Eliminating CFC-113 and Methyl Chloroform in Precision Cleaning Operations

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ELIMINATING CFC-113 AND METHYL CHLOROFORM IN PRECISION CLEANING OPERATIONS

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Bryan Baxter is employed by British Aerospace; Ron Stephenson is employed by Boeing Company; David Vickers is employed by Digital Equipment Corporation; John Stemniski is employed by Draper Laboratory; Bob Woodwell is employed by Honeywell; Abyd Karmali and Farzan Riza are employed by ICF Incorporated; and Richard Szymanowski is employed by Northern Telecom. 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.

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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 precision cleaning applications. It will prove useful to manufacturers world-wide because the procedures used to precision clean 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 precision 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 precision cleaning 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 precision 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 precision 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 precision 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 PRECISION CLEANING**

  This section provides some historical background on precision cleaning. In particular, it explains the reasons for industry's dependence on CFC-113 and MCF, and describes the factors that define precision cleaning applications.

- **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 precision cleaning process.

- **ALTERNATIVES TO CFC-113 AND METHYL CHLOROFORM**

  This section describes the operational principles, costs, and advantages and disadvantages of several alternative technologies.

- **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 PRECISION CLEANING

Precision cleaning is not easy to define. For this reason, we will briefly examine the history of, and requirements for, precision cleaning. This information will describe the characteristics that help to define precision cleaning applications. CFC-113 and, to a lesser degree, MCF have been the solvents of choice within the precision cleaning industry. In order to assist a plant in finding alternatives to CFC-113 and MCF, this manual will first explain the reasons for industry's historical dependence on these solvents. This understanding will be useful in evaluating alternatives later on.

Historical Perspective

Since the beginning of the Industrial Revolution, industry has been required to clean mechanical components. Before assembling manufactured parts, machining-lubricants and metallic residue (swarf) must be removed. Aliphatic hydrocarbons (paraffin, white mineral spirit, Stoddard solvent) were widely used in heavy engineering such as railroads, bridges, mining, shipbuilding, civil engineering, and chemical plants where dimensional tolerances were large and assemblies were not critically sensitive to contamination. This technology lasted unchanged for about 150 years. But the technology gradually changed with a growing concern for industrial safety, the need for increased solvent power, and the manufacturing of more precise components.

Precision component cleaning required the use of more effective cleaning technologies than those traditionally employed in heavy industries. The mass production of watches provided the basis for the modern precision engineering industry. The watch industry required a pure, chemically inert, nonflammable, and reasonably nontoxic solvent. This solvent would be used to clean small parts and finished assemblies, so that particles (dusts, metal swarf, etc.) and organic residues (oils, skin fats, etc.) were removed, and contaminant-free final assemblies could be made cheaply and quickly. Pure synthetic solvents filled this requirement.

From this precision engineering basis, the modern precision engineering industry has grown. The specifications of defense and space technology require this industry to achieve high levels of sophistication. Yet, the basic concepts of precision cleaning are still the same in modern industries. Precision cleaning requires solvents with the following characteristics:

- A volatile solvent that leaves no residues;
- Sufficient solvent power to remove organic soils;
- Low surface tension to penetrate small spaces;
- High density to assist the lift-off of small particles;
- Rapid drying;
- Low cost;
- Low toxicity;
- Nonflammability.

The next section discusses the applications which require these characteristics.

Industries Using CFC-113 and Methyl Chloroform for Precision Cleaning

Although precision cleaning is needed in a wide range of industries, several key factors define the applications where precision cleaning is required: These include those applications in which:

- Critical cleanliness standards of particulate and/or organic contami-nants need to be satisfied;
- Components have sensitive compatibilities;
- Components have physical characteristics such as geometry and porosity which make dewatering crucial in the cleaning process; and
- Components being cleaned are costly.

The following list provides an indication of the wide and varied applicability of precision cleaning operations.

- Electronics industry
  - Microelectronics
  - Recording heads and components for disk drives
  - Microswitches
  - Miniature precision potentiometers
  - Plastic electronics packaging
  - Servo motors
  - Solenoids
  - Slip ring assemblies.
- Medical
  - Heart pacemakers
  - Prosthesis manufacture
  - Contact lenses
  - Hospital oxygen systems
  - Kidney dialysis capillaries
  - Hypodermic needles.
- Defense
  - Inertial sensors and platforms
  - Hydraulic systems for aircraft and missiles
  - Decontamination of nuclear systems
  - Decontamination of chemical agents
  - Flushing fuel systems
  - Ball bearing manufacture and assembly.
- Aerospace
  - Manufacture of airframe components
  - Maintenance of avionics, auxiliary power generators, oxygen systems, undercarriages, flight controls, fuel systems.

A variety of particulate and nonparticulate contaminants are removed in precision cleaning operations. Particulate contamination includes scrap material created during cutting, drilling, grinding, and buffing of precision parts (e.g., silicon wafers and aluminum storage disk substrates). Nonparticulate contamination in-cludes waxes (used to hold silicon wafers during semiconductor manufacturing), fingerprint oils, and other contaminants.

As the term suggests, precision cleaning involves cleaning components to extremely strict standards of cleanliness. A good indication of the cleaning ability required for precision cleaning processes is provided in Exhibit 3, which shows the clearance on a computer disk drive relative to the size of various contaminants.

Industrial Dependence on CFC-113 and Methyl Chloroform

Although CFC-113 and MCF have relatively high ozone-depleting potentials, they possess other properties that have made them ideal for precision cleaning.

The characteristics that made CFC-113 the precision cleaning solvent of choice are its remarkable chemical stability (manifested directly exhibit 3 (size comparison)

in its compatibility to structural materials), its low toxicity, and nonflammability. These properties have allowed closed, superclean white-room assembly areas to be operated safely and effectively.

Probably the best example of the benefits of solvent compatibility is in the cleaning of beryllium, specifically in the inertial sensor industry. As the performance requirements of gyros increased for both defense and aerospace applications, there was a need for a structural material that combined low density with high dimensional stability. Hot pressed beryllium satisfied those requirements, with properties unique among metals. It has one distinct disadvantage -- chemical reactivity, especially with ionic chlorine. The availability of CFC-113 as a pure, stable cleaning solvent has allowed beryllium to be widely used as a structural material.

Another advantage of CFC-113 is its solvent abilities with high density polychlorofluoroethylene and polybromofluoroethylene compounds: liquids with densities of 1.8 to 2.4 g/cm^3 (at 158°F to 176°F). These compounds are used as flotation fluids in the gyro industry and are not soluble in common solvents. Furthermore, flotation fluids may contain other polymeric additives as property modifiers that must not be affected by whatever solvent is used. CFC-113 is compatible with all current flotation fluids and is extremely useful in this application.

MCF is also used in some precision cleaning applications (e.g., medical). Its physical properties, including its solvency, evaporation rate, and higher boiling point, make it an ideal product for removing certain soils. Like CFC-113, MCF is both nonflammable and low in toxicity. The lower cost of MCF is also a reason for its use as a cleaner.

Exhibit 4 provides a comprehensive list of the principal properties of CFC-113 and MCF.

Exhibit 4

PRINCIPAL PROPERTIES OF CFC-113 AND METHYL CHLOROFORM

	CFC-113	MCF
Formula	CCl_2FCClF_2	$CH_3\text{-}CCl_3$
Molecular Weight	187.39	133.4
Pounds Per Gallon at 68°F	13.16	11.16
Boiling Point °F	117.63	165.20
Freezing Point °F	- 31	- 30.4
Coefficient of Expansion Per °F	0.00089	0.00008
Surface Tension At 68°F Dynes/cm	19.6	25.56
Solubility % By Weight at 68°F -		
In Water	0.017	0.15
Of Water	0.0086	0.03
Flash Point (Tag Closed Cup) °F	None	None
Flammable Limits % By Volume in Air		
Lower	Nonflammable	8.0
Upper	Nonflammable	10.5
Toxicity P.E.L. in PPM*	1000	350
Specific Heat Liquid At 68°F Btu/(lb)(°F)	0.22	0.43
Latent Heat of vaporization at B.P. Btu/lb	63.12	103.18
Kauri-Butanol Value	31	124

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* P.E.L. is the Permissible Exposure Limit as defined under the Occupational Safety and Health Act.

Source: DuPont Company, Handbook of Standards for Solvents.

