Alternatives for CFC-113 and Methyl Chloroform in Metal Cleaning

Final

June 1991
Revised October 1994

Printed on Recycled Paper

ALTERNATIVES FOR CFC-113 AND METHYL CHLOROFORM IN METAL CLEANING

by

ICOLP Technical Committee*

Earl Groshart (Chairman)
George Bohnert
Charles Carpenter
Stephen Evanoff
John Golden
Greg Hollingsworth
Stewart Holm
Michael Oborny
Farzan Riza
Ronald Stephenson

Stephen O. Andersen
U.S. Environmental Protection Agency

Revised by

Stephen O. Andersen, U.S. Environmental Protection Agency
Nina Bonnelycke, U.S. Environmental Protection Agency
John Sparks, U.S. Environmental Protection Agency
Michael Zatz, ICF Incorporated

---

* ICOLP is the International Cooperative for Ozone Layer Protection. ICOLP corporate member companies include AT&T, British Aerospace Defense, Ford Motor Company, Hitachi, Honeywell, IBM Corporation, Mitsubishi Electric Corporation, Motorola Corporation, Ontario Hydro, Northern Telecom, Texas Instruments, and Toshiba Corporation. Industry association affiliates include American Electronics Association, Association Pour la Research et Development des Methodes et Processus Industriels, CANACINTRA (Mexico), Center for Global Change, Electronic Industries Association, Halogenated Solvents Industry Alliance (U.S.), Industrial Technology Research Institute of Taiwan, Japan Electrical Manufacturers Association, Korea Anti-Pollution Movement, and Korea Specialty Chemical Industry Association. Government and NGO affiliates include the City of Irvine (CA), National Academy of Engineering, Research Triangle Institute, Russian Institute of Applied Chemistry, Russian Ministry of Environmental Protection and Natural Resources, Swedish National Environmental Protection Agency, Technology Development Foundation of Turkey, Turkish Ministry of the Environment, United Nations Environment Programme, U.S. Air Force, and U.S. Environmental Protection Agency (EPA).

Earl Groshart, John Golden and Ronald Stephenson are employed by Boeing; George Bohnert is employed by Allied Signal Aerospace; Stephen Evanoff is employed by General Dynamics; Stewart Holm is employed by Halogenated Solvents Industry Alliance; Greg Hollingsworth is employed by Honeywell; Farzan Riza is employed by ICF Incorporated; Michael Oborny is employed by Sandia National Laboratories; and Charles Carpenter is employed by the U.S. Air Force. We would like to thank the many individuals and companies that provided insight and information that helped produce this manual. This manual was funded by the U.S. EPA and ICOLP.

Disclaimer

The U.S. Environmental Protection Agency (EPA), the International Cooperative for Ozone Layer Protection (ICOLP), the ICOLP committee members, and the companies that employ the ICOLP committee members do not endorse the cleaning performance, worker safety, or environmental acceptability of any of the technical options discussed. Every cleaning operation requires consideration of worker safety and proper disposal of contaminants and waste products generated from cleaning processes. Moreover, as work continues, including additional toxicity testing and evaluation under Section 612 (Safe Alternatives Policy) of the Clean Air Act Amendments of 1990 and elsewhere, more information on the health, environmental and safety effects of alternatives will become available for use in selecting among alternatives discussed in this document.

EPA and ICOLP, in furnishing or distributing this information, do not make any warranty or representation, either express or implied, with respect to its accuracy, completeness or utility; nor does EPA and ICOLP assume any liability of any kind whatsoever resulting from the use of, or reliance upon, any information, material, or procedure contained herein, including but not limited to any claims regarding health, safety, environmental effects or fate, efficacy, or performance, made by the source of the information.

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

Table of Contents

Table of Contents (Continued)

List of Exhibits

FOREWORD

This manual has been developed jointly by the International Cooperative for Ozone Layer Protection (ICOLP) and the U.S. Environmental Protection Agency (EPA) to aid the phaseout of ozone-depleting substances (ODSs) in metal cleaning applications. It will prove useful to manufacturers world-wide because the procedures used to clean metal parts apply to all manufacturers, regardless of location or size. The manual has been prepared by the U.S. EPA and an international committee of experts from the solvent cleaning industry. Committee members represent both developed and developing countries.

The manual describes a step-by-step approach for characterizing the use of ozone-depleting solvents and identifying and evaluating alternatives. It is a "how-to" document which describes all of the steps necessary to successfully phase out the use of CFC-113 and methyl chloroform (MCF) in metal cleaning applications. Many of the alternatives described are currently in use at major companies around the world. The manual addresses primary cleaning applications and gives brief descriptions of the commercially available alternatives to CFC-113 and MCF. The manual provides sufficient technical information on the solvent alternatives to enable users to gather more detailed information on their alternatives of choice. A list of equipment and materials vendors is provided to facilitate such further research.

The Montreal Protocol

The 1987 Montreal Protocol on Substances that Deplete the Ozone Layer and subsequent 1990 and 1992 amendments and adjustments control the production and consumption of ODSs internationally. As a result of the most recent meetings in Copenhagen in November 1992, two chemicals commonly used as solvents are scheduled to be phased out. The 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 1996, and in developing countries between 2006 and 2015, depending on decisions taken by the Parties to the Protocol in 1995. In addition, the 1992 amendments include a developed country production freeze and reduction schedule for hydrochlorofluorocarbons (HCFCs), with a phaseout in developed countries by the year 2030.

Exhibit 1 lists the countries that are Parties to the Montreal Protocol as of February 1994. In addition, many companies world-wide have corporate policies to expedite the phaseout of ozone-depleting chemicals. Exhibit 2 lists corporations around the world that have successfully phased out their use of ODSs.

In addition to providing regulatory schedules for the phaseout of ODSs, the Montreal Protocol established a fund that will finance the agreed incremental costs of phasing out ODSs by eligible developing countries that are Party to the Protocol. Eligible countries are defined as those developing countries having a total annual consumption of CFCs of less than 0.3 kg per person, and of MCF and carbon tetrachloride of less than 0.2 kg per person.

International Phaseout Schedules

Several countries have passed legislation to phase out CFC-113 and MCF earlier than target dates set by the Montreal Protocol in an effort to slow ongoing depletion of the stratospheric ozone layer. Their policies are summarized below.

Canada

Environment Canada, the federal agency responsible for environmental protection in Canada, enacted a CFC phaseout program more stringent than the Montreal Protocol. 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. Production, imports, and exports of CFCs are to be eliminated by January 1, 1996, with a 75 percent reduction by January 1, 1994. For carbon tetrachloride, the phaseout date is January 1, 1995 -- one year earlier than that mandated by the

Montreal Protocol. Halons were eliminated by January 1, 1994. Production, imports, and exports of MCF will be halted by January 1, 1996, with interim reductions of 50 percent by January 1, 1994, and 85 percent by January 1, 1995.

European Community

Under the Single European Act of 1987, the twelve members of the European Community (EC) are

Exhibit 1

PARTIES TO THE MONTREAL PROTOCOL

Algeria
Antigua and Barbuda
Argentina
Australia
Austria
Bahamas
Bahrain
Bangladesh
Barbados
Belarus
Belgium
Benin
Bosnia/Herzegovina
Botswana
Brazil
Brunei Darussalam
Bulgaria
Burkina Faso
Cameroon
Canada
Central African Republic
Chile
China
Colombia
Congo
Costa Rica
Cote d'Ivoire
Croatia
Cuba
Cyprus
Czech Republic
Denmark
Dominica
Ecuador
Egypt
El Salvador
EEC
Fiji
Finland
France
Gambia
Germany
Ghana
Greece
Grenada
Guatemala
Guinea
Guyana
Honduras
Hungary
Iceland
India
Indonesia
Iran
Ireland
Israel
Italy
Jamaica
Japan
Jordan
Kenya
Kiribati
Kuwait
Lebanon
Libyan Arab Jamahiriya
Liechtenstein
Luxembourg
Malawi
Malaysia
Maldives
Malta
Marshall Islands
Mauritius
Mexico
Monaco
Morocco
Myanmar
Namibia
Netherlands
New Zealand
Nicaragua
Niger
Nigeria
Norway
Pakistan
Panama
Papua New Guinea
Paraguay
Peru
Philippines
Poland
Portugal
Romania
Republic of Korea
Russian Federation
St. Kitts and Nevis
St. Lucia
Samoa
Saudi Arabia
Senegal
Seychelles
Singapore
Slovakia
Slovenia
Solomon Islands
South Africa
Spain
Sri Lanka
Sudan
Swaziland
Sweden
Switzerland
Syrian Arab Republic
Tanzania
Thailand
Togo
Trinidad & Tobago
Tunisia
Turkey
Turkmenistan
Tuvalu
Uganda
Ukraine
United Arab Emirates
United Kingdom
United States
Uruguay
Uzbekistan
Venezuela
Viet Nam
Yugoslavia
Zambia
Zimbabwe

Date: February 1994

Exhibit 2

SUCCESSFUL CORPORATE OZONE-DEPLETING SOLVENT PHASEOUTS

A-dec
ADC Telecommunications
Advanced Micro Devices
Alcatel Network Systems
Apple Computer
Applied Magnetics
Aishin Seiki
Alps Electric
AT&T
Cadillac Gage
Calsonic
Canon
Corbin Russwin Hardware
Casio Computer
Chip Supply
Citizen Watch
Clarion
Compaq Computers
Conner Peripherals
Commins Engine
Diatek
Fuji Photo Film
Fujitsu
Funac
Harris Semiconductors
Hewlett Packard
Hitachi
Hitachi Metals
IBM
Iki Electric
Isuzu Motors
ITT Cannon
Japan Aviation Electronics
Kilovac
Kohyo Seiko
Kyocera
Mabuchi Motor
Matsushita
MDM
Minebea
Minolta Camera
Mitsubishi Electric
Mitsubishi Heavy Industry
Mitsubishi Motors
Mitsui High-tech
Motorola
Murata Erie N.A.
Murata Manufacturing
National Semiconductor
NEC
NHK Spring
Nihon Dempa Kogyo
Nissan
Nissan Diesel Motor
Northern Telecom
NRC
NSK
Olympus Optical
Omron
OTC/SPX
Pacific Scientific EKD
Ricoh
Rohm
Sanyo MEG
Sanyo Energy
Seagate Technology
Seiko Epson
Seiko-sha
Sharp
Shin-etsu Polymer
SMC
Sony
Stanley Electric
Sumitomo Electric
Sumitomo Special Metals
Sun Microsystems
Suzuki Motor
Symmons Industries
Taiyo Yuden
Talley Defense Systems
Thomson Consumer Electronics
3M
Toshiba
Toshiba Display Devices
Toyota Motor
Unisia JECCS
Victor Japan
Yamaha
Yokogawa Electric
Zexel

subject to environmental directives issued by the EC Governing Council. 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 includes regulatory provisions for the production of substances that deplete the ozone layer. The EC phaseout schedule for CFC-113 production is more exacting than the Montreal Protocol. It called for an 85 percent reduction of CFC-113 production by January 1, 1994 and a complete phaseout by January 1, 1995. For MCF, the schedule called for a 50 percent cut in production by January 1, 1994 and a complete phaseout by January 1, 1996. While all members must abide by these directives, Council Regulation number 3322/88 of October 31, 1988 states that EC members may take even more extensive unilateral measures to protect the ozone layer.

European Free Trade Agreement Countries

The European Free Trade Agreement (EFTA) countries of Austria, Finland, Iceland, Norway, Sweden, and Switzerland, have each adopted measures to completely phase out fully-halogenated ODSs. Austria, Finland, Norway, and Sweden will completely phase out their use of CFC-113 in all applications by January 1, 1995. Sweden plans to phase out MCF by this date as well. In addition, some EFTA countries have set sector-specific interim phaseout dates for certain solvent uses. Austria phased out CFC-113 in a number of solvent cleaning applications by January 1, 1994. Norway and Sweden eliminated their use of CFC-113 on July 1, 1991 and January 1, 1991, respectively for all applications except textile dry cleaning.

Japan

On May 13, 1992, the Ministry of International Trade and Industry (MITI) requested its 72 Industrial Associations to phase out CFC and MCF usage by the end of 1995.

United States

The U.S. Clean Air Act (CAA), as amended in 1990, contains several provisions pertaining to stratospheric ozone protection. ODSs are categorized by the CAA as either Class I or Class II substances. Class I substances include MCF, three types of halons, carbon tetrachloride, and all fully-halogenated CFCs, including CFC-113. Class II substances include 33 types of hydrochlorofluorocarbons (HCFCs). The sections of the CAA important to users of this manual are discussed below.

- ***Section 112: National Emission Standards for Hazardous Air Pollutants***

  This section of the CAA requires the EPA to develop emissions standards for 189 chemical compounds listed as hazardous air pollutants (HAPs). The list of HAPs includes the chlorinated solvents as well as many organic solvents likely to be used in cleaning metal parts.

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

  These sections detail the phaseout schedule for both Class I and Class II substances. EPA accelerated the schedule in response to both former President George Bush's call for a more rapid phaseout and the recent amendments made to the Protocol in Copenhagen.

- ***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 and Class II substances during their manufacture, use, storage, or disposal.

- ***Section 611: Labeling***

  This section directed EPA to issue regulations requiring the labeling of products that contain or were manufactured with Class I and Class II substances. Containers in which Class I and Class II substances are stored must also be labeled. 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 label must clearly identify the ODS by chemical name for easy recognition by average consumers, and must be placed so that it is clearly legible and conspicuous.

