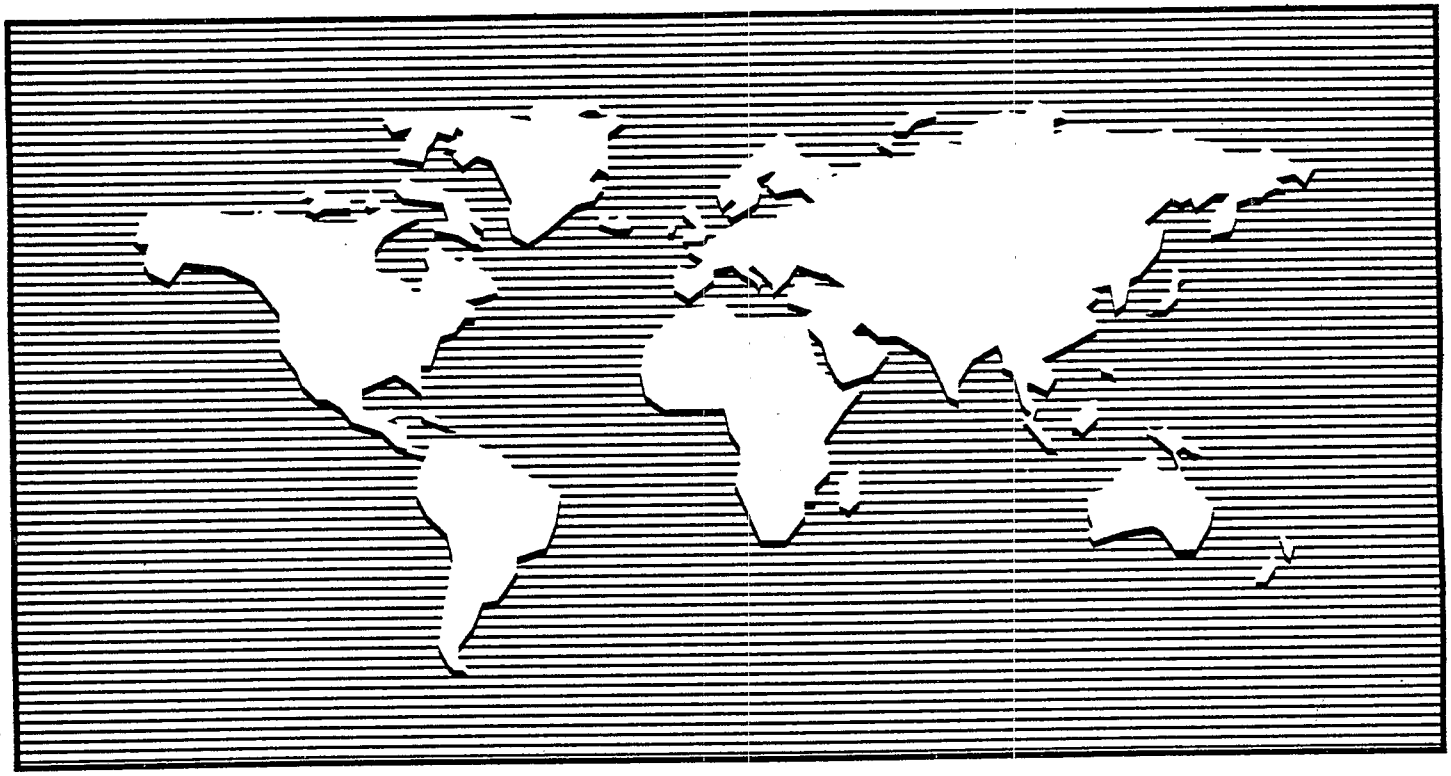
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Alternatives for CFC-113 And Methyl Chloroform in Metal Cleaning



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ALTERNATIVES FOR CFC-113 AND METHYL CHLOROFORM IN METAL CLEANING

by

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* ICOLP is the Industry Cooperative for Ozone Layer Protection. ICOLP corporate member companies include AT&T, Boeing Company, British Aerospace, Compaq Computer Corporation, Digital Equipment Corporation, Ford Motor Company, General Electric, Hitachi Limited, Honeywell, IBM, Matsushita Electric Industrial Company, Mitsubishi Electric Corporation, Motorola, Northern Telecom, Sundstrand, Texas Instruments, and Toshiba Corporation. Industry association affiliates include American Electronics Association, Electronic Industries Association, Japan Electrical Manufacturers Association and Halogenated Solvents Industry Alliance (U.S.). Government organization affiliates include the City of Irvine, California, the State Institute of Applied Chemistry (U.S.S.R.), the Swedish National Environmental Protection Agency, U.S. Air Force, and U.S. Environmental Protection Agency (EPA).

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FOREWORD

The 1987 Montreal Protocol on Substances that Deplete the Ozone Layer, and subsequent 1990 amendments and adjustments, restricts the production and consumption of ozone-depleting chemicals. Two such chemicals, chlorofluorocarbon 1,1,2-trichloro-1,2,2-trifluoroethane (commonly referred to as CFC-113) and 1,1,1-trichloroethane (commonly referred to as methyl chloroform or MCF), will be completely phased out in developed countries by years 2000 and 2005 respectively, and ten years later in developing countries.

Exhibit 1 lists the countries that are Parties to the Montreal Protocol as of April 1991. In addition, many companies worldwide have corporate policies to expedite the phaseout of ozone depleting chemicals. Exhibit 2 presents the corporate policies on CFC-113 reduction for some of these companies.

In addition to providing regulatory schedules for the phaseout of ozone-depleting chemicals, the Montreal Protocol established a fund that will finance the incremental costs of phasing out ozone-depleting substances by developing countries that are Party to the Protocol.

U.S. Clean Air Act Amendments

The U.S. Clean Air Act (CAA) was amended in 1990, and contains several provisions pertaining to stratospheric ozone protection. Section 602 of the CAA presents a list of ozone-depleting substances that are restricted under the CAA. These ozone-depleting substances are defined as Class I and Class II substances. Class I substances include all fully halogenated chlorofluorocarbons (CFCs) including CFC-113, three halons, MCF, and carbon tetrachloride. Class II substances are defined to include 33 hydrochlorofluorocarbons (HCFCs). The sections of the CAA that are of importance to users of this manual are discussed below.

Exhibit 1

MONTREAL PROTOCOL PARTICIPANTS

Argentina	Malawi
Australia	Malaysia
Austria	Maldives
Bahrain	Malta
Bangladesh	Mexico
Belgium	Netherlands
Brazil	New Zealand
Bulgaria	Nigeria
Burkina Faso	Norway
Cameroon	Panama
Canada	Poland
Chile	Portugal
Czechoslovakia	Singapore
Denmark	South Africa
Ecuador	Spain
Egypt	Sri Lanka
European Community	Sweden
	Switzerland
Finland	Syrian Arab Rep.
Fiji	Thailand
France	The Gambia
Germany	Trinidad and Tobago
Ghana	
Greece	Tunisia
Guatemala	Uganda
Hungary	USSR (includes Byelorussia and Ukraine)
Iceland	
Iran	
Ireland	United Arab Emirates
Italy	
Japan	United Kingdom
Jordan	United States
Kenya	Uruguay
Libya	Venezuela
Liechtenstein	Yugoslavia
Luxembourg	Zambia

Non-Ratifying Signatories: Congo, Indonesia, Israel, Morocco, Philippines, Senegal, Togo

Date: April, 1991

Exhibit 2

CORPORATE POLICIES ON CFC-113 REDUCTION SCHEDULE

Company	Reduction Schedule CFC-113
American Electronics Association Member Companies. U.S.	Phaseout 2000
AT&T. U.S.	Phaseout 1994
Canon. Japan	Phaseout 1994
Digital Equipment Corporation. U.S.	Phaseout 1995
Hitachi Corporation. Japan	Phaseout 1993
Honeywell. U.S.	Phaseout 1997
IBM. U.S.	Phaseout 1993
Intel Corporation. U.S.	Phaseout 1992
Matsushita. Japan	Phaseout 1995
Motorola. Inc.. U.S.	Phaseout 1992
Nissan Motor Corp.. Japan	Phaseout 1993
Northern Telecom. Canada	Phaseout 1991
Seiko-Epson. Japan	Phaseout 1993
Sharp Corporation. Japan	Phaseout 1995
Texas Instruments. U.S.	Phaseout 1994
Toshiba Corporation. Japan	Phaseout 1995
Volvo. Sweden	Phaseout 1994

Section 604 and Section 605: Phaseout of Production and Consumption of Class I and Class II Substances.

These provisions of the CAA present phaseout schedules for Class I & Class II substances. The phaseout dates for ozone-depleting substances listed in the CAA are more stringent than the Montreal Protocol. Exhibit 3 presents the phaseout schedule for CFC-113 and MCF. Other substances with ozone-deleting potential are also regulated under the Montreal Protocol and the CAA. While they are not used in solvent cleaning applications, these substances are used in other applications. Section 605 of the CAA presents provisions for the phaseout of HCFCs. The CAA freezes the production of HCFCs in 2015 and phases them out by 2030. Since these restrictions focus on production limitations, to the extent that these chemicals can be recovered, recycled, and reused, they may continue in commerce past the applicable phase-out dates.

Section 608: National Emissions Reduction Program

This section calls for EPA to promulgate regulations by July 1992 requiring emissions from all refrigeration sectors (except mobile air conditioners that are covered in Section 609) to be reduced to their "lowest achievable levels." Regulations affecting emissions from all other uses of Class I and Class II substances including solvent cleaning are to take effect by November 1995. This section also prohibits any person from knowingly venting any of the controlled substances, including HCFCs, during servicing of refrigeration or air conditioning equipment (except cars) beginning July 1, 1992, and requires the safe disposal of these compounds by that date.

Section 610: Nonessential Products Containing Chlorofluorocarbons

This provision directs EPA to promulgate regulations that prohibit the sale or distribution of certain "nonessential" products that release Class I & Class II substances during manufacture, use, storage, or disposal. In the CAA, Congress defined several products as nonessential including CFC-containing cleaning fluids for noncommercial electronic and photographic equipment, and CFC-propelled plastic party streamers and noise horns. In addition, Congress established guidelines to identify additional products that are nonessential. Regulations banning nonessential products that release Class I substances must be promulgated by November 15, 1991 and become effective November 15, 1992. In addition, the CAA bans the sale and distribution of certain products releasing Class II substances, including aerosols and pressurized dispensers and noninsulating foam, by January 1, 1994. Exemptions can be granted from the ban on aerosols and pressurized dispensers due to flammability and worker safety concerns.

Section 611: Labeling

This section of the CAA directs EPA to promulgate regulations by May 15, 1992 requiring labeling of products that contain or were manufactured with Class I or Class II substances and containers containing these substances. The label will read "Warning: Contains or manufactured with *[insert name of substance]*, a substance which harms public health and environment by destroying ozone in the upper atmosphere".

The CAA defines three types of products that must be labeled and specifies the time frame by which these products must be labeled. The three products and time frame are as follows:

- Effective May 15, 1993, containers in which a Class I or Class II substance is stored or transported, and products containing Class I substances must be labeled;

- Effective May 15, 1993, products manufactured with Class I substances must be labeled. However, products manufactured with Class I substances can be temporarily exempted from the labeling requirements of this section if EPA determines that there are no substitute products or manufacturing processes that (a) do not rely on the use of the Class I substance, (b) reduce the overall risk to human health and the environment, and (c) are currently or potentially available. If EPA temporarily exempts products

Exhibit 3

PHASEOUT DATES FOR CFC-113 AND METHYL CHLOROFORM UNDER THE U.S. CLEAN AIR ACT AND THE MONTREAL PROTOCOL

CFC PHASEOUT

Clean Air Act	Montreal Protocol
Reduce from 1986 levels by:	Freeze at 1986 production and consumption levels by July 1989
1991 - 15%	20% reduction from 1986 levels by January 1993
1992 - 20%	50% reduction from 1986 levels by January 1995
1993 - 25%	85% reduction from 1986 levels by January 1997
1994 - 35%	100% reduction from 1986 levels by January 2000
1995 - 50%	
1996 - 60%	Also call for future assessment to determine if an earlier complete phaseout by January 1997 is achievable
1997 - 85%	
1998 - 85%	
1999 - 85%	
2000 - 100%	

METHYL CHLOROFORM PHASEOUT

Clean Air Act	Montreal Protocol
Freeze at 1989 levels by 1991	Freeze at 1989 production and consumption levels by January 1993
Freeze at 1989 levels continues in 1992	30% reduction from 1989 levels by January 1995
Reduce from 1989 levels by:	70% reduction from 1989 levels by January 2000
1993 - 10%	100% reduction from 1989 levels by January 2005
1994 - 15%	
1995 - 30%	
1996 - 50%	
1997 - 50%	
1998 - 50%	
1999 - 50%	
2000 - 80%	
2001 - 80%	
2002 - 2004*	
2005 - 100%	

* New authority would be given to EPA to authorize, to the extent consistent with the Protocol, the production of methyl chloroform in an amount not to exceed 10% of baseline per year in 2002, 2003, and 2004 for use in essential applications for which no safe substitutes are available.

manufactured with Class I substances from the labeling requirement based on the lack of substitutes, the products must be labeled by January 1, 2015; and

- No later than January 1, 2015, products containing or manufactured with a Class II substance must be labeled. EPA may require such products to be labeled as early as May 15, 1993 if it determines, after notice and opportunity for public comment, that there are substitute products or manufacturing process available.

The CAA allows for petitions to be submitted to EPA to apply the requirements of Section 611 to products containing Class II substances or a product manufactured with Class I or II substances which are not otherwise subject to the requirements. This petition process will operate between May 15, 1993 and January 1, 2015. For products manufactured with Class I substances, a successful petition would result in the labeling of a product previously determined by EPA to be exempt. For products containing or manufactured with Class II substances, the petition process could lead to labeling of a product that had been left unlabeled by default.

Section 612: Safe Alternatives Policy

Section 612 establishes a framework for evaluating the environmental impact of current and future potential alternatives. Such regulation ensures that the substitutes for ozone-depleting substances will not create environmental problems themselves. The key provisions of Section 612 require EPA to:

- Issue rules by November 15, 1992 which make it unlawful to replace any Class I and Class II substances with a substitute that may present adverse effects to human health and the environment where EPA has identified an available or potentially available alternative that reduces the overall risk to human health and the environment.

- Publish a list of prohibited substitutes, organized by use sector, and a list of the corresponding alternatives;

- Accept petitions to add or delete a substance previously listed as a prohibited substitute or an acceptable alternative;

- Require any company which produces a chemical substitute for a Class I substance to notify EPA 90 days before any new or existing chemical is introduced into commerce as a significant new use of that chemical. In addition, EPA must be provided with the unpublished health and safety studies/data on the substitute.

To implement Section 612 EPA will (1) conduct environmental risk characterizations for substitutes in each end use and (2) establish the Significant New Alternatives Program (SNAP) to evaluate the future introduction of substitutes for Class I substances. EPA has also initiated discussions with NIOSH, OSHA, and other governmental and nongovernmental associations to develop a consensus process for establishing occupational exposure limits for the most significant substitute chemicals.

The environmental risk characterizations for the substitutes will involve a comprehensive analysis based on the following criteria: ozone-depleting potential, flammability, toxicity, exposure effects, energy efficiency, degradation impacts, air, water, and solid waste/hazardous waste pollution effects, and global warming potential. Economic factors will also be considered. EPA will organize these assessments by use sector (i.e. solvents, refrigeration, etc). The risk characterizations will result in risk-management strategies for each sector and substitute. EPA will then categorize a substance as unacceptable, acceptable with limitations on use or quantity, acceptable without comment, or delayed pending further study. Petitions will be allowed to change a substance's status with the burden of proof on the petitioner.

The SNAP program, effective November 15, 1992, will review future substitutes not covered in the initial risk characterization process. SNAP will evaluate a substitute based on the criteria established for the risk characterization and will classify it similarly.

Excise Tax

Congress has also placed an excise tax on ozone-depleting chemicals manufactured or imported for use in the United States. This tax provides a further incentive to use alternatives and substitutes to CFC-113 and MCF. The tax amounts are based on each solvent's ozone depleting potential.

Calendar Year	Tax Amount Per Pound	
	CFC-113	MCF
1991	$1.096	$0.137
1992	$1.336	$0.167
1993	$2.120	$0.265
1994	$2.120	$0.265
1995	$2.480	$0.310

The tax will increase by $0.310 per pound for CFC-113 and $0.045 per pound for MCF each year after 1995.

Other International Phaseout Schedules

European Community Directive

Under the Single European Act of 1987, the twelve members of the European Community (EC) are now subject to various environmental directives. The members of the EC are Belgium, Denmark, Germany, France, Greece, Great Britain, Ireland, Italy, Luxembourg, the Netherlands, Portugal, and Spain. Council Regulation number 594/91 of March 4, 1991 provides regulatory provisions for the production of substances that deplete the ozone layer. The EC phaseout schedule for CFC-113 production is more stringent than the Montreal Protocol. It calls for a 50 percent reduction of CFC-113 by the end of 1993, a 67.5 percent reduction by the end of 1995, an 85 percent reduction by the end of 1996, and complete phaseout by June 30, 1997. For MCF, the production phaseout schedule is as follows: 30 percent reduction by the end of 1995, 70 percent by the end of 2000, and a complete phaseout by the end of 2004. While all members must abide by these dates, Council Regulation number 3322/88 of October 31, 1988 states that EC members may take even more extensive measures to protect the ozone layer.

Other Legislation

Several other countries have adopted legislation that is more stringent than the terms of the Montreal Protocol. Environment Canada, the federal environmental agency responsible for environmental protection in Canada, also has a reduction program in place that is more stringent than the Montreal Protocol. All production and import of CFCs, for use in Canada, must be eliminated by no later than 1997. Environment Canada has also announced a series of target dates for the phaseout of CFCs in specific end uses. For solvent cleaning applications, such as metal and precision cleaning, it mandates a phaseout of CFC-113 by the end of 1994. Pending final consultations with end-users and producers of MCF, the target date for the phaseout of MCF will be 2000.

Japan has ratified the revised Montreal Protocol. The recent Ozone Layer Protection Act gives the Ministry of International Trade and Industry (MITI) the authorization to promulgate ordinances governing the use of ozone-depleting compounds. MITI and the Environmental Agency have established the "Guidelines for Discharge Reduction and Use Rationalization." Based upon these guidelines, various government agencies provide administrative guidance and advice to the industries under their respective jurisdictions. Specifically, MITI, the ministry overseeing several aspects of Japanese industry including the production and trade of controlled substances, prepares and distributes manuals, and encourages industry to reduce ozone-depleting compounds consumption through economic measures such as tax incentives to promote the use of equipment to recover and reuse solvents.

The EFTA (European Free Trade Agreement) countries (i.e., Austria, Finland, Iceland, Norway,

Sweden, and Switzerland) have each adopted measures to completely phaseout fully halogenated ozone-depleting compounds. Some of the EFTA countries have sector-specific interim phaseout dates for certain solvent uses. Norway and Sweden will phaseout their use of CFC-113 in all applications except textile dry cleaning by July 1 and January 1, 1991, respectively. Furthermore, Austria will phaseout CFC-113 in some solvent cleaning applications by January 1, 1992 and 1994. Austria, Finland, Norway, and Sweden will all completely phaseout their use of CFC-113 in all applications by January 1, 1995. Sweden also plans an aggressive phaseout date of 1995 for MCF.

Cooperative Efforts

The U.S. Environmental Protection Agency (EPA) has been working with industry to disseminate information on technically feasible, cost effective, and environmentally sound alternatives for ozone-depleting substances. As part of this effort, the U.S. EPA is working with the Industry Cooperative for Ozone Layer Protection (ICOLP*) to prepare a series of manuals to provide technical information on alternatives to CFC-113 and MCF. The manuals are based on actual industrial experiences that will serve as a guide to users of CFC-113 and MCF worldwide. These manuals will be updated periodically as technical developments occur.

The first manuals in the series are:

- Conservation and Recycling Practices for CFC-113 and Methyl Chloroform.
- Aqueous and Semi-Aqueous Alternatives to CFC-113 and Methyl Chloroform Cleaning of Printed Circuit Board Assemblies.
- Inert Gas Soldering/Low Residue Flux and Paste Alternatives to CFC-113 and Methyl Chloroform.
- Alternatives for CFC-113 and Methyl Chloroform in Metal Cleaning.
- Eliminating CFC-113 and Methyl Chloroform in Precision Cleaning Operations.
- Riveting Without CFC-113 and Methyl Chloroform.

This particular manual will take you, an individual in an industrial organization involved in metal cleaning operations, through a simple structured program to help you eliminate use of CFC-113 and/or MCF. This manual:

- Provides you with some background on metal cleaning;
- Guides you through a characterization of your existing process;
- Outlines the criteria to consider as you develop and select the appropriate alternative for your operations;
- Introduces several alternative technologies; and
- Presents detailed case studies on actual industrial applications of these technologies.

The alternatives to CFC-113 and MCF for metal cleaning discussed in the manual are:

- Aqueous cleaning
- Semi-aqueous cleaning
- Alternative solvents.

This manual will benefit all users of CFC-113 and MCF in metal cleaning. Ultimately, however, the success of your CFC-113 and MCF elimination strategies will depend upon how effectively you can coordinate your reduction and elimination programs. The development and implementation of alternatives to CFC-113 and MCF for metal cleaning present an exceptionally demanding challenge for your organization. The rewards for success are the contribution to global environmental protection and the increase in your company's industrial efficiency.

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* Appendix A presents more detailed information about ICOLP.

STRUCTURE OF THE MANUAL

This manual is divided into the following sections:

- **INTRODUCTION TO METAL CLEANING**

  This section provides a brief description of metal cleaning.

- **EXISTING CLEANING PROCESS CHARACTERIZATION**

  This section describes the tools to characterize metal cleaning operation. It is important to understand the relationship between metal cleaning and the other aspects of manufacturing processes and how CFC-113 and/or MCF are used.

- **ALTERNATIVE METHOD OVERVIEW**

  This section highlights the criteria for developing and selecting a non-CFC/MCF strategy for metal cleaning. Various technical and managerial considerations are discussed.

- **ALTERNATIVE MATERIALS AND PROCESSES**

  This section describes the operational principles and outlines the advantages and disadvantages of each technology.

- **WASTEWATER MINIMIZATION AND TREATMENT**

  This section presents methods to minimize and treat wastewater from aqueous and semi-aqueous cleaning processes.

- **CASE STUDIES OF INDUSTRIAL PRACTICES**

  This section describes case studies that illustrate the successful implementation of alternative technologies.

INTRODUCTION TO METAL CLEANING

Cleaning is an essential process in the production, maintenance, and repair of manufactured articles. As a surface preparation process, cleaning removes contaminants and prepares raw materials and parts for subsequent operations such as machining, painting, electroplating, inspection, and packaging. Cleaning is used in furniture and fixtures, primary metal industries, fabricated metal products, machinery, transportation equipment, and other miscellaneous manufacturing.