EXISTING CLEANING PROCESS CHARACTERIZATION

The first step in reducing and eventually eliminating the use of CFC-113 and MCF in precision 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 precision 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 precision 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 5 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 extensive, the information gathered using surveys and other means can be stored in an electronic database for future use. The creation of 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.

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 reduce its use of ozone depleting substances until an alternative, ODS-free method is chosen.

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. Further discussion of good housekeeping practices can be found 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. In doing this, a plant may render precision cleaning with CFC-113 or MCF unnecessary.

Whenever it is possible, a plant should separate components that require precision cleaning from those needing only gross 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 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?

Exhibit 5

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.

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. performance requirements, inspection, appearance)?

Soils removed through precision cleaning can be generally classified into two groups:

- Particulate contamination often must be identified with methods such as optical microscopy. Most optical and microchemical methods are sensitive to the nanogram or picogram level. It is better to perform the laboratory analysis of soils in-house. Sending contamination samples out risks further contamination of the sample. The following list presents some physical characteristics that can be used to identify and compare particulates.

Morphological
- Size
- Shape factor
- Crystal structure
- Interface angles
- Ratios
- Cleavage
- Invariants derived from fourier transform coefficients
- Surface features

Optical Properties
- Refractive index
- Dispersion (variation and refractive index with frequency or wavelength)
- Isotropy versus anistropy
- Birefringence
- Extraction angles
- Pleochroism

Microchemistry
- Precipitation reactions
- Recrystallization
- Solubility data
- Electronic series (plate out) of metals

A matrix of characteristics can be gradually developed for each type of particle contaminant found. A publication known as "The Particle Atlas" (see reference list) can help narrow the range of possibilities to be evaluated.

- Thin film chemical contamination occurs in many precision components. Sources of thin film chemicals include outgassing from sources such as lubricants, adhesives, coatings, polymeric and elastomeric materials. Chemical residues can also originate from sources such as fingerprints, machining fluids, coolants, and packaging. Methods to test the ability of the cleaning process in removing thin film chemical contamination are discussed later in the manual.

There are five additional categories of soils that are more often associated with gross cleaning rather than precision cleaning operations, but are described below for completeness.

- 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 soaps.

- 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 (synthetics): 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, their 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

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.

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 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.

As mentioned earlier, precision components that are made of beryllium are chemically reactive, especially with ionic chlorine. Care must be taken to select an alternative that is compatible with the substrate.

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). Therefore, 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 precision 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 when cleaning a part varies from industry to industry and from process to process. In general, precision cleaning is performed when cleanliness requirements are fairly stringent and/or component materials are sensitive.

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 Inspection.*** These tests are conducted under high-intensity or long-wave ultraviolet lamps primarily on large production parts, rather than test coupons. Examination reveals water-spotting, streaking or haze that might indicate insufficient rinsing.

- ***Electron or Optical Microscopy***. These tests can be conducted with test coupons or production parts to examine contamination residues, obtain photographic documentation, and observe crystal properties. When using electron microscopy, particular care must be taken to prevent the test coupon from introducing external contamination.

- ***Microchemistry***. This method characterizes microscopic residues on surfaces. This technique involves dissolving the residue with a drop of liquid, transferring the drop (and the dissolved contamination) to a microscopic slide, and performing the chemical analysis under a microscope. The most common residues analyzed are the crystal precipitates that form as a result of the reactions between specific contaminants and reagents.

- ***X-Ray Photoelectron Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA)***. XPS is a surface analysis technique that is particularly useful for identifying thin films on surfaces. The system can examine an area of one millimeter or more in diameter or, with small-spot ESCA, can be focused to a fine spot micrometers in diameter. Other useful chemical analysis techniques include Auger electron spectroscopy (AES), secondary ion mass spectroscopy (SIMS), and microscopic Fourier-Transform infrared spectroscopy (micro FT-IR).

- ***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.

- ***Residue Level.*** The test panel is rinsed with an appropriate solvent after cleaning. The solvent is then evaporated and the residue analyzed quantitatively and qualitatively using analytical instrumentation (EDS, SEM, IR, etc.).

- ***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. Standard precautions should be taken 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 placed in 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 of this method 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 contamination.

- ***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.

Compliance to Specifications

Many precision cleaning applications are subject to military or other 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. In such instances, it is necessary to negotiate 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.

- Accelerated testing involves the use of temperature, humidity, and chemical accelerants in environmental test chambers. Optical and electron microscopy, Auger electron spectroscopy (AES), and ESCA are useful analytical tools.

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. Process steps that may follow precision cleaning 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. Precision cleaning may not make sense if packaging contaminates the parts.

- ***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 leads to stress corrosion or loss of fatigue strength.

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. Precision cleaning operations must be controlled to maintain the required level of cleanliness. 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. Some alternative cleaning processes may have slower throughput due to optimized operations and special drying stages. For example, if a plant switches from a solvent cleaning to aqueous cleaning process, it must allow more time for drying. This added drying time reduces the throughput of the cleaning, and possibly manufacturing, process. If enough time is not given to dry parts, subsequent operations can be adversely affected. For batch cleaning processes, throughput may not be critical.

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, the addition of wastewater treatment facilities may be necessary.

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 cleaning 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 techniques for use with 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.

In some alternative processes, as the concentration of soils in the cleaning solution increases, parts may leave the cleaning solution with unacceptable amounts of residual soil. Therefore, plants should consider monitoring solutions regularly, using filtration, and having a post-rinse/wash step.

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.

$$\boxed{\begin{aligned} NPV &= Cost_0 + Cost_1/(1+i) + \\ &\quad Cost_2/(1+i)^2 + \ldots + Cost_n/(1+i)^n \end{aligned}}$$

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. The cost savings resulting from savings in solvent consumption should be included 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 precision cleaning, will create 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 certain 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 THE 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 precision cleaning:

- Determine where and why CFC-113 and methyl chloroform are consumed in precision cleaning operations;
- Characterize existing cleaning processes. This activity will help reveal how precision 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 plant with a better understanding of its 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.

ALTERNATIVES TO CFC-113 AND METHYL CHLOROFORM

A number of alternative cleaning processes and alternative solvents to eliminate CFC-113 and MCF are now available for precision 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
- Pressurized Gases
- Supercritical Fluids
- Gas Plasma Cleaning
- Ultraviolet/Ozone
- CO_2 Snow

Alternative Solvents:

- Aliphatic Hydrocarbons
- Perfluorocarbons
- Alcohol Cleaning with Perfluorocarbon
- Hydrochlorofluorocarbons
- N-Methyl-2-Pyrrolidone
- Other Organic Solvents
- Other Chlorinated Solvents
- Volatile Methyl Siloxanes

"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 precision 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, 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, chelates, saponifiers, emulsifiers, 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 6 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 trouble 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 less effective than phosphates.

Additives are either organic or inorganic compounds that provide additional 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 6

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 7 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. For example, parts with capillary spaces and blind holes may trap low surface tension cleaning solutions. This is particularly a concern in precision cleaning applications. Sometimes, high velocity sprays can improve the flushing action to remove the cleaning solution. However, in other cases, immersion cleaning may be more effective.

A number of disk drive and aerospace manufacturers currently use high velocity sprays for critical cleaning. It has been found that these sprays are effective in removing surface active agents when high purity water is used, and when the sprays have an increased turbulent layer and reduced laminar sublayer.

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. The current industry practice is to use a 40 kHz operating frequency for delicate operations. 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 fixtures on the ultrasonic equipment 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.