  Labeling regulations affecting Class I substances took effect on May 15, 1993. Products containing or manufactured with a Class II substance must be labeled no later than January 1, 2015.

- ***Section 612: Safe Alternatives Policy***

Section 612 establishes a framework for evaluating the overall environmental and human health impact of current and future alternatives to ozone-depleting solvents. Such regulation ensures that ODSs will be replaced by substitutes that reduce overall risks to human health and the environment. As a result of provisions set in Section 612, the Environmental Protection Agency:

- Issued rules in November 1992 that make it unlawful to replace any Class I and Class II substance with a substitute that may present adverse effects to human health and the environment when the EPA has identified an available or potentially available alternative that can reduce the overall risk to human health and the environment.
- Has published a list of prohibited substitutes, organized by use sector, and a list of the corresponding alternatives;
- Will accept petitions to add or delete a substance previously listed as a prohibited substitute or an acceptable alternative;
- Requires any company that produces a chemical substitute for a Class I substance to notify EPA 90 days before the 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 has (1) conducted environmental risk characterizations for substitutes in each end use and (2) established the Significant New Alternatives Program (SNAP) to evaluate the substitutes for Class I substances. EPA 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 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 are also considered. EPA has organized these assessments by use sector (i.e. solvents, refrigeration, etc). The risk characterizations result in risk-management strategies for each sector and substitute. EPA has also categorized each substance as unacceptable, acceptable with limitations on use or quantity, acceptable without comment, or delayed pending further study. Petitions are allowed to change a substance's status with the burden of proof on the petitioner.

In early 1994, the EPA issued a list of alternatives it found to be acceptable and unacceptable according to this framework in its Significant New Alternatives Policy (SNAP) Program ruling. The list will be updated regularly as new alternatives become available.

Excise Tax

As an incentive to reduce the production and consumption of ODSs in the U.S., Congress placed an excise tax on ODSs manufactured or imported for use in the U.S. Taxes do not apply to recycled chemicals. This tax provides a further incentive to use alternatives and substitutes to CFC-113 and MCF and to recycle used chemicals. The tax amounts are based on each chemical's ozone-depleting potential. These taxes have recently been increased as a part of the U.S. Congress' comprehensive energy bill of 1992.

Calendar Year	Tax Amount Per Pound	
	CFC-113	MCF
1991	$1.096	$0.137
1992	$1.336	$0.167
1993	$2.68	$0.211
1994	$3.48	$0.435
1995	$4.28	$0.535

Cooperative Efforts

Japan

The Japanese Ozone Layer Protection Act gives its Ministry of International Trade and Industry (MITI) the authorization to issue restrictions on ODSs. MITI and the Environmental Agency have established the "Guidelines for Discharge Reduction and Use Rationalization." Based upon these guidelines, various government agencies have provided administrative guidance and advice to the industries under their respective jurisdictions. Specifically, MITI worked with the Japan Industrial Conference for Ozone Layer Protection (JICOP) to prepare two manuals that provide technical information on alternatives to CFC-113 and MCF. The manuals are titled:

- Manual for Phasing-Out 1,1,1-Trichloroethane; and
- Manual for Reduction in the Use of Ozone-Depleting Substances.

MITI also encourages industry to reduce consumption of ODSs through economic measures such as tax incentives to promote the use of equipment to recover and reuse solvents.

Sweden

The Government/Industry/Research Institution sectors are conducting two major cooperative efforts targeting the phaseout of ODSs and chlorinated solvents:

- The TRE-project (Technology for Clean Electronics); and
- The AMY-project (Cleaning of Metallic surfaces).

In addition, direct support is being provided to industry for industrial scale introduction of new technologies. These are, to name a few, closed loop systems, microbiological cleaning systems, ion exchange technologies, electrochemical cleaning systems, vacuum evaporation systems, reverse osmosis, and alternative solvent-based systems.

United States

EPA has been working with industry to disseminate information on technically-feasible, cost-effective, and environmentally-sound alternatives to ODSs. As part of this effort, the Agency, along with ICOLP, prepared a series of manuals that provide technical information on alternatives to CFC-113 and MCF. Additional information about ICOLP can be found in Appendix A. The manuals are based on actual industrial experiences and serve as a guide to users of CFC-113 and MCF worldwide. These manuals will be updated periodically as technical developments occur.

The complete set of manuals produced includes:

- Alternatives for CFC-113 and Methyl Chloroform in Metal Cleaning.
- Aqueous and Semi-Aqueous Alternatives to CFC-113 and Methyl Chloroform Cleaning of Printed Circuit Board Assemblies.
- Conservation and Recycling Practices for CFC-113 and Methyl Chloroform.
- Eliminating CFC-113 and Methyl Chloroform in Aircraft Maintenance Procedures.
- Eliminating CFC-113 and Methyl Chloroform in Precision Cleaning Operations.
- No-Clean Soldering to Eliminate CFC-113 and Methyl Chloroform Cleaning of Printed Circuit Board Assemblies.

This particular manual provides those in an organization currently cleaning with ODSs with a simply-structured program to help eliminate their use of CFC-113 and/or MCF. Moreover, it presents alternative processes that can be used in metal cleaning. Many of these processes are currently in use around the world. The goal of the manual is to:

- Warn users of CFC-113 and MCF of the impending halt in production and the consequences to their operations;
- Identify the currently available and emerging alternatives for CFC-113 and MCF;
- Provide an overview of the tasks that are required to successfully implement an alternative process or chemical;
- Provide an overview of the environmental, health, safety, and other factors associated with alternatives and the benefits achievable from the phaseout of CFC-113 and MCF;
- Present detailed case studies on the actual industrial applications of these technologies to:
    -- Identify unresolved problems in eliminating CFC-113 and MCF; and
    -- Describe the equipment configuration of a typical facility after it has eliminated its use of CFC-113 and MCF.

This manual will benefit all users of CFC-113 and MCF in the metal cleaning industry. Ultimately, however, the success of a CFC-113 and MCF elimination strategy will depend upon how effectively reduction and elimination programs are organized. Experience has also shown that a strong education and training program for workers using new processes results in greater efficiency and a smooth transition away from CFC-113 and MCF. The development and implementation of alternatives to CFC-113 and MCF for metal cleaning present a challenge for most organizations. The rewards for success are the contribution to global environmental protection and an increase in industrial efficiency.

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 presents the initial steps a facility must take in order to reduce and eliminate CFC-113 and MCF usage in cleaning procedures. It emphasizes the importance of being familiar with the different aspects of the cleaning processes.

- **METHODOLOGY FOR SELECTING AN ALTERNATIVE CLEANING PROCESS**

  This section discusses various organizational, policy, technical, economic, and environment, health, and safety issues that should be considered when selecting a metal cleaning process.

- **ALTERNATIVE MATERIALS AND PROCESSES**

  This section describes the operational principles and outlines the advantages and disadvantages of several alternative technologies, including aqueous cleaning, semi-aqueous cleaning, aliphatic hydrocarbons, chlorinated solvents, other organic solvents, etc.

- **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 provides examples of successful applications 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 chemicals 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, chemically stable, and have low toxicity when properly formulated with adequate stabilizers.

Metal cleaning may be divided into two general 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 and reduce solvent emissions.

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 and beneath 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

The first step in reducing and eventually eliminating the use of CFC-113 and MCF in metal cleaning is designating a team to coordinate the effort. Team members should represent various plant functions including process design, production and production engineering, environmental control, occupational health and safety, quality control, and purchasing.

In order for the team to develop an effective program, it must first acquire a good overall knowledge of existing cleaning processes within its facility. This knowledge will help the team to identify and prioritize the cleaning operations to which it must direct its attention. Once these operations are identified, the team can analyze the processes to reduce CFC-113/MCF usage and determine cleaning requirements so that an optimal alternative may be selected for each application.

Acquiring an adequate knowledge of the metal cleaning processes in a facility can be accomplished through the use of surveys. The team should determine the quantities of CFC-113 and MCF used in every aspect of the plant's operations. If possible, the team should also visit the cleaning shop(s) to observe existing procedures, interview operators, and collect substrate and soil samples for laboratory tests. The study should include a flow chart of each manufacturing or maintenance process as well as tabular summaries of soils, substrates, and part geometry. Conducting the survey will allow the team to establish contacts and develop rapport with the individuals who will ultimately be affected by the process change. The cooperation and input of these individuals is essential to the success of the phaseout program.

After the study has been completed, the team should be able to characterize the different cleaning operations in the plant. The following sections suggest typical questions the team should be able to answer about existing cleaning processes, disposal practices, the soils being removed, and the substrates being cleaned.

Analyze Existing Cleaning Methods

In order to reduce and eliminate the use of CFC-113 and MCF in metal cleaning, the team must identify and analyze all of the processes that use these substances. Questions the team should be able to answer include:

- What processes incorporate CFC-113 and MCF?
- What quantity of CFC-113 and MCF is used in each process?
- Where do CFC-113 and MCF losses occur?
- Where does cleaning take place in the facility?
- What percentage of the time are the cleaning machines in use?
- How many parts are cleaned per day per machine?

An effective way to collect such information is through a written survey. Exhibit 3 shows an example of a survey that can be used to characterize CFC-113 and MCF usage in all aspects of the plant's operations. Of course, this survey should be modified to fit each individual plant.

In facilities where CFC-113 and MCF use is diverse and/or extensive, the information gathered using surveys and other means can be stored in an electronic database for future use. The creation of such a comprehensive database will allow the team to monitor progress and to pinpoint areas in the facility where consumption of ODSs remains high. Facilities may choose to design the tracking system themselves, hire a firm to create a custom system, or purchase an existing system from another company.

Through familiarizing itself with current usage patterns, the team will not only know which cleaning operations can utilize currently available alternative cleaning methods, but also which operations can reduce their use of CFC-113 and MCF until an acceptable method becomes available.

If the team finds that CFC-113 and MCF losses are fairly high, they may suggest ways to curb the loss, such as using covers on vapor degreasers and using wipe cloths and storage bags to save spilled CFC-113/MCF. Taking such measures will help the plant to reduce its use of ozone depleting substances until an alternative, ODS-free method is chosen.

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. If several similar cleaning operations exist throughout the plant, the team may choose to consolidate some of them into a central location. This could also allow for more efficient use of the cleaning materials and facilities and improved control of waste and emissions.

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 goal is to pinpoint ways the plant can:

- improve housekeeping to eliminate ODS use
- change production materials or processes to reduce or eliminate the soiling of parts
- change production materials so the soils can be cleaned using non-ODS cleaning technologies.
- consolidate operations

Practicing good housekeeping measures involves identifying all the CFC-113 and MCF uses within a plant and determining whether these solvents were intended for use in each application. In many cases, the ozone-depleting substances are used unnecessarily because of their convenience and excellent cleaning characteristics. By restricting CFC-113 and MCF use to intended or essential applications, a plant can significantly reduce its use of these solvents.

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. In such situations, it is to the plant's advantage to cease solvent cleaning in that application. The implementation of good housekeeping practices is further discussed in the Alternative Materials and Processes section of the manual.

Another way a plant can reduce or eliminate the use of CFC-113 or MCF is by evaluating the process that occurs before solvent cleaning, to see if changing the materials or the process itself can eliminate the soiling of parts or change the nature of the soil. For example, traditional machining, cutting, and press oil can often be replaced with volatile oil, which completely evaporates after use. This not only eliminates the need to clean, it also allows the plant to save money through the consolidation of processing oils. However, because these oils are usually volatile organic compounds (VOCs), their evaporation may contribute to smog formation. Therefore, they may not be desirable in all locations. Exhibit 4 presents numerous other ways to change process materials or procedures in order to eliminate the need for solvent cleaning.

Once all the unnecessary solvent cleaning operations are eliminated, the plant may want to consider consolidating remaining operations into one or a few locations. This will free-up floor space within the plant, make it easier to keep track of CFC-113 and MCF consumption, and possibly

Exhibit 3

CFC-113 AND METHYL CHLOROFORM USAGE PROFILE

SHOP NAME & LOCATION: ____

NAME OF CONTACT IN SHOP: ____

A. PROCESS IDENTIFICATION

Parts Cleaned (be as specific as possible):

____

Current Cleaning Method (e.g. open-top vapor degreasing, conveyorized vapor degreasing, cold cleaning, dip tank, hand-wipe, aerosol, etc.):

____

Number of Cleaning Machines in Shop Which Use CFC-113 or MCF:

____

Controls on Cleaning Equipment (e.g. covers, extended freeboard, cooling coils, etc.):

____

Other Uses (e.g., carriers, drying):

____

Substrates Typically Cleaned:

____

____

Soils Typically Removed (e.g., dirt, oil, grease) (attach MSDS for the soil if available):

____

____

Standards to be met (e.g., military, ASTM):

____

____

B. PRODUCTS USED

Generic Name of Solvent (circle one; use one survey for each chemical):

CFC-113 **MCF (1,1,1-trichloroethane)**

Trade Name of Solvent (e.g. Daiflon 113, Freon TF, Chlorothene SM, Triethane) (see Appendix C for additional tradenames):

____

Manufacturer (e.g. Daikin, DuPont, Dow, PPG) (see Appendix C for additional manufacturers):

____

C. USE HISTORY

Quantity Purchased and Used Yearly; specify units (e.g. liters, gallons):

	PURCHASED (quantity of solvent purchased or requisitioned by this shop for cleaning)	USED (quantity of solvent consumed in this shop for cleaning)
1991		
1992		
1993		
1994		

D. CFC-113 AND MCF DISPOSAL PRACTICES

	1991	1992	1993	1994
Quantity shipped out as waste for disposal (specify units):				
Disposal costs:				
Quantity shipped out for recycling (specify units):				
Cost of recycling:				
Quantity recycled on site (specify units):				
Quantity lost to the environment[1] (through leakage, spillage, testing, dragout, evaporation, etc.) (specify units)				

[1] This quantity can be calculated as follows: Quantity Lost = Quantity Purchased - Quantity shipped out as waste.