Chlorofluorocarbon 113 (CFC-113) and methyl chloroform (MCF) have been used for many solvent cleaning applications. These solvents exhibit good solvency for a wide variety of organic contaminants and are noncorrosive to the metals being cleaned. They have low heats of vaporization and high vapor pressures that are beneficial in vapor cleaning processes and allow evaporative drying of cleaned parts. Additionally, these solvents are non-flammable, have low toxicity, and chemically stable when properly formulated with adequate stabilizers.

Solvent cleaning may be divided into two types: cold cleaning and vapor degreasing. Cold cleaning is usually accomplished with solvents at, or slightly above, room temperature. In cold cleaning, parts are cleaned by being immersed and soaked, sprayed, or wiped with the solvent.

Vapor degreasing is a process that uses the boiling solvent vapor to remove contaminants. A basic vapor degreaser consists of an open-top steel tank that has a heat source at the bottom to boil the solvent and cooling coils near the upper section to condense the vapors.

Heat, introduced into the reservoir, boils the solvent and generates hot solvent vapor which displaces the lighter air and forms a vapor zone above the boiling solvent up to the cooling zone. The hot vapor is condensed when it reaches the cooling zone by condensing coils or a water jacket, thus maintaining a fixed vapor level and creating a thermal balance. The hot vapor condenses on the cool part suspended in the vapor zone causing the solvent to dissolve or displace the contaminants or soils.

Vapor degreasing is, in most applications, more advantageous than cold cleaning, because in cold cleaning the solvent bath becomes increasingly contaminated. Although the boiling solvent contains the contaminants from previously cleaned parts, these usually boil at higher temperatures than the solvent, resulting in the formation of essentially pure solvent vapors. In addition, the high temperature of vapor cleaning aids in wax and heavy grease removal as well as significantly reducing the time it takes for cleaned parts to dry.

EXISTING CLEANING PROCESS CHARACTERIZATION

To develop an effective program to reduce and eliminate the use of CFC-113 and MCF, you must first acquire a good knowledge of your plant operations. The types of questions you should be able to answer include the following:

- What materials/substrates are you cleaning?
- Where are the contaminants coming from?
- What types of contaminants are you removing?
- Why are you performing metal cleaning at your plant?
- Is this cleaning step necessary?
- What are the effects of metal cleaning on the upstream and downstream aspects of your process?
- What processes are using CFC-113 and MCF?
- Where do CFC-113 and MCF emission losses take place?
- Who purchases CFC-113 and MCF?
- Who accepts delivery of CFC-113 and MCF?
- How are CFC-113 and MCF handled from arrival to ultimate use?

Characterize Solvent Use

The first step in addressing the use of CFC-113 and MCF is to designate a team to coordinate the solvent reduction and elimination programs. Team members should represent various plant functions including process design, production and production engineering, environmental control, occupational health and safety, quality control, and purchasing. The team leader of the reduction and elimination programs should conduct a survey to determine the quantities of CFC-113 and MCF used in every aspect of the plant's operations. An example survey form that could be used for this purpose is shown in Exhibit 4. Material Safety Data Sheets are useful in identifying the composition of solvents.

The total quantity of CFC-113 and MCF used in your processing should be divided by the appropriate production unit for your operations to obtain the ratio of kilograms or pounds of CFC-113 and MCF used per production unit. This value will be your benchmark for reduction and elimination programs.

Determine if Solvent Cleaning Is Necessary

After identifying the processes where solvents are being used, the next step is to determine whether each cleaning step is necessary. The entire production system should be viewed with a focus on improved procedures, housekeeping, and process changes to eliminate soiling of parts.

Exhibit 4

CFC-113 AND METHYL CHLOROFORM USAGE PROFILE

A. Identification

Name of Product: _____

Manufacturer: _____

Purchase Number: _____

CFC or MCF Components:

	Chemical Name	Percent or Concentration
1.	_____	_____
2.	_____	_____
3.	_____	_____

B. Quantification of Usage Patterns

Quantity Purchased: (specify units)

1989: _____ 1991: _____

1990: _____ 1992: _____

C. CFC and MCF Disposal Practices

	1989	1990	1991	1992
Annual quantity shipped out as waste for disposal: (specify units)				
Annual disposal costs:				
Annual quantity shipped out for reclamation: (specify units)				
Annual cost of reclamation:				
Annual quantity lost to the environment: (specify units)				
Through leakage:				
Through spillage:				
Through testing:				
Through dragout and evaporation:				
By other means (specify) _____				
Unaccounted for:				

Source: U.S. EPA 1990

A suggested hierarchy of options is:

Reduce or eliminate soiling of parts:

- Improve housekeeping;
- Consolidate operations.

For example, in a number of metal finishing processes, solvent cleaning is followed by alkaline cleaning. The question to ask is whether alkaline cleaning can handle the soil loading if the solvent cleaning step is eliminated. The answer may be yes. Or, if chip removal is desired, can a mechanical means (such as air blow-off, water spray/flush) replace solvent cleaning?

Another useful step is to evaluate the processes where solvent is being used, and determine whether alternative materials would make solvent cleaning unnecessary. Exhibit 5 presents methods that could be considered. For example, if the process before the solvent cleaning step was changed as suggested in Exhibit 5, could the solvent cleaning step be eliminated? If the answer is no, it will be necessary to find alternative solvent cleaning methods. These alternatives are discussed later.

Characterize the Soils and Their Sources

A critical part of the initial stage of process evaluation is characterizing the soils and their sources. This study of existing materials and procedures will help identify means of eliminating the need for cleaning or reducing the amount of soil to be removed.

Conduct a factory survey to characterize the soils and identify their sources. This survey should include visits to each production process, observation of existing procedures, interviews with operators of the equipment, and collection of soil samples for preliminary laboratory tests. This process will provide firsthand experience and also establish contact and develop rapport with the individuals who will ultimately be effected by the process change. Their cooperation and input are essential to the success of the program.

The general category of the soils that are removed needs to be determined. The types of soils can be generally classified into five groups:

- Pigmented drawing compounds are used in process steps where the metal is extruded through dies to produce parts. The most commonly used pigmented compounds contain one or more of the following substances: whiting, lithopone, mica, zinc oxide, bentonite, flour, graphite, white lead, molybdenum disulfide, titanium dioxide, and soap-like materials.

- Unpigmented oil and grease include common shop oils and greases such as drawing lubricants, rust preventive oils, and quenching oils.

- Forming lubricants and fluids used for machining can be classified into three subgroups: (1) hydrocarbon-based oils: plain or sulfurized mineral and fatty oils (or a combination of the two), chlorinated mineral oils, and sulfurized chlorinated mineral oils, (2) soluble/emulsifiable oils: conventional or heavy duty soluble oils containing sulfur or other compounds, glycol ethers, glycols or other emulsifiers added, and (3) water soluble: chemical cutting fluids that are water soluble and contain soaps, amines, sodium salts of sulfonated fatty alcohols, and alkyl aromatic salts of sulfonates.

- Polishing and buffing compounds can also be classified into three subgroups: (1) liquids: mineral oils and oil-in-water emulsions or animal and vegetable oils with abrasive materials, (2) semi-solids: oil-based containing abrasives and emulsions or water-based containing abrasive and dispersing agents, and (3) solids: grease containing stearic acid, hydrogenated fatty acids, tallow, hydrogenated glyceride, petroleum waxes, and combinations that produce either saponifiable or nonsaponifiable materials in addition to abrasive materials.

- Miscellaneous surface contaminants such as lapping compounds, residue from magnetic particle inspection, hand oils, shop dirt, chips, airborne dust, finger grease, ink marks, barrier cream, or hand protective cream and metal pieces also exist.

Exhibit 5

METHODS TO ELIMINATE THE NEED FOR CLEANING

Soil Presently Removed by Chlorinated Solvent	Methods Which Reduce Solvent Use
Hydraulic Fluids - Phosphate Esters	Prevent spills and leaks. Sorbent materials can be used.
Magnetic Inspection Field Kerosene	Sorbent materials can be used. Water carriers to replace the organics can be considered.
Hydrocarbon Greases and Oils	Hand wiping stations can remove enough material to allow alkaline cleaning. Water soluble compounds can be used.
Fats and Fatty Oils	Handwipe or use alkaline cleaners.
Polishing Compounds -- Fats	Water-soluble compounds may be substituted. Cleaning at the polishing station should be considered.
Machining Compounds -- Cutting Fluids	Water-soluble compounds should be considered.
Corrosion Inhibiting Compounds	Alkaline-soluble compounds can be considered. Protective packaging may eliminate cleaning need.
Drawing Compounds	Water-soluble compounds can be used.
Forming Compounds	Water-soluble compounds can be used.
Ink Marks	Water-soluble inks can be used and removed with water-based cleaners. Use labels or tags until final marking applied.
Fingerprints	If all fabricated parts are handled with gloves, fingerprints will be minimized. Hand alkaline wipe to remove.
Mill Oils	Protective packaging eliminates cleaning need. Sorbent materials may be used to remove oils.

The sources of the soils must be identified. For example, are the soils:

- Received as raw material?
- Produced in forming/stamping operations?
- Produced in general machining operations?
- Produced in sub-assembly? and/or
- Received with vendor parts?

Once the soils and their sources have been identified, the solvent elimination process can be optimized. For example, the type of soils can be consolidated by reducing the number of processing/machining fluids and switching to water-soluble alternatives. It is common practice to use a wide variety of processing fluids; in most cases this can be avoided. Review the Material Safety Data Sheets for all the processing fluids that are being used and select the acceptable ones.

Try to use water-soluble and non-chlorinated, emulsifiable machining and metal forming lubricants. These products require smaller quantities to perform a given task, and are more compatible with alkaline cleaners than with halogenated solvents and are generally emulsified and removed from substrates at lower temperature-concentration conditions than are neat hydrocarbon oils. Lubricant spray applicators, which discharge a fine, well-controlled mist, can also decrease lubricant usage without affecting product quality.

Other types of alternative metal forming lubricants under development include "dry" lubricants and thin polymer sheeting which can be peeled from the surface after the metal forming operation.

The handling, packaging, and routing of parts through the production process should be reassessed to minimize the number of times a part is soiled and cleaned. Put particular emphasis on consolidating, if possible, cleaning operations into a centralized unit or location. This step improves control of waste, emissions, and usage.

Segregation and precleaning of parts can extend bath life and make cleaning more efficient. Heavily soiled parts should be routed separately through a single precleaning system, thereby concentrating soils in one cleaning process.

Characterize the Substrate

The selection of the cleaning process must be based not only on the soils being removed, but also on the substrates being cleaned. In evaluating alternative cleaning processes, it is important to characterize the substrate/material being cleaned. This includes evaluation of:

- The type of substrate used;
- The size and geometry of the part being cleaned;
- The porosity of the part.

Metals such as aluminum and alloys containing magnesium, lithium, and zinc require special consideration because of their sensitivity to attack by certain chemicals. For example, cleaners for aluminum are generally mildly alkaline (approximately 9-10 pH), while those for magnesium and steel are best used above 11 pH. Zinc and cadmium are subject to corrosion and pitting by alkaline solutions.

Parts with excessive porosity such as coatings, parts that have severely rough surfaces, parts that have permanent overlapping joints (i.e., rivet joints, skip welded, and crimp joints), and parts with blind holes and tubing can retain solution -- which can cause corrosion.

ALTERNATIVE METHOD OVERVIEW

In developing and selecting an alternative technology for metal cleaning, several criteria should be considered. These considerations include:

- Organizational
- Technical
- Economic
- Environmental, Health, and Safety

Organizational

Important considerations include:

- ***Compatibility with other corporate goals.*** Corporate policy might disallow the use of particular solvents because of their impact on product quality.
- ***Feasibility given existing organizational structure.*** Environmental concerns may already be the responsibility of a particular task force within the company. Some companies have made environmental performance a criterion for evaluating managerial performance.
- ***Compatibility with corporate environmental policy.*** Some alternatives generate other forms of emissions, effluents, or wastes that are also the subject of corporate environmental goals.

Technical

The technical feasibility of the alternative process must be evaluated on a case-by-case basis. The first step is to develop criteria for evaluating the alternative process taking into account applicable federal, state, and local regulations that might apply. As discussed in the Foreword Section, the Clean Air Act Amendments of 1990 have several provisions pertaining to stratospheric ozone protection that must be considered before selecting alternatives. These include Section 608: National Emissions Reduction Program, Section 611: Labeling, and Section 612: Safe Alternatives Policy.

Important technical considerations include:

- Chemical cleaning ability
- Physical and chemical characteristics of cleaning process
- Compliance to specifications
- Material compatibility
- Effect on subsequent processes
- Process control
- Production rate requirements
- Ease of new process installation
- Floor space requirements
- Operating and maintenance requirements.

Chemical Cleaning Ability

The question of cleanability can be the source of many hours of meetings, discussions, and testing. The degree of cleanliness required varies from industry to industry and from process to process. In some metal cleaning applications, cleanliness requirements are less stringent in terms of measurable residue while in industries where critical components are being cleaned, requirements may be more stringent. Meeting cleanliness standards in the aerospace industry may require the removal of all damaging contaminants. The high performance coatings and adhesives used on jet aircraft require, for example, a high degree of surface cleanliness to insure the integrity of the coatings and to guarantee that adhesives are not adversely affected.

The removal of contamination from a surface is not a single property of a solvent, but a combined relationship of several characteristics. Some of these characteristics include wetting, capillarity, detergency, solubility, and emulsification.

Several standard tests can be used to determine the cleaning ability of the alternative process. Some of these tests can be run on the shop floor (visuals, tissue paper test, water break, and acid copper test), whereas other tests would have to be performed in a laboratory.

- *Visual Examination.* This test is useful only for visible contamination, but it can be done in a production/plant environment.

- *Tissue Paper Test.* The cleaned surface is rubbed with white tissue paper and the tissue is observed for stains. This test is simple and can be done in the production/plant environment.

- *Water Break.* If the last clean rinse forms a continuous water film on the part as it is removed, the surface can be considered clean.

- *Acid Copper Test.* A ferrous panel is immersed in a copper sulfate solution. On clean surface areas, copper will be deposited by chemical activity, forming a strong adherent, semi-bright coating that is spot free.

- *Atomizer Test.* Water mist is applied to a clean dry surface with an atomizer. The cleanliness is determined by the value of the advancing contact angle.

- *Contact Angle of Water Drop.* A drop of water is placed on the test surface; the contact angle is then measured either photographically or by a contact angle goniometer. Although this is an accurate method of determining relative surface cleanliness, it can only be used under laboratory conditions.

- *Kerosene Viewing of Water Break.* The test panel is withdrawn from water and is immediately submerged in a transparent container of kerosene that is lighted from the bottom. Water breaks are displaced by kerosene. (Kerosene is combustible, so be careful when using this method.)

- *Radioactive Tracer.* A radioactive soiling compound is applied to the test piece, and the residual radioactivity is measured after cleaning. This is the most sensitive of the quantitative tests now available. Use standard precautions when working with radioactive materials.

- *Fluorescent Dye.* An oil soluble fluorescent dye is mixed with an oily soiling material and applied to the test panels. After the panels are cleaned, the retained soil is visible under ultraviolet or black light. Note that some cleaners may selectively remove tracer or fluorescent dyes.

- *Gravimetric.* The test panels are weighed before and after cleaning. The sensitivity of the method depends upon the sensitivity of the balance and the size of the panel.

- *Oil Spot.* A drop of solvent is used to degrease an area the size of the drop. The drop is picked up with a pipette and evaporated on ground glass. An evaporation ring indicates contamination.

- *Particulate Contamination.* A thin film of polyvinyl chloride is pressed against the test surface, heated to 240°F, and cooled. It is then carefully stripped from the surface and examined under the microscope. The particulate contaminants will be embedded in the vinyl sheet.

- ***Particle Removal Test.*** Particle removal can be tested by artificially contaminating surfaces with known particles of various sizes down to and below the size of interest for removal. Precision particles from submicron to tens of microns in size can be obtained. Nephelometric methods and membrane filtration methods such as ASTM-F24 are useful low-cost techniques for evaluating general cleaning.

- ***Chemical Analysis.*** Surface cleanliness can be evaluated and surface contaminants identified and quantified by using a number of analytical chemical techniques. The techniques most often used are Auger electron spectroscopy (AES), secondary ion mass spectroscopy (SIMS), x-ray photo-electron spectroscopy (XPS), and microscopic Fourier-Transform infrared spectroscopy (micro FT-IR).

- ***Optical Monitoring and Polarized Light Microscopy.*** Visual inspection using microscopy is relatively inexpensive and gives fast results.

- ***End Use Tests.*** These tests can be conducted to examine the effect of cleaning on subsequent process steps such as the application of protective coating (some of these are discussed later in this section).

Physical and Chemical Characteristics of the Cleaning Process

Physical and chemical characteristics include viscosity, surface tension, density, boiling point, freezing point, specific heat, and latent heat of vaporization. These properties determine the cleaning effectiveness.

Compliance to Specifications

In instances where cleaning requirements are governed by military or other specifications, it is necessary to either verify compliance by demonstrating that cleaning is adequate or renegotiate existing specifications before switching to alternative technologies.

Material Compatibility

In the selection of an alternative process, material compatibility is important. Issues to be considered include corrosion problems and compatibility with various process materials, such as metals, plastics, elastomers, composites, and other sensitive materials.

Compatibility problems can be evaluated by performing a number of corrosion tests:

- Intergranular attack testing determines if the cleaning solution unacceptably weakens the test metal by selectively removing material along grain boundaries.

- Stress corrosion (ASTM-G38) cracking (SCC) of parts can occur when susceptible materials (from which the parts are made) are corrosion sensitized during cleaning and are subsequently aged in a tension stress application. In general SCC tests are run by subjecting a test specimen of the same composition and heat treatment as the part, to a constant tension stress load after being exposed to the corrosive medium. A number of ASTM test methods specify complete test details for specimen configuration and stress loading. See TM-01-69 MACE standard "Laboratory Corrosion Testing of Metals for the Process Industry."

- Total immersion corrosion (ASTM 483) testing evaluates the general corrosive attack of a cleaner which can cause unacceptable dimensional changes in a metal surface. A number of specifications describe variations on this test (MIL-C-87936, ASTM F483). Metal cleaners for aluminum and aluminum alloys can be evaluated in accordance with ASTM D930. Cleaners for all other metals can be evaluated using ASTM D1280. For example, the test can be conducted by completely immersing a tared specimen into the test solution so that there is no air/solution interface. The specimen is allowed to sit undisturbed for 24 hours after which it is removed, rinsed, dried, and reweighed. Corrosion is measured as weight loss. The amount of allowable loss should be predetermined depending on the kind of material and use, but should be restricted to a few milligrams.

- Sandwich corrosion (ASTM F1110) testing measures the corrosivity of a cleaner trapped between fraying surfaces and then periodically exposed to various temperature and humidity conditions.

- Hydrogen embrittlement (ASTM F519-77) testing is conducted to determine if cleaners will adversely affect high strength steel. Testing can be conducted in accordance with ASTM F519, using both cadmium plated and unplated Type 1A steel specimens. The specimens are subjected to 45 percent of their ultimate tensile strength while immersed in the test solution. The specimens must not break for a minimum of 150 hours.

Effect on Subsequent Processes

Since cleaning is an integral part of manufacturing processes, it is critical that you examine the effect of cleaning on subsequent manufacturing steps. These include:

- *Application of Protective Coatings.* Cleaning is used extensively before and after the application of protective and/or decorative finishes. For example, surfaces cleaned before painting, enameling, or lacquering, give better adhesion of finishes. Similarly, cleaning is used to remove large amounts of oil contamination, prior to electroplating.

- *Inspection.* Inspections may be numerous, making speed and ease of part handling very important. Parts are cleaned to meet customer requirements and have to be inspected to identify any defects.

- *Assembly.* Assembly requires that parts be free from inorganic and organic contaminants. The cleaning process should leave the parts clean and dry, ready for assembly, and/or subsequent finishing.

- *Further Metal Working or Treatment.* In many instances, parts must be prepared for subsequent operations such as welding, heat treating, or further machining. Cleaning between steps allows the operator to start each new step with clean, dry parts. Before heat treatment, all traces of processing oils should be removed from the surfaces: their presence causes smoking, nonuniform hardening, and heat treatment discoloration on certain metals.

- *Machining.* By starting a machining operation with a clean surface, the chance of carrying imperfect parts through to other operations is minimized. Cutting oils used during machining give best results when applied to clean surfaces.

- *Packaging.* Final cleaning prepares parts for packing and shipping.

Process Control

Process control is part of a quality assurance program. Being satisfied with a process is key to a successful program. One example of good process control is checking cleaner solution strengths on a routine basis. Maintaining solution strength by making small, frequent additions is much more effective than making a few large additions.

Throughput of the Cleaning Process

Cleaning process throughput can be an important parameter, especially if cleaning is part of a continuous production process. For example, adhesion of finishes can be affected by moisture remaining on a surface to be coated. The rapid drying time associated with solvent cleaning provides an advantage in speeding up production processes. For batch cleaning processes, this factor may not be critical. Some alternative process may require slower throughput for optimized operations.

Ease of New Process Installation

Another consideration is whether the current manufacturing operation is flexible enough to allow installation of a new process. Would it be easy or would it disrupt the current process?

Floor Space Requirements

Equipment must be compatible with the plan and space constraints of your manufacturing floor. A

new process might require rearranging subsequent processes to optimize the floor plan. In some cases, alternatives take up more space than solvent cleaning processes. For example, most aqueous cleaning processes include a drying stage that requires additional floor space. Rearranging existing equipment or installing a new process also may trigger permitting requirements.

Operating and Maintenance Requirements

Each new process will require operating and maintenance procedures. The new process might be more cumbersome to operate and may require special operator training.

Maintenance of process equipment on a regular basis is critical. For example, cleaning of spray nozzles is necessary to remove soil contamination that would make them less effective. Pumps and valves should also be checked regularly.

Economic

Process economics is a key factor in the selection of alternative processes. Initial costs associated with an alternative process include capital costs of equipment, possible costs associated with waste treatment/handling equipment and costs for permit changes for new construction or new operating procedures. In addition, operating cost equations include material, labor, maintenance, and utility costs. Cost estimates for an alternative process can be developed through preliminary process design.

One simple approach is to calculate net present value (NPV) based on the discount rate and period of investment your company uses. The NPV is calculated as follows, where (n) is the number of years, and (i) is the discount rate.

$$NPV = Cost_0 + Cost_1/(1+i) + Cost_2/(1+i)^2 + \ldots + Cost_n/(1+i)^n$$

While traditional economic considerations such as rate of return and payback period are important, the CFC-113 and MCF reduction program can be justified on a basis of environmental protection and solvent supply reliability. An important component of the analysis should recognize that the price of CFC-113 and MCF will increase rapidly as supplies are reduced and then eliminated and taxes are imposed. Because of the considerable difference in ozone-depleting potential, the price increases of CFC-113 and MCF will vary. Include the cost savings resulting from savings in solvent consumption. Some new alternative processes are much less expensive than the current CFC and MCF processes being used.