Exhibit 7

AQUEOUS CLEANING PROCESS EQUIPMENT

IMMERSION WITH ULTRASONIC AGITATION	IMMERSION WITH MECHANICAL AGITATION	SPRAY WASHER
ADVANTAGES		
High level of cleanliness; cleans complex parts/ configurations Can be automated Usable with parts on trays Low maintenance May be performed at ambient temperature	Cleans complex parts and configurations Will flush out chips Simple to operate Usable with parts on trays Can use existing vapor degreasing equipment with some modifications.	High level of cleanliness Inexpensive Will flush out chips Simple to operate High volume Spray unit may be portable
DISADVANTAGES		
High cost Requires rinse water for some applications Requires new basket design Limits part size and tank volumes May require separate dryer	Requires rinse water for some applications Harder to automate Requires proper part orientation and/or changes while in solution May require separate dryer	Requires rinse water for some applications Not effective in cleaning complex parts May require separate dryer

Effective rinsing is a key part of aqueous cleaning in precision applications. Residues of water-based cleaning media, such as synthetic detergents, surfactants, and additives, may have a detrimental effect on component performance and reliability. Elements such as sodium and sulfur are common synthetic detergent materials that may remain on surfaces. Substances such as phosphorus, calcium, magnesium, chlorides, hydrocarbon films, amines, and nitrates are also potential residues of aqueous-based systems. Rinsing is particularly critical in parts with capillaries or complex geometry, where aqueous cleaning solutions might easily be trapped. 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 precision cleaning consists of three general process steps:

- Wash Stage
- Rinse Stage
- Dry Stage

Exhibit 8 provides a conceptual diagram of the different stages that make up the aqueous cleaning 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 which 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 precision 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 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

exhibit 8

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. Wastewater minimization and treatment is discussed in further detail later in this manual.

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. While it is most frequently used in metal cleaning, it is also used in electronics and precision 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 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. Exhibit 9 shows a schematic for a typical semi-aqueous cleaning process.

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.

exhibit 9

PRESSURIZED GASES

When removing particulate contamination, pressurized gases can serve as an alternative to cleaning with CFC-113 and MCF. Gases that are typically used include air, rare gases, carbon dioxide, chlorodifluoromethane (HCFC-22), and nitrogen. These gases, which may be stored at room temperature, are readily available in bulk and smaller quantities, and in numerous grades of purity.

Depending upon the pressurized gas that is used in the cleaning application, the advantages of cleaning with pressurized gases may include the following:

- Low viscosity
- Low toxicity
- High diffusivity
- Nonflammability
- Low capital cost

The drawbacks associated with the use of pressurized gases may include:

- Low density
- High pressure (may cause rupturing of seals)
- Often not effective for removing microscopic particles
- May not be appropriate for cleaning some critical components.

Process Chemistry

Air. Dry air is produced using ordinary air by removing hydrocarbons through oxidation. Carbon dioxide is removed from the air, and the air is then compressed and dried.

Clean dry air may be economically produced from pressurized air in-house. Specifically designed diaphragms and other noncontaminating pumps are available for this purpose. High efficiency filters, drying agents, and other equipment are also useful.

Rare Gases. Helium, neon, argon, krypton, and xenon are all rare gases. Unlike air, which reacts with many substances due to its high oxygen content, rare earth gases are noted for their extreme chemical inactivity. These monatomic gases are obtained by fractionation of liquid air.

Argon, the most abundant of the rare earth gases, is commercially available in cylinders ranging from 1,775 to 6,000 psig at 21.1°C. Argon is not toxic, but is an asphyxiant.

A problem inherent in cleaning with high pressure gases is the development of static charges. Ionizing guns are available from clean room equipment suppliers that can alleviate this problem.

Carbon Dioxide. Carbon dioxide, which can be recovered from a number of processes, is colorless, odorless, nonflammable, and slightly acidic. When used in pressurized cleaning, carbon dioxide does not contribute to global warming since its primary source is the air itself.

The gas is stable under most conditions, but will dissociate into carbon dioxide and carbon monoxide in the presence of free carbon at high temperatures. For example, at 1000°C, the equilibrium ratio of carbon dioxide to carbon monoxide is 0.7 percent to 99.3 percent.

Above the critical temperature of -31°C, all solid carbon dioxide converts to a gas. The gas can be shipped under its own vapor pressure of 830 psig at 21.1°C. Care must be taken when handling carbon dioxide because it is an asphyxiant, and cumulative amounts of the gas are poisonous.

HCFC-22. Chlorodifluoromethane, or HCFC-22, is colorless and nonflammable. Continued flooding of localized areas with liquid HCFC-22 causes rapid chilling, which helps to remove more tenacious contaminants.

At high temperatures, various metals may catalyze decomposition of HCFC-22. Silver is the most reactive with HCFC-22, followed by brass, bronze, aluminum, 1340 steel, copper, nickel, 18-8 stainless steel, and inconel. Magnesium and aluminum alloys with 2 percent or more magnesium are also particularly reactive with HCFC-22 in the presence of water. Natural rubber may also become swollen and degraded by the solvent.

HCFC-22 is often shipped as a liquified gas under its own pressure of 123 psig at 21.1°C. The gas is available in bulk and small disposable cans. Direct contact with liquid HCFC-22 may cause frostbite. The gas is considered to be nontoxic, but high concentrations can produce dizziness, narcosis, and nausea.

HCFC-22 has an ozone depletion potential (ODP) of 0.05. In comparison, MCF and CFC-113 have ODPs of 0.1 and 0.8 respectively. Because HCFC-22 is an ozone-depleting chemical, it's use is slated for reduction and elimination by the year 2030 under the 1992 amendments to the Montreal Protocol. The solvent is also subject to production control requirements under the Clean Air Act Amendments of 1990. Therefore, while HCFC-22 may be a viable short-term substitute to CFC-113 or MCF, its long-term use is limited.

To reduce the health and environmental impacts of HCFC-22, a plant should take measures to reduce emissions during use.

Nitrogen. Nitrogen can react with hydrogen, oxygen, and some metals at elevated temperatures. Reactive metals include calcium, barium, and magnesium. A very reactive form of nitrogen, called active nitrogen, is produced when it is passed through a glow discharge at low pressure. Active nitrogen combines with mercury, arsenic, zinc, calcium, sodium, phosphorous, and sulphur to produce nitrides.

Equipment Considerations

Typically, clean, dry, inert gas or air is fed to a pressurized gas gun at 100 psi. Many models offer 0.3 to 0.5 micron particle filtration with a maximum outlet pressure of ionized gas at 30 psi. Different ionizing and filtration techniques have been designed for specific needs. One model is reported to remove 3.0 micron size particles with 99 percent efficiency from bare silicon wafers.

Whether the ejected material produced by pressurized gas will damage surrounding surfaces depends on the composition of the contaminant and substrate. For example, metal dust can be easily removed from an assembly using pressurized gas. However, if the assembly includes an optical component with a sensitive coating, the component may be scratched by impinging particles. Particles with low mass may not damage the sensitive surfaces. Likewise, harder components may be resistant to scratching and indentation by particles.

Dislodged particles may also be a cause for concern because clean room requirements as well as surrounding structure may not tolerate increased levels of contamination. Ejected debris can be contained when small parts are being cleaned by performing the cleaning process in a laminar flow work station equipped with a high efficiency particulate air filter or an ultra-low penetration air filter. A vacuum may also be used with pressurized gas on some parts to capture dislodged contamination.

Process Details

Some of the primary considerations in choosing pressurized gases for precision cleaning include following properties:

- ***Surface chemistry***. This factor is ultimately responsible for the nature of the electrostatic forces between surfaces;

- ***Porosity***. Porous (and rough) surfaces possess the potential to mechanically lock contaminant and substrate and further hinder the cleaning process;

- ***Roughness of surface***. Large particles on a smooth surface may be removed more easily than small particles on a rough surface for the same reason;

- ***Size, shape, and homogeneity of the contaminant***. On a microscopic level, all surfaces possess ridges and valleys that make intimate contact between surfaces difficult. Adsorbed contamination on particles and other surfaces also hinders contact and prevents relatively short-range molecular interactions from occurring;

- ***Sensitivity of the surrounding area to ejected material***. Relatively inert gases and mixtures are most often used with specially designed equipment to meet cleanliness requirements without damaging the surrounding area.

SUPERCRITICAL FLUIDS

Supercritical fluids (SCFs) are a special category of pressurized gases. Specifically, they are fluids that are above their critical values for temperature and pressure. The critical region is characterized by the following conditions:

$0.9 < T_r < 1.2$ and
$1.0 < P_r < 3.0$

where T_r and P_r are the reduced temperature and pressure, respectively.
($T_r = T/T_{critical}$; and $P_r = P/P_{critical}$)

The technique of supercritical gas extraction exploits the powerful solvent abilities of such fluids at high temperatures and pressures. Relatively small adjustments to the temperature and pressure of supercritical fluids produce significant changes in density and solvent power. Exhibit 10 lists some of the properties of typical supercritical solvents.