NOTE: The total quantity of CFC-113 and MCF used should be divided by the quantity of goods produced to obtain the ratio of kilograms or pounds of CFC-113 and MCF used per production unit. This value can be a benchmark for reduction and elimination programs.

Exhibit 4

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, volatile oils, or lubricated steel sheets 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.

lower operating costs through reduced electricity and solvent use.

Analyze Solvent Disposal Procedures

In addition to analyzing the cleaning processes, the team should also analyze the facility's disposal practices. Being familiar with disposal practices will aid the team in further reducing CFC-113 and MCF usage. Questions the team should be able to answer include:

- How is CFC-113 and MCF reclaimed/disposed of after use?
- How often is the CFC-113 and MCF replaced in degreasing processes?

The team should ensure that the used CFC-113 and MCF is being treated and disposed of safely. An evaluation of disposal techniques will allow the team to investigate whether these solvents can be used for longer periods of time prior to disposal, thus further reducing the facility's usage of CFC-113 and MCF. In addition, the team will be able to evaluate the possibility of using spent solvent in subsequent cleaning operations where pure solvent is not needed.

Characterize the Soils and Their Sources

An important step in characterizing existing cleaning processes is identifying the soils to be removed and their sources. The purpose of this step is either to: 1) identify ways to eliminate the need for cleaning or reduce the amount of soil to be removed, or 2) select an alternative that can remove the identified soil from parts. A plant should be able to answer the following questions when identifying soils:

- What type of soils are being removed?
- Where are the soils coming from?
- What are the performance conditions around the substrate and soil (e.g. heat, cold, high stress)?
- Why is the soil being removed (e.g. inspection, coating, appearance)?

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.

Once the soils are identified, the sources should be determined. Soils are often

- received as raw material
- received with vendor parts
- produced in forming/stamping operations
- produced in general machining operations
- produced in sub-assembly

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 no-clean or water-soluble alternatives. It is common practice to use a wide variety of processing fluids; in most cases this can be avoided. Material Safety Data Sheets can be used to determine what processing fluid is best suited to a metal plant's needs. By using no-clean alternatives, a plant can significantly reduce operating expenses and keep capital costs at a minimum, since cleaning and waste treatment are no longer necessary.

If no-clean oils are not a viable option, water-soluble, non-chlorinated, emulsifiable machining and metal forming lubricants may also be acceptable processing fluids. 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 be used to 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.

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

When studies are conducted regarding alternative cleaning methods, it is critical that the team is familiar with the substrates being cleaned in each operation. Often, cleaning processes that are effective on one substrate cannot be used on another substrate, even if the soil is identical. Questions that the team should consider include:

- What material/substrate is being cleaned?
- What degree of cleanliness is required?
- What is the surface finish required?
- What coatings are on the surface?
- What is the size and geometric configuration of the part? Is there solvent entrapment potential associated with the part? How rough is the surface of the part?
- To what level of assembly has the part been dismantled?

As the team learns more about the substrates that are being cleaned, it will become aware of the properties that it must look for and the choices that it will be limited to in choosing a new cleaning chemical or process.

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 and zinc are mildly alkaline (approximately 9-10 pH) or contain inhibitors such as silicate to prevent alkaline attack on these soft metals, while those for magnesium and steel are best used above 11 pH. Zinc and cadmium are subject to corrosion and pitting by alkaline solutions.

Another material that requires special attention is titanium (and its alloys). It can be sensitive to attack (e.g., stress corrosion cracking) by residual chlorinated and fluorinated solvents, particularly if subjected to processes at temperatures greater than 662°F (350°C). It can also be vulnerable to a reduction in fatigue strength if subject to dry abrasive blasting. The team should be familiar with the parts that contain this metal.

Composite materials, which are used in aircraft and other products that require high strength and stiffness and low density, also warrant special attention. Examples of composite materials include Kevlar, graphite/epoxy, and Kevlar/graphite.

Parts with excessive porosity, parts that have severely rough surfaces, parts that have permanent overlapping joints, and parts with blind holes and tubing can retain cleaning solution, which may cause corrosion. Care must be taken to thoroughly dry these parts after cleaning.

Special care is also required during cleaning prior to nondestructive testing procedures such as penetrant inspection. In order to conduct an accurate penetrant inspection test, the product surface must be completely free of residual surface contamination. The presence of cleaner residue or other contaminants may shield flaws in the structure and prevent the inspection fluid from penetrating surface flaws or cracks. Therefore, care must be exercised to ensure that the cleaning method employed results in a sufficiently clean surface prior to inspection.

METHODOLOGY FOR SELECTING AN ALTERNATIVE CLEANING PROCESS

In developing and selecting an alternative chemical or process for metal cleaning, several criteria should be considered. These criteria can be broadly grouped into the following categories:

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

Organizational

The most important aspect of a corporate phaseout of ozone-depleting substances (ODSs) is the commitment of the corporate management to such a program. Without such a commitment, a facility would be hard-pressed to successfully complete its phaseout. Important considerations which pertain to the corporate organization include:

- ***Compatibility with other corporate goals.*** Corporate policy may not allow the use of particular solvents if the company is sensitive to public opinion. This would result from a corporate policy in which the opinions of the general public are to be considered in all decision-making.

- ***Compatibility with corporate environmental policy.*** Some alternatives generate other forms of emissions, effluents, or wastes that are also the subject of corporate environmental goals.

- ***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.

- ***Willingness to provide capital.*** Corporate management must be willing to make capital investments in new equipment in order to facilitate a phaseout of ODSs. They should understand that a capital outlay at the present time may result in significant cost savings in future years.

Policy and Regulatory

Any potential alternative chemical or process must be examined for compliance with a variety of government regulations and laws. At the very least, alternatives must comply with the mandates of the 1987 Montreal Protocol on Substances that Deplete the Ozone Layer and its subsequent amendments and adjustments. In addition, alternatives must meet federal and local regulations that apply in the country where the alternative is to be implemented. In the United States for example, alternatives must comply with the sections pertaining to stratospheric ozone protection in the Clean Air Act Amendments of 1990. These include Section 608: National Emissions Reduction Program, Section 611: Labeling, and Section 612: Safe Alternatives Policy. Alternatives must also follow strict regulations on emissions of volatile organic compounds (VOCs) in some metropolitan areas.

Technical

The technical feasibility of an alternative process is dependent on a number of important considerations. While these considerations will vary from facility to facility depending on location and function, a number of these considerations are universal in their applicability. Important criteria to consider when evaluating an alternative cleaning process for its technical adequacy include the following:

- Cleaning ability
- Compliance to specifications
- Material compatibility
- Effect on subsequent processes
- Process control
- Throughput of the cleaning process
- Ease of new process installation
- Floor space requirements
- Operating and maintenance require-ments.

Cleaning Ability

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. For example, gross metal cleaning in the manufacture of heavy machinery will not require a high level of cleanliness. On the other hand, the high performance coatings and adhesives used on jet aircraft require a high degree of surface cleanliness to insure the integrity of the coatings.

The successful removal of contamination from a surface is not a property of the solvent alone, but a combined relationship of the cleaner, the substrate, the soils, and the cleaning conditions. Characteristics of the cleaner or solvent that greatly affect its cleaning ability include wetting, capillary action, detergency, solubility, and emulsification.

Several standard tests can be used to determine the cleaning ability of an alternative chemical or 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 discoloration. 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. In addition, the presence of a surfactant on the test surface may result in a false reading.

- ***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. (Because kerosene is combustible, care must be taken 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.

- ***Elemental Analysis***. A surface carbon determination is one of the most accurate methods of identifying small amounts of organic residues such as oils remaining after the cleaning of metal parts. A test part is introduced into an electric resistance furnace and carbon dioxide is introduced at 958°F (500°C). Measurements are taken using a non-dispersive infrared analyzer (wave length = 4240 nm). The sensitivity is 0.01 mg/m^2 and the accuracy is 0.5 percent carbon content.

- ***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 contamina-tion.

- ***Particulate Contamination***. A thin film of polyvinyl chloride is pressed against the test surface, heated to 240°F (115°C), 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).

Compliance to Specifications

Standards and specifications often complicate the search for alternative chemicals or processes by requiring the use of a specific cleaner or solvent for a specific cleaning application. This is a particularly important consideration in the maintenance of military equipment.

In instances where cleaning requirements are governed by military or other specifications, it is necessary to either verify compliance by using the indicated cleaners or solvents only, or renegotiate existing specifications before switching to alternative technologies.

Material Compatibility

In the selection of an alternative process, material compatibility is as important as the cleaning ability of the cleaner itself. Issues to be considered include: the possibility for corrosion or chemical attack of metals, plastics, composites, and other sensitive materials; swelling or deformation of elastomers; and damage to coatings or adhesives present on the surface.

Compatibility can be evaluated by performing a number of tests including:

- Intergranular attack testing determines if the cleaning solution unacceptably weakens the test metal by selectively removing material along grain boundaries.
- Stress corrosion cracking (SCC) (ASTM-G38) 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, possibly with variations in temperature. 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 or gain. 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 confined between fraying surfaces and periodically exposed to specified 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 to examine cleaning effectiveness and the effect of cleaners on subsequent manufacturing steps. These steps may include:

- ***Inspection***. Inspections may be numerous, making speed and ease of handling of parts very important. Parts are cleaned to meet customer requirements and must 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.
- ***Packaging***. Final cleaning prepares parts for packing and shipping.
- ***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 and passivation of ferrous metal alloys, and anodizing and chemical conversion coating of aluminum.
- ***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, since their presence causes smoking, nonuniform hardening, and heat treatment discoloration on certain metals. Residual contaminants remaining on a surface during heat treatment can cause intergranular attack, which may lead to stress corrosion or the loss of fatigue strength.

- ***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.

Potential residues remaining after cleaning with an alternative product or process must be evaluated for their compatibility with subsequent processes. This is especially important in cleaning prior to nondestructive testing (NDT) inspection.

Process Control

Process control is part of a quality assurance program. Being satisfied with a process is vital to a successful program. One example of good process control is checking cleaner solution concentration on a routine basis. Maintaining proper solution concentration by making small, frequent additions is much more effective than making a few large additions. The proper automated chemical dispensing equipment, which can be activated by a timer or by conductivity of the solution, is a good method for control.

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 processes may require slower throughput for optimized operations along with special drying stages.

Ease of New Process Installation

The ease with which a solvent cleaning process using CFC-113 or MCF can be converted to or replaced by an alternative cleaning process will have a direct bearing on the choice of alternative. Issues associated with the installation of the new process include facility preparation, production/ service downtime, user awareness/education, qualification testing, and transition between the two processes. In some cases, wastewater treatment facilities may be required.

Floor Space Requirements

Equipment must be compatible with the plan and space constraints of the facility's 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, compared to a single vapor degreaser, most aqueous cleaning processes include a minimum of two wash/rinse tanks and a drying device. The result often is an increase in the amount of floor space required. However, some cabinet spray washers are designed to wash, rinse, and dry in the same cabinet, thereby minimizing the need for multiple tanks. Rearranging existing equipment or installing a new process also may trigger additional permitting requirements.

Operating and Maintenance Requirements

Each new process may require a modification of operating and maintenance procedures. In these cases, not only will there be the need to develop and test the new procedures, but special operator training may be needed to familiarize operators with the proper procedures associated with the new cleaning technologies.

Due to the fact that process parameters are likely to require more close control when substituting an alternative process, maintenance of process equipment on a regular basis is critical. For example, cleaning of spray nozzles is necessary to remove soil contamination, and pumps and valves should 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.

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

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. It is important to recognize that the price of CFC-113 and MCF will continue to rise rapidly as the supplies are reduced and higher 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 in all cost calculations. Many of the alternative processes can be much less expensive than the current CFC-113 and MCF processes being used.

Environmental, Health, and Safety

Important environment, health, and safety issues to consider when evaluating an alternative cleaning process 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, in the United States, some cities have taken steps to phase out ozone-depleting compounds (ODCs) more quickly than the U.S. Clean Air Act requires. Other areas have strict laws regulating the use of VOCs. In addition to the phaseout requirements under the Clean Air Act, there are a number of provisions in effect that will also impact the selection of alternatives. These provisions include Section 608: National Emissions Reduction Program, Section 610: Nonessential Products Containing Chlorofluorocarbons, Section 611: Labeling, and Section 612: Significant New Alternatives Policy. These and other provisions must be considered before selecting alternatives. In Europe, "Best Available Technology (BAT)" guidelines have been developed in order to control VOC emissions from solvent cleaning processes. These guidelines outline recommended equipment design and operating practices for use in cold cleaning, vapor degreasing, and "in-line" cleaning. The guidelines also address treatment and disposal of waste materials from solvent cleaning operations. This includes not only spent solvent, but contaminants such as solids and oils as well.

