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Guide to Cleaner Technologies

Alternatives to Chlorinated Solvents for Cleaning and Degreasing

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GUIDE TO
CLEANER TECHNOLOGIES

ALTERNATIVES TO CHLORINATED SOLVENTS FOR CLEANING AND DEGREASING

Office of Research and Development
United States Environmental Protection Agency
Cincinnati, Ohio 45268

NOTICE

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This *Guide to Cleaner Technologies: Alternatives to Chlorinated Solvents for Cleaning and Degreasing* has been subjected to U.S. Environmental Protection Agency peer review and administrative review and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency.

This document is intended to provide alternatives to chlorinated solvents for pollution prevention in cleaning and degreasing processes. Site-specific selection of a technology will vary depending on shop and manufacturing process applications. It is the responsibility of individual users to make the appropriate application of these technologies. Compliance with environmental and occupational safety and health laws is the responsibility of each individual business and is not the focus of this document.

FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the U.S. EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

Reducing or eliminating the utilization or generation of hazardous material at the source or recycling these solvents on site is one of EPA's primary pollution prevention goals. Economic benefits to industry may also be realized by reducing disposal costs and lowering the liabilities associated with hazardous waste disposal.

Publications in the U.S. EPA series, Guides to Pollution Prevention, provide an overview of several industries and describe options to minimize waste in these industries. Their focus is on the full range of operations in existing facilities. Many of the pollution prevention techniques described are relatively easy to implement in current operations without major process changes.

This *Guide to Cleaner Technologies: Alternatives to Chlorinated Solvents for Cleaning and Degreasing* summarizes information collected from U.S. Environmental Protection Agency programs, peer-reviewed journals, industry experts, vendor data, and other sources. The cleaner technologies are categorized as commercially available or emerging. Emerging technologies are technologies that are in various stages of development, and are not immediately available for purchase and installation. For each technology, the *Guide* addresses its pollution prevention benefits, operating features, application, and limitations. Elimination or reduction in the use of chlorinated cleaning and degreasing solvents is the main focus of the technologies covered in the *Guide*.

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OVERVIEW

What Is Cleaner Technology?

A *cleaner technology* is a source reduction or recycling method applied to eliminate or significantly reduce hazardous waste generation. *Source reduction* includes product changes and source control. *Source control* can be further characterized as input material changes, technology changes, or improved operating practices.

> *Source reduction precedes recycling in the hierarchy of pollution prevention options. Pollution prevention should emphasize source reduction technologies over recycling, but, if source reduction technologies are not available, recycling is a good approach to reducing waste generation. Therefore, recycling should be used where possible to minimize or avoid the need to treat wastes after viable source reduction options have been evaluated and/or implemented.*

The cleaner technology must reduce the quantity and/or toxicity of the waste produced. It is also essential that final product quality be reliably controlled to meet acceptability standards. In addition, the cost of applying the new technology relative to the cost of similar technologies should be considered.

Why Clean and Degrease?

> *Cleaning is done to remove soils that interfere with process performance or give an undesirable appearance.*

Cleaning and degreasing in industry generally applies to removal of contamination from hard surfaces. The contamination is any unwanted material that adheres to a surface, such as films, particulates, and oxidation products. Films include oil or grease lubricants, hydraulic fluids, preservatives, and possibly paint coatings. Particulates may include dust, soil matter, metal fines, or product material in an industrial process. Oxidation coatings includes rust in iron-bearing components (hydrous ferric oxides) and oxide coatings of highly anodic metals, such as aluminum. The hard surface to which cleaning and degreasing is done may be a single material, such as a pure metal or alloy, glass, ceramic, or plastic. Alternatively, it may be a composite material, such as metal parts that are connected by welding, brazing, or soldering, and printed circuit board assemblies that consist of electronic components and interconnects embedded in a laminate substrate, usually made of glass epoxy, polyimide, or other polymeric material.