SCFs have high diffusitivity and low density and viscosity compared to liquid solvents such as CFC-113 and MCF. This combination of characteristics allows for rapid extraction of contaminants and phase separation. Supercritical gas extraction has been found to be particularly effective for removing substances with medium molecular weight and relatively low polarity. In cleaning applications, the fluid itself can be easily recovered because of its high volatility.

The advantages of SCFs are similar to those of pressurized gases. Some additional advantages of SCFs include:

- Flexibility in altering the properties of the solvent;
- Ability to achieve cleaning selectivity;
- Rapid phase separations, which results in rapid cleaning time;
- Low operating costs (e.g., utilities).

The greatest drawback of cleaning with SCFs is the need to operate at high pressures, which can introduce significantly higher capital costs than cleaning with pressurized gas. Another disadvantage is the possibility that substrates may be adversely effected by the requisite high temperature and pressure conditions.

Initial results of the application of SCFs to precision cleaning indicate significant promise. Exhibit 11 presents the applications of supercritical carbon dioxide that have been tested so far as a potential replacement for precision cleaning with CFC-113 and MCF. It is important to confirm that the cleanliness achieved in each application matches the precision cleaning requirements.

Process Chemistry

Exhibit 12 shows a schematic diagram of the carbon dioxide supercritical cleaning process. The solvent fluid is pressurized and then heated to its supercritical state. It is then introduced into the extraction vessel at the selected extractor operating conditions. The carbon dioxide in the extractor can either be in solid or liquid phase. In the extractor, the supercritical fluid selectively solubilizes one or more contaminants from the source material. The solute-rich SCF exits the extractor and undergoes a temperature and/or pressure change. This change decreases the solubility of the solute in the fluid, which causes the solute and fluid to separate in the separator vessel.

Process Details

In order to determine whether SCF is a technically feasible and economically viable alternative, a plant must evaluate the phase equilibrium properties of the SCFs. This is important because fluids in high-pressure phase often exhibit complex behavior. Phase equilibrium and mass transport data are used to size equipment, determine utility requirements, and estimate costs. Important parameters to consider include:

- the number of phases present;

- the composition and density of each phase;
- the equilibrium changes associated with temperature, pressure, and composition variation.

Exhibit 10

DATA FOR TYPICAL SUPERCRITICAL SOLVENTS

Solvent	Critical Temperature (deg. C)	Critical Pressure (atm)	Density (g/cm3)
Methane	-83	45.4	0.16
Ethylene	9	49.7	0. 2 2
Chlorotrifluoromethane	29	38.7	0.58
Carbon dioxide	31	72.8	0.47
Ethane	32	48.2	0.20
Nitrous oxide	36	71.5	0.45
Sulfur hexafluoride	45	37.1	0.74
Propylene	92	45.6	0.23
Propane	97	41.9	0.22
Ammonia	132	111.3	0.24
Trichlorofluoromethane	198	43.5	0.55
n-Hexane	234	29.3	0.23
Isopropanol	235	47.0	0.27
Ethanol	243	63.0	0.28
Toluene	318	40.6	0.29
Water	374	217.7	0.32

Exhibit 11

SUPERCRITICAL CARBON DIOXIDE APPLICATIONS

Hardware	Materials/Components Cleaned	Contaminants Removed
Spacecraft	High voltage cables	Silicone oils
	Bearings	
		Lubricants
	Rivets	
Radar	Connectors	
	Flux residues	
	Transformers	
	Dielectric oils	
	Cables	
Laser	Optical benches	
Machine oils		
	O-rings	
		Plasticizers
Gas system	Seals	
		Plasticizers
		Monomers
Cleaning aid	Cotton ball/wipers	
Organic extractables		
	Cotton tipped applicators	Triglycerides
Adhesive residues		

exhibit 12 (basic model)

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.

ULTRAVIOLET LIGHT/OZONE CLEANING METHOD

The UV/ozone cleaning process has been used successfully to remove thin organic films from a number of different surfaces, including glass, quartz, mica, sapphire, ceramics, metals, silicon, gallium arsenide, and polyamide cement.

Process Overview

UV/ozone cleaning is a simple process that is relatively inexpensive to set up and operate. Under the proper conditions, the process can produce clean surfaces in less than one minute. Furthermore, these surfaces will remain clean during storage under UV/ozone.

The basic UV/ozone cleaning process involves the exposure of a contaminated surface to UV light in the presence of ozone. Cleaning occurs as a result of various photosensitized oxidation processes. Contaminant molecules are excited and/or dissociated by the absorption of short-wavelength UV light. These molecules and the free radicals produced by dissociation react with atomic oxygen to form simpler, volatile molecules such as carbon dioxide, water vapor, and nitrogen that can easily leave the surface.

There are several variables that determine the effectiveness of UV/ozone cleaning. These include: contaminants present, precleaning procedure, UV wavelengths emitted, distance and atmosphere between the UV source and the surface to be cleaned, contact angle of the light, and length of time of the exposure.

Testing must be performed to determine optimal conditions for different surfaces to be cleaned and contaminants to be removed. The part being cleaned should be kept as close as practicable to the UV light source, to maximize the rate of cleaning. Surfaces that have multiple contaminants or thick layers of contaminants require precleaning in order for the UV/ozone process to work. UV/ozone will efficiently clean organic contamination, but particles and inorganic components are more difficult to remove with this process.

Because the UV/ozone process requires no moving parts, it is easy to maintain and operate. However, both the use of UV light and the presence of excessive ozone can be dangerous to humans. UV light can cause eye injuries, and ozone causes respiratory distress. Special design considerations are necessary to accommodate the low workplace limits for ozone (0.1 ppm).

The UV/ozone process may also cause damage to the surface being cleaned. Staining and discoloration of materials can result from improper wavelengths and exposure times. Overexposure of materials to UV light can also cause corrosion. One positive side effect of the UV/ozone process is the neutralization of static charges on insulator surfaces.

Possible Applications

The UV/ozone cleaning process has numerous applications. Its primary use is substrate cleaning prior to thin film deposition, such as is necessary in the production of quartz crystal resonators. The process is also used for cleaning and storing metal tools, masks, resonator parts, and storage containers. Other applications that have been identified for UV/ozone cleaning include: photoresist removal, the cleaning of vacuum chamber walls, photomasks, silicon wafers, lenses, mirrors, solar panels, and gallium-arsenide wafers.

Future Developments

Future developments in UV/ozone cleaning procedures will come from further testing and experimentation with specific applications. Cleaning techniques can be refined considerably.

CO_2 SNOW

CO_2 snow is a relatively new cleaning technique that can be used to replace CFC-113 and MCF in a variety of cleaning applications. CO_2 snow is produced when liquid CO_2, which is stored at high pressure (> 800 psi) at ambient temperature, moves through specially designed orifices, or "jets". The CO_2 expands and cools rapidly, generating a combination of solid CO_2 particles, or "snow", and gas. During cleaning, the snow is directed at the contaminated surface, and cleaning occurs as a result of the momentum transfer between the solid CO_2 particles and particulate contamination. The collisions loosen the particulates from the surface, and the gaseous CO_2 sweeps them away. The level of cleaning can be controlled by adjusting the spray force, and the size of the area to be cleaned is changed by varying the spray pattern.

CO_2 snow removes particulate and organic contamination from parts ranging from small, extremely delicate items to large structures. Examples of military applications of CO_2 snow cleaning include restoring silicon wafers to original optical performance; removing thin molecular films such as Krytox, T-15u, and pump oil; and cleaning optical components such as glass mirrors, reflective optical elements, optical filters, and windows. Commercial applications include removing sanding residue from automobile body panels, nylon residue from disk drive parts, laser ablated metal from sunshields, cleanroom debris from light valves, and carbon epoxy dust from UV coatings.

The following are several advantages to cleaning using CO_2 snow:

- Does not damage sensitive surfaces (e.g., gold coatings and pristine silicon);
- Does not degrade material or change internal properties;
- Leaves no detectable residue;
- Meets stringent cleaning requirements -- provides superior cleaning performance compared to conventional solvent spray methods;
- Environmentally compatible. CO_2 does not damage the ozone layer and is not hazardous;
- Does not generate waste or residue, so clean-up and disposal problems are eliminated;
- Cost effective, since CO_2 is readily available and inexpensive compared to most solvents;
- Efficient. Spraying time is significantly shorter in comparison to solvent spray cleaning methods. For example, CO_2 reduced the cleaning time of aircraft windows from three days to one hour, thus saving $1.3 million a year.