- ***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, less toxic, and less dependent on raw materials.

- ***Public perceptions***. 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 to contribute to ozone depletion and global warming***. Each potential alternative must be evaluated for its contribution to ozone depletion as well as global warming. In most cases, it will be considered unacceptable to replace a high ozone depletor with a nonozone-depleting substance that has a high global warming potential (GWP). The focus during the phaseout of ozone-depleting substances should be on finding substitutes that do not contribute significantly to other environmental problems. The U.S. EPA is evaluating the ozone-depleting potential (ODP) and GWP of alternatives as a part of its overall risk characterization 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 energy efficiency of an alternative cleaning process will have direct impacts on both the cost of maintaining a process as well as on the environment via global warming concerns. Energy issues are being evaluated by the U.S. EPA as part of the overall risk characterization under Section 612 of the Clean Air Act.

- ***Effects on emissions, effluents, and wastes generated***. Every alternative has different effects on water, air, and land pollution. It is preferable to eliminate environmental problems, rather than to transfer them from one medium to another. The phaseout of CFC-113 and MCF in cleaning operations will reduce or eliminate the need to dispose of spent solvent. However, processes such as aqueous cleaning, which are sometimes used in metal cleaning, will result in large amounts of wastewater that may have to be treated before being discharged to a POTW. The emissions, effluents, and waste streams of alternatives are being evaluated as part of the overall risk characterization that the U.S. EPA is conducting for Section 612 of the Clean Air Act.

- ***VOC concerns***. Limitations on VOC emissions may influence the selection of an alternative. In many areas, switching solvents requires repermitting and the adoption of more stringent controls. 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 to hazardous chemicals where possible. Exposure limits such as those determined by the Occupational Safety and Health Administration (OSHA) in the U.S. should be considered before selecting alternatives. The American Conference of Governmental and Industrial Hygienists also provides threshold limit values (TLVs) for different chemicals. Personal protective equipment such as gloves, safety glasses, and shop aprons can be used to increase worker safety. Work procedures and practices should be reviewed and modified to accommodate the properties of the alternative cleaner. A toxicologist should also be consulted if the cleaner or cleaning process is new to the facility. As part of the implementation strategy for Section 612 of the Clean Air Act Amendments, the U.S. EPA has 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 a material or process will require the review of fire protection engineers and insurance carriers. Flammability should be evaluated and adequate fire control measures implemented before switching to a cleaning process which involves potentially flammable substances. Flammability is being evaluated as part of the overall risk characterization that is being conducted by the U.S. EPA under Section 612 of the Clean Air Act.

REVIEW OF EXISTING PROGRAM

The following sequence of activities should be performed to develop a maintenance cleaning program that eliminates the use of CFC-113 and MCF in metal cleaning:

- Determine where and why CFC-113 and methyl chloroform are consumed in metal cleaning operations;
- Characterize existing cleaning processes. This activity will help reveal how metal cleaning integrates with other manufacturing processes and determine whether cleaning is necessary;
- Characterize current solvent material, process control methods, operating procedures, and disposal practices, and determine the sources of any solvent losses. This step will help identify "housekeeping" measures to reduce solvent consumption at little or no net cost to the facility;
- Characterize the substrate materials being cleaned. This step includes identifying the type and geometry of materials being cleaned;
- Characterize the soils and their sources; and
- Establish criteria that must be considered before selecting an alternative cleaning process. These criteria include organizational, policy, technical, economic, environmental, health, and safety issues.

These steps will provide a better understanding of cleaning needs, allow for the elimination and/or consolidation of certain cleaning operations, and develop a systematic procedure for selecting an alternative cleaning process. With this understanding, the next section describes some major alternative processes to solvent cleaning using CFC-113 and methyl chloroform.

ALTERNATIVE MATERIALS AND PROCESSES

A number of alternative cleaning processes and alternative solvents to eliminate CFC-113 and MCF are now available for metal cleaning operations. The choice of an alternative depends on a variety of factors, including the cleanliness required and economic, technical, health, safety, and environmental issues. It may also be possible to reduce and/or eliminate deposition of soils which require cleaning, allowing the use of a less aggressive cleaning method. Therefore, the conversion to an alternative cleaning process may be made simpler by evaluating the ability to reduce contamination.

The following sections describe the major advantages, disadvantages, and key process details associated with the most promising 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. The following alternatives are addressed in this manual:

"Good Housekeeping" Practices

Alternative Cleaning Processes:

- Aqueous
- Semi-Aqueous
- Gas Plasma Cleaning

Alternative Solvents:

- Aliphatic Hydrocarbons
- Other Chlorinated Solvents
- Other Organic Solvents
- N-Methyl-2-Pyrrolidone
- Volatile Methyl Siloxanes
- Hydrochlorofluorocarbons

"GOOD HOUSEKEEPING" PRACTICES

As previously mentioned, one of the primary components of a successful phaseout strategy is the identification of uses of the solvent to be eliminated. An accurate picture of solvent usage will allow the phaseout team to focus its efforts on those areas where large quantities of solvent are used and where alternatives are readily available. This solvent use characterization can also be used to decrease consumption immediately through the classification of uses as either legitimate and improper uses.

Many of the metal cleaning applications in which CFC-113 and MCF are being used are neither necessary nor intended uses. When these substances were introduced to plants years ago, they were intended for specific applications. However, their excellent cleaning ability, coupled with the availability of these solvents, has often resulted in their extensive use.

One method of significantly reducing a plant's usage of CFC-113, and especially MCF, is the implementation of "good housekeeping" measures. These measures should be designed to limit use of these substances to applications for which they are intended, and to eliminate their use in other convenience applications. The first step in this "good housekeeping" procedure is to identify all uses of the solvents.

Use of CFC-113 and MCF should be evaluated using surveys, shop inspections, and whatever additional means are necessary. The resulting data should be cataloged so that it can be compared with future data. Computerizing the cataloging system may make tracking usage patterns easier in the long run.

Once the survey of current uses is completed, the solvent substitution team should evaluate each of the uses to determine whether or not the solvent being used was intended for use in that application. In cases where it is decided that the solvent was not meant to be used in a specific application, this usage should be eliminated immediately and replaced with the originally intended solvent or cleaning process. Investigations should also be conducted to learn how CFC-113 or MCF came to be used for the unintended application. The results of this investigation should help to prevent the same problem from occurring in other applications or with other chemicals.

After the cataloging system is in place, arrangements can be made to monitor and log all future purchases and dispersements of CFC-113, MCF, and all other solvents. Several players in the airline industry, using an approach such as this, have had substantial success in controlling their consumption not only of ozone-depleting solvents, but of other solvents as well, thereby experiencing significant cost savings. One major airline in Europe has reported a reduction in CFC-113 and MCF usage of more than 50 percent through "good housekeeping" measures alone.

AQUEOUS CLEANING

Aqueous cleaners use water as the primary solvent. They often incorporate surfactants and builders with special additives such as pH buffers, corrosion inhibitors, saponifiers, emulsifiers, chelates, deflocculants, complexing agents, antifoaming agents, and other materials. These ingredients can be formulated, blended, and concentrated in varying degrees to accommodate the user's cleaning needs. Exhibit 5 presents an overview of the advantages and disadvantages of aqueous cleaning.

Process Chemistry

Aqueous cleaners are made up of three basic components: (1) the builders which make up the largest portion of the cleaner and create stable soil emulsions once soils are removed from a surface, (2) the organic and inorganic additives which promote cleaning and cleaner stability, and (3) the surfactants and wetting agents which are the key constituents and remove or displace soils from surfaces and initiate the emulsification process. As 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, pyrophosphates, and condensed phosphates, alkali metal hydroxides, silicates, carbonates, bicarbonates, and borates. A blend of two or more builders is typically used in aqueous cleaners.

Although phosphates are the best overall builders, discharge of cleaning solutions containing phosphates is often subject to environmental regulations, thereby limiting their use. Chelating agents such as the sodium salt of ethylenediamine tetra acetic acid (EDTA), the trisodium salt of nitrilotriacetic acid (NTA), and gluconates used with other builders can be employed instead of phosphates. Silicates are sometimes difficult to rinse and may cause problems in subsequent plating and painting operations if not completely removed. They may also cause fouling in process equipment such as filters and pumps. Hydroxides are effective on difficult soils. They saponify effectively because of their high pH. Carbonates are an inexpensive alkaline source but are less effective builders than phosphates.

Additives are organic or inorganic compounds that provide further cleaning or surface modifications. Glycols, glycol ethers, chelating agents, and polyvalent metal salts are common additives.

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. The use of surfactants reduces the surface tension of water, allowing the water to penetrate into tightly spaced areas where it could not otherwise reach.

The use of a nonfoaming cleaner is extremely important in alkaline cleaning applications performed using a spray technique.

Nonionic surfactant is generally the only type of surfactant that results in minimum foaming and provides good detergency. Therefore, it is often used in spray applications. All types of surfactants can be used for immersion cleaning, although cationic surfactants are rarely used.

Exhibit 5

AQUEOUS CLEANING

ADVANTAGES

Aqueous cleaning has several advantages over organic solvent cleaning.

- Safety -- Aqueous systems have fewer worker safety problems 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.
- Flexibility -- 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 water-based lubricants and coolants to replace oil-based lubricants for environmental and other reasons. Water-based lubricants are well 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 dissolution. These include saponification (chemical reaction), displacement, emulsification, dispersion, and others. Particles are effectively removed by surface activity coupled with the application of mechanical energy.
- Ultrasonics Applicability -- Ultrasonics are much more effective in water-based solvents than in CFC-113 or MCF solvents.
- Material and Waste Disposal Cost -- Aqueous cleaning solutions are generally less expensive than solvents and, when properly handled, will reduce waste disposal costs.

DISADVANTAGES

Depending upon the specific cleaning application there are also disadvantages.

- Cleaning Difficulty -- Parts with blind holes, small crevices, and tubing may be difficult to clean and/or dry, and may 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, particularly from surfactants, can be 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. Drying equipment is often required.
- Floor Space -- In some instances aqueous cleaning equipment may require more floor space.
- Capital Cost -- In some cases, new facilities will need to be constructed.
- Material Compatibility -- Corrosion of metals or delayed environmental stress cracking of certain polymers may occur.
- Water -- In some applications high purity water is needed. Pure water can be expensive.
- Energy Consumption -- Energy consumption may be higher than solvent cleaning if applications require heated rinse and drying stages.
- Wastewater Disposal -- In some instances, wastewater may require treatment prior to discharge.

Process Equipment

Typical aqueous cleaning equipment can be classified into two general categories: in-line and batch. In-line equipment is generally highly automated and allows for continuous processing of the product being cleaned. Batch cleaning requires that operators load and unload the cleaning equipment after each cycle is completed. Given equal cleaning cycle times, in-line cleaners allow for a significantly higher throughput than batch cleaners.

The in-line and batch equipment can be further classified according to the method by which the cleaner is applied to the part to be cleaned. The three basic methods of aqueous cleaning are immersion, spray, and ultrasonic. Exhibit 6 presents an overview of the advantages and disadvantages of these three types of equipment.

Immersion equipment cleans by immersing parts in an aqueous solution and using agitation or heat to displace and float away contaminants. Agitation can be either mechanical or ultrasonic.

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, higher spray pressure is more effective in removing soil from metal surfaces. Aqueous cleaners that are specifically designed for spray application are prepared with low foaming detergents.

The spray design should be able to reach all part surfaces by mechanically manipulating the part or the spray nozzles. Although spray cleaning is effective on a wide variety of parts, some part configurations may be difficult to clean using currently available spray technology. In such cases, immersion cleaning may be more effective.

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

Ultrasonics equipment works well with water-based processes. Because the cavitation efficiency is higher for water than for CFC-113 and MCF, the removal of particles from surfaces is usually more effective in aqueous versus organic solvent media. A plant should exercise caution in the design of the cleaning process to insure that cavitation erosion of part surfaces is not a problem. Certain part geometries are also sensitive to ultrasonic agitation.

It is important to optimize system operations 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 to walls, fixtures, and other parts will impact cleaning performance. 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 leaching and absorption of sonic energy.

Both ultrasonic and spray equipment can be used together to great advantage, especially in rinsing. Low pressure (40-80 psi) spray at relatively high volumes is good for initial rinsing. It is critical to keep the part wet at all times prior to final drying. A secondary immersion-ultrasonic rinse is especially useful for parts with complex geometry or blind holes.

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

Process Details

The aqueous cleaning procedure used in metal cleaning consists of three general process steps:

- Wash Stage
- Rinse Stage
- Dry Stage

Exhibit 7 provides a conceptual diagram of the different stages that make up the aqueous cleaning

Exhibit 6

AQUEOUS CLEANING PROCESS EQUIPMENT

IMMERSION WITH ULTRASONIC AGITATION	IMMERSION WITH MECHANICAL AGITATION	SPRAY WASHER
ADVANTAGES		
High level of cleanliness; cleans complex parts/ configurations	Cleans complex parts and configurations	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	Usable with parts on trays	Simple to operate
May be performed at ambient temperature	Can use existing vapor degreasing equipment with some modifications.	High volume
		Spray unit may be portable
DISADVANTAGES		
High cost	Requires rinse water for some applications	Requires rinse water for some applications
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
Limits part size and tank volumes	May require separate dryer	
May require separate dryer		

exhibit 7

process. The following is a description of the three stages.