> *Oils and greases, polishing compounds, solder flux residues, adhesives, and inks represent some of the many types of soils that require cleaning.*

The types of contaminants and materials to be cleaned are specific to each industry. However, the reason for cleaning and degreasing usually is that the contaminants would interfere with the performance of a certain process or the contamination is undesirable from the standpoint of product performance or appearance. In metal finishing, for example, cleaning is performed to remove oils and greases used for lubrication, machine tool cutting, quenching, and rust prevention. Metals polishing and buffing compounds present difficult cleaning problems because they contain waxes and abrasives and can form metal soaps during use. In the electronics industry, cleaning consists primarily of removing solder flux residue, photoresist residue, and particulates (drill debris) of metal and circuit board material. Other contaminants that may be encountered in numerous other industries include adhesives, fingerprints, inks, cured paints, mineral oil, mold release compounds, asphalt, tar, sealants, waxes, and toners.

> *Chlorinated solvent properties and characteristics are shown in Table 1.*

Traditionally, industries that use chlorinated solvents for cleaning and degreasing include

Table 1. Properties[a] and Characteristics of Chlorinated Solvents

Physical Properties and Characteristics	CFC-113 CCl_2FCClF_2	TCA CH_3CCl_3	TCE $CHClCCl_2$	PERC CCl_2CCl_2	METH CH_2Cl_2
Ozone-Depleting Potential (ODP)[b]	0.8	0.1	—	—	—
Photochemical Reactivity (RCRA-listed)	No	No	Yes	Yes[c]	—
Molecular Weight (grams per mole)	187.4	133.5	131.4	165.9	84.9
Boiling Point (°C)	47.6	72-88	86-88	120-122	40
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[d]	31	124	130	91	132
Vapor Pressure (mm Hg)	285	100	58	14	350
OSHA PEL 8-hr TWA (ppm)	1000	350	50	25	500[e]
Flash Point (°C)	None	None	None	None	None

[a] Applicable at 25°C.

[b] ODP relative to CFC-11, which is 1.0.

[c] PERC is not photochemically reactive, but it is not exempt under the Clean Air Act.

[d] *Value expresses the solvency of the solvent for Kauri rosin; higher values correspond to higher solubility.*

[e] The Occupational Safety and Health Administration (OSHA) has proposed lowering the PEL of METH to 25 ppm or lower (U.S. Department of Labor, 1991).

- Metal finishing
- Airframe manufacturing
- Automotive manufacturing
- Machine parts manufacturing
- Electronics manufacturing and assembling
- Glass fabrication and finishing
- Repair, overhaul, and equipment maintenance.

Because there is no universal definition of "clean," process developers must adopt their own criteria for judging cleanliness using methods that meet their individual needs. Underestimating the level of cleanliness required for a particular application may lead to a loss of product performance or quality, while overestimating may cause time, energy, and materials to be wasted. As a working definition, "clean" is usually the level of cleanliness required for any of the following to occur:

- Mechanical devices function according to design specifications
- Electronic or electrical devices perform reliably over their expected service lifetimes
- Organic coatings adhere properly to a substrate
- Product finish meets performance and appearance criteria.

Traditionally, chlorinated hydrocarbon solvents have been used to remove oils, fats, waxes, and other organics from surfaces. Chlorinated solvents have been widely used until recently because they are very effective cleaners and are safe to workers because they are nonflammable. The solvents most commonly used are 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113); 1,1,1-trichloroethane (TCA; also called methyl chloroform, or MCF); trichloroethylene (TCE); tetrachloroethylene (also called perchloroethylene, or PERC); and dichloromethane (also called methylene chloride, or METH). Some properties and characteristics of these solvents are described in Table 1.

Traditionally, three methods have been used for cleaning and degreasing:

- Vapor degreasing
- Cold cleaning
- Spot cleaning.

Vapor degreasing is a robust cleaning process.

In **vapor degreasing**, a solvent is heated to its boiling point so that vapor is created which can then contact parts suspended above the liquid surface. The vapor condenses on the cooler parts, dissolves the contaminants and flushes the liquid mixture back into the hot liquid. Vapor rising past the parts is condensed by a cooling jacket that slows the eventual loss of solvent to the atmosphere. Because the contaminants usually have higher boiling points than the solvent, the vapor itself remains relatively pure. The cleaning process is complete when the parts warm up and vapor no longer condenses on them. Then the parts are removed and they quickly dry in air, due to the high vapor pressure of the solvents.

Process time for vapor degreasing usually is about 10 minutes; however, additional time would be needed for loading and unloading parts. CFC-113, TCA, TCE, and PERC are commonly used in vapor degreasing.