Environmental, Health, and Safety

Important considerations include:

- ***Compatibility with appropriate federal, state, and local regulations.*** State and local regulations on ozone-depleting chemicals, VOCs, effluents of waste can be more stringent than their federal counterparts. For example, some cities have taken steps to phase out ozone-depleting compounds (ODCs) more quickly than the U.S. Clean Air Act requires. In addition, to the phaseout requirements under the Clean Air Act there are a number of provisions that will go into effect over the next few years that will also impact the selection of alternatives. These provisions include Section 608: National Emissions Reduction Program, Section 611: Labeling, and Section 612: Safe Alternatives Policy. These and other provisions must be considered before selecting alternatives.

- ***Compatibility with regulatory trends.*** Since new environmental policy is emphasizing pollution prevention and risk reduction, it is prudent to move to cleaner products and processes that are less polluting, less energy-intensive, and less dependent on raw materials.

- ***Public perceptions.*** Recent legislation, such as "right-to-know" laws has provided the public with more information about the chemicals used by specific plants and their associated risks.

Public information has made plants more accountable to the concerns of neighboring communities.

- *Potential of alternatives for ozone depletion and global warming.* Each alternative must be evaluated for its contribution to ozone depletion and global warming. These issues will be evaluated as part of the overall risk characterization that will be conducted by EPA under Section 612 of the Clean Air Act.

- *Energy efficiency.* As energy costs rise, it is important to consider the energy requirements of each alternative. The use of energy efficient alternatives is also desirable from a global warming perspective. Energy issues will be evaluated as part of the overall risk characterization under Section 612: Safe Alternatives Policy of the Clean Air Act.

- *Effects on emissions, effluents, and wastes generated.* Determine whether environmental problems are eliminated or merely transferred from one medium to another. Each alternative has differing effects on water, air, and land pollution. Issues such as these will be evaluated as part of the overall risk characterization that EPA will conduct as part of Section 612: Safe Alternatives Policy of the Clean Air Act.

- *VOC concerns.* In many areas, switching solvents can take you from an existing to a new/modified source, subject to repermitting and more stringent controls. Limitations on VOC emissions may influence your choice of alternative. In the U.S., for example, certain states have legislation that restricts the use of solvents that are VOCs. Some states also ban the use of substances (e.g., methylene chloride in New Jersey) because of possible toxic health effects. Application-specific exemptions and containment criteria may also exist, so VOC regulatory provisions should be researched thoroughly. The air toxics provisions of the 1990 Clean Air Act Amendments target 189 toxic air pollutants. Of these, 149 are organic compounds.

- *Toxicity and Worker Safety.* Alternatives should minimize occupational exposure. The Occupational Health Safety Administration (OSHA) has set Personal Exposure Limits (PELs) for many chemicals and should be considered before selecting alternatives. In addition, the American Conference of Governmental and Industrial Hygienists provides threshold limit values (TLVs) for different chemicals. As part of the implementation strategy for Section 612 of the Clean Air Act Amendments, EPA has also initiated discussions with NIOSH, OSHA, and other governmental and nongovernmental associations to develop a consensus process for establishing occupational exposure limits for the most significant substitute chemicals.

- *Flammability.* Fire and explosion hazards are very important considerations. In some instances changes in process will have to be brought to the attention of insurance carriers. Flammability will be evaluated as part of the overall risk characterization that will be conducted by EPA under Section 612 of the Clean Air Act.

REVIEW OF EXISTING PROGRAM

Following the recommendations presented so far for developing a non-CFC-113 and MCF cleaning program. the following sequence of activities should be performed/carried out next:

- Determine where and why CFC-113 and methyl chloroform are consumed in metal cleaning operations:
- Characterize existing cleaning processes. This activity will help you understand how metal cleaning integrates with other manufacturing processes and determine whether cleaning is necessary:
- Characterize the soils and their sources. Identify the type of soils being removed and the steps to be taken to reduce the soiling of parts;
- Characterize the substrate materials being cleaned. This step will assist in identifying the type, shape, and geometry of materials being cleaned;
- Establish criteria for selecting an alternative cleaning process. These criteria include organizational, technical. environmental, health. and safety issues that must be considered before selecting an alternative process.

The benefits resulting from these steps include a better understanding of cleaning needs, elimination and consolidation of certain cleaning operations, and development of a systematic procedure for selecting an alternative cleaning process. With this understanding, the next section describes some major alternative processes to solvent based cleaning.

ALTERNATIVE MATERIALS AND PROCESSES

A number of alternative cleaning processes and alternative solvents to CFC-113 and MCF are now available for metal cleaning operations. The choice of an alternative depends on cleaning needs and process selection factors.

Alternative Cleaning Processes:

- Aqueous
- Semi-Aqueous

Alternative Solvents:

- Hydrochlorofluorocarbons
- Aliphatic Hydrocarbons
- N-Methyl-2-Pyrrolidone
- Miscellaneous Solvents

The following sections describe the major advantages, disadvantages, and key process issues of several alternatives.

Provision of this material in no way constitutes EPA or ICOLP recommendation or approval of any company or specific offering. These technologies should be evaluated on a case-by-case basis. A list of vendors and references at the end of this manual may be a useful additional source of information.

AQUEOUS CLEANING

Aqueous cleaners use water as the primary solvent. Synthetic detergents and surfactants are combined with special additives such as builders, pH buffers, inhibitors, saponifiers, emulsifiers, deflocculants, complexing agents, antifoaming agents, and other materials. These agents provide multiple degrees of freedom in formulation, blending, and concentration, and provide useful synergistic effects. Exhibit 6 presents an overview of the advantages and disadvantages of aqueous cleaning.

The key stages of an aqueous cleaning process are (see Exhibit 7):

- Washing
- Rinsing
- Drying
- Wastewater Treatment and Disposal

Although each of these steps is an important and integral part of the aqueous cleaning process, rinsing and drying may not be necessary in all circumstances and wastewater disposal may be completely integrated into other steps through the use of recycled baths.

Process Design and Implementation

To implement an aqueous cleaning process, conduct an overall evaluation of the following:

- The cleaner's effectiveness (i.e., whether it has good cleaning chemistry for your needs);
- The process equipment (i.e., mechanical considerations);
- Other process characteristics (e.g., wetting agents).

Process Chemistry

Aqueous cleaners are comprised basically of three major types of components: (1) the builders which make up the largest portion of the cleaner, (2) the organic and inorganic additives which promote better cleaning or affect a metal's surface, and (3) the surfactants and wetting agents.

As we noted earlier, being able to tailor the cleaner formulation gives aqueous cleaning great flexibility. Molecular structure, which has significant effects on the properties, can be varied over a wide range. For example, the number of carbons on the molecule (whether straight chain, branched chain, or ring structure) and the ratio of the hydrophilic to hydrophobic moiety can be tailored to achieve the desired cleaning requirements.

Builders are the alkaline salts in aqueous cleaners. They are usually a blend selected from the following groups: alkali metal orthophosphates and condensed phosphates, alkali metal hydroxides, silicates, carbonates, bicarbonates, and borates. A blend of two or more of these builders is typically used in aqueous cleaners.

Phosphates are the best overall builders. However discharge of cleaning solutions containing phosphates is subject to environmental regulations. Chelating agents such as ethylenediamine tetra acetic acid (EDTA) and nitrates can be used instead of phosphates. Silicates are sometimes difficult to rinse and may cause trouble in subsequent plating operations if not completely removed. Carbonates and hydroxides are cheap sources of alkalinity and are also effective builders.

Additives are either organic or inorganic compounds that provide additional cleaning or surface modifications. Chemical compounds such as glycols, glycol ethers, chelating agents, and polyvalent metal salts, could be considered additives. Some of these materials could be subject to VOC concerns.

Exhibit 6

AQUEOUS CLEANING

ADVANTAGES

Aqueous cleaning has several advantages over organic solvent cleaning.

Safety -- Aqueous systems have few problems with worker safety compared to many solvents. They are not flammable or explosive. Consult material safety data sheets for information on health and safety.

- Cleaning -- Aqueous systems can be designed to clean particles and films better than solvents.
- Multiple Degrees-of-Freedom -- Aqueous systems have multiple degrees-of-freedom in process design, formulation and concentration. This freedom helps aqueous cleaning provide superior cleaning for a wider variety of contamination.
- Removal of Inorganic or Polar Soils -- Aqueous cleaning is particularly good for cleaning inorganic or polar materials. Many machine shops are using or converting to water-based lubricants and coolants versus oil-based for environmental and other reasons. These are ideally suited to aqueous cleaning processes.
- Oil and Grease Removal -- Organic films, oils, and greases can be effectively removed by aqueous chemistry.
- Multiple Cleaning Mechanism -- Aqueous cleaning functions by several mechanisms rather than just solvency. These include saponification (chemical reaction), displacement, emulsification, dispersion, and others. Particles are effectively removed by surface activity coupled with the application of energy.
- Ultrasonics Applicability -- Ultrasonics are much more effective in water-based solvents than in CFC-113 or MCF solvents.
- Chemical Cost -- Aqueous cleaning solutions are generally less expensive than solvents.

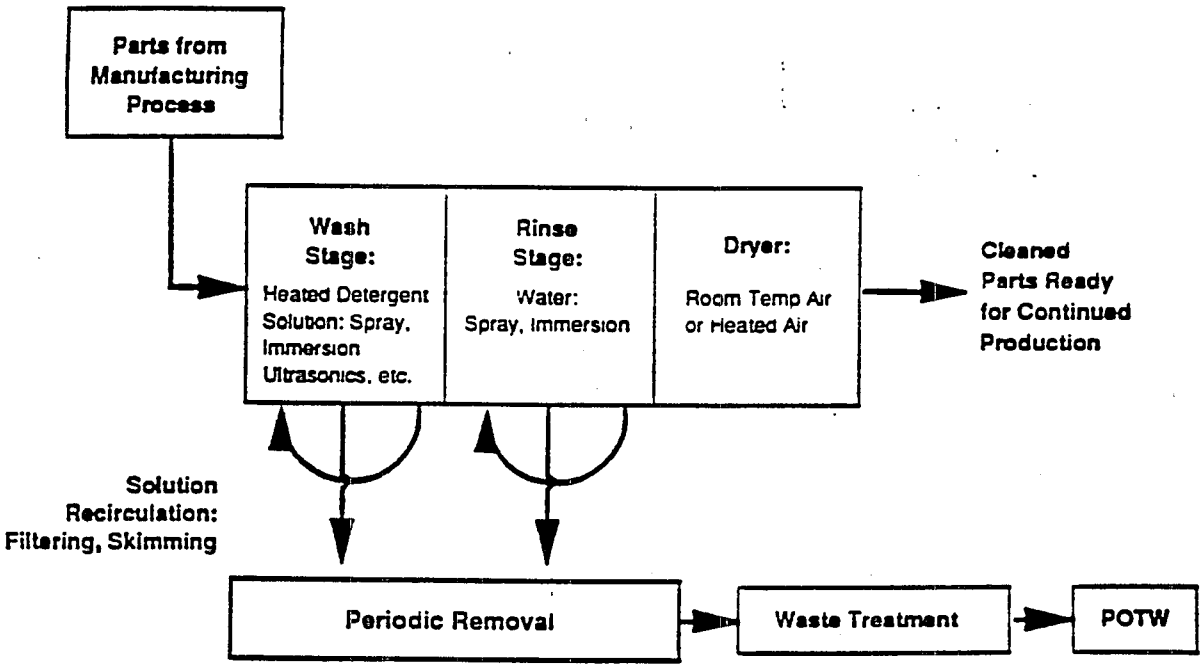
DISADVANTAGES

Depending upon the specific cleaning application there are also disadvantages.

- Cleaning Difficulty -- Parts with blind holes and small crevices may be difficult to clean, and will require process optimization.
- Process Control -- Solvent cleaning is a very forgiving process. To be effective, aqueous processes require careful engineering and control.
- Rinsing -- Some aqueous cleaner residues can be difficult to rinse. Some surfactants are especially difficult to rinse. Trace residues may be detrimental for some applications and materials. Special caution should be taken for parts requiring subsequent vacuum deposition, liquid oxygen contact, etc. Rinsing can be improved using DI water or alcohol rinse.
- Drying -- It may be difficult to dry certain part geometries with crevices and blind holes. A piece of drying equipment is often required.
- Floor Space -- In some instances aqueous cleaning equipment may require more floor space.
- Material Compatibility -- Corrosion of metals or delayed environmental stress cracking of certain polymers may occur.
- Water -- In some applications high purity water is needed. Depending on purity and volume high purity water can be expensive.
- Energy Consumption -- Energy consumption may be higher than solvent cleaning in applications that require heated rinse and drying stages.
- Wastewater Disposal -- In some instances use of aqueous cleaning may require wastewater treatment prior to discharge.

Exhibit 7

CONFIGURATION OF AQUEOUS CLEANING PROCESS IN THE METAL CLEANING INDUSTRY



Source: EPA 1989a

Surfactants are organic compounds that provide detergency, emulsification, and wetting in alkaline cleaners. Surfactants are unique because of their characteristic chemical structure. They have two distinct structural components attached together as a single molecule. A hydrophobic half has little attraction for the solvent (water) and is insoluble. The other half is hydrophilic and is polar, having a strong attraction for the solvent (water) which carries the molecule into solution. Their unique chemical structure provides high affinity for surface adsorption. Surfactants are classified as anionic, cationic, nonionic, and zwitterionic (amphoteric). Surfactants most useful in metal cleaning are anionic and nonionic.

In spray wash alkaline cleaning virtually zero foam can be tolerated, therefore, surfactants must be selected that do not foam under the selected process conditions.

Nonionic surfactant is generally the only type that results in minimum foaming and provides good detergency. For immersion cleaning all types of surfactants can be used; however, in most cases the anionic or nonionic type are used.

Process Equipment

Aqueous cleaning equipment can be characterized as:

- In-line equipment for high throughput cleaning requirements;
- Batch equipment for low throughput, such as maintenance applications or small production processes.

The in-line and batch equipment can be further subdivided into immersion, spray, and ultrasonic equipment. Exhibit 8 presents an overview of the advantages and disadvantages of these three types of equipment.

Immersion equipment cleans the parts by immersing them in a solution and using some form of agitation to add the energy needed to displace and float away contaminants. Soil is removed from the metal surface by convection currents in the solution, the currents are created by heating coils or by some mechanical action.

Spray equipment cleans parts with a solution sprayed at medium-to-high pressure. Spray pressure can vary from as low as 2 psi to 400 psi or more. In general, the higher the spray pressure, the more mechanical help is provided in removing soil from metal surfaces. Spray cleaners are prepared with low foaming detergents which are not as chemically effective as those used in immersion cleaners, but are still effective because of the mechanical agitation.

Although spray cleaning is effective on most parts, certain configurations such as the interior of an automobile tail pipe have soiled areas that are inaccessible to the sprayed cleaning solution. In these instances, immersion cleaners are more effective.

A high pressure spray is an effective final rinse step. Pressures may range from 100 psi in less critical applications to 500 psi or even 2000 psi in critical applications. Optimization of nozzle design such as spray pattern, drop size and formation, pressure/velocity, and volume are very important and have a major impact on effectiveness. A final spray is much cleaner than an immersion bath, since the final water touching the part can be highly pure and filtered.

Ultrasonics equipment works well with water-based processes. Because the cavitation efficiency is high, the removal of particles from surfaces is usually more effective in aqueous versus organic solvent media. Ultrasonic cavitation efficiency is typically less effective in CFCs and MCF than with water-based chemistry. Process design requires caution to insure that cavitation erosion of part surfaces is not a problem. Certain part geometries are also ultrasonic sensitive.

It is important to optimize your system's capabilities when using ultrasonic systems. Since good ultrasonic cleaners have few standing waves, reflection from the surface and the walls is an important consideration. The number of parts and their orientation is very important for good cleaning. The fixturing should be low mass, low surface energy, and nonabsorbing cavitation resistant material such as a stainless steel wire frame. Avoid using plastics for fixtures because of

Exhibit 8

AQUEOUS CLEANING PROCESS EQUIPMENT

IMMERSION WITH ULTRASONIC AGITATION	IMMERSION WITH MECHANICAL AGITATION	SPRAY WASHER
ADVANTAGES		
Highest level of cleaning; cleans complex parts/ configurations	Usable with parts on trays	High level of cleanliness
Can be automated	Will flush out chips	Inexpensive
Usable with parts on trays	Simple to operate	Will flush out chips
Low maintenance	Cleans complex parts and configurations	Simple to operate
	Can use existing vapor degreasing equipment with some simple engineering changes.	High volume
		Portable
		Short lead time
DISADVANTAGES		
Highest cost	Requires rinse water for some applications	Requires rinse water for some applications to prevent film residues
Requires rinse water for some applications	Harder to automate	Not effective in cleaning complex parts
Requires new basket design	Requires proper part orientation and/or changes while in solution	May require separate dryer
Long lead time	May require separate dryer	
Can't handle heavy oils		
Limits part size and tank volumes		
May require separate dryer		

leaching and absorption of sonic energy. It is also important to optimize the size of the load to the size of the tank. Both ultrasonic and spray equipment can be used to great advantage, especially in rinsing. There are benefits for both immersion ultrasonics and spray using high-purity water. Low pressure (40-80 psi) at relatively high volumes is good for initial rinsing. It is critical to keep the part wet at all times prior to final drying. The spray design should be able to reach all part surfaces by mechanically manipulating the part or the spray nozzles. A secondary immersion-ultrasonic rinse is especially useful for parts with complex geometry or holes.

In some instances final rinsing with DI water or an alcohol, such as isopropanol, can remove residues and prevent water spots.

Other Process Considerations

Product design can have a significant influence on cleanability. The choice of materials and part configuration should be reviewed for opportunities to make changes that have a major influence on the success of water-based cleaning.

Care should be taken to prevent cleaning fluids from being trapped in holes and capillary spaces. Low surface tension cleaners sometimes penetrate spaces and are not easily displaced by a higher surface tension, pure water rinse. Penetration into small spaces is a function of both surface tension and capillary forces.

Water-based cleaning is sometimes not as forgiving as CFC-113 and MCF cleaning. Good engineering and process control are more critical in preventing problems. Useful parameters for process control include bath temperatures, pH, agitation, rinse water quality, and cleaning bath quality. Part inspection by a method such as contact angle, turbidity, or ASTM F24 can be very useful. Valuable bath and water quality measurements could include conductivity/resistivity, particle count, turbidity, and TOC (total organic carbon).

Drying presents the major challenge when switching to aqueous cleaning. For simple parts, this obstacle may be minimal, but for complex parts drying may require considerable engineering and experimentation. Solvent equipment that is currently in use has no real provision for drying; the thermodynamics of CFC-113 and MCF are favorable to spontaneous evaporation.

Aqueous cleaning requires careful consideration of drying materials. Evaporative removal of bulk water is usually not practical from the perspective of energy use or process time. Compact turbine blowers with filtered outputs can mechanically remove 90 percent or more of the water. Design options in blowers include variation of pressure, velocity, and volume flow. Other sources of air include dedicated compressors or plant air; great care must be taken to assure desired air quality by appropriate filtration of oil, particles, and moisture. When using such options, economics and noise reduction are other considerations. Humidity and air conditioning control, and the associated economics, may be an issue for the equipment and the plant.

Evaporative drying following mechanical water removal can be accomplished using infrared heating, clean dry air-heated or at ambient temperature, or vacuum heated drying. Dryers can be designed for either in-line or batch operations. Drying design should always be confirmed by experimentation.

Wastewater treatment and recycling is an important consideration. Some detergents and surfactants are biodegradable, while others are not. In many applications the cleaning bath is changed infrequently and a relatively low volume of wastewater is discharged. In others, the water can be evaporated to leave only a small volume of concentrated waste for recycling.

Recycling or regeneration of the cleaner/detergent solution is feasible and should be considered. This can be accomplished using a combination of oil skimming techniques, coalescing separators, and ultrafiltration (ceramic membranes).

Details on wastewater treatment and recycling are presented later in this manual.

SEMI-AQUEOUS CLEANING

Hydrocarbon/surfactant cleaners are emulsion cleaners that can be substitutes for CFC-113 and MCF in metal cleaning applications. Hydrocarbon/surfactants have been included in many different cleaners formulated for different purposes. Hydrocarbon/surfactants are used in cleaning processes in two ways. They are either emulsified in water solutions and applied in a manner similar to standard aqueous cleaners or they are applied in concentrated form and then rinsed with water. Because both methods use water in the cleaning process, the hydrocarbon/ surfactant based process is commonly known as a semi-aqueous process (see Exhibit 9).

Advantages

The advantages of semi-aqueous cleaning solutions include the following:

- Good cleaning ability especially for heavy grease, tar, waxes, and hard to remove soils;
- Compatible with most metals and plastics;
- Suppressed vapor pressure (especially if used in emulsified form);
- Non-alkalinity of process prevents etching of metals thus helping to keep metals out of the waste streams;
- Reduced evaporative loss;
- Potential decrease in solvent purchase cost;
- A rust inhibitor can be included in the formulation to protect parts from rusting.

Disadvantages

The disadvantages include:

- Rinsability problems, because residues can be left;
- Recycling or disposal cost of wastewater could make the process less economically viable;
- Flammability concerns if a concentrated cleaner is used in spray cleaners. However, the flammability issue can be solved with proper equipment design;
- Some cleaners have objectionable odors;
- Some of the cleaners are VOCs;
- Drying equipment may be required in some applications; and
- Some cleaners can auto-oxidize. For example, d-limonene (a type of terpene) can auto-oxidize from contact with air. This can be reduced using an antioxidant additive.

Cleaning Process

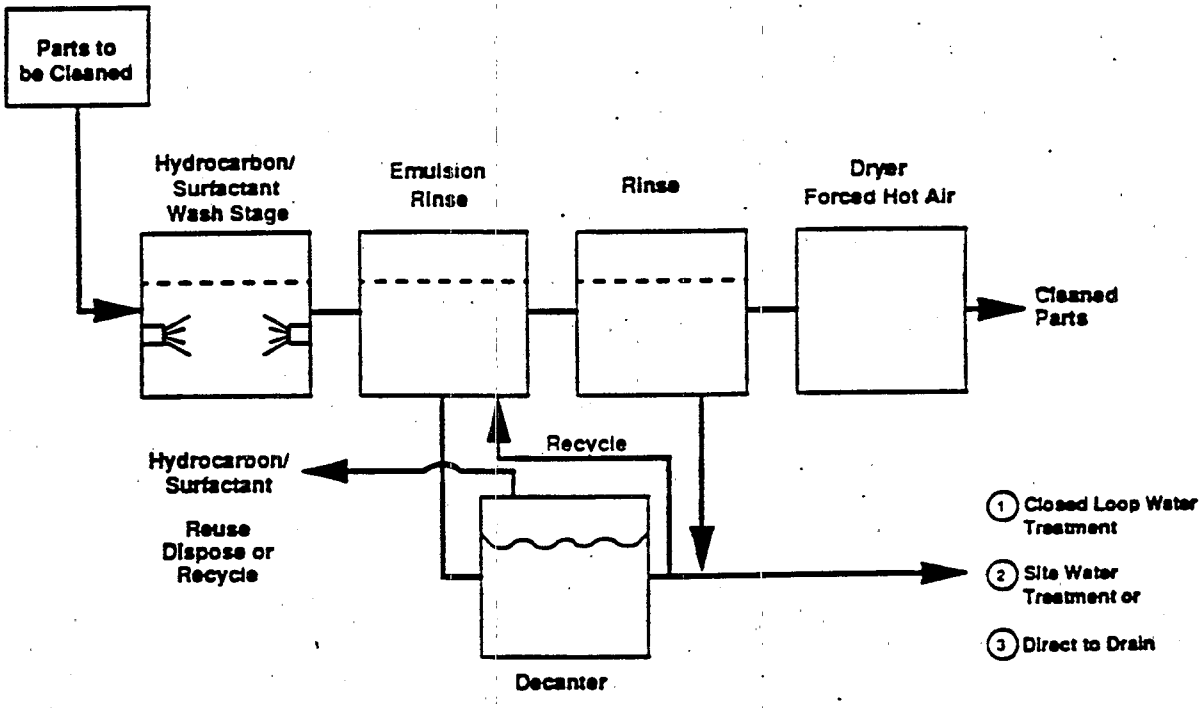
The steps in a typical semi-aqueous cleaning process are analogous to aqueous applications. Equipment for use with semi-aqueous processes is also similar to aqueous cleaning equipment designs.