Wash Stage. The wash stage in an aqueous cleaning process refers to the application of a water-based cleaner, often containing detergents and surfactants. The method of cleaner application is primarily dependent on the part or surface being cleaned.

Relatively small assemblies may be immersed in a tank which contains the cleaning agent. Often this solution will be heated to improve cleaning. If immersion tanks are used, contamination build-up in the cleaning solution must be monitored. When the level of contamination becomes too high, the cleaner should be treated and reused or disposed of. Parts that are too large for immersion tanks may be cleaned using a hand-held wand-type spray washer.

Rinse Stage. In the rinse stage of the aqueous cleaning process, all of the cleaning solution applied during the wash stage is removed from the part being cleaned. As the cleaner is removed, all of the contaminants which have been displaced and/or solubilized are also removed from the part. The rinse is often performed using water with no additives or, in some cases, deionized water. However, rinse aids are sometimes added to water to cause the water to form a sheet rather than "bead up." This sheeting action reduces water spots and aids in quicker, more uniform drying.

The rinse processes used in metal cleaning are identical to those employed in the wash stage - immersion or spray. In some cases, several rinse stages are required.

Dry Stage. The dry stage is a vital part of an aqueous cleaning process. For simple parts, drying may be relatively easy, but for complex parts, drying is often more difficult.

There are several drying methods currently employed after the aqueous cleaning of metal parts. The first is the use of a drying oven. These units evaporate excess water through the application of heat and can accommodate a wide variety of parts. The second drying option is a manual wipe with a dry cloth or mop to absorb the excess water from the clean part. This method is not adequate for parts with small crevices and/or closely spaced components since a cloth or mop may not be able to fit into the small spaces where water may be trapped. A third method for removing excess water is through forced air drying. In this method, hot air is blown onto the cleaned part to force water off the part. Applications where the air is blown at an angle of approximately 45° are known as air knives. A fourth method for drying parts after cleaning is the use of dewatering oils. These oils, when placed on a cleaned surface, displace moisture and provide a thin film preservative on the part. As an alternative to these four drying methods, some plants choose to let the cleaned parts dry in air. Given enough drying time, all residual water should evaporate, leaving a clean, dry part. However, air drying increases the risk of corrosion and may leave residual salts from evaporation on the component.

If the forced air drying method is used, compact turbine blowers with filtered outputs may be used as a source of air. Blowers are capable of removing 90 percent or more of water from parts. Design options in blowers include variation of pressure, velocity, and volume flow. Other sources of air include dedicated compressors and plant air. Plants should use filters to remove oil, particles, and moisture to achieve the desired level of air quality. When using the forced air drying method, issues such as noise, humidity, and air conditioning may have to be considered.

Regardless of the drying method selected, a plant should test the method's effectiveness before it is implemented.

Other Process Details

The following are additional process details that will influence a facility's decision regarding the feasibility of aqueous cleaning.

Removal of Cleaning Fluids. Care should be taken to prevent cleaning fluids from becoming 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.

Improving Process Control. Water-based cleaning is sometimes not as forgiving as CFC-113 and MCF cleaning. A plant may have to experiment with process control in order to achieve optimal washing with aqueous cleaning. Different parameters that may need to be varied include bath temperatures, pH, agitation, rinse water quality, and cleaning bath quality. Parts can be inspected for cleanliness using tests such as the Contact Angle test or ASTM-F24 test, as described in the Technical section of the Methodology for Selecting an Alternative Cleaning Process.

Wastewater Issues. One of the major drawbacks associated with the use of aqueous cleaning is the fact that wastewater treatment may be required prior to discharging spent cleaner and rinse water. In some 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. Plants that make extensive use of aqueous cleaning may find themselves with substantial wastewater treatment needs. Facilities considering a switch to aqueous cleaning should consult with their local water authorities to determine the need for pre-treatment of wastewater prior to discharge.

Water 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 membrane filtration (ceramic or polypropylene membranes). Vendors of aqueous cleaners sometimes pick-up spent cleaner from customers, recycle it, and re-sell it.

SEMI-AQUEOUS CLEANING

Semi-aqueous cleaning involves the use of a nonwater-based cleaner with a water rinse. It is applicable to electronics, metal, and precision cleaning processes, although it is most frequently used in metal cleaning. Semi-aqueous cleaners can consist of a wide variety of chemical constituents. Examples of semi-aqueous cleaning formulations are hydrocarbon/surfactant mixtures, alcohol blends, terpenes, and petroleum distillates.

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

- Good cleaning ability; typically superior to aqueous cleaning 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 stream and minimizing potential adverse impact to the substrate;
- Reduced evaporative loss;
- Potential decrease in solvent purchase cost;
- A rust inhibitor can be included in the formulation to protect parts from rusting.

Drawbacks associated with the use of semi-aqueous cleaning processes include:

- Rinsability problems; thus residues may remain on the part;
- Disposal of spent solvent after water recycling may increase costs;
- Flammability concerns, particularly if a concentrated cleaner is used in a spray application. 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;
- Some cleaners can auto-oxidize in the presence of air. One example of such a cleaner is d-limonene (a terpene hydrocarbon isomer). This can be reduced using an antioxidant additive;
- Some constituents pose potential exposure risks to workers. For example, ethylene glycol methyl ether has displayed evidence of potential risk in laboratory animals.

Process Equipment

The equipment normally used in a typical semi-aqueous cleaning process is similar to that used in aqueous applications: immersion equipment and spray equipment.

While equipment that has been designed specifically for use with concentrated semi-aqueous cleaners is available, some vapor degreasing units can be modified to become immersion wash tanks. However, rinse tanks are usually also required.

Immersion equipment is still the simplest method of cleaning metal parts. The primary distinction of semi-aqueous immersion cleaning from aqueous immersion cleaning is that, due to the high solvency of hydrocarbon/surfactant blends, less mechanical energy may be required to achieve a satisfactory level of cleanliness. However, to achieve a higher level of cleanliness, agitation must be added to the process, either mechanically or with ultrasonics, or the cleaning solution must be heated.

As with aqueous cleaning, a mechanical spray can improve the cleaning performance of the semi-aqueous cleaning solution. It is important to note that, if a spray is used with a concentrated hydrocarbon/surfactant blend, the atomized solution is prone to combustion and special care must be taken to prevent fire risks. One such prevention measure is the use of a nitrogen blanket which displaces oxygen from the spray chamber, thereby reducing fire risk.

One semi-aqueous cleaning option, called "spray-under immersion," combines both immersion and spray cleaning techniques. In this equipment, high pressure spray nozzles are placed below the surface of the liquid. This prevents the formation of atomized solution and decreases risk associated with flammability. Workpiece movement may also be used to enhance cleaning without increasing the flammability hazard of the semi-aqueous cleaner.

Process Details

Just as the equipment used in semi-aqueous cleaning processes is similar to that used in aqueous cleaning, so too are the cleaning stages. The semi-aqueous cleaning process consists of a wash stage, a rinse stage, and a dry stage.

There are two primary differences between the aqueous and semi-aqueous cleaning processes. The first is the cleaner which is used in the wash stage. As mentioned, rather than the simple detergent and water mixture used in aqueous cleaning, semi-aqueous processes make use of any one of a number of cleaning agents, including hydrocarbons, alcohols, and terpenes.

The cleaner is applied to the part being cleaned using some form of mechanical energy. As mentioned, however, due to the fact that semi-aqueous cleaners generally have higher solvency power than aqueous cleaners, less mechanical energy is usually needed to achieve an acceptable level of cleanliness.

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 to 30°F (-7 to -1°C) of their flash point to remove difficult soils. When using cleaners that are ignitable, it is best to apply them using methods that do not mist such as spray-under immersion or ultrasonics. If the cleaners are used in vapor or spray cleaning, they should be used with an inert atmosphere or other protective equipment.

The second difference between the aqueous and semi-aqueous cleaning process lies in the addition of a second, emulsion wash stage after the initial wash and before the rinse. In this stage, the part is immersed in an emulsion which further cleans the part and helps to remove soils from the part's surface. This step results in less contamination of the rinsewater, making recycling of the rinsewater easier than it would be otherwise. The emulsion cleaner is sent to a decanter where the soils are removed from the cleaner. The cleaner can then be reused in the emulsion wash.

A rinse with clean water removes the residues left by the wash step(s). The rinse step is necessary when concentrated cleaners are used because of their low volatility (which prevent them from evaporating from the parts cleaned in the wash stage). However, the rinse step may not be necessary when a dilute hydrocarbon emulsion is used, provided the level of cleanliness needed does not require removal of the residue from the wash stage. In some instances, a fast evaporating 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 in aqueous cleaning. The removal of excess water from the part prepares it for further processing and prevents it from rusting. The same types of drying methods used in aqueous cleaning -- heat, forced air, manual wipe, dewatering oils, ambient air drying -- are also used in semi-aqueous processes.

Another similarity between aqueous and semi-aqueous processes is the possible need for wastewater treatment. In order to avoid processing excessive quantities of wastewater, some plants may choose to recycle their spent cleaners. Some currently available semi-aqueous cleaners can be easily separated from the rinse water. This allows the rinse water to be recycled or reused. The waste cleaner can then be burned as fuel.

GAS PLASMA CLEANING

Gas plasma cleaning is typically used as a final clean in a multi-stage process to achieve surfaces completely free of organic contamination. It is used in a variety of industries, including electronic, automotive, medical, textiles, and plastics to clean and surface treat microelectronic devices, plastic automotive bumpers, stainless steel syringe needles, angioplasty balloon catheters, plastic lenses, golf balls, lawnmower distributor covers, and other products.

Gas plasma cleaning involves using electrically excited, nontoxic gas such as oxygen or air to remove thin layers of organic residues. The electrically excited gas, called plasma, is made up of electrons, ionized atoms, and neutral molecular fragments (free radicals). The molecular fragments combine with the organic surface films to form small quantities of volatile gaseous by-products such as carbon dioxide, water vapor, and trace amounts of carbon monoxide and other hydrocarbons.

The advantages of using plasma cleaning include the following:

- Process gases are relatively cheap, nontoxic, and noncaustic. Examples of gases are air, oxygen, argon, helium, and silicon tetrafluoride;
- Because the reactions occur on the surface of the part, the bulk of the part is unaffected;
- Gas plasma cleaning is compatible with most metals, ceramics, and glass materials;
- Plasma cleaning offers a high level of worker safety because cleaning takes place in a closed vacuum chamber and the reaction by-products are evacuated through a vacuum pump as soon as they are formed;
- Operating costs are low compared to solvent cleaning because there is no need to regularly monitor, replenish, and dispose of chemicals;
- The plasma cleaning process cleans and surface treats at the same time. Gas removes organic contaminants and chemically combines with the material surface to enhance its chemical properties for adhesive bonding -- it makes the surfaces more polar and allows adhesives to fill surface micro-pores and form stronger covalent bonds;
- By-product vapors do not require scrubbing and can be vented to the atmosphere through standard hose exhaust.

There are also several disadvantages to using gas plasma cleaning. These include the following:

- Capital costs are initially high and the equipment is highly specialized. Reactor costs are typically $20,000 to $130,000.
- For space systems such as satellite optical components that must be cleaned during use, the plasma gases must be provided at launch or produced chemically;
- It may be difficult to determine exactly how long the process should last. Outer contaminant layers are stripped faster and at lower energies than layers close to the original surface. A possible reason for this could be that the inner contaminant layers are exposed to more UV radiation from the plasma itself, and therefore cross-polymerize and form stronger bonds with the surface of the part. This uncertainty could lead to overuse of process gas supplies;
- Using oxygen as a process gas produces a visible film on the surface of gold mirrors. Such a film may be difficult to remove and, if left on the mirror, can increase light scattering;
- Plastics may be superficially etched by oxygen after extended cleaning;
- The energy of the process must be limited to avoid sputtering, a phenomenon that can damage the elements being cleaned;
- Because cleaning capacity is low, gross contamination must be removed prior to plasma cleaning.

Process Chemistry

Cleaning occurs through the combined action of UV light and atomic oxygen fragments reacting with organic residues on the part. Although some chemical reactions between the plasma and contaminants are not understood, most of the by-products formed are the result of conventional chemical reactions. The reaction is similar to the normal combustion of hydrocarbons, but at lower temperatures (25°C - 50°C). The highly energized ions and UV light help break apart the hydrocarbons and provide the activation energy necessary to start the chemical reactions. The formula for the two stages of reactions may be written as:

$$O_2 + \text{RF energy} \rightarrow 2O + \text{ions} + \text{electrons} + \text{UV light \& visible light}$$

$$C_xH_y + \text{O plasma} \rightarrow CO_2 + H_2O + CO + \text{smaller hydrocarbons}$$

The quantity of by-product gas generated is so low that one year of plasma cleaning produces the equivalent of approximately 10 minutes of automobile exhaust.

Process Equipment

A typical plasma cleaning system consists of a vacuum chamber made of aluminum, a vacuum pump, a radio-frequency generator, a gas flow module, and a microprocessor-based controller. The vacuum chamber, which can be cylindrical or planar, holds the components for cleaning. Within the vacuum chamber is a set of electrodes, which may be in the form of a cage or removable shelves. During cleaning, the radio-frequency source is connected across these electrodes. The radio-frequency generator supplies the energy for creating plasma. The control equipment governs the composition of the reagent gas, the flow-rate of the reagent gas, the radio-frequency power, the reactor's operating pressure, and the processing time. Most applications use the closed-vacuum chambers in batch mode, but continuous cleaning is also possible.