Cold cleaning generally is performed in a tank containing TCA or CFC-113 at room temperature. The components to be cleaned are usually agitated mechanically or ultrasonically. The primary disadvantage of cold cleaning compared with vapor degreasing is that its cleaning performance degrades with use because the solvent becomes "loaded" with dissolved contaminants.

Spot cleaning refers to localized cleaning of a workpiece. A typical method of spot cleaning is to use a lint-free cloth saturated with solvent. Spot cleaning is commonly used in repair operations, for example, to remove solder flux residue after replacing an electronic component on a circuit board or to remove a small amount of lubricant on a mechanical device. Methylene chloride, CFC-113, and TCA are commonly used in spot cleaning. In spot cleaning, excess solvent is allowed to evaporate from the workpiece. Clean solvent typically is kept in a closed container to prevent unnecessary loss.

Solvents and Cleaners

Solvents are used to dissolve soils.

A *solvent* could be defined as any substance that can dissolve another substance. For example, pure water is a solvent for many polar and ionic compounds. Petroleum hydrocarbons are good solvents for many nonpolar organic compounds. In most of the industrial trade literature the term *solvent* refers to nonaqueous substances, whereas the term *cleaner* refers to substances that use water. Cleaners are water-based and generally contain additives that allow them to remove contaminants. These conventions generally are adhered to in this *Guide*.

Cleaners clean by displacing, dissolving, or chemically altering a contaminant.

Cleaning and degreasing can be grouped broadly as being *chemical*, *electrochemical*, or *mechanical* in nature. The **chemical properties** possessed by a cleaner or solvent determine whether the cleaner or solvent acts by *displacing*, *dissolving*, or in some way *chemically altering* the contaminant on a substrate and hence causing its removal. Cleaners and solvents are designed to implement one or more of these mechanisms, depending on the nature of the contaminant to be removed. Details about these chemical mechanisms are given in Sections 2 and 3 along with general descriptions of various cleaner and solvent components.

Electrochemical methods often are employed prior to electroplating and consist of applying a current (direct, reverse, or periodic) through a workpiece. Water decomposition causes small bubbles of hydrogen (direct) or oxygen (reverse) to form at the metal surface and helps to lift away contaminant particles. The metal itself usually is immersed in an alkaline solution to increase electrical conductivity and to maximize cleaning performance.

Mechanical methods control fluid impingement on a surface and vary considerably with the type of process equipment being used. Some form of mechanical energy almost always is used to enhance the chemical or electrochemical cleaning process. Simple agitation, air sparging, turbulent flow, spraying, and ultrasonic action are typical methods used to enhance cleaner performance. (See U.S. EPA companion publication, *Guide to Cleaner Technologies: Cleaning and Degreasing Process Changes*.) The bulk physical properties of a cleaner or solvent also affect the cleaning process by determining how a liquid interacts with a surface. For example, surface tension affects a fluid's ability to penetrate small spaces such as cracks and holes as well as getting between the contaminant and substrate to help displace the contaminant.

Pollution Problem

In the 1970s, it was realized that some chlorofluorocarbons (CFCs) undergo chemical changes in the upper atmosphere that subsequently lead to the destruction of stratospheric ozone. It is this "ozone layer" that filters out much of the sun's harmful ultraviolet radiation. For this reason, the world community has since sought to eliminate production and use of CFCs. According to the Montreal Protocol on Substances That Deplete the Ozone Layer, signed in 1987 by 45 nations including the United States, agreements were made to restrict the production and use of ozone-depleting chemicals. The Montreal Protocol and its London Amendments (1990) led to further changes in the U.S. Clean Air Act, which was amended by President Bush on November 15, 1990. The Clean Air Act Amendments (CAAA) established a time frame to eliminate all fully halogenated CFCs, certain chlorinated hydrocarbons, and hydrochlorofluorocarbons (HCFCs).

Class I ozone layer-depleting substances must be phased out by 1996.