The four major steps used in the cleaning process are:

- Wash step with a hydrocarbon/ surfactant;
- Rinse step with water;
- Drying process to remove excess water;
- Wastewater disposal.

Exhibit 9

SEMI-AQUEOUS PROCESS FOR IMMISCIBLE HYDROCARBON SOLVENT



In cases where extreme cleanliness is required, the hydrocarbon/surfactant cleaning can be followed by a fully aqueous wash step with an alkaline detergent and a deionized water rinse. As in aqueous cleaning, it is important to note that both the wash and the rinse stage are recirculating; these solutions are not continuously discharged.

In the wash step, the hydrocarbon/surfactant cleaner is applied to the part being cleaned with some form of mechanical energy. Low flash point hydrocarbon/surfactant cleaners are generally not heated; however, some are slightly warmed when the cleaner is used in a diluted form. High flash point hydrocarbon/surfactant cleaners may be heated to within 20-30°F of their flash point to remove difficult soils. Cleaners that are ignitable should not be used in vapor or spray cleaning without an inert atmosphere or other protective equipment. Application methods that avoid misting such as spray-under immersion, spin-under immersion, or ultrasonics should be used. Dilute hydrocarbon emulsion cleaners formulated with water may be heated. Less mechanical energy is needed when using a hydrocarbon/surfactant solution than when using an aqueous solution because of the high solvency of hydrocarbon/ surfactant cleaners.

A rinse with clean water removes the residues left by the wash step. The rinse step is necessary when concentrated hydrocarbon/ surfactant cleaners are used because of their low volatility (which prevent them from evaporating from the parts cleaned in the wash stage). The rinse step may not be necessary when a dilute hydrocarbon/surfactant emulsion is used, if the level of cleanliness needed does not require removal of the residue from the wash stage. In some instances, alcohol is used as a final rinse step. The rinse step may also serve as a finishing process and in some instances is used to apply rust inhibitors to the parts.

The drying step serves the same function as it does in aqueous cleaning. The removal of remaining water from the part prepares it for further processing or prevents it from rusting. Heated or high velocity room temperature air are the principal drying agents. As in aqueous cleaning, the drying step may not be needed if the parts are rust inhibited, are not immediately needed, and/or are moved immediately to another wet process.

The wastewater disposal step is always an important part of the cleaning process. As in aqueous cleaning most of the contaminants in the wastewater are removed by decanters and filters as the solution is recirculated in the tank.

Some available hydrocarbon/surfactant cleaners can be easily separated from the rinse water. This allows the rinse water to be recycled or reused. The waste hydrocarbon/surfactant can then be burned as fuel. In such cases, contaminants, like oil and grease, removed from the part being cleaned are retained in the hydrocarbon/surfactant phase, thereby greatly reducing the contamination loading in the water effluent.

Process Equipment

Equipment for use specifically with concentrated hydrocarbon/surfactants is available. As with aqueous cleaning, this equipment can be classified as immersion or spray equipment, either batch or in-line equipment.

Immersion equipment is the simplest design used in hydrocarbon/surfactant-based cleaning. The immersion equipment works with but is not limited to the dilute emulsion solutions which do not present the combustion (flammability) danger of the concentrated hydrocarbon/ surfactants. These pieces of equipment may operate in batch or in-line configuration. Certain solvent vapor degreasers can be retrofitted to allow immersing of the parts into the bath of emulsion cleaner. The parts are simply dipped into the bath which may or may not be heated. Because of the solvency of the hydrocarbon/ surfactants, little mechanical energy needs to be added to achieve adequate cleanliness. Higher cleanliness can be achieved by adding agitation to the process, either mechanically or with ultrasonics, or by heating the cleaning solution.

As with aqueous cleaning, a mechanical spray improves the cleaning performance of the solution. When using concentrated hydrocarbon/ surfactants, the atomized solution is prone to combustion and special care must be taken to prevent it. Nitrogen blanketing displaces oxygen from the spray chamber which is enclosed to prevent sparks from entering.

When using concentrated hydrocarbon/surfactant in immersion equipment, "spray-under immersion" can be performed. In this equipment, high pressure spray nozzles are placed below the surface of the liquid. This prevents the formation of atomized solution and decreases flammability. Mechanical agitation, workpiece movement, and at properly designed ultrasonic agitation may also be used.

HYDROCHLOROFLUORO-CARBONS

Several HCFCs (e.g., HCFC-225ca, HCFC-225cb, HCFC-141b, and HCFC-123) have been proposed as possible CFC-113 and MCF substitutes. Exhibit 10 presents physical properties of these chemicals.

There are several issues to keep in mind as you make your decision:

- HCFCs have an ozone-depleting potential (ODP); while the ODP is significantly lower than CFC-113, HCFCs are subject to production control requirements imposed by the Clean Air Act Amendments of 1990, and are targeted for phaseout by 2030.
- HCFCs are also subject to Section 608: National Emissions Reduction Program that will set Lowest Achievable Emission Levels (LAEL) for HCFCs, Section 611: Labeling that will require labeling of all products manufactured with or containing HCFCs, and Section 612: Safe Alternatives Policy that will conduct overall risk characterization and set occupational exposure limits for the use of HCFCs.
- Some HCFCs are currently available only in limited quantities for customer evaluation; commercial production is expected soon.
- These solvents have good cleaning performance.

Blends of different HCFCs are also possible. Several companies have now developed constant boiling blends of HCFC-123 and HCFC-141b. These solvent blends are an acceptable alternative to CFC-113 and MCF for removing heavy grease and water-soluble oil residues. They are equivalent to CFC-113 and MCF for removing light oils, but far less effective for buffing compounds.

If you choose blends as an alternative to CFC-113 and MCF, it is important to consider possible process design changes. For example, conventional degreasers require modification to extend freeboards and lower condenser temperatures. In addition, provisions such as superheated-vapor drying or increased dwell times in freeboard are desirable to reduce dragout losses and can be incorporated into the design.

The high volatility of HCFC cleaning solutions require special equipment design criteria. In addition, the economic use of HCFCs may require special emission control features for vapor degreasers (see Exhibit 11a, b, and c). These include:

- Automated work transport facilities;
- Hoods and/or automated covers on top entry machines;
- Facilities for work handling that minimize solvent entrapment;
- Facilities for superheated vapor drying;
- Freeboard deepened to width ratios of 1.0 to 2.0;
- Main condenser operating at 45° to 55°F;
- Secondary condenser operating at -30° to -20°F;
- Dehumidification condenser operating at -30 to -20°F (optional);
- Seals and gaskets of chemically compatible materials;
- Stainless steel construction;
- Welded piping containing a minimum of flanged joints;
- A gasketed water separator or refrigerated desiccant dryer for methanol blends;
- A cool room to work in is recommended;

- Controlled exhaust from refrigeration unit to prevent excessive heat from reaching the separator chambers.

Material compatibility is another important consideration. The HCFC-123/HCFC-141b blends require compatibility testing with magnesium, zinc and other metals. In addition, the solvent blends have shown some adverse effects with plastics such as ABS, acrylic, and Hi-Impact Styrene. Like metals, plastics need to be tested on an individual basis.

Exhibit 10

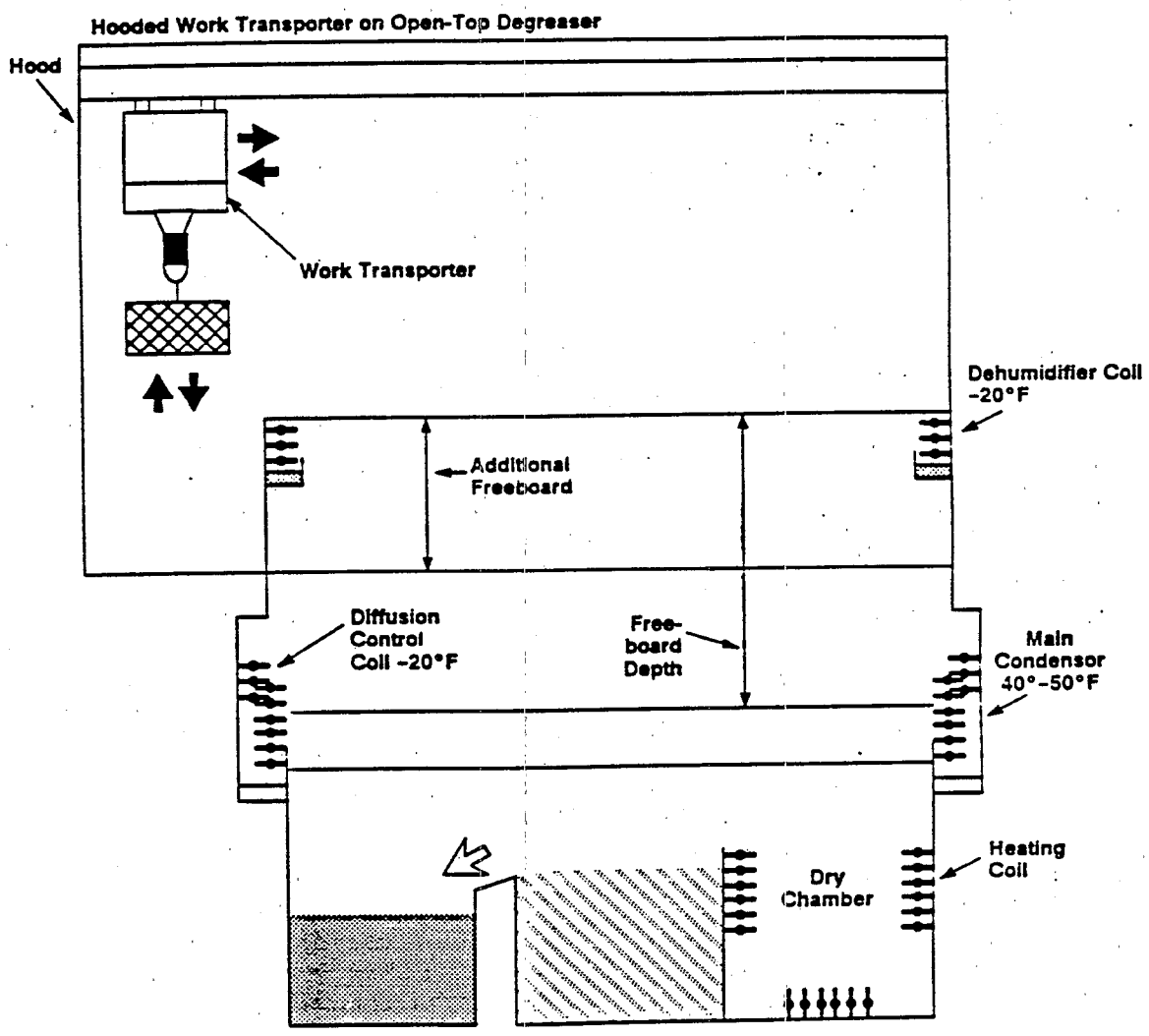
PHYSICAL PROPERTIES OF HCFCs AND OTHER SOLVENT BLENDS

	CFC-113	MCF	HCFC-225ca	HCFC-225cb	HCFC-141b/[1] HCFC-123/ Methanol
Chemical Formula	CCl_2FCClF_2	CH_3CCl_3	$CF_3CF_2CHCl_2$	$CClF_2CF_2CHClF$	CH_3CFCl_2/ CF_3CCl_2H/ CH_3OH
Ozone Depleting Potential	0.8	0.1	~0.05	~0 05	0.08-0.13
Boiling Point (°C)	47.6	73.9	51.1	56.1	29.8
Viscosity (cps) @ 25°C	0.68	0.79	0.59	0.61	0.47
Surface Tension (dyne/cm)	17.3	25.56	16.3	17.7	18.3
Kauri-Butanol Value	31	124	34	30	76
Flash Point °C	None	None	None	None	None
Toxicity	Low	Low	Underway	Underway	Near Completion

[1] Several other HCFC-141b/HCFC-123 blends exist. Chemical manufacturers recommend a blend of HCFC-141b/HCFC-123 (80 wt.%/20 wt.%) for straight oils and an azeotrope of HCFC-141b/HCFC-123/methanol for semi-synthetic and synthetic oils.

Exhibit 11a

ADVANCED DESIGN DEGREASER FOR USE WITH LOW BOILING POINT SOLVENTS

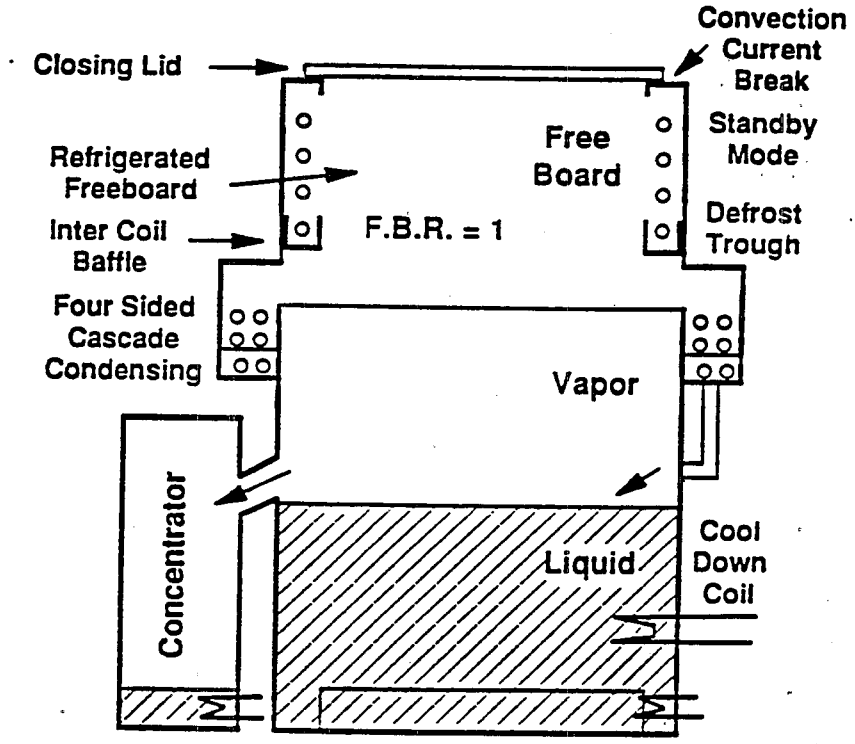


Source: DuPont

S16060-4

Exhibit 11b

STACKED LOW EMISSION DEGREASER WITH SOLVENT SAVING FEATURES



Solvent Saving Features
(not shown)

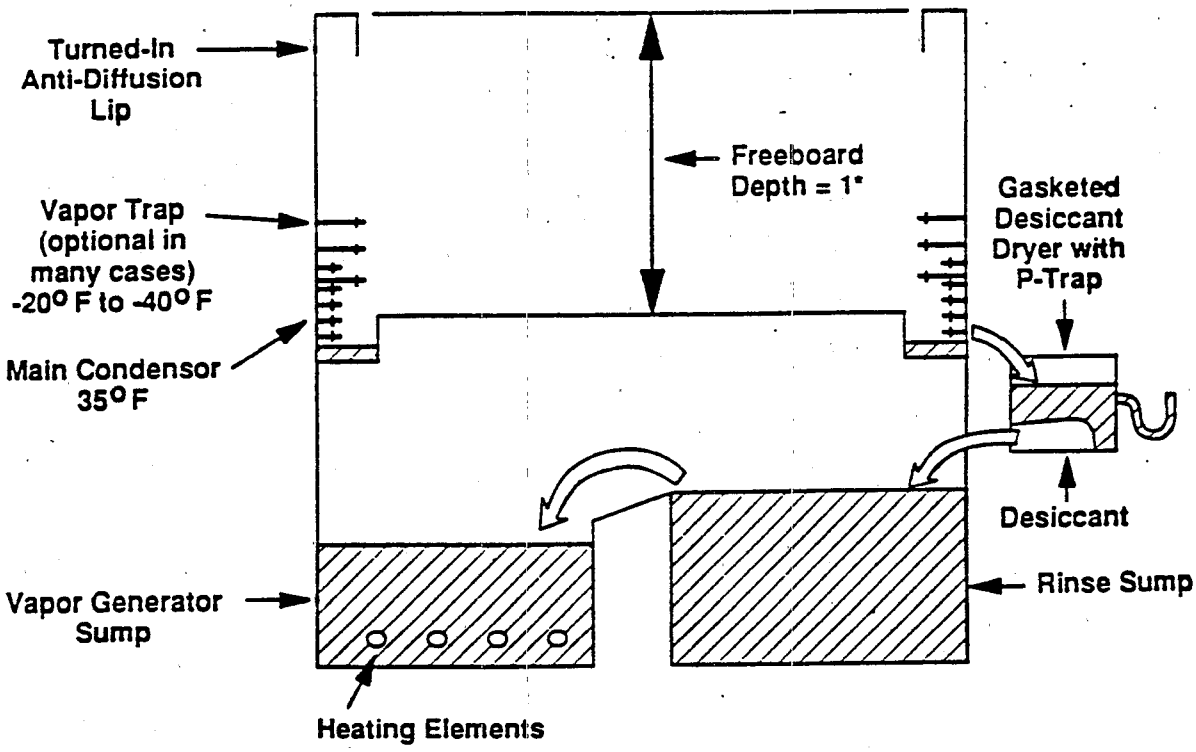
- Screwed pipe joints
- Correct sealing material
- Correct pump seals
- Minimum number of pipe joints
- Degreaser enclosure
- Mechanical handling with optional rotation
- Correct size basket

Source: ICI

115131-2

Exhibit 11c

ADVANCED DESIGN DEGREASER FOR USE WITH LOW BOILING POINT SOLVENTS



*Machine Width = w; w = 1 indicates 100% Freeboard

Source: Allied-Signal

I15131-3

N-METHYL-2-PYRROLIDONE

N-Methyl-2-Pyrrolidone, also referred to as M-Pyrol® or NMP is miscible with water and most other organic solvents including esters, ethers, alcohols, ketones, aromatic and chlorinated hydrocarbons, and vegetable oils. It has powerful solvent properties as evidenced by its physio-chemical properties. These properties include a solubility parameter of 11.0, high purity, high flash point, and low volatility.

Testing of NMP for specific cleaning applications is underway. Initial results indicate that NMP is effective in ultrasonics applications and cavitates at both room temperature and elevated temperatures in its 100 percent active form. Metal substrates that have been successfully tested with NMP include carbon steels, stainless steel 304, 316, 317, Carpenter 20CB3 Admiralty brass, Cupro-Nickel and ferralium. Several polymeric materials such as Epoxy-Urethane are sensitive to NMP. Exhibit 13 summarizes the solvent's principal properties. Exhibit 12 shows two typical process equipment designs that have been used successfully for both batch and in-line operations.

Exhibit 12

SUMMARY OF PROPERTIES OF N-METHYL-2-PYRROLIDONE

Empirical Formula	C_5H_9NO
Molecular Weight	99.1
Freezing Point	-24.4°C (-11.9°F)
Boiling Point	202°C (395°F) @ 760 mm
Vapor Pressure (20°C)	0.29 mm
Viscosity (25°C)	1.65 cp
Specific Gravity	1.027
Interfacial Surface Tension (25°C)	40.7 dynes/cm
Flash Point (open cup)	95°C (204°F)
(closed cup)	93°C (199°F)
Explosive limits	0.058 grams/filter - lower limit
	2.18% vapor in air - 360°F (182°C)
	0.323 grams/liter - upper limit
	12.24% vapors in air - 370°F (188°C)
Heat of Combustion	719 K cal/mol
Specific Heat	0.40 K cal/kg at 20°C
Heat of Vaporization	127.3 K cal/kg (230 BTU/lb)
Miscibility with Other Solvents	Completely miscible with water and most organic solvents including alcohols, ethers, ketones, aromatic and chlorinated hydrocarbons and vegetable oils.

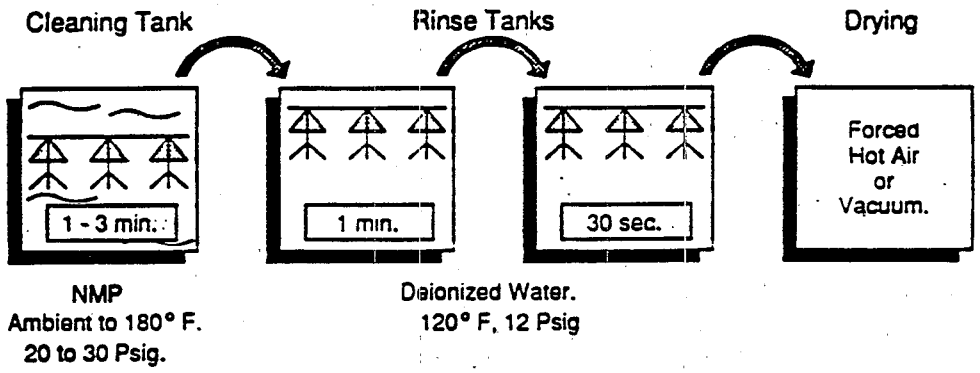
Source: GAF Chemical

Exhibit 13

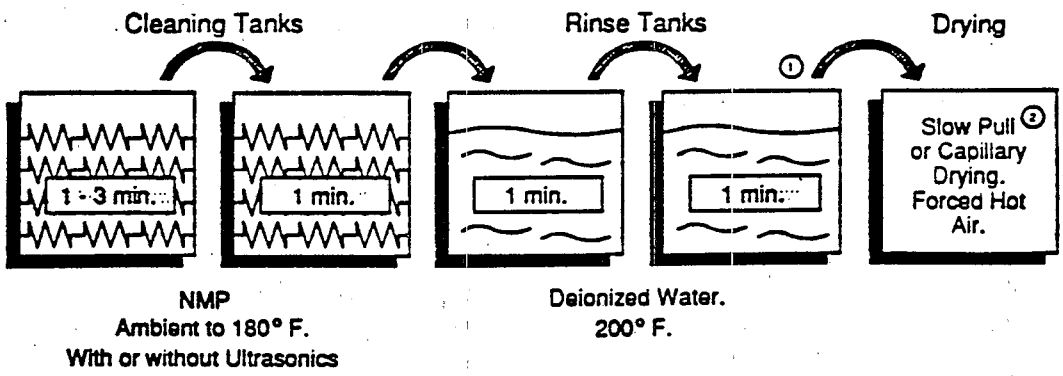
NMP CLEANING PROCESSES

SPRAY WASH CLEANING

(Spray under immersion recommended.)