Many sizes of systems are currently available for cleaning applications, ranging from small, modified microwave ovens to large chambers designed to hold several car bumpers. As mentioned earlier, the initial cost of a plasma cleaning system is relatively high: one medium-sized system is approximately $60,000. However, the operating costs are fairly low. One tank of industrial grade oxygen gas costs approximately $20, and will last more than a year for light cleaning. Furthermore, training time is low because of the ease of using plasma cleaning equipment.

Process Details

To use the gas plasma cleaning system, parts are placed on the electrodes inside the vacuum chamber. The vacuum is then pumped down to about 0.05 Torr. While pumping continues, the gas is introduced to the system at a regulated pressure of 0.1 to 1 Torr. The radio frequency generator, operating at 13.56 MHz, supplies the excitation power. A pale blue gas occurs when the radio-frequency source is connected across the electrodes.

The power, time, pressure, gas flow rate, and gas type can be varied to optimize the cleaning process. Most systems offer automatic control of these process variables. Multi-step processes can be stored in the controller memory, which allows for high consistency and repeatability.

The cleaning time depends greatly on the specific process, but generally ranges from a few seconds to a few hours. Sophisticated plasma systems are capable of strip rates exceeding 1 micron per minute at temperatures near 200°C. Lower cost industrial systems are capable of rates up to 0.2 microns per minute at 100°C or less. Most cleaning can occur in less than 15 minutes, assuming larger contaminants have already been removed through another cleaning process such as hot water rinsing or wiping. Thicker organic residues up to 0.001 inches may be removed in about 30 minutes at 150°C.

ALIPHATIC HYDROCARBONS

There is a wide range of aliphatic hydrocarbon solvents that can be used in metal cleaning (see Exhibit 8). Petroleum fractions, commonly known as mineral spirits or kerosene, are derived from the distillation of petroleum and are used extensively in maintenance cleaning (e.g., auto repair). They are most often used in single-stage cleaning operations in open-top equipment using ambient air drying. Synthetic aliphatic hydrocarbons, which offer closer control of composition, odor, boiling range, evaporation rate, etc., are employed in OEM cleaning processes as well as in maintenance operations.

The advantages of aliphatic hydrocarbon cleaners include:

- Superior cleaning ability for a wide variety of soils, especially heavy grease, tar, waxes and hard to remove soils. Low surface tension allows good penetration into areas with closely spaced parts or components.

- Compatible (non-corrosive) with most rubbers, plastics and metals.

- They employ no water and can therefore clean water-sensitive parts.

- Reduced evaporative loss.

- No wastewater is produced.

- Waste streams from those products with flash points greater than 140°F (60°C) may be classified as nonhazardous.

- Synthetic aliphatic hydrocarbons are not regulated as hazardous air pollutants under the U.S. Clean Air Act.

- Recyclable by distillation. High stability and recovery.

The disadvantages include:

- Flammability concerns. However, these concerns can be mitigated with proper equipment design, and some products are available with flash points greater than 200°F (93°C).

- Slower drying times than CFC-113 and MCF.

- VOC control may be required.

- Some grades have low Occupational Exposure Limits.

- Odors may cause some worker discomfort.

The steps in a typical aliphatic hydrocarbon cleaning process are analogous to those for aqueous or semi-aqueous processes, with the exception that the rinse step may be replaced with additional wash steps. Equipment designs for use with aliphatic hydrocarbons are modified aqueous equipment designs, primarily to account for flammability and VOC concerns.

The major steps in the cleaning process are typically:

- Wash steps (1 to 3 stages depending on degree of cleaning needed) with an aliphatic hydrocarbon cleaner;

- Drying step, often using forced air;

- VOC emission control by destruction or recovery from solvent laden air, if required; and

- Waste solvent recovery and/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 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 that can provide protection against ignition conditions. This protection is required because fine droplets can ignite at temperatures below the bulk fluid flash point.

Fluids with flash points below approximately 104°F (40°C) 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 59°F (15°C) between the fluid flash point and the cleaning temperature is recommended. For systems with poor 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. If the dryer is not operating at 59°F (15°C) below the flash point of the fluid, sufficient air flow should be provided so that the effluent air composition is well below the Lower Explosive Limit of the system.

Regardless of whether or not it is required by law, 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 capturing solvent vapors from spent drying air. Numerous vendors market this type of recovery equipment. In some cases, however, the VOC concentration in the air may be too low to facilitate recovery and catalytic incineration may be required to destroy the VOCs.

For waste recovery, the best reclamation technology for aliphatic hydrocarbons is usually filtration and distillation. One of the advantages of some of the aliphatic hydrocarbon solvents with few impurities and narrow distillation range is the high recovery rate in distillation. Should some disposal of residual solvent be necessary, fuel substitution or incineration are good options. Some companies specialize in the service of recycling these solvents and their services may be contracted by a solvent user.

Exhibit 8

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

OTHER CHLORINATED SOLVENTS

One of the most appealing substitutes for CFC-113 and MCF in terms of process similarity is the use of another chlorinated solvent which does not contribute to ozone-depletion. The solvents normally used in cleaning applications are trichloroethylene, perchloroethylene, and methylene chloride. While these substances are ideal due to the fact that they can be used in vapor degreasing applications, as are CFC-113 and MCF, they may have significant health and environmental impacts which, if not properly addressed, make their use less attractive.

These three cleaning solvents have undergone extensive testing in recent years for safety, health, and environmental impacts. As a result of this testing, two of the solvents -- trichloroethylene and perchloroethylene -- have been classified as VOCs (although the U.S. EPA has recently proposed that perchloroethylene be exempted from regulation as a VOC), and all three have been classified as hazardous air pollutants in the U.S. These classifications have significant implications for chlorinated solvent use in the U.S. since they require that emissions control measures be employed and extensive records be kept when using these solvents. In November 1993, the U.S. EPA proposed national emission standards for hazardous air pollutants (NESHAPs) used in existing and new halogenated solvent cleaning applications. The standards, which were developed under the requirements of Title III (Hazardous Air Pollutants) of the Clean Air Act, cover both vapor degreasing and immersion cleaning with trichloroethylene, perchloroethylene, and methylene chloride, as well as with MCF. The standards are expected to be finalized by November 1994. After that time, companies operating existing equipment will have two years to comply with the requirements.

Under the proposal, companies are required to install emission control equipment and to implement automated parts handling and specified work practices in order to meet emission standards. Alternatively, companies may choose to comply with either an idling mode emission limit, in conjunction with parts handling and work practice requirements, or a limit on total emissions. Exhibit 9 presents the proposed control equipment combinations and the alternative idling limits for different types of equipment. Exhibit 10 lists the alternative total emissions limits.

Within 90 days of the finalization of the standards, companies must submit an initial notification of each solvent cleaning machine. Companies are expected to implement one of the compliance options within two years, and to submit an initial compliance report within 30 days of the end of the two-year period. Cleaning machines that begin operation after the proposal date are expected to comply with the standards upon start-up or on the date the standards are finalized, whichever is later. Following the submission of the initial compliance report, companies are required to submit annual compliance reports. Noncompliance reports, if necessary, are submitted quarterly. The operators of batch vapor and in-line vapor and cold cleaning machines are required to obtain an operating permit from the EPA or the operator's state, if the state has an EPA-approved permitting program. Companies that choose to comply with the alternative emission limit are required to keep a monthly log of solvent additions and removals, and to use mass-balance equations to calculate their total emissions. The emissions, based on a three-month rolling average, must be equal or less than the total emissions limit.

In addition to being VOCs and/or hazardous air pollutants, two of the nonozone-depleting chlorinated solvents have been shown to be carcinogenic to animals in extensive toxicity testing. This discovery has prompted the International Agency for Research on Cancer to classify both perchloroethylene and methylene chloride as "possibly carcinogenic to humans." In addition, many governments have set very low permissible worker exposure limits for all three chlorinated solvents. The U.S. Occupational Safety and Health Administration (OSHA) has set worker exposure limits at 100 parts per million (ppm) for perchloroethylene and trichloroethylene, and 500 ppm for methylene chloride. A proposal has been submitted to lower the permissible exposure limit (PEL) for methylene chloride to 25 ppm.

Chlorinated solvents are subject to hazardous waste regulations in some areas, including the U.S. where they are covered under the Resource Conservation and Recovery Act (RCRA). Users of these solvents must be aware of and comply with all regulations governing use, storage, and disposal of these materials.

Despite the many possible environmental and safety effects associated with the use of chlorinated solvents, they are feasible substitutes for CFC-113 and MCF in metal cleaning provided adequate control measures are used. Exhibit 11 summarizes the solvent properties of these other chlorinated solvents.

Exhibit 9

CONTROL EQUIPMENT COMBINATIONS AND ALTERNATIVE IDLING LIMITS UNDER NESHAPs

Cleaner Type (m^2 solvent/air interface area)	Control Equipment Combination Options[a,b]	Alternative Idling Limit (kg/hr)[b]
Batch Vapor ($\leq$ 1.21 m^2)	1. FBR=1.0, FRD, RRD 2. FBR=1.0, BPC, RRD 3. BPC, FRD, RRD 4. CVR, FRD, RRD	0.15
Batch Vapor (> 1.21 m^2)	1. BPC, FRD RRD 2. BPC, DWL, RRD 3. DWL, FRD, RRD 4. BPC, FRD, SHV 5. BPC, RRD, SHV 6. FBR=1.0, RRD, SHV 7. DWL, RRD, SHV	0.15
In-Line[c] (Existing)	FBR=1.0, FRD	0.10
In-Line[c] (New)	SHV, FRD	0.10
Batch Cold Cleaning	CVR, Water Layer	N/A

[a] FBR - freeboard ratio
FRD - freeboard refrigeration device
RRD - reduced room draft
BPC - biparting cover
CVR - manual cover
DWL - dwell
SHV - superheated vapor

[b] Compliance with the proposed equipment or idling emission standard also requires automated parts handling and work practices

[c] Includes both vapor and cold cleaning equipment

Exhibit 10

ALTERNATIVE TOTAL EMISSIONS LIMITS UNDER NESHAPs

(BASED ON THREE-MONTH ROLLING AVERAGE)

	Average Emission (kg/m^2-month)
Batch Vapor (Existing and New)	109.8
In-Line Vapor & Cold Cleaning (Existing)	153.2
In-Line Vapor & Cold Cleaning (New)	98.5
Batch Cold Cleaning	N/A

Exhibit 11

PROPERTIES OF CHLORINATED SOLVENTS

Physical Properties	CFC-113	MCF	Trichloro-ethylene	Perchloro-ethylene	Methylene Chloride
Ozone Depleting Potential	0.8	0.12	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	73.8	87	121	4.0
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
U.S. OSHA PEL 8 hr. TWA (ppm)	1000	350[a]	100	100	500[b]
Flash Point (°C)	None	None	None	None	None

---

[a] Obtained from HSIA White Paper 1989.

[b] A proposal has been submitted to lower the PEL of methylene chloride to 25 ppm.

Source: UNEP 1991.

OTHER ORGANIC SOLVENTS

The solvent cleaning industry has used a wide range of other organic solvents for electronics, metal, and precision cleaning. Some of the solvents commonly used include ketones, alcohols, ethers, and esters. These solvents can be used in either a heated state or at room temperature in a dip tank, or in hand-wipe operations. However, due to the fact that most are flammable, these types of organic solvents are most often used at room temperature in a process commonly known as cold cleaning.

The ketones form a group of very powerful solvents (see Exhibit 12). In particular, acetone (dimethyl ketone) and methyl ethyl ketone (MEK) 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. It is important to note that MEK is often classified as a hazardous air pollutant, as it is in the U.S. Even so, it is extremely widely used in a variety of applications.

Alcohols such as ethanol and isopropanol, and several glycol ethers are used alone and in blends in 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 extreme care must be exercised while using the lower flash point alcohols (see Exhibit 13).

A relatively new method of organic solvent cleaning employs a special vapor degreaser designed for use with alcohols. One class of such equipment uses an alcohol vapor zone to clean the parts, and has a perfluorocarbon or nitrogen (inert gas) vapor blanket above the alcohol. This blanket effectively reduces the flammability risk associated with the heated alcohol. However, because of the extremely high global warming potential of perfluorocarbons, their use is being severely restricted in many countries, including the United States. Acceptable applications of perfluorocarbons are being limited to only those applications in which no other currently available alternative that is not an ozone-depleting substance is acceptable. A new line of chemicals known as hydrofluorocarbons (HFCs) is currently being developed for use in general cleaning applications and to replace perfluorocarbons in alcohol vapor degreasers. The second class of alcohol vapor degreasing equipment does not make use of an inerting agent such as perfluorocarbons. In these systems, there are numerous safety devices built into the equipment, including air monitors, automatic sprinkler systems, and automatic shutoff capabilities. Nevertheless, when using this equipment, workers must exercise extreme caution to reduce the risk of explosion. Both methods of alcohol vapor degreasing are currently being used in industry.