As mentioned earlier, CO_2 snow is dispensed through specially designed orifices or jets. In some cases the nozzle is a part of a hand-held gun, while in other cases, nozzles are placed inside automated jet spray cleaning systems.

There are several variations of the hand-held gun currently commercially available, including the fixed-orifice gun and variable-orifice gun. The fixed-orifice gun emits a constant stream of CO_2 snow. The nozzle determines the spray pattern and force, and snowflake size. Various interchangeable nozzles are available for use with this gun. The operator can clean large quantities of similarly sized parts, achieving consistent results with a fixed-orifice gun. The variable-orifice gun has an adjustable orifice that allows the operator to vary the snowflake size and spray force. It is useful when various contaminants need to be removed from a wide range of parts composed of different materials.

The semi- and fully-automated jet spray cleaning systems offer moisture-free, temperature-controlled cleaning environments. Because nozzle location and nozzle motion can be programmed, these systems offer high repeatability with minimal operator interaction. Often, these cleaning systems are equipped with multiple nozzle capabilities that allow for a wide range of applications (e.g., CO_2 jet spray, hot N2 gas).

ALIPHATIC HYDROCARBONS

There is a wide range of aliphatic hydrocarbon solvents that can be used in precision cleaning (see Exhibit 13). 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 manufacturing 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 of using aliphatic hydrocarbons 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 aliphatic hydrocarbon 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 necessary 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 a 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 13

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

PERFLUOROCARBONS

Perfluorocarbons (PFCs) offer possible solutions to current CFC-113 and MCF users, particularly in cleaning parts for high accuracy gyros, before assembly and during strip down and rework. 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.

Process Chemistry

The PFCs are a group of compounds in which all the hydrogen atoms of a hydrocarbon are substituted by fluorine. Because of the extreme electronegativity of the fluorine atom, this total substitution results in extreme chemical stability in all of the compounds. The compounds are virtually inert chemically, have low toxicity, are completely nonflammable, and have no ozone depletion potential. As a result of this very low chemical activity, PFCs can be used in medical applications and are safe in contact with pure oxygen at high pressures. The excellent chemical stability of these fluids also makes them compatible with all gyro construction materials including beryllium. Exhibit 14 summarizes the compatibility of PFCs with various other materials.

Because their base hydrocarbons can vary, PFCs can have a wide range of molecular weights and structures. This results in a wide range of boiling points. One manufacturer identified six compounds available commercially with boiling points ranging from 29°C to 160°C, at 1 atm.

All the PFC compounds are strong infrared absorbers. This capability, coupled with the PFCs' extremely long atmosphere lifetimes, result in the chemicals having a very significant global warming potential. Another drawback of PFCs is their very low solvency power, which makes them unlikely to be very useful for removing oils.

Another major disadvantage of PFCs is their high cost, resulting from complex synthetic production processes. A typical low to mid-range boiling PFC, for example, is approximately $90 US per kg (late 1990).

Process Equipment

Design of equipment for gyroscope or other precision parts cleaning must be specific to each application. One requirement for all equipment, however, is that it must be hermetically sealed. Unless effective sealing is achieved, the loss of PFC will be prohibitively expensive (even considering the high cost and strategic importance of the products) and environmentally unacceptable because of its high global warming potential.

Process Details

All current high density flotation fluids are soluble in certain PFCs, allowing them to be used for flushing filled assemblies.

High pressure spraying with PFCs appears to be a very effective method of particle removal.

Exhibit 14

PERFLUOROCARBON (PFC) COMPATIBILITY WITH VARIOUS MATERIALS

Class of Material	Observation
Rubbers	<1% linear swell, ± 1% change in weight
Polyethylene, polypropylene	<1% shrinkage, zero change in weight
Nylons	Negligible change in dimensions or weight
Polystyrene	Variable, generally negligible, shrinkage (e.g., 0.2%)
"Perspex" ("Plexiglass")	<0.2% shrinkage, slight loss in weight
FTFE (unfilled)	2-3% linear swell, up to 10% increase in weight
PVC (Rigid)	Negligible change
PVC (Flexible)	Extraction of plasticizer, loss of flexibility (in hot Flutec)
Electronic circuit boards*	± <0.1% dimensional change, zero change in weight
Copper and brass	Slight tarnishing (from dissolved oxygen)
Other Common metals	No effect detectable
Silicone and microcircuit chips	No known effect
Adhesives Adhesive tapes Paper Enamelled wires Insulating tapes Paints Other surface coatings and sealants	No adverse effects detected in any samples tested up to the present time

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* Including: SRBP, Epoxy, DAP, Silicone, Melamine, Polyester, with filler materials of all common types.

ALCOHOL CLEANING WITH PERFLUOROCARBON

Alcohols such as methyl, ethyl, and isopropyl have been used extensively for cleaning printed circuit boards and precision components. They are very effective in removing rosin and polar activators commonly used in flux.

Safety is the primary difficulty in using alcohols, which are highly flammable. Both flame and explosion proofing are necessary equipment characteristics to prevent operator injury and equipment damage. Using a perfluorocarbon (PFC) "blanket" adequately suppresses the flammability of the alcohol vapor, thereby allowing for temperatures sufficiently high for distillation.

PFCs are relatively immiscible with alcohol; the two may be used together with little or no mixing.

There are several advantages to using alcohol as a solvent for precision cleaning. These include the following:

- Alcohol, being extremely polar, has great solvency and allows for greater freedom in removing particulate and organic contamination than CFC-113.
- PFCs are nonflammable, have low toxicity and reactivity, and have no ozone-depleting potential.
- Relatively small amounts of alcohol are required for each cleaning. This amount varies with the process.
- The nonflammable nature of the alcohol-PFC vapor allows for continuous distillation, thus permitting clean rinses.
- Since alcohol and PFC have different boiling points, an operating temperature between the two will allow for selective boiling and will prevent the percentage of alcohol in the vapor from rising to a point where the vapor becomes flammable. Adding water to the alcohol raises the alcohol's flash point above the PFC's boiling point.
- Alcohol and PFC are "clean" agents; i.e., they leave no residue. They also evaporate readily at low temperatures.

There are also several drawbacks associated with the use of alcohol/PFC cleaning. These include the following:

- Safety systems must be designed to automatically cease operations if the PFC level drops below the level necessary to prevent explosion.
- PFCs have a high global warming potential.
- PFCs are expensive.
- Pure alcohols are not effective at removing nonpolar contaminants like grease.
- High capital cost of equipment.
- Uncertain development time and costs.

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 15 presents physical properties of these chemicals. HCFCs have been attractive alternatives due to their good cleaning performance, and their 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 15

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 Potential	0.8	0.1	~0.05	~0.05	0.11
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 precision 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 requires special equipment design criteria. In addition, the economic use of HCFCs may require special emission control features for vapor degreasers (see Exhibit 16a, 16b, and 16c). 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 HCFC blends may require compatibility testing with titanium, magnesium, zinc and other metals. Solvent blends have shown some adverse effects with plastics such as ABS, acrylic, and Hi-Impact Styrene. Therefore, plastics also need to be tested on an individual basis.

exhibit 16a

exhibit 16b

exhibit 16c

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 17 summarizes the solvent's principal properties. Exhibit 18 shows two typical process equipment designs that have been used successfully for both batch and in-line operations.

Exhibit 17

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 18

OTHER ORGANIC SOLVENTS

The precision cleaning industry has always used a wide range of miscellaneous solvents. In most applications, such solvents are used in manual operations. They are often applied using camel or sable hair brushes during assembly or rework. Typical solvent cleaning applications include:

- Local defluxing after solder rework operations;
- Defluxing after special solder operations (e.g., strain gauge lead attachment);
- Varnish applications (e.g., small scale in-situ coil impregnations).

Some of the solvents commonly used include organic solvents such as ketones, alcohols, ethers, and esters, and chlorinated solvents such as trichloroethylene, perchloroethylene, and methylene chloride. Chlorinated solvents will be described in further detail in the next section.