IMMERSION TANK CLEANING



① May be spray rinsed.

② Slow incremental removal from DI water. Effective on flat surfaces.

Source: GAF Chemicals Corporation

115131-4

ALIPHATIC HYDROCARBONS

There is a wide range of aliphatic hydrocarbon solvents that can be used in metal cleaning (see Exhibit 14). Petroleum fractions, commonly known as mineral spirits or kerosene, are used extensively in maintenance cleaning (e.g., auto repair). These operations are single stage, open top processes using ambient air drying. In most cases such processes are not suitable for original equipment manufacturing cleaning. Synthetic aliphatic hydrocarbons, which offer closer control of composition, odor, boiling range, evaporation rate, etc., are employed in OEM cleaning processes and will be discussed below.

The advantages of aliphatic hydrocarbon cleaners include:

- Good cleaning ability for a wide variety of soils, especially heavy grease, tar, waxes and hard to remove soils. Low surface tension allows good penetration.
- Compatible (non-corrosive) with most rubbers, plastics and metals.
- They employ no water, hence can clean water sensitive parts.
- Low odor and low toxicity grades available.
- Reduced evaporative loss.
- No wastewater stream.
- Recyclable by distillation. High stability and recovery.

The disadvantages include:

- Flammability concerns. However, these concerns can be mitigated with proper equipment design.
- Slower drying times than halogenated solvents.
- VOC control may be required. However, equipment, such as carbon adsorption and condensers, exist to recover solvent from effluent air.
- Some grades have low Occupational Exposure Limits.

The steps in a typical hydrocarbon cleaning process are analogous to aqueous or semi-aqueous processes. Equipment designs for use with hydrocarbons are modified aqueous equipment designs.

The major steps in the cleaning process are typically:

- Wash steps (1 to 3 stages depending on degree of cleaning needed) with a hydrocarbon cleaner;
- Drying step, using forced air;
- VOC recovery from solvent laden air, if required; and
- Waste solvent recovery or disposal.

The wash steps involve liquid-phase cleaning at temperatures sufficiently below the flash point of the fluid. Ultrasonics or other agitation processes such as immersion spraying, parts rotation or fluid pumparound can be used to augment cleaning action. Spraying or misting processes, where fine droplets are formed, should be employed only in an inert environment or with equipment with other protection against ignition conditions. This protection is required because fine droplets can ignite at temperatures below bulk fluid flash point.

Fluids with flash points near 40°C (104°F) should be operated in unheated equipment, at ambient temperatures. For higher flash points, hot cleaning can be employed to boost cleaning action. For systems with good temperature control (independent temperature sensors, cutouts, level indicators, etc.), a safety margin of 15°C (27°F) between the fluid flash point and the cleaning temperature is recommended. For systems with poorer temperature control, a larger margin should be employed.

Each wash step should be followed by a drain period, preferably with parts rotation, to minimize solvent dragout from stage to stage.

In multistage processes, fluid from one bath is periodically transferred to the preceding bath as its

soil level builds up. Fresh solvent is added only to the final bath to ensure the highest cleanliness of parts, and spent solvent is removed only from the first stage.

The drying step normally uses forced air, which may be heated. Either the dryer should operate at 15°C below the flash point of the fluid, or sufficient air flow should be provided so that the effluent air composition is well below the Lower Explosive Limit of the system.

The VOC recovery step is an important part of the cleaning process. Depending on the solvent chosen, either carbon adsorption or condensation are the best technologies for recovering solvent vapors from spent drying air and lip vent air. Numerous vendors market this type of recovery equipment.

In the waste recovery area, the best reclamation technology for these products is usually filtration and distillation. One of the advantages of the low olefin content and narrow distillation range is that the recovery in distillation is high. Should some disposal of residual solvent be necessary, fuel substitution or incineration are good routes.

Exhibit 14

PROPERTIES OF ALIPHATIC SOLVENTS

PRODUCT	Lb./Gal. 60°F	Sp. Gr. 60°/60°F	Boiling Range °F	Fl. Pt. °F TCC	KB	Evap. Rate[1]
Mineral Spirits	6.37	0.764	305-395	105	32	0.1
Odorless Mineral Spirits	6.33	0.760	350-395	128	27	0.1
140 Solvent	6.54	0.786	360-410	140	30	0.1
C10/C11 Isoparaffin	6.25	0.750	320-340	107	29	0.3
C13 N-Paraffin	6.35	0.760	320-340	200	22	0.1
C10 Cycloparaffin	6.75	0.810	330-360	105	54	0.2
Kerosene	6.60	0.790	330-495	130	30	-

1 n-Butyl Acetate=1

Note:

KB = Kauri Butanol Value
Fl. Pt. = Flash Point

MISCELLANEOUS SOLVENTS

The metal finishing industry has used a wide range of solvents for cleaning. Some of the solvents, commonly used, include:

- Ketones;
- Alcohols;
- Glycol Ethers;
- Esters; and
- Other chlorinated solvents.

The ketones form a group of very powerful solvents (see Exhibit 15a). In particular, acetone (dimethyl ketone) and ethyl methyl ketone are good solvents for polymers and adhesives. In addition, acetone is an efficient dewatering agent. However, their flammability (note that acetone has a flash point of 0°F) and incompatibility with many structural polymers (e.g., stress cracking of polyether sulphone, polyether ketone, and polycarbonate) means that they should only be used with care and in small quantities.

Alcohols such as ethanol, isopropanol, and several glycol ethers are used for a number of applications. These solvents are chosen for their high polarity and for their effective solvent power. The alcohols have a range of flash points and care must be exercised while using the lower flash point alcohols (see Exhibit 15b). Solvents in this family, particularly certain glycol ethers, can cause swelling, cracking, and structural degradation of polymeric and elastomeric materials.

Esters, such as dibasic esters and aliphatic mono esters, have good solvent properties. They offer good cleaning for a variety of grimes and soils. Most of these materials are readily soluble in alcohols, ketones, ethers, and hydrocarbons, but are only slightly soluble in water. Dibasic esters have high flash point and low vapor pressure. They are only slightly soluble in high paraffinic hydrocarbons. Dibasic esters are so low in vapor pressure that a residual film will remain on a surface after application. Aliphatic esters, generally acetates, range in formula from ethyl acetate to tridecyl acetate. The higher grades (hexyl acetate and heavier) are commonly used in degreasing. They fall into the combustible or non-combustible flash point range. They have acceptable compatibility with most polymers. These esters can be dried from a surface by forced air drying with no residual film.

Other chlorinated solvents such as trichloroethylene, perchloroethylene, and methylene chloride also are effective cleaners. However, trichloroethylene and perchloroethylene have been shown to exhibit photochemical reactivity and are regulated as smog precursors. These substances also have been shown to be carcinogenic to animals, and care should be taken in their use. Chlorinated solvents are subject to hazardous waste regulations under the Resource Conservation and Recovery Act (RCRA). Users of these solvents must be aware of and comply with all federal, state, and local regulations governing use, storage, and disposal of these materials. In addition to being classified as hazardous waste, these solvents are subject to reporting requirements under the Superfund Amendments and Reauthorization Act (SARA) Title III. Occupational exposure standards have also been set for the use of these solvents and must be considered when selecting these alternatives. Chlorinated solvents might be selected substitutes for CFC-113 and MCF in some cases. Recent developments in emission control technology as described in the discussion of HCFCs, might mitigate some effects of these substances. Exhibit 16 summarizes the properties of these other chlorinated solvents.

Exhibit 15a

PROPERTIES OF KETONES

KETONES	Formula	Mol. Wt.	lbs per gal	B.P. °F	F.P. °F	Evap Rate CCl_4 =100	Coefficient of Expansion Per °F	Surface Tension @ 68°F Dynes/cm
ACETONE	CH_3COCH_3	58.08	6.58	132-134	-138.6	139	0.00080	23.7
METHYL ETHYL KETONE	$CH_3COC_2H_5$	72.10	6.71	174-177	-123.5	97	0.00076	24.6
DIETHYL KETONE	$C_2H_5COC_2H_5$	86.13	6.80	212-219	-43.5	-	0.00069	24.8
METHYL n-PROPYL KETONE	$CH_3COC_3H_7$	86.13	6.72	214-225	-108.0	66	0.00062	25.2
CYCLOHEXANONE	$(CH_2)_5CO$	98.14	7.88	266-343	-49.0	12	0.00051	-
METHYL ISOBUTYL KETONE	$(CH_3)_2CHCH_2COCH_3$	100.16	6.68	234-244	-120.5	47	0.00063	22.7
METHYL n-BUTYL KETONE	$CH_3COC_4H_9$	100.16	6.83	237-279	-70.4	32	0.00055	25.5
METHYL CYCLOHEXANONE (Mixed Isomers)	$(CH_3)C_5H_9CO$	112.17	7.67	237-343	-	7	0.00042	-
ACETONYL ACETONE	$CH_3COC_2H_4COCH_3$	114.14	8.10	365-383	15.8	-	0.00052	39.6
DIISOPROPYL KETONE	$(CH_3)_2CHCOCH(CH_3)_2$	114.18	6.73	237-261	-	-	-	-
METHYL n-AMYL KETONE	$CH_3(CH_2)_4COCH_3$	114.18	6.81	297-309	-31.9	15	0.00057	-
DIACETONE	$(CH_3)_2C(OH)CH_2COCH_3$	116.16	7.82	266-356	-65.2	4	0.00055	29.8

KETONES	Formula	Sol % by Wt. @ 68°F		Flash Pt (TCC) °F	Flammable Limits % by Volume in Air		Toxicity MAC in ppm	Spec. Heat Liq. @ 68°F Btu/(lb)(°F)	Latent Heat @ B.P. Btu/lb
		In Water	O' Water		Lower	Upper			
ACETONE	CH_3COCH_3	∞	∞	0	2.6	12.8	1000	0.51	224
METHYL ETHYL KETONE	$CH_3COC_2H_5$	26.8	11.8	28	1.8	11.5	250	0.53	191
DIETHYL KETONE	$C_2H_5COC_2H_5$	$3.4^{104\ F}$	4.6	55	-	-	250	0.56	163
METHYL n-PROPYL KETONE	$CH_3COC_3H_7$	4.3	3.3	45	1.6	8.2	200	-	180
CYCLOHEXANONE	$(CH_2)_5CO$	2.3	8.0	145	1.1	-	100	0.49	-
METHYL ISOBUTYL KETONE	$(CH_3)_2CHCH_2COCH_3$	2.0	1.8	64	1.4	7.5	100	0.55	148
METHYL n-BUTYL KETONE	$CH_3COC_4H_9$	$3.4^{77°F}$	$3.7^{77°F}$	73	1.2	8.0	100	0.55	148
METHYL CYCLOHEXANONE (Mixed Isomers)	$(CH_3)C_5H_9CO$	0.2	3.0	118	-	-	100	$0.44^{58°F}$	-
ACETONYL ACETONE	$CH_3COC_2H_4COCH_3$	∞	∞	174	-	-	-	-	-
DIISOPROPYL KETONE	$(CH_3)_2CHCOCH(CH_3)_2$	0.6	-	75	-	-	-	-	-
METHYL n-AMYL KETONE	$CH_3(CH_2)_4COCH_3$	0.4	1.5	120	-	-	100	-	149
DIACETONE	$(CH_3)_2C(OH)CH_2COCH_3$	∞	∞	48	-	-	50	$0.50^{58°F}$	200

Source: DuPont Company, Handbook of Standards for Solvents

Exhibit 15b

PROPERTIES OF ALCOHOLS

PRODUCT	Lb./Gal. 60°F	Sp. Gr. 20°/20°C	Boiling Range °F	Fl. Pt. °F TCC	Evap. Rate[1]
Methanol	6.60	0.792	147-149	54	3.5
Ethanol, Prop. Anhydrous	6.65	0.799	165-176	49	1.8
Ethanol, Spec. Industrial Anhydrous	6.65	0.795	167-178	50	1.8
Isopropanol, Anhydrous	6.55	0.786	179-182	53	1.7
n-Propanol	6.71	0.806	205-208	74	1.0
2-Butanol	6.73	0.809	207-215	72	0.9
Isobutanol	6.68	0.803	225-228	85	0.6
n-Butanol	6.75	0.811	241-245	97	0.5
Amyl Alcohol (primary)	6.79	0.815	261-282	120	0.3
Methyl Amyl Alcohol	6.72	0.808	266-271	103	0.3
Cyclohexanol	7.89	0.949	320-325	142	0.05
2-Ethylhexanol	6.94	0.834	360-367	164	0.01
Texanol	7.90	0.950	471-477	248[2]	0.002

1 n-Butyl Acetate=1
2 C.O.C.

Source: Southwest Chemical Company, Solvent Properties Reference Manual

Exhibit 16

PROPERTIES OF OTHER CHLORINATED SOLVENTS

Physical Properties	CFC-113	MCF	Trichloro-ethylene	Perchloro-ethylene	Methylene Chloride
Ozone Depleting Potential	0.8	0.1	0	0	-0
Chemical Formula	CCl_2FCClF_2	CH_3CCl_3	$CHClCCl_2$	CCl_2CCl_2	CH_2Cl_2
Molecular Weight	187.38	133.5	131.4	165.9	84.9
Boiling Point (°C)	47.6	72-88	86-88	120-122	39.4-40.4
Density (g/cm^3)	1.56	1.34	1.46	1.62	1.33
Surface Tension (dyne/cm)	17.3	25.4	29.3	31.3	N/A
Kauri Butanol Value	31	124	130	91	132
Toxicity	Low	Low	Medium	Medium	Medium
OSHA PEL 8 hr. TWA (ppm)	1000	350[a]	50[a]	25[a]	500[a]
Flash Point (°C)	None	None	None	None	None

[a] Obtained from HSIA White Paper 1989.

Source: UNEP 1989.

WASTEWATER MINIMIZATION AND TREATMENT

Wastewater generated from aqueous and semi-aqueous based cleaning processes used in the metal cleaning industry might require pretreatment prior to discharge to the sewer system to meet local, state, or federal regulations. The amount of pollutants and the quantity of wastewater generated depend on the cleaning process. The type of treatment technology used depends solely on the quality and quantity of the wastewater generated.

Contaminants

The wastewater generated from aqueous and semi-aqueous based cleaning processes can contain organic contaminants along with dissolved or suspended metals. An additional problem encountered with alkaline cleaners is the high pH of the wastewater.

Organic Matter

Organic matter in the wastewater results from removal of oil and grease from the parts being cleaned and from the chemical constituents of the cleaners.

Generally considered a single type of pollutant, oil and grease are not categorized by any chemical formula, but rather as a general type of semi-liquid material that may contain fatty acids, fats, soaps, and other similar materials. Oily wastewater can be placed into five categories:

- ***Free oil***: oil which rises rapidly to the surface under quiescent conditions;
- ***Mechanical dispersions***: fine oil droplets ranging in size from microns to a few millimeters in diameter which are stabilized by electrical charges or other forces but not through the influence of surface active agents;

  Chemically stabilized emulsions: oil droplets similar to mechanical dispersions but with enhanced stability resulting from surface active agents at the oil/water interface;

- ***"Dissolved" oil***: truly soluble chemical species plus very finely divided oil droplets (typically less than 5 microns diameter). This form generally defies removal by normal physical means;
- ***Oil-wet solids***: oil adhering to the surface of particulate material in the wastewater.

Organic matter such as oil and grease contribute to visual and olfactory problems, interfere with normal oxygen transfer from air to water, and exert both a biological oxygen demand (BOD) and a chemical oxygen demand (COD). The measure of organic matter in a waste stream is generally characterized by measuring the BOD and COD. BOD is a measure of the oxygen consuming characteristic of organic matter. COD measures oxygen consuming pollutants in wastewater. COD measures the total oxidizable carbon in the wastewater and relates to the chemically bound oxygen in the water. BOD relates to the dissolved oxygen.

Most aqueous and semi-aqueous chemicals used in cleaner formulations are biodegradable. The term "biodegradable" may be misleading, because it may take too long for these chemicals to break down into their constituent elements to be considered "environmentally acceptable."

Metals

Metals can exist either in suspension or solution. Metals in suspension are metal chips and fines removed from the parts being cleaned. Dissolved metals are metals in solution. Dissolved metals in aqueous-based wastewater generally arise from metals that are etched off as a result of the alkalinity of the solution.

pH

A high pH, or alkaline content, can harm aquatic life. Aqueous cleaning wastewater generated in the metal cleaning industry is generally alkaline (i.e., has a pH greater than 7) and in most instances, it has a pH ranging from 9 to 12 and must be neutralized prior to discharge.

Wastewater Minimization

Before discussing wastewater treatment options, we discuss methods for minimizing the amount of wastewater generated from aqueous and semi-aqueous cleaning processes. One of the key factors in minimizing wastewater is to optimize the cleaning process.

Optimizing the cleaning process includes:

- Avoiding unnecessary loading
- Removing sludge promptly
- Monitoring the cleaning solution
- Maintaining equipment
- Designing more efficient process features.

Avoid Unnecessary Loading

In addition to consuming cleaner, an excessive amount of loading causes the soils removed from the parts to interfere with cleaning. These solids form scale on the heating tubes and reduce heat transfer efficiency. Excessive loading requires regular maintenance and increases discharge of wastewater.

When using alkaline cleaners, alkalinity may be reduced by the acidity of the soils being removed, reaction of the alkali with the carbon dioxide in the air used for agitation, and reaction of the cleaner components with the hard water salts. This reduction in alkalinity consumes the cleaner and reduces bath life. Solutions to such problems include using mechanical agitation, soft water, demineralized water, or deionized water, and frequent replacement of the used alkaline cleaner.

Remove Sludge and Soils Promptly

Removing sludge and soils promptly from cleaning tanks will reduce cleaner use by increasing the time before the entire tank needs to be cleaned out.

Alkaline cleaners are available that allow the separation of excess oily soils from the cleaning solution. These formulations use surfactants that are good detergents but poor emulsifiers. Agitation of the bath during cleaning keeps the soil suspended. After a prolonged period of inactivity, such as overnight, the oily soils float to the surface and can be skimmed off. Although this method is effective with mineral oil, it is less effective with fatty oils.

Similarly there are also semi-aqueous cleaning systems that have a hydrocarbon phase that dissolves the soils but does not dissolve in the water phase. When allowed to stand without agitation, this hydrocarbon phase easily separates out.

Monitor Cleaning Solution Routinely

If solution strengths are analytically checked on a routine basis, solution strength can be maintained more effectively by making small and frequent additions rather than a few large ones. Analytical checks can be performed by the operator using simple titration techniques (for example, the addition of a given amount of reagent to a known volume of cleaner and indicator can result in a color change). Full scale titration tests may be performed by a laboratory on a less frequent basis. An accurate log of all tests and cleaner additions should be kept.

Maintain Equipment

All equipment should be regularly maintained. Metal tanks should be properly coated with protective finishes. Deionized water should be used in tanks with plastic lining. Spray nozzles should be inspected regularly to avoid clogging. Another important item that should be maintained is float valves that supply make-up water. Leaks in these valves can cause dilution of cleaner. It is also important to determine whether plastic material used in equipment is compatible with the hydrocarbon material used in the semi-aqueous process.

Consider Other Process Design Features

Other process design features that reduce wastewater discharge include:

- Use of demineralized water for cleaning needs that cannot tolerate minor residue on the parts. Rinsing should be carried out using demineralized water. This water reduces the amount of sludge generated during wastewater treatment and may allow the direct use of rinse water as make-up water for the wash tank;
- Counterflow rinse systems should always be used to reduce overall water consumption and subsequent treatment requirements;
- Fog nozzles use much less water than conventional spray systems.

Wastewater Treatment Technologies

Wastewater generated from these processes can have a wide range of pollutants; therefore, the treatment technologies applied will depend on the type of pollutant present and the quantity of wastewater being generated. The wastewater treatment equipment and processes discussed below are categorized based on the type of pollutant being treated.

Oil and Grease

Gravity Separator. This treatment technology takes advantage of the difference in specific gravity between water and oil and grease. Gravity separators are the most common devices employed in waste treatment to separate grease and non-emulsified oils. The technique does not always remove very finely divided (colloidal) oily or scummy material. The process generates an oily dispersion that may have to be treated prior to disposal. Relative energy requirements are low. The treatment process involves retaining the oily waste in a holding tank and allowing gravity separation of the oily material which is then skimmed from the wastewater surface.

In instances where the quantity of wastewater to be treated is small, a simple skimmer attached to a tank can be used to remove the free floating oils -- a process commonly used in metal cleaning. The oil skimmers either are operated continuously during cleaning or are operated once a day before the cleaning process is started. It should be noted that during the removal of oil, other suspended solids, like metal fines and chips, are also removed.

Ultrafiltration. Ultrafiltration is a low pressure (10-150 psi) membrane process for separating high molecular weight emulsified oils and particulate matter less than 0.2 microns in diameter. A semi-permeable membrane, incorporated in membrane modules, performs the separation. The wastewater feed is pumped under pressure tangentially through the membrane modules. Water and low-molecular weight solutes such as salts and some surfactants, pass orthogonal to the direction of flow through the membrane pores as permeate. The solution may be reused or further treated prior to disposal. Emulsified oil and suspended solids cannot pass through the membrane pores and are retained as a concentrate. Capital cost for ultrafiltration equipment and operating costs associated with pumping the solution at elevated pressure are higher than other treatment methods. Material and disposal cost savings can provide an acceptable return on investment in cases where recycling of the permeate solution is possible.

Wastewater flows across the membrane surface at high velocity. This cross-flow characteristic differs from the perpendicular flow of ordinary filtration,

where "cake" builds up on the filter surface, requiring frequent filter replacement and cleaning. Tangential-flow prevents filter cake buildup, resulting in high filtration rates that can be maintained continuously, eliminating the cost for frequent membrane cleaning.

Data from aerospace industry investigators indicate that a ceramic ultrafiltration system can be used to recover the entire cleaner (builder and surfactant package) used in aqueous cleaners and that the efficiency of oil removal is best when using ultrafiltration. However, the ultrafiltration process must be closely tailored for the particular aqueous cleaner in order to prevent excessive loss of specific components.

Coalescing. The basic principle of coalescence involves the preferential wetting of a coalescing medium by oil droplets that accumulate on the medium and then rise to the surface of the solution as they combine to form larger particles. The important properties of the coalescing media are its wettability for the oil and its large surface area. Polypropylene and monofilament line are sometimes used as coalescing media. Floating absorption blankets or pillows are available from a number of suppliers. The active material is generally a blown polypropylene, which is highly oleophilic, but will not remove active ingredients from the cleaner.

Because of its simplicity, coalescing provides high reliability and low capital and operating cost. It cannot be used, however, to remove emulsified oils, if they are present, they must be pretreated before being sent to the coalescing unit.