In November 1992, the participating countries voted to advance the deadline for phasing out ozone layer-depleting substances (OLDS Class I) to January 1, 1996. The OLDS Class I list includes CFCs and halons, among which are CFC-113 and TCA, which are the substances most important to cleaning. Under the agreement, countries are allowed to seek exemptions for essential uses for which no technically feasible alternatives are available. EPA has petitioned for metered-dose inhalers for medical purposes and for 4 other small-use needs. The expected ban on Class II OLDS, which includes the HCFCs, is between 2020 and 2040 or earlier, as stipulated by the London Amendments to the Montreal Protocol.

Potential Solutions

Cleaner technologies now exist or are being developed that would reduce or eliminate the use of CFC-113 and TCA for many cleaning and degreasing operations. There are two main strategies in developing cleaner technologies:

- **Alternative cleaning and degreasing substances** that are non-ozone depleting or have lower ozone depletion potentials; are nonhazardous (measured by Occupational Safety and Health Act [OSHA] and National Institute of Safety and Health [NIOSH] criteria); have low toxicities, low odor, and high flash points; produce low emissions of volatile organic compounds (VOCs); and are effective for removing contaminants.
- **Process changes** that use different technologies for cleaning or that eliminate the need for cleaning.

This *Guide* is concerned with the first strategy, alternative cleaning and degreasing substances. A discussion of process changes is given in the companion U.S. EPA publication, *Guide to Cleaner Technologies: Cleaning and Degreasing Process Changes.* Both alternative cleaning and degreasing substances and process changes may have limitations that should be evaluated carefully by potential users with their specific applications in mind.

What's In This Guide?

This application guide describes primarily chemical alternatives to chlorinated solvents that can be used to reduce waste in cleaning and degreasing operations. The two main objectives of this application guide are

- To identify commercial and developing cleaning systems and other technologies that eliminate the use of ozone-depleting chlorinated solvents and reduce the use of smog-producing high-VOC solvents.
- To provide resources for obtaining more detailed engineering information about these technologies.

The following questions are addressed:

- What alternative solvents or cleaners are available or under development that would reduce or eliminate pollution?
- Under what circumstances might one or more of these alternative solvents or cleaners be applicable to a given operation?
- What pollution prevention, operating, and cost benefits could be realized by adopting the new technology?

Other Questions Affecting Investment Decisions

Other questions affecting the decision to choose an alternative technology include

- Might new pollution problems arise when implementing cleaner technologies?
- Are tighter, more complex process controls needed?
- Will product quality and operating rates be affected?
- Will new operating or maintenance skills be needed?
- What are the overall capital and operating cost implications?

To the extent possible, these questions are addressed in this guide. The cleaner technologies described in this guide are applicable under different sets of product and operating conditions. If one or more alternative solvents and cleaners are sufficiently attractive for use as replacements for chlorinated and high-VOC solvents, the next step of the user is to obtain detailed engineering data from vendors of the technology in order to perform an in-depth evaluation of the technology potential. Section 6 provides information on trade associations that may be helpful in obtaining technical data. Furthermore, the user may benefit greatly by inquiring among others in related industries who have already implemented one of the technologies mentioned in this guide. Both alternative cleaning solutions and process changes may have limitations that should be carefully evaluated by potential users for the specific applications.

Who Should Use This Guide?

This application guide has been prepared for plant process and system design engineers and for personnel responsible for process improvement and design. Process change descriptions within this guide allow engineers to evaluate options so that cleaner technologies can be considered for existing plants and factored into the design of new cleaning and degreasing operations.

Sufficient information is presented to select one or more candidate technologies for further analysis and in-plant testing. The guide does not recommend any technology over any other. It presents concise summaries of applications and operating information to support preliminary selection of cleaner technology options for testing in specific processes. Sufficient detail is provided to allow identification of possible technologies for immediate application to eliminate or reduce waste production.

The keywords given below will help you quickly scan the available and emerging technologies covered in this guide.

Keywords

Cleaner Technology
Pollution Prevention
Source Reduction
Source Control
Recycling
Solvent Substitute
Alternative Solvent
CFC Replacement
Cleaning/Degreasing
Metal Cleaning
Defluxing
Aqueous Cleaners
Semi-Aqueous Cleaners
Petroleum Hydrocarbons
Hydrochlorofluorocarbons (HCFCs)
Miscellaneous Organic Solvents
Supercritical Fluids
Carbon Dioxide Snow
Catalytic Wet Oxidation Cleaning
Absorbent Media Cleaning

Summary

The cleaner technologies described in this guide are divided into two groups based on their maturity:

- Commercially available technologies—Section 2
- Emerging technologies—Section 3.