Organic 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 19). 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, the flammability of both solvents (note that acetone has a flash point of 0°F) and their incompatibility with many structural polymers (e.g., stress cracking of polyether sulphone, polyether ketone, and polycarbonate) mean 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. However, certain glycol ethers, can cause swelling, cracking, and structural degradation of polymeric and elastomeric materials. The alcohols have a range of flash points. Extreme care must be exercised while using the lower flash point alcohols (see Exhibit 20).

As mentioned earlier, one method of organic cleaning involves the use of an alcohol vapor zone to clean the parts, and a perfluorocarbon vapor blanket above the to reduce the flammability risk of the heated alcohol. A different class of alcohol vapor degreasing equipment does not make use of an inerting agent such as perfluorocarbons. Instead, these systems have numerous safety devices built into the equipment, including air monitors, automatic sprinkler systems, and automatic shutoff capabilities. Nevertheless, when using both types of equipment, workers must exercise extreme caution to reduce the risk of explosion.

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 esters 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. In fact, 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 noncombustible 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.

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 19

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	$C_2H_5COC_2H_5$	$3.4^{104°F}$	4.6	55	-	-	250	0.56	163
METHYL n-PROPYL KETONE	$CH_3COC_3H_7$	4.3	3.3	45	1.6	8.2	200	-	180
CYCLOHEXANONE	$(CH_2)_5CO$	2.3	8.0	145	1.1	-	100	0.49	-
METHYL ISOBUTYL KETONE	$(CH_3)_2CHCH_2COCH_3$	2.0	1.8	64	1.4	7.5	100	0.55	148
METHYL n-BUTYL KETONE	$CH_3COC_4H_9$	$3.4^{77°F}$	$3.7^{77°F}$	73	1.2	8.0	100	0.55	148
METHYL CYCLOHEXANONE (Mixed Isomers)	$(CH_3)C_5H_9C0$	0.2	3.0	118	-	-	100	$0.44^{58°F}$	-
ACETONYL ACETONE	$CH_3COC_2H_4COCH_3$	∞	∞	174	-	-	-	-	-
DIISOPROPYL KETONE	$(CH_3)_2CHCOCH(CH_3)_2$	0.6	-	75	-	-	-	-	-
METHYL n-AMYL KETONE	$CH_3(CH_2)_4COCH_3$	0.4	1.5	120	-	-	100	-	149
DIACETONE	$(CH_3)_2C(OH)CH_2COCH_3$	∞	∞	48	-	-	50	$0.50^{58°F}$	200

Source: DuPont Company, Handbook of Standards for Solvents

Exhibit 20

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

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 21 presents the proposed control equipment combinations and the alternative idling limits for different types of equipment. Exhibit 22 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 precision cleaning provided adequate control measures are used. Exhibit 23 summarizes the solvent properties of these other chlorinated solvents.

Exhibit 21

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 (≤ 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 22

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 and Cold Cleaning (Existing)	153.2
In-Line Vapor and Cold Cleaning (New)	98.5
Batch Cold Cleaning	N/A

Exhibit 23

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 CH_2Cl_2		CCl_2FCClF_2	CH_3CCl_3	$CHClCCl_2$	CCl_2CCl_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 132		31	124	130	9	1
U.S. OSHA PEL 8 hr. TWA (ppm)	1000	350[a]	100	100	500[b]	
Flash Point (°C)	None	None	None	None	None	

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[a] Obtained from HSIA White Paper 1989.

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

Source: UNEP 1991.

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 24 presents the properties of three VMS blends as compared to CFC-113 and MCF. Exhibits 25 and 26 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 24

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 25

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 26

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

WASTEWATER MINIMIZATION AND TREATMENT

Pre-Treatment of Water

Because the cleanliness of precision components rinsed with water is largely determined by the quality of the rinsewater, a plant should understand its requirements for water supply and quality of water. For example, plants should remember that in some areas, water is in short supply and in others areas, the quality of water is not suitable for precision cleaning. Other factors to consider regarding water supply, quality, and pre-treatment include:

- Water supply requirements vary between machines and with various recycling schemes;
- Water supply requirements range from 0.5 gpm to 10 gpm with 3 to 5 gpm being most common. Systems that recycle water require additional water only to make up for evaporation;
- Pre-treatment of water may be required to reduce hardness and suspended particulates, or to reduce machine maintenance. Water softening can be done with off-the-shelf water softening packages;
- Water with hardness greater than four should not be used with saponifiers;
- Tap water costs less and wets better than purified deionized water, but can introduce contaminants or interfere with the cleaning chemistry;
- Highly deionized water can cause problems.

Typically, aqueous and semi-aqueous cleaning use tap water and/or deionized water. If the tap or deionized water is inadequate for the specific application, water treatment may be required.

The following treatment methods and equipment can be used to adjust water quality:

- Mechanical filtration to remove suspended particles;
- Sedimentation (to allow suspended particles to settle);
- Coagulation (to remove fine particles in colloidal suspension);
- Carbon filtration (to adsorb gases, vapors, organic substances, and colloidal solids);
- Bacteria filtration (to remove bacteria and other microorganisms);
- Irradiation with ultraviolet light (to destroy bacteria and other microorganisms);
- Water softening (to remove calcium and magnesium);
- Reverse osmosis (to remove dissolved solids, colloids, and microorganisms).

Depending on the initial water quality, different combinations of the above units are used to achieve the desired quality level.

Post-Treatment of Water

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 precision 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 stainless steel or lined with plastic lining 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 precision 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 precision components. 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 27 presents a conceptual design of a semi-continuous wastewater treatment system that treats wastewater generated from precision 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.

SUMMARY AND REVIEW

The manual has described the necessary steps to develop a program to eliminate the use of CFC-113 and MCF in precision cleaning operations. In doing so, it has:

- Summarized the reasons for the precision cleaning industry's historical dependence on CFC-113 and MCF;
- Outlined the steps necessary to characterize existing manufacturing processes and precision cleaning needs;
- Detailed the key organizational, technical, economic, and environmental criteria to consider when developing a phaseout program;
- Discussed the many new alternative cleaning processes and solvents for precision cleaning, and summarized their operational principles, advantages and disadvantages;
- Presented methods and options to minimize wastewater from the use of aqueous and semi-aqueous cleaning processes.

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 industrial experiences of some of the alternative technologies discussed earlier.

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 or ICOLP, ICOLP committee members, and the companies that employ the ICOLP committee members.

- ***Case Study #1:*** Aqueous Process for Cleaning Disk Drives.
- ***Case Study #2***: Alcohol with Perfluorocarbon Process for Cleaning Various Precision Components.
- ***Case Study #3:*** Aqueous Process for Cleaning Inertial System Parts.

CASE STUDY #1: AQUEOUS PROCESS FOR CLEANING DISK DRIVES

Case study #1 describes the work conducted by Digital Equipment Corporation (Digital) at its Colorado Springs Facility, to significantly reduce CFC-113 use and to identify alternative solvents.

Introduction

Digital designs and manufactures a variety of disk drives and controllers. The products range from 5 1/4" to 14" disks, from a few hundred megabytes to more than 1.5 gigabytes per spindle.

Disk drives are manufactured in cleanroom environments. The electromechanical components require precision cleaning from particles to submicron sizes and from ionic and organic film residues.

Digital previously used CFC-113 extensively for precision cleaning of components. In 1987, Digital adopted an overlapping, three-phased approach to reduce and eventually eliminate CFCs from its manufacturing operations. CFC consumption for 1987 was 62 tons. Early conservation efforts have led to substantial reductions - to 56 tons in 1989 and 45 tons in 1990. Projections for 1991 are 15 to 20 tons. The goal is for virtually complete elimination by the end of 1991.

Phases I and II -- CFC Reductions

Phase I was designed to achieve immediate reductions through engineering enhancements, process improvements, and operating discipline. Phase I efforts which have been implemented successfully, focused on short lead time and low cost immediate reduction in CFC emissions.

Phase II is a strategy during transition to alternatives. It accommodates near and mid-term efforts to achieve significant reductions in CFC consumption beyond that of the Phase I effort. Phase II addresses longer lead time and higher cost solutions. In this phase, Digital has implemented carbon adsorption columns, closed or nearly-closed systems, balloon accumulators, and other conservation devices.