Chemical Treatment. Chemical treatment is often used to breakdown stable oil-water emulsions. Chemical treatment consists of three steps: (1) coagulation -- breaking of the emulsion, (2) flocculation -- agglomeration of the tiny oil droplets to form larger droplets, and (3) sedimentation -- the removal of oil from water.

Chemicals (e.g., polymers, alum, ferric chloride, and organic emulsion breakers) break emulsions by neutralizing repulsive charges between particles, precipitating or salting out emulsifying agents, or altering the interfacial film between the oil and water. After the addition of the coagulant, another chemical, called the flocculent, is added to agglomerate the tiny oil droplets into larger oil drops so that they can be easily separated. Typical flocculents are high molecular weight polymers.

The disadvantage of this process is that chemical treatments used to break the emulsions generate sludge that has to be disposed of. This requirement increases cost, particularly if the level of emulsified oil needs special chemical treatment.

Organics

Organics present in the wastewater from aqueous and semi-aqueous based processes are generated from contaminants like the hydrocarbon chemicals and surfactants used in the chemical cleaners and finishing and pigment compounds used in the processing of the metal parts in the metal industry. Although oil and grease are organic in nature, they are not considered organic pollutants under this definition. It is known that many organic compounds are eliminated during the treatment steps for the removal of waste oil and grease. High molecular weight organics are much more soluble in oil than in the water and are skimmed off with the removed oil.

Carbon adsorption. This system involves passing the wastewater through a chamber containing activated carbon to remove the dissolved organic from the wastewater. Carbon adsorption is one of the most efficient organic removal processes available. In addition, it is reversible, thus allowing activated carbon to be regenerated by the application of heat and steam and then reused.

Some general rules relating to carbon adsorption capacity are:

- Higher surface area gives a greater adsorption capacity;
- Larger pore size gives a greater adsorption capacity;
- Adsorptivity increases as the solubility of the solute decreases. For hydrocarbons, adsorption increases with molecular weight;
- Adsorption capacity decreases with increasing temperature;

- For solutes with ionizable groups, maximum adsorption is achieved at a pH corresponding to the minimum ionization.

The rate of adsorption is also an important consideration. For example, while capacity is increased with the adsorption of higher molecular weight hydrocarbons, the rate of adsorption is decreased. Similarly, while temperature increases decrease capacity, they may increase the rate of removal of solute from solution.

Carbon adsorption requires pretreatment to remove excess suspended solids, oil, and grease. Suspended solids in the stream entering the carbon adsorption bed should be less than 50 parts per million (ppm) to minimize backwash requirements. Oil and grease should be less than 10 ppm. High levels of oil and grease can block the pores of the activated carbon, making it ineffective in the adsorption of organic matter.

Activated carbon columns are typically placed in series or parallel in wastewater treatment plants. A minimum of two columns is generally used in continuous operation: when the activated carbon in one column is used up and is being regenerated, the other column removes the contaminants. An economical treatment process, the major cost of activated carbon is associated with regeneration.

pH

Aqueous cleaning wastewater is alkaline and can have a pH ranging from 7 to 12, depending upon the cleaning process, and in particular, on the type and strength of the chemical cleaner used. Adding sulfuric or hydrochloric acid adjusts the pH of wastewater. The major investment cost associated with this treatment is the cost of the mixing tank. The operating costs, which are primarily the cost of material, are low.

Dissolved Metals

Precipitation. The most commonly used technique to treat dissolved metals consists of hydroxide precipitation followed by sedimentation. Reagents commonly used to effect the precipitation include alkaline compounds such as lime and sodium hydroxide. The treatment chemicals may be added to a mix tank or directly to the sedimentation device such as a clarifier. The major advantage of a clarifier is the short retention time required for settling of the metal precipitates. However, the cost of installing and maintaining a clarifier are high. The sludge generated has to be disposed according to Federal/state/or local regulations.

The performance of hydroxide precipitation depends on several variables. The most important factors affecting precipitation effectiveness are:

- Addition of sufficient excess hydroxide to drive the precipitation reaction to completion;
- Maintenance of an alkaline pH throughout the precipitation reaction and subsequent settling;
- Effective removal of precipitation solids.

In some instances flocculating agents are added to enhance the sedimentation process. Hydroxide precipitation, however, produces sludge that needs to be disposed of -- a fact which increases treatment cost.

Ion-Exchange. This system uses the reversible interchange of ions between a solid and a liquid so that there is no permanent change in the structure of the solid, the ion-exchange material. Ion exchange is used in a number of wastewater treatment applications, particularly in water softening and deionization, to remove dissolved metals from solution. The utility of ion exchange rests with the ability to reuse the ion-exchange materials. Eventually the resin beds will lose their efficiency and have to be either regenerated or replaced, thereby producing either concentrated wastewater or a volume of contaminated resin to be disposed of properly. Relative energy costs for this system are low. For example, in the wastewater treatment reaction to remove lead (Pb):

$$2\,Na^{+}\,R + Pb^{2+} = Pb^{2+}\,R_2 + 2\,Na^{+}$$

The exchanger R in the sodium-ion form is able to exchange for lead and, thus, to remove lead from the wastewater and to replace it with an equivalent quantity of sodium. Subsequently, the lead-loaded resin may be treated with a sodium chloride

solution, regenerating the sodium form so that it is ready for another cycle of operation. The regeneration reaction is reversible: the ion exchanger is not permanently changed.

Conceptual Design of a Wastewater Treatment System

In most aqueous and semi-aqueous cleaning systems the wash and rinse water is recycled and reused for a certain period of time before being discarded. Because of stringent environmental regulations, high water costs, and high energy costs, recycling of wastewater is recommended. Exhibit 17 represents a conceptual design of a semi-continuous wastewater treatment system that treats wastewater generated from the metal cleaning industry.

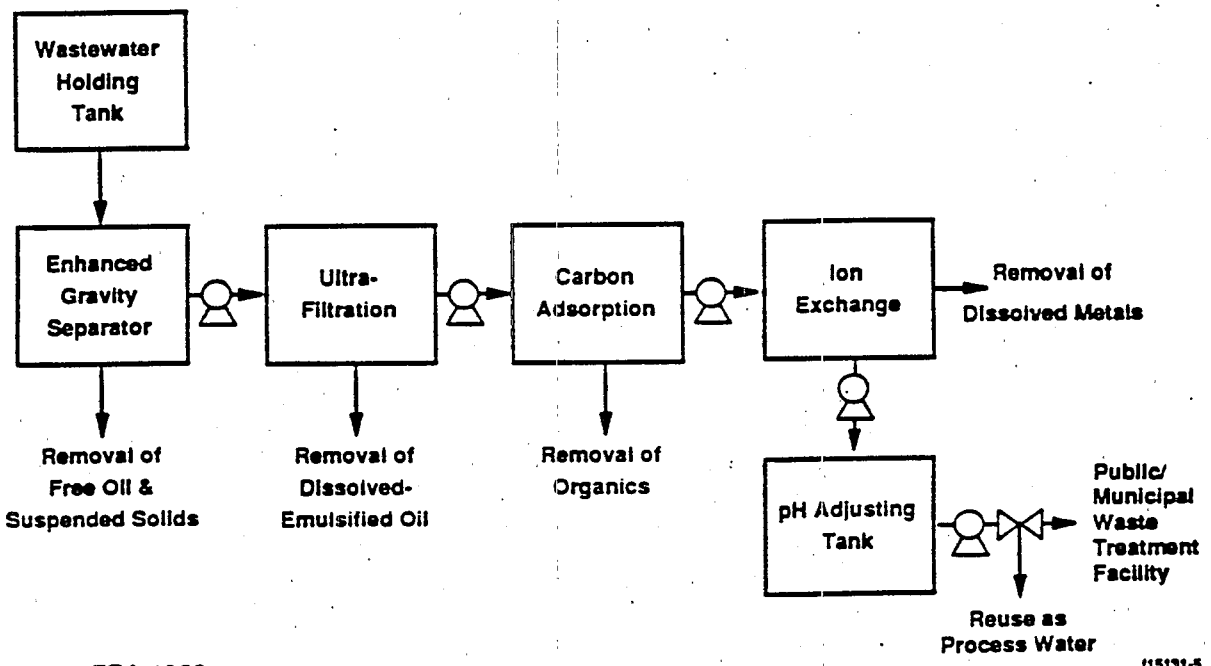
The system consists of six unit operations. Unit 1 is a holding tank where the wastewater generated is periodically discharged. Unit 2 is an enhanced gravity separator that removes free floating oil and suspended solids. Unit 3 is a ultrafiltration device that removes the emulsified-dissolved oils. Unit 4 is an ion-exchange column used to remove dissolved metals. Unit 5 is an activated carbon bed used to remove organic matter. Unit 6 is a pH adjusting tank. The final wastewater discharged from this system can be either reused as process water for an aqueous or semi-aqueous cleaning process or discharged to the Public Owned Treatment Works (POTWs).

Contract Hauling of Wastewater

For small users of aqueous and semi-aqueous cleaning processes it might be more economical to contract waste treatment rather than treating it in-house. In some cases, the volume of wastewater can be reduced to make it more economical for shipment (hauling) by evaporating excess water. Most companies that contract haul the waste generally treat it in large treatment facilities such as large wastewater treatment plants or large incinerators where it is burned as fuel. Waste from semi-aqueous processes is a fuel source for incinerators.

Exhibit 17

SEMI-CONTINUOUS WASTEWATER TREATMENT PROCESS



Source: EPA 1989a

SUMMARY AND REVIEW

The discussions presented in this manual have described a step-by-step approach to eliminating CFC-113 and methyl chloroform in solvent cleaning processes. The steps include:

- Determine where and why CFC-113 and methyl chloroform is used in cleaning operations:
- Characterize existing cleaning processes:
- Establish criteria for selecting alternative cleaning processes;
- Review alternatives that could be used to replace solvent cleaning and determine which alternative best suits the cleaning needs:
- Consider options for wastewater minimization and treatment.

The next section presents some case studies that provide examples of successful programs on alternatives being implemented in industry. The case studies are followed by references and list of vendors that may be an additional source of information.

CASE STUDIES OF INDUSTRIAL PRACTICES

The following section presents case studies of alternative technologies.

Mention of any company or product in this document is for informational purposes only and does not constitute a recommendation, either express or implied, of any such company or product by EPA, ICOLP, ICOLP committee members, and the companies that employ the ICOLP committee members.

The case studies presented include:

- ***Case Study #1:*** Evaluation of Aqueous Cleaning for Aluminum and Ferrous Alloys
- ***Case Study #2:*** Selection of Aqueous Process for Cleaning Components for Solenoid Valves
- ***Case Study #3:*** A Five Phase Program for Developing Alternative Cleaning
- ***Case Study #4:*** Program to Eliminate Wipe Solvents Containing CFC-113
- ***Case Study #5:*** Biodegradable Replacements for Halogenated Solvents and Cleaners
- ***Case Study #6:*** Replacement of Solvent Degreasing for Engineering Prototype Parts, Precision Machine Parts, and Various Cleanroom Items
- ***Case Study #7:*** Program to Eliminate Methyl Chloroform Use in Steel Chair Manufacturing Operations

CASE STUDY #1: EVALUATION OF AQUEOUS CLEANING FOR ALUMINUM AND FERROUS ALLOYS

Case Study #1 is an overview of the work conducted by Boeing since mid-1987 to evaluate aqueous cleaners and the aqueous cleaning process. The current status of the program encompasses the use of aqueous cleaning for aluminum and ferrous alloys. Work on titanium and magnesium alloys, although virtually complete, is still in progress.

Selection of Cleaners for Evaluation

An initial list of 10 cleaners was developed from vendor listings available through the literature, by selecting companies recognized as Boeing suppliers in other product areas. Selection criteria of the cleaners for evaluation include indicated cleaning effectiveness, low toxicity materials, and regeneration capability. As the project progressed, more contacts were made both within the aerospace industry and with other chemical suppliers. These contacts led to the eventual evaluation of 48 aqueous cleaner formulations, all meeting the initial selection criteria.

Cleaning Effectiveness Testing

The evaluation of aqueous cleaners began with the specification of the soil to be removed and the determination of cleaning performance. Most industrial specifications require only that a cleaner "leave no visible residue." Two specifications were found that detail test soils to be removed (SAE AMS 1536 and 1537) and the amount of soil removal required, as measured by weight. Cleaners for the evaluation were expected to remove all visible soils, so the measurement of soils removed by weight was not applicable. In addition, vapor degreasers at Boeing are often general cleaning operations that must remove a variety of soils from a number of substrate materials. For these reasons, no particular standard cleaning specification appeared applicable.

Immersion Cleaning

Immersion cleaning effectiveness tests were conducted on aluminum, steel, and titanium test panels using as test soils "permanent" marking ink, general purpose lubricating grease, silicone grease, general purpose lubricating oils, rust preventive compound, tar, lipstick (not a shop soil but a highly visible hydrocarbon mixture), solder flux, and machining wax. Cleaners were made up in bench-scale quantities (2 liters), and generally operated at two concentrations and over a temperature range based on suppliers' recommendations. Agitation was limited to that necessary for temperature control. Immersion time was set at 20 minutes with qualitative evaluation of the cleaning effects performed every five minutes. Cleaning was followed by immersion rinsing in warm water.

Degreasers were described as vigorous if a particular soil was completely removed within 10 minutes. Other terms were used to describe removal or visible effect on soils at particular time intervals. After the completion of testing, cleaners that indicated an ability to quickly remove a broad spectrum of soils were judged as "most effective." This judgment was made recognizing that, for a specific cleaning operation, degreasers that ranked lower in overall effectiveness may be appropriate choices for the removal of particular soils.

Spray Cleaning

A single-nozzle spray tank was constructed for the evaluation of spray cleaners. Cleaners were evaluated using the same soils and substrates described for immersion cleaning. However, cleaning time was limited to 15 minutes and some evaluations were conducted at five seconds interval for light hydrocarbon oils. Cleaning was followed by spray rinsing with room temperature water. Effectiveness was again based on broad spectrum soils removal.

Ultrasonic Cleaning

Evaluation was conducted using a laboratory scale ultrasonic cleaning bath with a capacity of about two liters. Cleaners were evaluated using the same soils and substrates described for immersion cleaning, but with the addition of some tubing materials for test substrates. Cleaning time was limited to 15 minutes. Cleaning was followed by spray rinsing with room temperature water. Effectiveness was again based on broad spectrum soils removal.

Results of Cleaning Effectiveness Tests

Based on the qualitative evaluation of cleaning effectiveness, a number of conclusions were drawn:

- Several cleaners were evaluated that were determined to be highly effective cleaners. All cleaners tested showed at least some ability to remove general purpose lubricating oils. However, the vigorous cleaners were readily apparent by their effects on the other test soils, ink, and silicone grease in particular. The vigorous cleaners were then permitted to enter the more extensive test phase of the program described in the following sections.

- The effect of substrate on cleaning effectiveness was not strong, some indication that soils were harder to remove from steel than from aluminum.

- As expected the effect of temperature was significant in testing at room temperature, degreasers that showed some effectiveness were generally much more active when heated. Temperature for the cleaning process was limited to 140°F to prevent flash drying onto substrate surfaces.

- As expected the effect of agitation was also significant. Spray cleaning and ultrasonic cleaning generally took half the time of low agitation immersion cleaning.

Metallurgical Testing

Metallurgical tests were conducted to assure that the aqueous cleaners did not cause any adverse effects on substrate materials.

Etch Testing

Etch testing was conducted according to Boeing specifications. Test metals were immersed in the cleaners at operating concentration and temperature for 24 hours. The amount of weight lost by the test metals determined the acceptability of the cleaners. All vigorous cleaner candidates passed this test. Cleaners that would not pass this test were apparent in immersion cleaning effectiveness testing, due to the staining and gassing observed.

Intergranular Attack and End Grain Pitting

Intergranular testing was carried out according to Boeing specifications. Metal test specimens were exposed to cleaners at operating concentration and temperature for 30 minutes. Specimens were then cross-sectioned to determine that intergranular attack in excess of 0.0002 inches and end grain pitting in excess of 0.001 inches had not occurred. All vigorous cleaner candidates passed this test.

Sandwich Corrosion

Sandwich corrosion testing was carried out using Boeing specifications. Results of sandwich corrosion tests indicate the corrosion that can occur if, during the rinse cycle, the cleaners are not adequately removed from the surface. In general, alkaline-based cleaners were marginal to failing on this test. The terpene-based emulsion cleaners tested, however, did not indicate any corrosion potential.

Hydrogen Embrittlement of High Strength Steel

Testing was conducted in accordance with ASTM F519, using both cadmium plated and unplated Type 1A steel specimens. In this test, the specimens are subjected to 45 percent of their ultimate tensile strength while immersed in the test cleaner. The specimens must not break for a minimum of 150 hours. The terpene-based emulsion cleaners passed all tests. The alkaline-based cleaners passed the test with bare steel but failed with cadmium-plated steel due to caustic driven cadmium reembrittlement of the steel test specimen.

Effects on Subsequent Processes

Substituting the aqueous cleaning process for vapor degreasing must not adversely affect the chemical processes that follow. What was unknown was whether any residue from the aqueous cleaners would affect subsequent processes. The most straightforward method to look for adverse effects was judged to be the quality of subsequent finishes. The following tests were conducted by using the candidate aqueous cleaners prior to finishing aluminum, followed by standard quality control tests in accordance with specification requirements:

- *Chromate conversion coating* -- 168-hour salt spray;
- *Chromic acid anodizing* -- 336-hour salt spray;
- *Chromate conversion coating followed by epoxy primer* -- wet and dry adhesion tests, impact resistance, 3,000-hour scribe line corrosion test, and 30-day acidified salt spray coupled with CRES;
- *Chromic acid anodizing followed by epoxy primer* -- wet and dry adhesion tests, impact resistance, 3,000-hour scribe line corrosion test, and 30-day acidified salt spray coupled with CRES;
- *Chromate conversion coating followed by epoxy primer and epoxy enamel* -- wet and dry adhesion tests, impact resistance, 3,000-hour scribe line corrosion test, and 30-day acidified salt spray coupled with CRES;
- *Chromic acid anodizing followed by epoxy primer and epoxy enamel* -- wet and dry adhesion tests, impact resistance, 3,000-hour scribe line corrosion test, 30-day acidified salt spray coupled with CRES;
- *Phosphoric acid anodizing followed by adhesive bonding* -- crack extension test;
- *Phosphoric acid anodizing followed by epoxy primer* -- wet and dry adhesion tests and 3,000-hour scribe line corrosion test.

The following tests were conducted by using the candidate aqueous cleaners prior to finishing steel, followed by standard quality control tests for specification requirements:

- *Stainless steel passivation* -- salt spray verification test;
- *Cadmium plating* -- adhesion;
- *Chromium plating* -- adhesion;
- *Cadmium-titanium alloy plating* -- adhesion.

None of the tests for subsequent effects have indicated a failure due to the use of the aqueous cleaners.

Toxicological and Industrial Hygiene Analysis

Candidate cleaners were initially selected to be low toxicity materials, based on supplier information. However, Boeing requires that all new materials be evaluated prior to their use. These evaluations are still in progress for several of the effective cleaner candidates. Evaluations of d-limonene and the glycol ethers have been completed and will be made available to other organizations on request.

Cleaner Regeneration

All the cleaners selected for evaluation have some degree of soil rejection capability. Soil rejection capability is accomplished by the surfactant package included in the cleaner. The surfactant package reduces surface tension for effective contact by the cleaner's active ingredients, but then does not allow the removed hydrocarbon soils to be emulsified in the cleaner. As a consequence, oils and greases float on the top of a quiescent emulsion cleaner tank. The soil rejection capability provides an opportunity to regenerate the cleaner, greatly extending operating life and reducing the volume of hazardous waste generation. Rejected hydrocarbon soils can be removed from an operating aqueous cleaner in several ways: skimming off the oil, absorption using floating absorption blankets or pillows, using a coalescer, and through ultrafiltration.

CASE STUDY #2: SELECTION OF AQUEOUS PROCESS FOR CLEANING COMPONENTS FOR SOLENOID VALVES

Case Study #2 describes a program implemented at Honeywell to select an aqueous cleaning process for cleaning components of solenoid valves.

Honeywell, Skinner Valve Division, produces solenoid valves for use in fluid control. The majority of components are 300 and 400 series stainless steels with some brass and aluminum. Parts typically range in size from one-half inch in diameter by one inch long to two inches in diameter by four inches long. Operations performed include turning, milling, drilling, threading, broaching, and welding. Valves are used in a variety of applications such as gasoline pumps, medical oxygen equipment, and photocopying equipment.

Current Process

The major cleaning objective is to remove cutting oils and chips from blind holes. Final cleaning is performed prior to welding and assembly. All work moves through two vapor degreasers equipped with hoods, programmable hoists, ultrasonics, and attached recovery stills. Parts are degreased between operations and also before assembly. Parts are racked in metal trays approximately 10 inches x 16 inches, loaded three at a time into a rotating basket. Typical trays hold 40 to 200 parts depending on size. Total cycle time is five minutes. Annual volume is 1.2 million valves. Each valve contains five or six major components and each component is degreased at least two to three times. This results in over 16.5 million parts passing through the degreasing operations. Consumption of CFC-113 for 1989 was 54,000 lbs.

Alternative Selection Process

In response to the concerns with CFC-113, the Environmental Health and Safety group at Honeywell issued a policy for all divisions to reduce usage and ultimately eliminate CFC-113. A central group was formed to study the problem and relay information and findings to other divisions.

It was decided to avoid any replacement of CFC-113 with "in kind" HCFCs because of pending legislation that would ultimately regulate these solvents. In addition, HCFCs were not expected to be in production until 1992 and would require newer and more expensive equipment. Costs of HCFCs were expected to be at least equal to or greater than CFC-113.

Because there were no tight spaces to trap a cleaning fluid (as there might be for surface mounted electronic components) the low surface tension and high evaporative rate of CFC-113 were not a factor. The cleaning of parts between machining operations did not require a high degree of cleanliness; removal of the bulk of the oil and all of the loose chips would be sufficient.

Health and safety factors were considered. No substance that was more toxic or presented a greater health risk than the current process would be accepted.

Lastly, cost was a large factor. It was established through vendor tests that relatively inexpensive equipment could fill the cleaning needs and still achieve a less than two-year payback.

At Skinner Valve, two engineers were given the task of meeting the corporate goals. Using both corporate resources and cleaning equipment vendors, these engineers outlined the following steps to replace CFC-113 as a metal cleaning fluid.

- Develop an objective and guidelines;
- Identify information sources;
- Identify baseline what, why, where, how, cost;
- Establish current material flow;

- Identify equipment options;
- Run test on vendors equipment;
- Compare test results between different type of cleaning machines;
- Identify cleaning solution options;
- Identify waste handling options;
- Perform financial analyses;
- Order Phase I equipment;
- Install and debug equipment;
- Review results of Phase I equipment;
- Order Phase II equipment;
- Install Phase II equipment; and
- Obsolete vapor degreasers.

Cleaning Requirements

The factory has been restructured into a cell concept with Just in Time (JIT) manufacturing. This structure required decentralized degreasing operations, preferably units small and inexpensive enough to place one at every work station.