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 and in high paraffinic hydrocarbons. Dibasic esters generally have a high flash point and low vapor pressure. Dibasic esters are so low in vapor pressure that a residual film may remain on a surface after application, thereby necessitating a water rinse stage. 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, and have acceptable compatibility with most polymers. These esters can be dried from a surface by forced air drying with no residual film.

As with chlorinated solvents, many of the organic solvents are toxic and have low worker exposure limits. Prior to implementing such products, a plant should coordinate a review by an occupational health professional to ensure that the products are being used in a safe manner. All possible efforts should be made to protect workers from prolonged exposure to toxic chemicals.

Many organic solvent alternatives to CFC-113 and MCF also have problems with odor. Even though volatility and airborne concentrations can be reduced, the relatively strong odors of some of these solvents may build up. Without adequate ventilation and possibly masks for workers, these odors may reach a level which will cause discomfort for workers. Therefore, care should be taken to reduce the odor build-up in any location.

Other issues to consider when evaluating organic solvents as CFC-113 and MCF substitutes include VOC emissions and waste disposal. In many locations, most of the organic solvents will be considered VOCs, and their use will require emissions control. In addition, spent solvent may be considered hazardous waste. If it is, the solvent will require special handling and disposal practices.

Exhibit 12

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)	$(CH_3)C_5H_9C0$	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	$C_2H_5COC_2H_5$	$3.4^{104^\circ F}$	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	$CH_3COC_4H_9$	$3.4^{77^\circ F}$	$3.7^{77^\circ F}$	73	1.2	8.0	100	0.55	148
METHYL CYCLOHEXANONE (Mixed Isomers)	$(CH_3)C_5H_9C0$	0.2	3.0	118	-	-	100	$0.44^{58^\circ F}$	-
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	$0.50^{58^\circ F}$	200

Source: DuPont Company, Handbook of Standards for Solvents

Exhibit 13

PROPERTIES OF ALCOHOLS

CHEMICAL	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

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 14 summarizes the solvent's principal properties. Exhibit 15 shows two typical process equipment designs that have been used successfully for both batch and in-line operations.

Exhibit 14

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 15

VOLATILE METHYL SILOXANES

Volatile methyl siloxanes (VMSs) are relatively new alternatives to CFC-113 and MCF in precision and electronics cleaning. They remove most surface contaminants in precision metal working and optics processing, as well as most nonionic soils in electronics processing.

VMSs are low molecular weight silicone fluids that occur in both linear and cyclic form. Commercially available formulations are often made up of blends of several different VMS fluids. VMSs have been used for many years as ingredients in cosmetics and a variety of personal care products, but have not been traditionally used in solvent cleaning applications.

The primary benefits associated with the use of VMSs in cleaning applications include:

- Good cleaning capabilities for a variety of contaminants, including oils, greases, cutting fluids, silicone fluids, and waxes (when heated);
- Ability to evaporate without leaving a residue;
- Low surface tension allows VMSs, like CFC-113, to spread rapidly and penetrate tightly-spaced areas;
- Compatibility with a wide variety of substrates, including most plastics and elastomers;
- Easily recoverable and reusable. VMSs are recycled by distillation and/or filtration, depending on the contaminants present;
- No rinsing is needed, thereby eliminating any wastewater concerns.

The major drawbacks associated with the use of VMSs in precision cleaning include:

- Flammability. The most flammable VMS blend currently available has a flash point of 30°F and is classified as flammable. The least flammable blend has a flash point of 135°F and is classified as combustible.
- Longer drying times than CFC-113 and MCF. The evaporation rates of VMS blends are comparable to that of butyl acetate.
- Some constituents of VMS blends have very low recommended exposure limits on the order of 10 ppm. Overall toxicity testing on VMS blends is not yet complete.

The VMS blends used in cleaning are pure distilled methyl polysiloxanes that contain no additives and are clear in color. Because VMSs have low Kauri-Butanol values, they are excellent solvents for surface soils such as oils, greases, cutting fluids, silicone fluids, yet harmless on most elastomers and plastics. Exhibit 16 presents the properties of three VMS blends as compared to CFC-113 and MCF. Exhibits 17 and 18 list the compatibility of VMS fluids with certain elastomers and plastics.

VMSs are used as cleaning and rinsing agents. The most volatile VMS blend can also function as a drying agent. Parts rinsed with this blend will dry in less than one minute at room temperature. Less volatile VMS blends take longer to dry. Moderate heat may be applied to speed up the drying process.

VMSs can be used in existing cleaning equipment that is designed to safely handle flammable or combustible liquids. For example, equipment that uses isopropyl alcohol can be easily adapted for use with VMS fluids. In addition, CFC-113 or MCF vapor degreasers can be modified for VMS use. Mechanical agitation or ultrasonics can be added to enhance or speed the cleaning process.

Exhibit 16

PROPERTIES OF SAMPLE VMS BLENDS

	CFC-113	MCF	VMS Blend 1	VMS Blend 2	VMS Blend 3
Molecular Weight	187	133	162	236	310
Flash Point (°F)	none	none	30	94	135
Freezing Point (°C)	-35	-37	-68	-86	-76
Boiling Point (°C)	47	74	100	149	192
Evaporation Rate (butyl acetate = 1.0)	17	6	3	1	0.1
Viscosity at 25°C	0.68	0.79	0.65	1.0	1.5
Specific Gravity at 25°C	1.56	1.31	0.76	0.82	0.85
Surface Tension at 25°C (dynes/cm)	17.3	25.5	15.9	16	18
Heat of Vaporization at 150°F (cal/gm)	35	56.7	46	44	36
Kauri-Butanol Value	31	124.8	16.6	15.1	13.4

Exhibit 17

COMPATIBILITY OF SAMPLE VMS BLENDS WITH ELASTOMERS

1 week immersion at 50°C (percent swell)

Polymer	Common Name	VMS Blend 1	VMS Blend 2	VMS Blend 3
Acrylonitrile-Butadiene	Buna N	8.1	0	.4
Chlorosulfonated Polyethylene	Hypalon	2.4	-1.8	-1.9
EPDM Rubber	Nordel	-3.9	-6.6	-8.6
Fluoroelastomer	Viton A	-1.7	0	0
	Viton B	-1.2	-1.2	0
Isobutylene-Isoprene	Butyl Rubber	3.5	-5.8	-4.0
Natural Polyisoprene	Natural Rubber	16.0	11.5	4.9
Polychloroprene	Neoprene	58.5	56.9	53.9
Polysiloxane	Silicone	-7.1	-8.3	-8.3

Exhibit 18

COMPATIBILITY OF SAMPLE VMS BLENDS WITH PLASTICS

1 day immersion at 50°C (percent weight change)

Polymer	VMS Blend 1	VMS Blend 2	VMS Blend 3
Nylon	-0.5	0	-0.3
Acrylic	-0.2	0	-0.1
Polysulphone	-0.1	0	-0.1
PET	0	0	0
Polycarbonate	-0.1	0	-0.1
Polyvinyl Chloride	-0.1	0	0
Acetal	-0.2	0	-0.1
ABS	-0.3	0	-0.1
Polypropylene	0.6	0	0.1
PBT	-0.3	0	-0.1
Polyetherimide	-0.1	0	0
PVDF	0	0	0
Polystyrene	0.4	0	0.1
Chlorinated Polyvinyl Chloride	0	0	0
PTFE	0	0	0
Ionomer	0.6	0	0
Acrylic Clear	-0.2	0	0
High Impact Polystyrene	0	0	0
Polycarbonate B	-0.1	0	-0.1
Polypro	0.3	0	0.1
PVC	-0.1	0	0
Nylon B	-0.2	0	0.2
WHMW Polyethylene	0.6	0	0.1
HPDE	0.2	0	-0.6

HYDROCHLOROFLUOROCARBONS FOR ESSENTIAL APPLICATIONS

Faced with the phaseout of CFC-113 and MCF, some users of these solvents have looked toward several hydrochlorofluorocarbons (HCFCs) (e.g., HCFC-225ca, HCFC-225cb, HCFC-141b, and HCFC-123) as possible substitutes. Exhibit 19 presents physical properties of these chemicals. HCFCs have been attractive alternatives due to their nonflammability, good cleaning performance, and similarity in application method to CFC-113 and MCF. However, due to their environmental and health impacts, the use of these substances in solvent cleaning applications will be severely limited. At the present time, the only HCFC that can be used legally in metal cleaning in the U.S. is HCFC-141b. Under the SNAP rule (described in the Foreword), HCFC-141b use will be allowed in existing equipment until January 1, 1996. After January 1, 1996, the use of HCFC-141b in any metal cleaning application will be allowed only as a replacement for CFC-113, and then only with a special exemption granted by the U.S. EPA. At the time of revision of this manual, the use of HCFC-225 had not yet been approved for metal cleaning applications, although a SNAP submission was pending.

Exhibit 19

PHYSICAL PROPERTIES OF HCFCs AND OTHER SOLVENT BLENDS

	CFC-113	MCF	HCFC-225ca	HCFC-225cb	HCFC-141b
Chemical Formula	CCl_2FCClF_2	CH_3CCl_3	$CF_3CF_2CHCl_2$	$CClF_2CF_2CHClF$	CH_3CFCl_2
Ozone Depleting 0.11 Potential	0.8	0.1	~0.05	~0.05	
Boiling Point (°C)	47.6	73.9	51.1	56.1	32.1
Viscosity (cps) @ 25°C	0.68	0.79	0.59	0.61	0.43
Surface Tension (dyne/cm)	17.3	25.56	16.3	17.7	18.4
Kauri-Butanol Value	31	124	34	30	76
Flash Point °C	None	None	None	None	None
Toxicity	Low	Low	Underway	Underway	Near Completion

Therefore, these substances are no longer being recommended for use in solvent cleaning applications, where workers will be exposed to the chemicals for long periods of time. In addition, two major manufacturers have withdrawn all of their HCFC-123 formulations previously marketed for solvent cleaning applications. HCFC-141b is currently available and is manufactured by several chemical companies for use in solvent cleaning applications. Previous formulations of HCFC-141b included mixtures with HCFC-123 and methanol, but current formulations have dropped the use of HCFC-123. The major drawback associated with the use of HCFC-141b is its relatively high ODP of 0.11. This is only slightly below the ODP of MCF (0.12), a product which HCFC-141b is to be replacing. Because of the similarity in ODP, HCFC-141b is generally seen as an unacceptable substitute to MCF. In the U.S., for example, the Environmental Protection Agency has banned the use of HCFC-141b as a substitute for MCF in solvent cleaning applications, and has limited its use as a substitute for CFC-113. For these reasons, it is unlikely that HCFC-141b will be a suitable substitute for MCF in metal cleaning applications.

At the present time, it appears HCFC-225 is a good substitute for CFC-113 in general metal and precision cleaning. It is similar to CFC-113 in its chemical and physical properties and compatible with most plastics, elastomers, and metals. Thus, HCFC-225 has been applied as a CFC-113 replacement, where other alternatives can not be applied, with relatively few changes in equipment or process operations. Its ability to replace MCF, however, is limited because the solvency of HCFC-225 is low compared with that of MCF. When combined with other solvents such as petroleum, HCFC-225 may serve as an adequate substitute to MCF. All of the toxicological testings of HCFC-225ca and HCFC-225cb planned under PAFT-IV were completed in early 1994. Data from acute toxicity studies indicate that HCFC-225cb has very low toxicity. As a result, an Acute Exposure Limit (AEL) of 250 ppm has been set for HCFC-225cb, while the more toxic HCFC-225ca has an AEL of 25 ppm. Twenty-eight day inhalation studies also demonstrate no significant effects, and evidence from several genotoxicity studies indicates that neither isomer is a genetic hazard. At present, there is a capacity for the commercial production of a few thousand metric tons HCFC-225 (as a mixture of HCFC-225ca and HCFC-225cb). It is anticipated that this capacity will increase soon to meet worldwide demand.

As a means of addressing the ODP of HCFCs, the Parties to the Montreal Protocol developed a phaseout schedule for HCFCs at their November 1992 meeting in Copenhagen. Under the new amendment, HCFC consumption must be frozen at the base level by 1996; cut by 90 percent from the base level by 2015; cut by 99.5 percent by 2020; and cut by 100 percent by 2030. The base level is equal to 3.1 percent of 1989 CFC consumption plus 100 percent of 1989 HCFC consumption. This phaseout is prompting many potential users of HCFCs to switch directly to other alternatives.

If HCFCs must be used, it is important to consider the process design changes that may be required in order to reduce emissions. For example, on conventional degreasers, freeboards should be extended and condenser temperatures should be lowered. In addition, provisions such as superheated-vapor drying or increased dwell times in freeboard are desirable to reduce dragout losses.

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 20a, 20b, and 20c). 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 (7° to 13°C);
- Secondary condenser operating at -30° to -20°F (-34° to -29°C);

- Dehumidification condenser operating at -30 to -20°F (-34° to -29°C)(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. Certain blends may require compatibility testing with titanium, 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.

ex 20a

ex 20b

ex 20c

WASTEWATER MINIMIZATION AND TREATMENT

In order to meet local, state, or federal regulations, wastewater generated from aqueous and semi-aqueous based cleaning processes may require pretreatment prior to discharge to a publicly owned treatment works (POTW) or the sewer system. The type of treatment technology used depends primarily on the quality and quantity of the wastewater generated.