Phase III -- CFC Alternatives

Feasibility Study

Phase III efforts have been targeted to finding a permanent alternative to ozone-depleting CFCs in manufacturing operations. Initial efforts focused on an extensive feasibility study. This part of the project involved literature searches, vendor searches, and laboratory work with potential alternatives. Laboratory studies included testing a variety of organic, semi-aqueous, and aqueous solvent systems for particle removal, film removal, residues, and material compatibility with the variety of metal and polymer parts, coatings, and platings used in disk drive hardware. The decision was made to pursue an aqueous cleaning alternative for the bulk of precision cleaning.

Internal Consortium

Digital has several other plants that assemble disk drives or provide component hardware to be used in the drives. The company established a cooperative effort that allowed better utilization of funding, knowledge, and resources in a division of labor.

Process Design

The initial activity involved the selection of specific aqueous chemistry for process parameters and then an optimization of these variables. Primary design activities focussed on material compatibility, such as corrosion of metals and effects on polymers.

Test Program For Cleaning Effectiveness

Cleaning effectiveness was evaluated using a variety of tools. Optical microscopy, a very valuable method, can be used to count and size particles down to about one micron.

Particles made of a variety of materials such as aluminum oxide, stainless steel, nickel, glass, and polystyrene latex can be obtained in sizes from submicron to several tens of microns. These particles were used to artificially contaminate test coupons. Coupons were cut from disk drive materials, providing the same surface material and structure as actual production hardware. The particles were counted and sized to obtain initial frequency distributions either manually with a microscope or by using image analysis equipment. The contaminated parts were subjected to the treatment combination of fractional factorial experiments, and the effectiveness of the various combinations evaluated.

Similar testing was conducted using chemical film contamination where hydrocarbon oils and ionic contamination were used to contaminate the parts. Measurement can be conducted using optical microscopy or surface energy measurements (contact angle) or by more sophisticated methods such as X-Ray Photoelectron Spectroscopy (XPS).

Test Program For Rinsing

A key element of aqueous cleaning is removal of cleaning chemistry from the parts. Trace residues of ionic and organic films left behind can be detrimental to product function.

Experiments using contact angle, optical and chemical microscopy, and XPS are useful for identifying process residues and quantities in testing optimum methods of rinsing.

Test Program for Material Compatibility

Material compatibility was tested by evaluation before and after cleaning using optical microscopy, scanning electron microscopy (SEM), EDS (energy dispersive x-ray spectrometer), and XPS. Metals were tested for corrosion by acceleration in environmental chambers. Plastics were mechanically and environmentally stressed and cycled to evaluate the effects of surfactants on specific polymers.

Implementation

Digital is adopting an aqueous cleaning alternative for the majority of the precision cleaning requirements for disk drive cleaning. Based on the testing described above, a synthetic detergent blend of nonionic and anionic surfactants with additives (such as builders, inhibitors, dispersing agents, buffers, and others) will be used in an ultrasonic immersion process.

Rinsing will be conducted in three stages: an initial high-volume, low-pressure spray; a second stage immersion-ultrasonic rinse; and a final high-pressure spray rinse. The nozzle used in the sprays will be optimized for pressure, flow-rate, spray pattern, and other parameters.

Drying will be performed using a mechanical dewatering stage with high velocity and high volume of filtered air to remove the bulk water, followed by evaporative drying of residual moisture.

CASE STUDY #2: ALCOHOL WITH PERFLUOROCARBON CLEANING PROCESS

Case study #2 discusses the work carried out by British Aerospace (Dynamics) Ltd. (BADL) to develop two prototype cleaning systems that could use an alternative solvent and eliminate the use of CFC-113.

Introduction

BADL designs and manufactures a wide range of defensive missile systems which involves the manufacture of many subsystems. These include flight and ground equipment, electronics, guidance equipment, and control systems - all of which require the use of CFC-113 as a precision cleaning agent.

In common with most companies in the aerospace industry, BADL has set up an extensive Design Support Laboratory. Other organizations refer to these groups as Materials and Process Laboratories (M + PL). Their function is varied and is concerned with the fine tuning of designs which, among many other factors, includes contamination and the means of its prevention.

Company Requirements

The following characteristics of BADL's business defined the options and alternatives to CFC-113:

- Many of the manufacturing activities were relatively small. No single, large, high-throughput plant existed, especially in the electronics and precision engineering areas.

- As a major military contractor, BADL's manufacturing contracts often run for many years and thus represent technologies of varying dates. Changes to long-standing designs to enable different cleaning techniques to be introduced would require expensive requalification and would not be supported by customers.

- Considerable amounts of CFC-113 were used in dewatering processes to give rapid spot-free drying of electronics, small parts, and optics.

- BADL's business is supported by large numbers of subcontractors, many of whom are relatively small and use small scale batch cleaning methods.

- The bulk of BADL's CFC-113 applications were carried out in superclean, white room working conditions.

- Certain special materials such as beryllium, were used in both the sensor manufacture and in the space component divisions. These would require a careful choice of cleaning solvent, because of the sensitivity to corrosive attack.

Company Response

Following the approach by one of BADL's suppliers of CFC-113, the alcohol/perfluorocarbon cleaning process was considered as a useful alternative to CFC-113 for both electronics and small parts cleaning.

The process, which is described in the previous section, is based on the principle of adding a perfluorocarbon (PFC) to isopropanol (IPA). Components are immersed in the hot alcohol, cleaned by ultrasonic agitation, and then removed through the vapor resulting in a warm, dry, alcohol-free product. Alternatively, parts can be held within the vapor and spray cleaned with pure alcohol.

In order to move from the conceptual phase to design and implementation, BADL formed a cooperative venture with several partners: its supplier of perfluorocarbon, an industrial partner who could assist in the design of cleaning equipment and provide the industrial environment for the realistic evaluation of the process, and an industrial partner with experience in the manufacture of solvent cleaning machines.

Through this cooperative venture, BADL was able to design two prototype machines:

- A printed circuit board (PCB) cleaner; and
- A general purpose cleaner.

PCB Cleaner

This prototype was designed primarily to clean PCBs of all types including single sided through-hole, SMT and hybrids. The basic principles of the machine are shown in Exhibit 28. Mixed PFC and IPA vapor, generated by remote hot water heating of a PFC/IPA sump (A), volatilizes and the mixed vapors rise into a cleaning tank (B). This tank is closed by hermetic lid (C). The vapors condense on the cooling coils (D), with the condensate returning to the three tanks (E1), (E2), and (E3) each of which contains IPA and PFC. An inner gauze lid, (F), interconnected to the main lid is fitted to break up aerosols of alcohol from the spray, and vapors rising above the cooling coils are condensed on the refrigerated panel (G). Air and vapor displaced by the thermal expansion of the air in the cleaning tank passes via valves to the pressure balancing volume (H) thus preventing loss of vapors on heat-up and cool-down.

To operate the system, a holder containing the test circuits is fitted manually and the interlocked lids closed. Clean alcohol is pumped via pneumatic pump (J) from tank (E1) to spray heads (K) arranged on both sides of the PCBs; dirty alcohol flows back via the appropriate valve to (E1). The boards can then be rinsed with PFC (also from E1) to remove residues of contaminated alcohol from the first cleaning stage. This process of alcohol and PFC spray cleaning can be repeated twice more from tanks (E2) and (E3), so that the work pieces are cleaned with successively cleaner solvent.

In common with all vapor degreasing systems, this PFC /alcohol machine is self-cleaning. The majority of the solvent distillate returns to tank (E3) and the overflow weirs over into (E2) and (E1) and then into the sump. By this means, the soil is collected in the sump and tank (E3) always remains clean. The working fluid in the tank is the alcohol; dirty alcohol can be removed from the sump and replaced automatically by clean material pumped into tank (E3). Level sensors detect and automatically adjust both the PFC and alcohol levels throughout the system.

General Purpose Cleaner

During the development of the first prototype machine results of a research program on the effects of ultrasonic cleaning on microelectronics was published. This work showed that ultrasonic cleaning carried out under normal conditions did not damage electronic components nor sensitize them to long-term deterioration.

In the design of the first prototype, ultrasonic cleaning was not incorporated because of concerns about possible long-term damage. However, recent research has documented that ultrasonics do not have damaging impacts on properly designed boards. These results have greatly simplified the design of the second cleaner.

The second cleaner is also a batch operation with fully automatic under-lid handling of components. Parts are cleaned by an automatically programmed combination of hot alcohol immersion and ultrasonic cleaning; parts are dried before leaving the machine with heated PFC. Clean, dry, warm components are presented at the end of the sequence. Like the first prototype, this machine is also fitted with a hermetic lid system to eliminate solvent loss.