Several different levels of cleaning are required. These were broken down into three levels:

Level 1 includes those parts that must be completely cleaned with no oil or chips and completely dry with no residue. "Oxygen service" parts are the most demanding since they will be used in oxygen regulators and medical equipment. No hydrocarbons can be allowed. Inspection is done under ultraviolet light and the cleaned parts are handled with cotton gloves and placed in plastic bags until final assembly.

Level 2 includes normal cleaning prior to assembly or welding. Parts must be free of dirt and oil, with no chips, and dry.

Level 3 includes parts primarily between operations and is intended to remove the bulk of the oil and chips so that a part can be handled and located for the next operation. Depending on the next operation, it is not necessary for the part to be dry, for example, tumbling and passivation.

Ranking the work by levels provided a better breakdown of the numbers involved and how many locations and types of machines would be required. Tests were performed on representative samples of the different types of parts and the different levels of cleaning required.

After the decision was made to use an aqueous system, the question of waste material was still a major concern. Options included shipping waste solution and rinse water off site; this was rejected as being too expensive. On-site treatment was a less costly answer.

Honeywell considered on-site treatment and disposal into the sewer which would require constant monitoring and would become more difficult as more facilities attempted to discharge aqueous wastes to the sewer. Other treatments considered included ultrafiltration and evaporation. Evaporation was chosen for this application because rinse water volumes were low and the absence of a liquid waste stream limited the risk of spills and avoided the possibility of exceeding treatment limits.

General Description

The approach taken was to select the equipment first and then find the best cleaning solution for each application. The selection of cleaning solutions is still in progress. The preference of this team is to use one of the nonemulsifying cleaners to facilitate oil separation.

Three separate systems were selected: mechanical agitation, spray washers, and ultrasonics.

Mechanical Agitation

In general these units consist of a tank with a movable rack. The rack is set to submerge the work piece in a heated solution and move the work piece up and down a set frequency. Working temperatures range from room temperature to

180°F; agitation can be varied with respect to length and speed of the stroke. One system purchased also contains a heated rinse. Oil skimmers are either belt or disk type units with a separate secondary oil-water separator. Trays are filled at the rate of one every 15 minutes; the operator places the tray onto the work rack and starts a five-minute cycle. Solution temperature is set at 135°F. The parts are oriented to prevent cupping and dragout. At the end of the wash cycle, trays are either put through a rinse cycle or are allowed to dry and cool.

Spray Washers

Units consist of a small conveyor that passes parts under a series of high pressure spray nozzles. After washing, parts are passed under an air knife to blow off excess solution. Parts are then dropped into baskets and moved to the next operation. The bulk of these parts continue on to other "wet" operations such as tumbling and passivation. Working temperature is 135°F. A disk type oil separator is utilized.

Ultrasonic

Ultrasonic cleaners are reserved for the highest level of cleanliness. For critical parts, a prewash in an agitating washer is used. An immersion tank with bottom mounted transducers providing 1,400 watts input is used. A four- to five-minute cycle at 135°F followed by a three-bath counter flow rinse is utilized. Parts are then dried in a heated tunnel or a top loading oven.

Key items necessary to implement technology

- Upper management support.
- Shop support. It was necessary to work with operators and supervisors to integrate the aqueous cleaning process.
- Time allocation. Sufficient time was allocated to do the necessary research and experimentation to find the best available technology.

Costs of Technology

Total costs for the existing CFC-113 cleaning system and a projected cost for the replacement system was established. Material costs were based on current consumption and price of CFC-113. The consumption estimate incorporated reductions in CFC-113 use resulting from conservation practices adopted at Skinner Valve. However, the CFC-113 price calculation did not take into account the future price increase and the excise tax.

Additional costs items included waste removal and utility costs. Labor costs were assumed not to change. Salvage value of vapor degreasers was taken as zero, since it was difficult to determine what if any market value they might have.

Cycle times for aqueous processes are usually longer and throughput rates are lower. However, aqueous machines costs less than vapor degreasers, thus allowing the purchase of multiple units.

The largest savings occur in material costs. Cleaner cost for one machine were estimated at $35 to $50. This is based on the utilization of the cleaner for up to one month. Actual use shall depend on the volume and type of soils being removed. Costs of the aqueous cleaner is about the costs of two gallons of CFC-113.

Based on the project equipment list and current CFC-113 cost, Skinner Valve expects to have a payback period of less than one and half year. If existing vapor degreasers can be sold or transferred to another division, payback will be even shorter.

CASE STUDY #3: A FIVE-PHASE PROGRAM FOR DEVELOPING ALTERNATIVE CLEANING

Case Study #3 is an overview of the progress made by General Dynamics Fort Worth Division (GD/FW) to eliminate halogenated solvent vapor degreasing and MCF ambient immersion cleaning. After establishing a working team with representatives from all functional departments in 1987, criteria were established to identify acceptable alternatives and concrete goals and milestones were set. The project was divided into the five phases discussed below.

Phase I -- Soil, Cleaner, and Parts Identification/ Characterization

In Phase I, the soils and production operations that generate parts requiring degreasing were characterized. Concurrently, the chemist on the team began identifying alternative cleaning materials and processes. Formulations that contained any hazardous or restricted constituents were excluded as well as materials which could emit VOCs or toxic air emissions.

Phase II -- Cleaner Evaluation and Optimization

The Phase II evaluation focused on cleaning capability using a combination of water break, ultraviolet light, and acid copper immersion to determine cleanliness. Over fifty commercially available aqueous detergent and emulsion cleaners, nine terpene hydrocarbon formulations, and several CFC-113 blends (for comparative purposes) were screened. Concentrations and temperatures were varied for three fixed immersion periods. Cleaners were also tested for any gross corrosion or adverse effects on materials. Six products were selected by mid-1988. Five were selected as general degreasing substitutes. The sixth, a terpene hydrocarbon, was selected as an option for removing high-molecular-weight (asphaltic or paraffinic) soils.

Phase III -- Performance Confirmation and Materials Compatibility Evaluation

In Phase III, the five general degreasing substitutes were evaluated in detail for compatibility with substrate materials, surface coatings, adhesives, bonding materials, and downstream metal finishing processes. (These evaluations were similar to those shown in case study #1.) Compatibility with a variety of honeycomb core materials and laminates was also examined. Three materials were selected as candidates for further investigation as general degreasing substitutes. Additional options for heavy asphaltic soil removal were developed, and ultrasonics was investigated to facilitate cleaning of tubes and heavy asphaltic soils.

Phase IV -- Pilot-Scale Performance, Factory Evaluation

The Phase IV factory evaluation and pilot study of the final three candidate materials began in mid-1989. In Phase IV, laboratory performance was confirmed on production-sized parts, longer-term operational stability of the solutions was investigated, foaming characteristics were examined, operating and maintenance procedures were developed, an economic analysis was conducted, and a toxicological and environmental impact assessment was performed.

Phase V -- Development of Recycling Process

In Phase V, several engineers screened oil removal technologies and selected a recycle process based on a ceramic membrane ultrafiltration for further investigation. The three products were approved

for full-scale implementation in early 1990. Development of the ceramic membrane ultrafiltration technology operating parameters was completed in 1990. One product was identified as being completely recyclable at operating temperatures and concentration. Process emissions would be limited to an oily emulsion and solution from the membrane cleaning procedure.

Full-scale implementation is scheduled for 1992-95 and will include an ultrafiltration system to facilitate the recycling of heavily soiled solutions.

Overall, the project has achieved a number of its objectives:

- Identified several commercially available water-based cleaners as effective substitutes for halogenated solvent degreasing;
- Identified alternative cleaners and cleaning methods for heavy asphaltic and paraffinic soils not cleaned in aqueous immersion cleaners;
- Established a data base to tailor optimum operating conditions for particular degreasing requirements;
- Concluded that efficient cleaning systems can be designed for all parts configurations, including long narrow tubes, using a variety of off-the-shelf equipment; and
- Demonstrated that using a specific ultrafiltration technology cleaning solutions can be recycled at operating concentrations and temperatures.

CASE STUDY #4: PROGRAM TO ELIMINATE WIPE SOLVENTS CONTAINING CFC-113

Case Study #4 is an overview of how Air Force Plant #4, Fort Worth, Texas, developed a way to eliminate CFC-113 use by formulating a low vapor pressure wipe solvent and by finding a different technique for the disposal of wipe solvent cloths.

Currently, Volatile Organic Compound (VOC) emissions from wipe solvent are controlled at Air Force Plant #4 by using CFC-113 blended with hydrocarbon solvents. CFC-113 blends reduced wipe solvent VOC emissions by over 60 tons per year (tpy). However, because of the CFC-113 blends, the wipe solvent operations are emitting over 230 tpy of CFC-113.

Air Force Plant #4 is located in an ozone nonattainment area. Air Force Plant #4 does not want to continue to have CFC emissions from the wipe solvent operations. Commercial low vapor pressure wipe solvents would result in an estimated 40 tpy increase in VOC emissions.

Air Force Plant #4 is planning wipe solvent operations that would not increase VOC emissions over that currently emitted using the CFC-113 blends.

General Dynamics/Fort Worth Division developed a plan which involves capturing a patent-pending low vapor pressure wipe solvent before it evaporates. Cloths are used in conjunction with the solvent in the wipe solvent (cleaning) operations. Most of the solvent will evaporate from the cloth if the cloth is left exposed to the air for longer than 15 to 30 minutes. Placing solvent-laden cloths in bags immediately after use in the cleaning operation prevents solvent evaporation.

Laboratory evaluation of the bagging concept using metallized plastic bags showed that a maximum of 94 percent of the solvent could be captured. When the bagging concept was evaluated in the factory, there were mixed results depending on the attitude of the individual. A highly responsible worker could achieve about 90 percent capture. A worker with no interest in cooperating can lower the capture to 30 percent. Typically, the factory evaluations resulted in a 60 to 70 percent capture.

The solvent used is a new, proprietary, lower vapor pressure solvent blend that has no CFCs. General Dynamics/Fort Worth Division is seeking to patent this blend. When other solvents are used in conjunction with the bagging concept, the capture rate is much lower because more solvent evaporates from the cloth during use in the cleaning operation.

If the bags are tied off by the end of the an eight-hour shift and placed in the disposal cans designated for solvent-laden cloths, then the initial capture can be retained with less than a one percent loss. The disposal cans are emptied daily, and bagged cloths compacted directly into fibre drums. A gasketed drum lid prevents solvent evaporation from the drum contents. The compaction of the solvent-laden cloths into drums is planned to occur within 2 days after its initial use in the cleaning operation.

The compacted solvent-laden cloths will have sufficient energy value to be used as supplemental fuel in cement kilns. If the drums of compacted cloths are not used for energy recovery, they will be incinerated at a commercial hazardous incinerator.

If the overall solvent capture rate exceeds 40 percent, the Air Force Plant #6 will achieve lower VOC emissions than the current CFC-113 blend wipe solvent operations. Since the new wipe solvent contains no CFC-113, most of the CFC-113 emissions will be eliminated.

CASE STUDY #:5 BIODEGRADABLE REPLACEMENTS FOR HALOGENATED SOLVENTS AND CLEANERS

Case Study #5 is an overview of the work conducted since 1987 by the Air Force Engineering and Services Center, Tyndall Air Force Base, Florida, to determine biodegradable substitutes for halogenated solvents and cleaners used in depot-level maintenance operations. All of the preliminary testing, including full-scale screening, necessary to begin implementation of non-halogenated solvents and cleaners for metal finishing throughout the Air Force has been completed.

Background

Solvents and cleaners are used at the Air Force Air Logistics Centers (ALCs) to remove wax, grease, oil, and carbon from aircraft parts before repairing or electroplating. Most of these solvents are, or contain ozone-depleting agents. Many are classified as toxic, and cannot be treated in industrial waste treatment plant (IWTPs) that remove organic chemicals by biological processing. The process wastes must be shipped to approved landfills for disposal.

Purpose

The purpose of this program is to:

- identify halogenated solvents for removing wax, grease, oil and burnt-on carbon that can be replaced with biodegradable solvents;
- identify the biodegradable solvents that can be used;
- develop procedures for, and implement, their use; and
- develop procedures for testing future solvents.

The program has been conducted under contract to EG&G Idaho, Incorporated by scientists and engineers of the Idaho National Engineering Laboratory. The program had three phases: Phase 1 - Solvent Selection and Performance Evaluation; Phase II - Extended Performance Testing; and Phase III - Full Scale Testing.

Phase 1 - Solvent Selection and Performance Evaluation

Phase I included five major tasks:

- identification of the industrial processes at the Air Force Depot-Level maintenance organizations in which solvents/cleaners are used, the procedures for their use, and the processes following their use such as inspection, electroplating, etc.;
- development of quality assurance methods and procedures;
- identification of enhancement methods; and
- screening of solvents to evaluate the performance of the biodegradable solvents for (a) removing wax, oil, grease, and carbon, (b) biodegradability, and (c) corrosiveness.

If a solvent passed the first three screening evaluations, it was then tested for corrosiveness. The product was required to biologically degrade within six hours. Cleaning efficiency, equivalent to current processing, was required.

Phase II - Extended Performance Testing

Extended performance tests on solvents passing the screening tests in Phase I, were conducted at the field test facility at Tinker AFB, Oklahoma. Tests included enhancement methods (effects of temperature, mixer agitation, and ultrasonic agitation); cleaning capacity for wax, oil, and grease as a function of solvent loading; rinsing and drying requirements; and impact on the biological treatment plant at Tinker AFB's IWTP.

Information on the toxicity of selected biodegradable solvents was obtained from the manufacturers and entered in a database.

The solvents were tested to determine their cleaning efficiency. Preliminary tests showed that process enhancement was needed if aircraft parts are to pass the "white glove" test. Hence, tests were conducted using ultrasonic and mixer agitation at various temperatures, with and without rinsing. To test solvent performance, the selected solvents were loaded with various amounts of masking wax, carbonized oil/xylene, or hydraulic fluid, and their cleaning efficiency was measured as a function of solvent loading.

Biological acclamation tests were started on Exxon Exxate 1000 loaded with oil/xylene. In the pilot-scale solids contact clarifier at Tinker AFB, the metal sludge floated to the surface. Subsequent jar tests showed that all of the selected solvents either float or disperse the sludge. However, flotation of the metal sludge can be prevented by adding aluminum sulfate, ferric ion, or magnesium ion. Additionally, magnesium ion addition caused the plant to be more susceptible to upsets from influent changes, and as a result, is not recommended. A product, Fremont 776, was added to the program during Phase III. The product passed all the screening tests that the others had, and did not float or disperse the sludge. Extended corrosion testing indicated that general corrosion occurred in some cases with enhancement techniques, especially with the aqueous solvents. In all cases, no hydrogen embrittlement occurred.

An ASTM guideline is being developed for determining biodegradability. The guideline is based on the Phase I screening procedure and an eight-day protocol that was completed. Protocol testing began by examining the selection of phenol as a test control compound. Also, tests were conducted to define the percentage of error associated with chemical oxygen demand (COD) measurements. The relative error increases as the lower limit of detection is approached and decreases at higher COD analyses. The error appears to be linear. Repeatability tests were also conducted, and COD and adenosine triphosphate (ATP) averages were plotted. The data from the TIC/TOC (total inorganic/total organic carbon) analyses had less variability than the data from COD and TOC analyses. A set of guidelines is being developed by the Air Force and will be submitted for review to the ASTM task group on biological effects and environmental fate. An ASTM set of guidelines will be developed by the ASTM task group on Biological Effects and Environmental Fate. The set of guidelines will include the screening test, the eight-day test protocol and the 21 day test as steps in a series of logical events that industry can use in determining the biodegradability of solvents for use in individual waste treatment plants.

The solvents to be used in the full-scale Phase III tests were selected. They included:

- Exxon Exxate 1000;
- Bio-Tek # 140 Saf-Solv;
- Orange-Sol De-Solv-It;
- 3-D Supreme; and
- Fremont 776.

Phase III - Full Scale Testing

Phase III testing included cleaning Air Force production parts in an intermediate scale 100-gallon agitated tank in a cabinet spray washer and in a full-scale cleaning tank at Tinker AFB.

Results

Each of the solvents tested in the full-scale test program could be applied in cleaning processes at Tinker AFB. As expected from earlier testing, the solvents differed greatly in their performance depending on soil type. Specific recommendations for solvent use are included below.

3-D Supreme. The cabinet spray washer and full-scale tests both indicated that 3-D Supreme was an effective cleaner for Air Force parts. Applied in an agitated tank, it would provide an acceptable

alternative to vapor degreasers now in service. The solvent is effective in removing oils, grease and carbon deposits but should not be considered for wax removal. For both 3-D Supreme and Fremont 776 rinsing the parts with steam or high pressure spray at intermediate points in the cleaning cycle would enhance the cleaning substantially and reduce the overall cleaning-cycle time.

The major drawback in using 3-D Supreme is the impact of disposal of used baths on the solids contact clarifier (SCC) sludge bed at the IWTP. The 3-D Supreme causes the SCC sludge to float. Several solutions to this problem are the addition of small amounts of ferric chloride ($FeCl_3$) to the IWTP process stream; or replace the current polymer addition with an iron bearing polymer. The operator time and chemical and equipment expenses involved could be costly.

It is necessary, when disposing of used 3-D Supreme through an activated sludge system, to maintain a constant feed source to acclimate the bacteria to the material. The microorganisms in the activated sludge (AS) basin feed mostly on phenol and to a lesser extent on other organic constituents in the wastewater. As long as phenol is intermittently available, the organisms will feed on it and will not acclimate to removing other organic constituents as efficiently or completely. Given the constant availability of 3-D Supreme, the organisms would acclimate, as evidenced by reduction in COD and TOC concentrations in the eight-day tests. However, large fluctuations of phenol concentrations would hamper that adjustment. If the solvent were stored and fed into the system continuously, the microorganisms should acclimate and degrade the material.

Fremont 776. The Fremont 776 is in use in a cabinet spray washer, which has been used for cleaning fuel control assemblies. The solvent did not remove molybdenum disulfide grease or wax and did not seem to emulsify the hydraulic oil The full-scale test results showed Fremont 776 being less effective than 3-D Supreme as a cleaner. However, the product performed adequately on oils, grease and carbon soil. The major advantage of Fremont 776 is that it can be released to the industrial wastewater system and treated at the IWTP without modification of the processes in that facility.

Orange Sol De-Solv-It. When enhanced with agitation and elevated temperature, Orange Sol, De-Solv-It is a moderately effective wax remover. The jar tests demonstrated that neither ferric chloride nor aluminum sulfate could prevent the SCC sludge from floating when Orange-Sol was present. For this reason, Orange-Sol should not be added to the Tinker AFB wastewater systems unless the oil and water separator can be shown to remove the material. Attempts to emulsify the Orange-Sol in the jar tests using a high-speed blender were ineffective. Being that resistant to emulsification speaks well for its removal by the oil and water separation system. A study to determine how De-Solve-It effects the oil-water separator will be conducted. Another consideration is that Orange Sol De-Solve-It is expensive, $14.90 per gallon.

Exxon Exxate 1000. Exxate 1000 proved moderately effective for removing wax and could be used in applications such as those described for the Orange-Sol. Application of Exxon's Exxate 1000 has several drawbacks. First, floating the sludge of the metals treatment system occurred, the same problem as with the Orange-Sol. Concentrations of ferric chloride, high enough to ensure the SCC sludge would settle, lowered the pH to a level that was harmful to the activated sludge. Unless the ferric chloride treatment were coupled with a pH adjustment downstream for the SCC, the activated sludge system would be upset. Low pH conditions would also shift the metal precipitation equilibrium, raising the concentration of heavy metals downstream from the SCC. For these reasons, the ferric chloride treatment is not recommended for use with Exxate 1000.

Aluminum sulfate was successful in preventing the floatation of the SCC sludge, with Exxate 1000 present in the waste stream, but the method is costly. The chemical and its handling would be expensive, and the amount of SCC sludge would be increased substantially.

Additionally, considerations are: the distinctive odor of the solvent resulted in complaints of headaches and other discomfort and may require special ventilation considerations; like Orange-Sol, the De-Solv-It, the Exxon product is expensive, $6.24 gallon; the pilot-scale run data demonstrated that the solvent biologically degraded and did not disrupt the activated sludge basin operation.

Bio-Tek # 140 Saf-Solv. The Bio-Tek product was dropped because full-scale testing showed inadequate cleaning of aircraft parts.

Conclusions

The major conclusions of this case study are:

- The Bio-Tek product was eliminated after the 100-gallon tank test due to poor full-scale cleaning efficiencies.
- 3-D Supreme outperformed Fremont 776 in the cabinet spray washer tests. The cabinet spray washer operators stated that the 3-D Supreme cleaned better than detergents currently in use.
- The organic-based solvents, Orange-Sol De-Solv-It and Exxon Exxate 1000, were not tested in the cabinet washer due to explosion hazards.
- Orange-Sol proved to be the best wax remover in the 100-gallon tank test. Exxate 1000 was also moderately effectively for wax removal.
- 3-D Supreme cleaned parts very well in the full-scale tests, removing oil, grease and carbon well enough for 81 percent on the parts to pass normal Air Force inspections. Eight-one percent equals or exceeds current standards. One hundred percent of the parts with only oil and grease passed.
- When soiled with oil, grease and carbon, 64 percent of the parts cleaned with the Fremont 776 passed the inspections. The organic-based solvents did not remove the oil, grease and carbon as well as the water-based solvents.
- Twenty percent of the Orange-Sol parts and 20 percent of the Exxate 1000 parts passed the inspections. The organic-based solvents did remove wax moderately.
- Some parts were successfully painted without blasting, a normal paint preparation step.
- When introduced in quantity, the Fremont 776 product is the only product which will not affect the industrial waste treatment plant. The other solvents while biodegradable, require corrective measures to prevent sludge flotation, and in some cases to initiate biodegradation in the activated sludge system.

CASE STUDY #6: REPLACEMENT OF SOLVENT DEGREASING FOR ENGINEERING PROTOTYPE PARTS, PRECISION MACHINE PARTS, AND VARIOUS CLEANROOM ITEMS

At Company A, CFC-113 in a number of different applications is being replaced. This results in annual CFC-113 reductions of 136,000 lbs. The following are examples of some of these operations.

Engineering Model Shop Prototype Parts

Aqueous spray cleaning has replaced CFC-113 vapor degreasing and cold cleaning of engineering model shop prototype parts. A glove box spray cabinet removes water soluble and solvent-soluble lubricants from parts. A hand held spray wand operating at 400 psi and a flow rate of 2.5 gpm recirculates a heated (100°F) solvent-assisted alkaline cleaner. Dilute concentrations of the cleaner are used to reduce foaming.

Corrosion of the mild steel spray cabinet has been eliminated by the use of a liner. Slight discoloration of some aluminum parts has occurred because of inadequate final rinsing.

Total equipment cost was less than $5,000. Annual CFC-113 savings amount to 24,000 lbs. ($67,200 at 1990 prices).

Precision Machined Parts

Ultrasonic cleaning with a solvent assisted alkaline cleaner has replaced CFC-113 cold cleaning of precision machined piece parts. Removal of machine lubricants (water and solvent soluble) using bench top ultrasonic cleaners at each work station has replaced sloshing parts in CFC-113 solvent.