Wastewater Quality

Wastewater may contain organic contaminants along with dissolved or suspended metals. Additionally, when using alkaline cleaners, wastewater can have a pH that is too high for discharge to a POTW or sewer.

Organic Matter

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

Oil and grease are generally considered a single type of pollutant. They are not categorized by any chemical formula, but rather as a 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 that 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 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 create visual and olfactory problems in the water, interfere with normal oxygen transfer from air to water, and exert both a biochemical oxygen demand (BOD) and a chemical oxygen demand (COD). BOD is a measure of the oxygen consuming characteristics of organic matter. COD measures the total oxidizable carbon in the wastewater. BOD differs from COD in that BOD relates to the dissolved oxygen in water, while COD relates to the chemically bound oxygen in the water. The measure of organic matter in a waste stream is generally characterized by measuring the BOD and COD.

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

Metals

Metals can exist either in suspension or solution. Metals in suspension are chips and fines removed from the parts being cleaned. Dissolved metals in aqueous-based wastewater generally arise from metals that are etched off parts 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). In most instances, the wastewater has a pH ranging from 9 to 12, and must be neutralized prior to discharge to a POTW or sewer.

Wastewater Minimization

Before considering wastewater treatment options, a plant should investigate methods to minimize the amount of wastewater generated from aqueous and semi-aqueous cleaning processes. One important step in minimizing wastewater is optimizing 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 more of the cleaner, an excessive amount of loading will cause the soils removed from the parts to interfere with cleaning. These soils can form scale on the heating tubes and reduce heat transfer efficiency. Excessive loading requires regular maintenance and increased discharge of wastewater.

When using alkaline cleaners, alkalinity may be unintentionally 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 replacing the used alkaline cleaner frequently.

Remove Sludge and Soils Promptly

Removing sludge and soils promptly from cleaning tanks reduces 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 keeps the soils suspended. After a period of inactivity (e.g. 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 analyzed on a routine basis, solution strength can be maintained more effectively by making small and frequent additions rather than a few large ones. Analyses 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. The plant should keep an accurate log of all tests and cleaner additions.

Maintain Equipment

All equipment should be regularly maintained. Metal tanks that are not fabricated with stainless steel should be properly coated with protective finishes. Tanks that hold deionized water should be constructed of stainless steel or lined with plastic in order to prevent rapid rusting. Spray nozzles should be inspected regularly to avoid clogging.

Additional important items to maintain are the 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 can reduce wastewater discharge include:

- Use of demineralized water during rinsing, to clean parts that cannot tolerate minor residue. 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 metal cleaning 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. The 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. Gravity separators are the most common devices employed in waste treatment to separate grease and nonemulsified 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.

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. The oil skimmers are either 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.

The treatment of wastewater from a semi-aqueous cleaning process should not involve the removal of gross amounts of oil and grease if a decanter is used with properly designed cleaning equipment. The removal of dissolved organic material and small amounts of suspended oils may be required.

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 from liquids. A semi-permeable membrane, incorporated in membrane modules, performs the separation. The wastewater feed is pumped across the membrane surface at high velocity. Water and low-molecular weight solutes such as salts and some surfactants pass through the membrane pores as permeate. This 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.

The cross-flow characteristic of ultrafiltration 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 cleaning systems, and that the efficiency of oil removal is best when using ultrafiltration. However, the ultrafiltration process must be specifically tailored to the aqueous cleaner used in order to prevent excessive loss of specific components.

The capital cost of ultrafiltration equipment and operating costs associated with pumping wastewater at high pressure are greater than the costs of 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.

Coalescing. During the coalescence process, oil droplets wet a coalescing medium. As the oil droplets combine to form larger particles, they rise to the surface of the solution. The most important properties of the coalescing media are its ability to absorb 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 that 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 costs. It cannot be used, however, to remove emulsified oils; if emulsified oils are present, the wastewater must be pretreated before being sent to the coalescing unit.

Chemical Treatment. Chemical treatment is often used to break down 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.

Coagulants (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 so it breaks down. After the addition of the coagulant, the flocculent is added to bring the tiny oil droplets together to form larger oil drops, so that they can easily be separated from the wastewater. 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. The cost of chemicals and sludge disposal can be high.

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 from the finishing and pigment compounds used in the processing of metal parts. 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 wastewater through a chamber containing activated carbon in order to remove the dissolved organic material 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 regarding carbon adsorption capacity include:

- Higher surface area provides greater adsorption capacity;

- Larger pore size provides 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 same factors can also affect the rate of adsorption. For example, while adsorption capacity is greater when removing higher molecular weight hydrocarbons, the rate of adsorption is decreased. Similarly, while higher temperatures decrease capacity, they may increase the rate of removal of solute from solution.

Before carbon adsorption is performed, wastewater should be pretreated 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 the carbon 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 being regenerated, the other column removes the contaminants.

Carbon adsorption is an economical treatment process. The greatest cost associated with the technology is regenerating the activated carbon.

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 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, if a clarifier or similar device is being used, directly to the sedimentation device. The greatest advantage of using a clarifier is the short retention time it takes for metal precipitates to settle. However, the cost of installing and maintaining a clarifier are high. The sludge that is generated must be disposed according to federal, state and social 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.

It is important to note that the use of hydroxide precipitation produces sludge that must be disposed, thus increasing treatment cost.

In Japan, ferrite precipitation is frequently used in place of hydroxide precipitation. It has the advantages of precipitating the metals at lower concentrations (by a factor of about two). Furthermore, a market already exists for the precipitates in the technical ceramics industry. Its disadvantages are higher operating costs and the considerable quantities of dissolved iron left in the effluent water. Regulations on ferrous and ferric ions should be investigated.

Ion-Exchange. Ion exchange is used in a number of wastewater treatment applications, particularly in water softening and deionization, to remove dissolved metals from solution. The process involves the reversible interchange of ions between a solid, called the ion-exchange material, and a liquid so that there is no permanent change in the structure of the solid. 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. 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, remove lead from the wastewater and replace it with an equivalent quantity of sodium. Subsequently, the lead-loaded resin may be treated with a sodium chloride solution, which regenerates the sodium form so that it is ready for another cycle of operation. The regeneration reaction is reversible and the ion exchanger is not permanently changed. Relative energy costs for this system are low.

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 21 presents a conceptual design of a semi-continuous wastewater treatment system that treats wastewater generated from metal cleaning industries.

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 POTW.

Contract Hauling of Wastewater

For small users of aqueous and semi-aqueous cleaning processes, it may be more economical to contract wastewater treatment rather than treating it in-house. In some cases, the volume of the wastewater can be reduced to make it more economical for shipment (hauling) by evaporating excess water. Most companies that contract haul 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 can be a fuel source for incinerators.

ex 21

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 a list of vendors that may serve as 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 temper-ature 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 tempera-ture 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 22):

- 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 22

References

Bailey, P.A. 1977. The treatment of waste emulsified oils by ultrafiltration. *Filtration and Separation*: 53-55.

Bansal, I.K. 1975. Ultrafiltration of oily wastes from process industries. AICHE Symposium Series: 93-99.

Baran, Yu,. V., A.M. Ovsyankin, V.V. Ushakov, and G.M. Franchuk. 1986. Cleaning metal surfaces with electroaerodynamic aerosol jets.

Bhattacharyya, D., A.B. Jumawan, R.B. Grieves, and L.R. Harris. 1979. Ultrafiltration characteristics of oil-detergent-water systems: membrane fouling mechanisms. *Separation Science and Technology*, 14(6): 529-549.

Burow, Richard F. 1993. Volatile methyl siloxanes (VMS) as replacements for CFCs and methyl chloroform in precision and electronics cleaning. 1993 CFC and Halon Alternatives Conference: 654-661.

Chevez, A.A., et al. 1990 (November). Substitution of cleaners with biodegradable solvents, phase II, extended performance testing. Draft. ESL-TR-93. Air Force Engineering and Services Center, Engineering and Services Laboratory.

Cohen, L.E., and J.A. Hook. 1987 (February). Corrosion of anodized aluminum by alkaline cleaners: causes and cures. *Plating and Surface Finishing*: 73-76.

Cohen, L.E. 1987 (November). How clean is your 'CLEAN' metal surface? *Plating and Surface Finishing*: 58-61.

Daufin, G., J.P. Labbe, and J. Pagetti. 1977. Corrosion inhibition of an aluminum-silicon-magnesium alloy in alkaline media. *Corrosion Science* 17: 901-912.

Hughes Aircraft Company. 1993. Eliminate CFC cleaning with Eco-Snow^{TM} (a presentation of the company's CO^2 snow cleaning product).

Jansen, G., and J. Tervoort. 1984 (November). Longer bath life in alkaline cleaning. *Product Finishing*: 6-12.

Kaliniichuk, E.M., I.A. Makarov, and I.I. Vasilenko, and N.A. Sukhovukhova. 1973. Purification of petroleum-refinery waste waters by coagulation and regeneration of the coagulant sludge. Consultants Bureau: 756-761.

Lee, S., Y. Aurella, and H. Rogers. 1984. Concentration polarization, membrane fouling and cleaning in ultrafiltration of soluble oil. *Journal of Membrane Science* 19: 23-38.

Linford, H.B. and E.B. Saubestre. 1950 (December). Cleaning and preparation of metals for electroplating. *Plating and Surface Finishing*: 1265-1269.

Lipp, P., C.H. Lee, and C.J.D. Fell. 1988. A fundamental study of the ultrafiltration of oil-water emulsions. *Journal of Membrane Science* 36: 161-177.

American Society for Metals. 1964. *Metals Handbook, Volume 2.* pages 317-325.

American Society for Metals. Surface Cleaning Finishing and Coatings. in *American Metals Handbook, 9th Edition, Volume 5*.

Paquin, Don. 1994 (March). The gas plasma alternative to wet cleaning. *Precision Cleaning*: 45-48.

Priest, W. 1978 (March). Treatment of waste oil emulsions by ultrafiltration. *Water and Waste Treatment*: 42-43.

Risotto, Stephen. 1994 (March). Regulatory watch: Summary of EPA's proposed NESHAPs for solvent cleaning. *Precision Cleaning*: 50.

Schrantz, J. 1990. Rinsing -- a key part of pretreatment. *Industrial Finishing*: 24-29.

Seislowski, S. 1990 (February). Cleaning basics part 2 - soils. *Metal Finishing*: 43-46.

Shukla, S.B. 1979 (June). Role of detergent raw materials. *Chemical and Petro-Chemicals Journal* 20-23.

Spring, S. 1974. *Industrial Cleaning*. New York: Prism Press. pages 25, 150, and 188.

United Nations Environment Programme (UNEP). June 30, 1989. Electronics, Degreasing and Dry Cleaning Solvents Technical Options Report.

U.S. Environmental Protection Agency. 1989a (December). Technical assessment of aqueous and hydrocarbon/surfactant based cleaning processes in the electronics, precision instruments, and metal cleaning industries -- Draft Report. Office of Toxic Substances. Washington, D.C.

U.S. Environmental Protection Agency. 1989b (August). Waste minimization in metal parts cleaning. Office of Solid Waste. Washington, DC.

U.S. Environmental Protection Agency. 1990 (March). Manual of practices to reduce and eliminate CFC-113 use in the electronics industry. Office of Air and Radiation. EPA 400/3-90-003. Washington, D.C.

Wikoff, P.M., et al. 1989 (September). Substitution of wax and grease cleaners with biodegradable solvents: phase I. ESL-TR-89-04. Air Force Engineering and Services Center, Engineering and Services Center, Engineering and Services Laboratory.

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

INTERNATIONAL COOPERATIVE FOR OZONE LAYER PROTECTION

The International 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
British Aerospace Defense
Ford Motor Company
Hitachi
Honeywell
IBM Corporation
Mitsubishi Electric Corporation
Motorola Corporation
Ontario Hydro
Northern Telecom
Texas Instruments
Toshiba Corporation

In addition, ICOLP has a number of industry association and government organization affiliates. Industry association affiliates include American Electronics Association, Association Pour la Research et Development des Methodes et Processus Industriels, CANACINTRA (Mexico), Center for Global Change, Electronic Industries Association, Halogenated Solvents Industry Alliance (U.S.), Industrial Technology Research Institute of Taiwan, Japan Electrical Manufacturers Association, Korea Anti-Pollution Movement, and Korea Specialty Chemical Industry Association. Government and NGO affiliates include the City of Irvine (CA), National Academy of Engineering, Research Triangle Institute, Russian Institute of Applied Chemistry, Russian Ministry of Environmental Protection and Natural Resources, Swedish National Environmental Protection Agency, Technology Development Foundation of Turkey, Turkish Ministry of the Environment, United Nations Environment Programme, U.S. Air Force, and U.S. Environmental Protection Agency (EPA). The American Electronics Association, Electronic Industries Association, City of Irvine, California, Japan Electrical Manufacturers Association, Swedish National Environmental Protection Agency, U.S. EPA, U.S. Air Force, and the Russian 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:

Ms. Allison Morrill
Project Manager
ICOLP
2000 L Street, N.W.
Suite 710
Washington, D.C. 20036
Tel: (202) 737-1419
Fax: (202) 296-7472

APPENDIX B

LIST OF VENDORS FOR CFC-113 AND METHYL CHLOROFORM SOLVENT CLEANING SUBSTITUTES

This is not an exhaustive list of vendors. Vendors can be cited in any 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, ICOLP, or the committee members, either express or implied, of any product or service offered by such entity.