CASE STUDY #3: AQUEOUS PROCESSES FOR CLEANING INERTIAL SYSTEM PARTS

Case study #3 details the work carried out at a U.S. Air Force Base technical center to identify aqueous processes that could replace the use of CFC-113 and MCF.

Introduction

The Aerospace Guidance and Metrology Center (The Center), located at the Newark Air Force Base in Ohio, repairs a variety of inertial guidance and navigation systems and related components. The repair processes require extensive cleaning to remove contamination from parts made of aluminum, copper, beryllium, steel, and other materials. The contamination includes particulates and nonparticulates. Many assemblies have critical tolerances that mandate precision cleaning of the component parts before reassembly. The critical tolerances of some devices are such that particulate contamination as small as 0.5 microns can cause the device to fail.

Traditionally, CFC-113 and MCF have been the solvents most frequently used to meet The Center's stringent cleaning requirements. Prior to 1989, the Center purchased over 600,000 pounds of CFC-113 annually. The policy of The Center is to completely eliminate the use of CFC-113 and MCF for cleaning by the end of 1995.

Several cleaning procedures previously based on CFC-113 and/or MCF were changed to aqueous processes in late 1989 and early 1990. This conversion has resulted in many benefits in addition to reduced solvent use. Work is continuing to extend the use of aqueous processes throughout The Center's cleaning operations as a major contribution to achieving the goal in its military policy.

Aqueous Process as an Alternative

Aqueous cleaning was considered as an attractive alternative to CFC-113 and MCF for several reasons. First, The Center already possessed a sophisticated ultrasonic cleaning device specifically designed to use water and biodegradable detergents for cleaning metal parts. The Center's engineers believed that many of the parts that were being cleaned with CFC-113 and/or MCF could be precision cleaned in the ultrasonic cleaner.

Another reason involved perceived difficulties in obtaining approval to change processes. Since any procedural change in the repair practices performed by The Center must be approved by the appropriate military office, it is normally difficult to make changes. One such office, however, had originally required aqueous cleaning but subse-quently authorized CFC-113 and MCF to be used instead. Therefore, The Center expected that they would be willing to approve aqueous cleaning if it were demonstrated to clean equal to or better than the CFC-113/MCF based processes. It was felt this should provide a basis for approaching other military offices to permit changes.

Finally, the aqueous processes using biodegradable detergents were attractive because of their relative low cost, their availability, and their nonhazardous nature.

Testing and Implementation of Aqueous Procedures

Teams were formed to investigate and develop an acceptable aqueous process for each cleaning operation selected as a candidate for conversion from CFC-113 or MCF. The team members were from engineering, production, and quality assurance sections. The team concept proved to be very effective. One reason for this was that the cross feed of ideas contributed significantly to the solution of many of the original (and inevitable) problems encountered. In addition, the new processes were readily accepted when they were subsequently approved for implementation because all the participating sections had been involved in the design stage.

The teams experimented until they were able to fit an aqueous cleaning process to the specific procedure being examined. For the experiment to be a success, it had to produce results that were at least as good as the CFC-113 or MCF based process. These experiments proved that high quality deionized water was essential to the success of the aqueous process. The many other factors that came into play included: process development of proper techniques for drying the parts, development of a procedure to bag the parts after cleaning to ensure cleanliness during travel from the cleaning site to the reassembly site, development of fixtures to permit proper orientation of the parts within the ultrasonic cleaning chamber, and controls to prevent the effects of electrostatic charge in the cleaning area from causing recontamination of the cleaned parts.

Extensive testing and evaluation were performed to convince the team itself and local management that the new process should be substituted for the old. The thoroughness of the testing and evaluation proved adequate to convince the military office to approve the process changes.

Personnel from the physical science laboratory at The Center were instrumental in determining the effects of aqueous cleaning and in providing documentation. A variety of tests were used to evaluate the cleanliness achieved from the aqueous procedures and, also, to determine if the part was damaged by the procedure, either chemically or metallurgically. Testing had to be tailored to the geometry and composition of the parts involved. It included, as applicable, optical microscopy, scanning electron microscopy, particle counts, water break tests, and other techniques. Functional tests were also used on some parts as an indicator to determine if the parts were clean and damage free. Once it was determined that a part could be successfully cleaned with an aqueous process, the part was subjected to a cleaning time in the ultrasonic environment that would approximate the expected cumulative cleaning time of the part's life. This test was to ensure that no damage would be experienced as a result of the new cleaning process during the life of the part.

The lab also conducted controlled tests with a variety of metals common to The Center's parts and a variety of commercially available biodegradable detergents to determine the amount of metal that would be removed through exposure to each detergent. This information was used to select an appropriate detergent for application where minimum metal removal was desired.

Results

To date, eight cleaning operations that previously used CFC-113 and/or MCF have been successfully converted to aqueous processes using the ultrasonic cleaner; no CFC-113, MCF, or other solvents are now used in these operations. The aqueous processes are sophisticated and require technician care to insure that parameters such as deionized water quality, water temperature, vacuum oven drying time, and temperature are maintained.

Benefits from the conversion include not only decreased solvent usage, but also improved yields, reduced process time, and reduced exposure of the technicians to hazardous chemicals.

Future Plans

The results of its experience with aqueous processes has encouraged The Center to continue converting CFC-113 and MCF based processes to aqueous processes. However, not all future conversions will be centered around the specific ultrasonic cleaner used with the original process conversions. Additional testing in The Center's laboratory has produced successful results using aqueous processes involving water spray booths, conventional ultrasonic cleaners, and other equipment. The Center has learned that the process must be tailored to the specific cleaning operation to obtain the least expensive and most practical solution that meets the process requirements.

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GLOSSARY

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.

Aerosol spray -- A means of atomizing liquids by propelling them from a pressurized container by a soluble gas. Apart from the fact that CFC gases can be used as the propellant, CFC-113 mixtures may be the propelled liquid.

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.

Chlorocarbon -- An organic chemical composed of chlorine and carbon, e.g., carbon tetrachloride.

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.

COD -- An abbreviation for chemical oxygen demand.

Defluxing -- The removal of flux residues after a soldering operation. Defluxing is a part of most high-reliability electronics production.

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

Flux -- An essential chemical employed in the soldering process to facilitate the production of a solder joint. It is usually a liquid or solid material, frequently based on rosin (colophony).

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.

Hydrocarbon -- An organic chemical composed only of hydrogen and carbon. Gaseous or volatile hydrocarbons are flammable.

Hydrocarbon derivative -- An organic hydrocarbon whose molecule has been modified by adding atoms other than hydrogen and carbon, e.g., alcohols.

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 are often used in this application.

Hydrochlorocarbon -- An organic chemical composed of hydrogen, chlorine and carbon, e.g., trichloroethylene.

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.

Pentafluoropropanol -- A fluorinated alcohol.

Perchloroethylene -- A perhalogenated chlorocarbon solvent used extensively in industrial degreasing and for dry cleaning.

Precision cleaning -- Though not a perfect definition, this term refers to the cleaning of high-precision mechanical parts and electronic sensory devices, as opposed to general metal cleaning. This is usually done under controlled atmospheres, notably in "clean-rooms" with low particulate contamination.

Printed circuit -- A printed circuit is an electronic component designed for interconnecting the other components. It usually consists of a metallic conductor pattern on an organic insulating substrate. After fabrication, it is known as a printed circuit board (PCB); after assembly where components are added, it is known as a printed wiring assembly (PWA).

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.

Solvent containment -- Means of preventing or reducing the emission of CFC or other solvents into the environment. This technique usually involves improving the design of the equipment in which the solvent is used and preventing losses.

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.

1,1,1-trichloroethane -- A hydrochlorocarbon solvent with an estimated ODP of 0.1. Also known as methyl chloroform.

Vapor phase cleaning -- A cleaning process, usually with CFC-113 solvent or hydrochlorocarbon solvents, where the final rinse of the parts being cleaned is achieved by condensing solvent vapors on the parts.

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, U.S. EPA, U.S. Air Force, Swedish National Environmental Protection Agency, and 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, non-proprietary 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; and

- Legislation that has been enacted or is in place internationally, nationally, and locally.

Information about ICOLP can be obtained from:

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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.