The cleaner is maintained between 120° and 140°F. Cleaning time is 10 to 30 seconds at a frequency of 40 kHz. A deionized water rinse and air dry follow the cleaning step. Emphasis is placed on thorough rinsing and drying.

Total capital equipment cost for 75 bench top ultrasonic units was $26,000. Annual CFC-113 savings amount to 86,000 lbs. ($240,800 at 1990 prices).

Various Cleanroom Items

CFC-113 used in wiping and rinsing applications in cleanrooms was replaced with a volatile aqueous cleaner. The cleaner is a blend of high purity water, isopropyl alcohol, ammonium hydroxide and two surfactants. It is essentially 100 percent volatile and leaves ultra-low cleaner residue. Items cleaned include gloves, finger cots, and clean bench work surfaces. Wet cleaning was necessary because dry wiping and blow-off were determined to be inadequate for the desired cleanliness level.

After nonvolatile residue testing, minor surface tests, cleanroom wipe evaluation, corrosion and electrical contact checks all showed positive results, this technology was implemented. However, some rusting of tool steel fixtures has occurred. (Rusting is prevented with proper drying.)

The cleaner is packaged and dispensed in precleaned spray bottles. The cleaner costs approximately $1 per gallon for materials. Annual CFC-113 savings from this technology amounts to 26,000 lbs. ($72,800 at 1990 prices).

CASE STUDY #7: PROGRAM TO ELIMINATE METHYL CHLOROFORM USE IN STEEL CHAIR MANUFACTURING OPERATIONS

Case Study #7 is an overview of how LA-Z-BOY, Monroe, Michigan, a large manufacturer of furniture, converted a methyl chloroform vapor degreasing process to a semi-aqueous based process. The company previously had used methyl chloroform to clean oil and metal fines from stamped carbon steel chair parts prior to painting. LA-Z-BOY decided to switch to a semi-aqueous based process using Bio T Max (a citrus terpene based cleaning agent). LA-Z-BOY is satisfied with the new semi-aqueous based cleaning process and has found considerable improvement in paint adhesion compared to their old system.

Process Description

Installing the Bio T cleaning process involved modifying the existing vapor degreaser tank so that it could be used as a dip tank for the wash stage. The capacity of this tank is 1,558 gallons. The rinse tank used for the semi-aqueous process is an old wash tank that had been previously utilized in the facility. The rinse tank has a capacity of 1,100 gallons. Both the wash and rinse tanks were fitted with spray nozzles and 95 gpm feed pumps to recirculate the water.

The wash and rinse stages are operated at room temperature using DI water as the cleaning medium. The concentration of Bio T in the wash tank is maintained at 8-10 percent concentration.

Parts to be cleaned are placed on hooks on a monorail, and undergo the following sequence of steps (see Exhibit 18):

- Parts are processed through the wash and rinse stages. The wash and rinse cycles last about 5-10 minutes depending on the level of soil loading and the throughput required. The time in the wash and rinse tanks is set by adjusting the speed of the monorail.

- Next, the parts are painted by processing them through a water based paint tank and a paint rinse tank. Parts are painted using an electro-deposition process using water based paints. The paint process is the same as that used with the old vapor degreasing process.

- After painting, the parts are passed through a dryer. The dryer is also the same as that used with the old vapor degreasing process.

- After the parts exit the dryer, they are unloaded and new parts are loaded onto the monorail. The loaded parts then enter the wash stage and repeat the above sequence of steps.

The semi-aqueous system is set up so that the permeate from the rinse tank that contains the carry over of Bio T from the wash tank is fed back to the wash tank. Both tanks are made up with DI water to maintain the tank water level. This is necessary to make up for water loss due to drag out and evaporation.

The semi-aqueous cleaning system is equipped with an on-line filter used to remove residue metal fines and chips, and an oil absorbent filters used to remove free floating oil. It has been noted that during the night when the system is shut down, oil separates and floats to the top. This oil is skimmed off before the unit is turned on in the mornings.

Capital and Operating Costs

LA-Z-BOY estimates that the capital costs associated with this process is $8,211. This is based on costs for:

- Two sock type filtering systems (100 gpm);

- Two bottom feed pumps (3,450 rpm, 95 gpm);

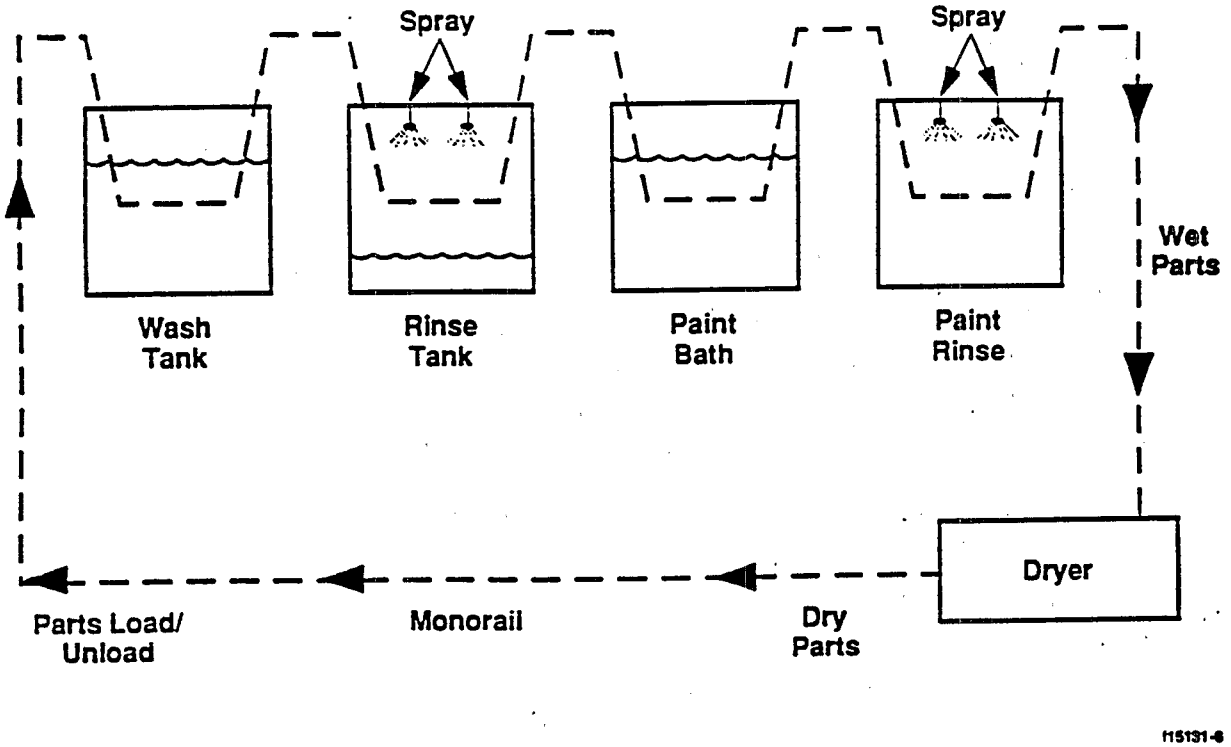
- Sandblasting and painting of rinse tank;

- Miscellaneous parts, pipe fittings, etc;
- 5 drums (each 55 gallons) initial fill for the semi-aqueous process; and
- Labor.

LA-Z-BOY estimates that the operating costs of the semi-aqueous based process is about half that of the methyl chloroform based process. This is based of the fact that one drum of Bio T is used per month. At a cost of $16.5 per gallon, this results in monthly costs of $907.5. The monthly cost of the solvent process was estimated at $1.836. This includes cost of virgin solvent & costs of disposal of waste solvent. The cost calculations for the solvent and semi-aqueous process do not include energy costs of operating the vapor degreaser and the recirculating pumps respectively. However, it is believed that the aqueous process energy costs are not higher than the solvent process energy costs.

Exhibit 18

AQUEOUS PROCESS FOR CARBON STEEL CHAIR PARTS



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List of Vendors for CFC-113 and Methyl Chloroform Solvent Cleaning Substitutes*

Alternative Solvents

Allied-Signal
PO Box 1139 R
Morristown, NJ 07960
Tel: (201) 455-4848
Fax: (201) 455-2745

Arco Chemical Company
3801 West Chester Pike
Newton Square, PA 19073

Dow Chemical
2020 Dow Center
Midland, MI 48674
Tel: (517) 636-8325

Exxon Chemical Company
P.O. Box 3272
Houston, TX 77001
Tel: (800) 231-6633

Daikin Industries, Ltd.
Chemical Division
1-1 Nishi Hitotsuya
Settsu-Shi, Osaka 566
Japan
Tel: 81-6-349-5331

DuPont Chemicals
Customer Service
B-15305
Wilmington, DE 19898
Tel: 1-800-441-9450

GAF Chemicals Corporation
1361 Alps Rd.
Wayne, NJ 07470
Tel: (201) 628-3847

ICI Americas Inc.
P.O. Box 751
Wilmington, DE 19897
Tel: (302) 886-4469

Aqueous Cleaners

Ardrox
16961 Knott Avenue
La Mirada, CA 90638
Tel: (714) 739-2821

Brulin
2920 Dr. Andrew J. Brown, Ave.
PO Box 270
Indianapolis, IN 46206
Tel: (317) 923-3211

DuBois Chemicals, Inc.
511 Walnut Street
Cincinnati, OH 45202
Tel: (513) 762-6839

Freemont Industries, Inc.
Valley Industrial Park
Shakopee, MN 55379
Tel: (612) 445-4121

* This is not an exhaustive list of vendors. For more names check the Thomas Register. Vendors can be cited in subsequent editions of this document by sending information to ICOLP. ICOLP's address is provided in Appendix A. Listing is for information purposes only, and does not constitute any vendor endorsement by EPA or ICOLP, either express or implied, of any product or service offered by such entity.

Hubbard-Hall, Inc.
P.O. Box 790
Waterbury, CT 06725
Tel: 203-754-2171

Modern Chemical Inc.
P.O. Box 368
Jacksonville, AR 72076
Tel: (501) 988-1311
Fax: (501) 682-7691

Parker-Amchem
32100 Stephenson Highway
Madison Heights, MI 48071
Tel: (313) 583-9300

W.R. Grace & Co.
55 Hayden Avenue
Lexington, MA 02173
Tel: (617) 861-6600

Intex Products Co.
P.O. Box 6648
Greenville, SC 29606
Tel: (803) 242-6152

Oakite Products, Inc.
50 Valley Road
Berkeley Heights, NJ 07922
Tel: (201) 464-6900

Qual Tech Enterprises, Inc.
1485 Bayshore Blvd.
San Francisco, CA 94124
Tel: (415) 467-7887
Fax: (415) 467-7092

3-D Inc.
2053 Plaza Drive
Benton Harbor, MI 49022
Tel: (800) 272-5326

Aqueous Cleaning Equipment

American Metal Wash
360 Euclid Avenue
PO. Box 265
Canonsburg, PA 15317
Tel: (412) 746-4203
Fax: (412) 746-5738

Branson Ultrasonics Corp.
41 Eagle Road
Danbury, CT 06813-1961
Tel: (203) 796-0400

Electrovert Corp.
4330 Beltway Place
Suite 350
Arlington, TX 76017
Tel: (817) 468-5171

Jensen Fabricating Engineers
P.O Box 362
East Berlin, CT 06023
Tel: (203) 828-6516

Bowden Industries
1004 Oster Drive NW
Huntsville, AL 35816
Tel: (205) 533-3700
Fax: (205) 539-7917

Crest Ultrasonics Corp.
Scotch Rd.
Mercer County Airport
P.O. Box 7266
Trenton, NJ 08628
Tel: (609) 883-4000

Graymills
3705 N. Lincoln Ave.
Chicago, IL 60613
Tel: (312) 268-6825

J. M. Ney Company
Neytech Division
Bloomfield, CT 06002
Tel: (203) 342-2281
Fax: (203) 242-5688

Stoelting Inc.,
502 Highway 67
PO Box 127
Kiel, WI 53042
Tel: (414) 894-2293
Fax: (414) 894-7029

Hydrocarbon/Surfactant

Crest Ultrasonics Corp.
P.O. Box 7266
Scotch Road
Mercer County Airport
Trenton, NJ 08628
Tel: (609) 883-4000

DuPont Chemicals
Customer Service
B-15305
Wilmington, DE 19898
Tel: 1-800-441-9450

Golden Technologies Company, Inc.
Biochem Systems Division
15000 W. 6th Avenue
Suite 202
Golden, CO 80401
Tel: (303) 277-6577
Fax: (303) 277-6550

Penetone Corporation
74 Hudson Avenue
Tenafly, NJ 07670
Tel: (201) 567-3000

Union Camp
P.O. Box 37617
Jacksonville, Fl 32236
Tel: (904) 783-2180

Alcohol Cleaning Equipment

Electronic Control Design
13626 South Freeman Road
Milwaukie, OR 97222-8825
Tel: (503) 829-9108
Fax: (503) 659-4422

Unique Industries
11544 Sheldon St.
P.O. Box 1278
Sun Valley, CA 91353
Tel: (213) 875-3810

Detrex Corporation
P.O. Box 569
401 Emmett Ave.
Bowling Green, KY 42102
Tel: (502) 782-1511

Electrovert Corp.
4330 Beltway Place
Suite 350
Arlington, TX 76017
Tel: (817) 468-5171

Orange-Sol Inc.
Dennis Weinhold
P.O. Box 306
Chandler, AZ 85244
(602) 497-8822

Petroferm
5400 East Coast Highway
Fernandina Beach, FL 32034
Tel: (904) 261-8286
Fax: (904) 261-6994

Herbert Streckfus GmbH
Elektronik-Sondermaschinenbau
7814 Eggenstein 1
Kruppstrabe 10
Germany
Tel: (0721) 70222-24
Telex: 7 826 566
Ttx: 721119
Fax: 0721/785966

KLN Ultraschall GmbH
Siegfriedstr. 124
D-6148 Heppenheim
Germany
Tel: 6252/14-0
Teletex: 625290
Fax: 6262/14-277

Streckfuss USA, Inc.
3829 W. Conflans
P.O. Box 153609
Irving, TX 75015-3409
Tel: (214) 790-1614

GLOSSARY

Acute toxicity -- The short-term toxicity of a product in a single dose. Can be divided into oral, cutaneous and respiratory toxicities.

Adsorption -- Not to be confused with absorption. Adsorption is a surface phenomenon which some products can exhibit, whereby they can form a physicochemical bond with many substances.

Alcohols -- A series of hydrocarbon derivatives with at least one hydrogen atom replaced by an -OH group. The simplest alcohols (methanol, ethanol, n-propanol, and isopropanol) are good solvents for some organic soils, notably rosin, but are flammable and can form explosive mixtures with air: their use requires caution and well-designed equipment.

Aqueous cleaning -- Cleaning parts with water to which may be added suitable detergents, saponifiers or other additives.

Azeotrope -- A mixture of chemicals is azeotropic if the vapor composition is identical to that of the liquid phase. This means that the distillate of an azeotrope is theoretically identical to the solvents from which it is distilled. In practice, the presence of contaminants in the solvent slightly upsets the azeotropy.

Biodegradable -- Products in wastewater are classed as biodegradable if they can be easily broken down or digested by, for example, sewage treatment.

BOD -- An abbreviation for biochemical oxygen demand.

CFC -- An abbreviation for chlorofluorocarbon.

CFC-113 -- A common designation for the most popular CFC solvent, 1,1,2-trichloro-1,2,2-trifluoroethane, with an ODP of approximately 0.8.

Chelation -- is the solubilization of a metal salt by forming a chemical complex or sequestering. One way of doing this is with ethylenediaminetetra-acetic acid (EDTA) salts which have a multi-dentate spiral ligand form that can surround metallic and other ions.

Chlorofluorocarbon -- An organic chemical composed of chlorine, fluorine and carbon atoms, usually characterized by high stability contributing to a high ODP.

Chronic toxicity -- The long-term toxicity of a product in small, repeated doses. Chronic toxicity can often take many years to determine.

COD -- An abbreviation for chemical oxygen demand.

Detergent -- A product designed to render, for example, oils and greases soluble in water, usually made from synthetic surfactants.

Fatty acids -- The principal part of many vegetable and animal oils and greases, also known as carboxylic acids which embrace a wider definition. These are common contaminants for which solvents are used in their removal. They are also used to activate fluxes.

Greenhouse effect -- A thermodynamic effect whereby energy absorbed at the earth's surface, which is normally able to radiate back out to space in the form of long-wave infrared radiation, is retained by gases in the atmosphere, causing a rise in temperature. The gases in question are partially natural, but man-made pollution is thought to increasingly contribute to the effect. The same CFCs that cause ozone depletion are known to be "greenhouse gases", with a single CFC molecule having the same estimated effect as 10,000 carbon dioxide molecules.

HCFC -- An abbreviation for hydrochlorofluorocarbon.

HFC -- An abbreviation for hydrofluorocarbon.

Hydrocarbon/surfactant blend -- A mixture of low-volatile hydrocarbon solvents with surfactants, allowing the use of a two-phase cleaning process. The first phase is solvent cleaning in the blend and the second phase is water cleaning to remove the residues of the blend and any other water-soluble soils. The surfactant ensures the water-solubility of the otherwise insoluble hydrocarbon. Terpenes and other hydrocarbons are often used in this application.

Hydrochlorofluorocarbon -- An organic chemical composed of hydrogen, chlorine, fluorine and carbon atoms. These chemicals are less stable than pure CFCs, thereby having generally lower ODPs.

Metal cleaning -- General cleaning or degreasing of metallic components or assemblies, without specific quality requirements or with low ones.

Methyl chloroform -- See 1,1,1-trichloroethane.

ODP -- An abbreviation for ozone depletion potential.

Ozone -- A gas formed when oxygen is ionized by, for example, the action of ultraviolet light or a strong electric field. It has the property of blocking the passage of dangerous wavelengths of ultraviolet light. Whereas it is a desirable gas in the stratosphere, it is toxic to living organisms at ground level (see volatile organic compound).

Ozone depletion -- Accelerated chemical destruction of the stratospheric ozone layer by the presence of substances produced, for the most part, by human activities. The most depleting species for the ozone layer are the chlorine and bromine free radicals generated from relatively stable chlorinated, fluorinated, and brominated products by ultraviolet radiation.

Ozone depletion potential -- A relative index indicating the extent to which a chemical product may cause ozone depletion. The reference level of 1 is the potential of CFC-11 and CFC-12 to cause ozone depletion. If a product has an ozone depletion potential of 0.5, a given weight of the product in the atmosphere would, in time, deplete half the ozone that the same weight of CFC-11 would deplete. The ozone depletion potentials are calculated from mathematical models which take into account factors such as the stability of the product, the rate of diffusion, the quantity of depleting atoms per molecule, and the effect of ultraviolet light and other radiation on the molecules.

Ozone layer -- A layer in the stratosphere, at an altitude of approximately 10-50 km, where a relatively strong concentration of ozone shields the earth from excessive ultraviolet radiation.

Saponifier -- A chemical designed to react with organic fatty acids, such as rosin, some oils and greases etc., in order to form a water-soluble soap. This is a solvent-free method of defluxing and degreasing many parts. Saponifiers are usually alkaline and may be mineral (based on sodium hydroxide or potassium hydroxide) or organic (based on water solutions of monoethanolamine).

Solvent -- Although not a strictly correct definition, in this context a product (aqueous or organic) designed to clean a component or assembly by dissolving the contaminants present on its surface.

Surfactant -- A product designed to reduce the surface tension of water. Also referred to as tensio-active agents/tensides. Detergents are made up principally from surfactants.

Terpene -- Any of many homocyclic hydrocarbons with the empirical formula $C_{10}H_{16}$, characteristic odor. Turpentine is mainly a mixture of terpenes. See hydrocarbon/surfactant blends.

Volatile organic compound (VOC) -- These are constituents that will evaporate at their temperature of use and which, by a photochemical reaction, will cause atmospheric oxygen to be converted into potential smog-promoting tropospheric ozone under favorable climatic conditions.

APPENDIX A

INDUSTRY COOPERATIVE FOR OZONE LAYER PROTECTION

The Industry Cooperative for Ozone Layer Protection (ICOLP) was formed by a group of industries to protect the ozone layer. The primary role of ICOLP is to coordinate the exchange of non-proprietary information on alternative technologies, substances, and processes to eliminate ozone-depleting solvents. By working closely with solvent users, suppliers, and other interested organizations worldwide, ICOLP seeks the widest and most effective dissemination of information harnessed through its member companies and other sources.

ICOLP corporate members include:

- AT&T
- Boeing Company
- British Aerospace
- Compaq Computer Corporation
- Digital Equipment Corporation
- Ford Motor Company
- General Electric
- Hitachi Limited
- Honeywell
- IBM
- Matsushita Electric Industrial Company
- Mitsubishi Electric Corporation
- Motorola
- Northern Telecom
- Sundstrand
- Texas Instruments
- Toshiba Corporation

In addition, ICOLP has a number of industry association and government organization affiliates. Industry association affiliates include American Electronics Association (AEA), Electronics Industries Association, Japan Electrical Manufacturers Association and Halogenated Solvents Industry Alliance (U.S.). Government organization affiliates include the City of Irvine, California, the State Institute of Applied Chemistry (U.S.S.R.), the Swedish National Environmental Protection Agency, the U.S. Air Force, and the U.S. Environmental Protection Agency (EPA). The American Electronics Association, the Electronic Industries Association, the City of Irvine, California, the Japan Electrical Manufacturers Association, the Swedish National Environmental Protection Agency, the U.S. EPA, the U.S. Air Force, and the U.S.S.R. State Institute of Applied Chemistry have signed formal Memorandums of Understanding with ICOLP. ICOLP will work with the U.S. EPA to disseminate information on technically feasible, cost effective, and environmentally sound alternatives for ozone depleting solvents.

ICOLP is also working with the National Academy of Engineering to hold a series of workshops to identify promising research directions and to make most efficient use of research funding.

The goals of ICOLP are to:

- Encourage the prompt adoption of safe, environmentally acceptable, nonproprietary alternative substances, processes, and technologies to replace current ozone-depleting solvents;
- Act as an international clearinghouse for information on alternatives;
- Work with existing private, national, and international trade groups, organizations, and

government bodies to develop the most efficient means of creating, gathering, and distributing information on alternatives.

One example of ICOLP's activities is the development and support of an alternative technologies electronic database "OZONET." OZONET is accessible worldwide and has relevant information on the alternatives to ozone-depleting solvents. OZONET not only contains technical publications, conference papers, and reports on the most recent developments of alternatives to the current uses of ozone-depleting solvents, but it also contains:

- Information on the health, safety and environmental effects of alternative chemicals and processes;
- Information supplied by companies developing alternative chemicals and technologies;
- Names, addresses, and telephone numbers for technical experts, government contacts, institutions and associations, and other key contributors to the selection of alternatives;
- Dates and places of forthcoming conferences, seminars, and workshops;
- Legislation that has been enacted or is in place internationally, nationally, and locally.

Information about ICOLP can be obtained from:

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