Pollution Prevention Strategy, Section 4, discusses the impact of regulations on the potential for cleaner technologies. The Cleaner Technology Transfer Considerations, Section 5, discusses the various technical, economic, and regulatory factors that influence the selection and use of a cleaner technology.

Reference

U.S. Department of Labor, Occupational Safety and Health Administration (OSHA). 1991. "Occupational Exposure to Methylene Chloride." 29 CFR Parts 1910, 1915, and 1926, Proposed Rule. *Federal Register, 56*(216):57036-57141.

SECTION 2
AVAILABLE TECHNOLOGIES

How to Use the Summary Tables

Seven available alternatives to chlorinated solvents for cleaning and degreasing are evaluated in this section:

- Aqueous cleaners
- Semi-aqueous cleaners
- Petroleum hydrocarbons
- Hydrochlorofluorocarbons (HCFCs)
- Miscellaneous organic solvents
- Supercritical fluids
- Carbon dioxide snow.

Tables 2 and 3 summarize descriptive and operational aspects of these technologies. They contain evaluations or annotations describing each available cleaner technology and give users a compact indication of the range of technologies covered to allow preliminary identification of those technologies that may be applicable to specific situations.

Descriptive Aspects

Table 2 describes each available cleaner technology. It lists the **Pollution Prevention Benefits, Reported Application, Benefits,** and **Limitations** of each technology.

Operational Aspects

Table 3 shows the key qualitative operating characteristics for the available materials and technologies. The rankings are estimated from descriptions and data in the technical literature and are based on comparisons to the materials that these alternatives would replace.

Process Complexity is qualitatively ranked as "high," "medium," or "low" based on such factors as the number of process steps involved and the number of material transfers needed. Process complexity is an indication of how easily the new technology can be integrated into existing plant operations. A large number of process steps or input chemicals, or multiple operations with complex sequencing, are examples of characteristics that would lead to a high complexity rating.

The summary tables will help identify possible candidate cleaner technologies.

The **Required Skill Level** of equipment operators also is ranked as "high," "medium," or "low." Required skill level is an indication of the level of sophistication and training required by staff to operate the new technology. A technology that requires the operator to adjust critical parameters would be rated as having a high skill requirement. In some cases, the operator may be insulated from the process by complex control equipment. In such cases, the operator skill level is low but the process complexity is high.

Table 3 also lists the **Waste Products and Emissions** from the available cleaner technologies. It indicates tradeoffs in potential pollutants, the waste reduction potential of each, and compatibility with existing waste recycling or treatment operations at the plant.

Use the information in the text, from the references, and from industry and trade groups to get more detail on the best candidates.

The **Cleaner Cost per Gallon** column provides a preliminary measure of economics to be compared with the cost for solvents currently used. Due to the diversity of cost data and the wide variation in plant needs and conditions, it is not possible to give specific cost comparisons. Cost analysis must be plant-specific to adequately address factors such as the type and age of existing equipment, space availability, production volume, product type, customer specifications, and cost of capital. Where possible, sources of cost data are referenced in the discussions of each cleaner technology.

The **Energy Use** column provides a qualitative assessment of the energy requirements associated with each alternative.

Table 2. Available Technologies for Alternatives to Chlorinated Solvents for Cleaning and Degreasing: Descriptive Aspects

Technology Type	Pollution Prevention Benefits	Reported Application	Operational Benefits	Limitations
Aqueous Cleaners	• No ozone depletion potential • May not contain VOCs • Many cleaners reported to be biodegradable	• Excellent for removing inorganic and polar organic contaminants • Used to remove light oils and residues left by other cleaning processes • Used to remove heavy oils, greases, and waxes at elevated temperatures (>160°F)	• Remove particulates and films • Cleaner performance changes with concentration and temperature, so process can be tailored to individual needs • Cavitate using ultrasonics	• Nonflammable and nonexplosive; relatively low health risks compared to solvents; consult Material Safety Data Sheet (MSDS) for individual cleaner • Contaminant and/or spent cleaner may be difficult to remove from blind holes and crevices • May require more floor space, especially if multi-stage cleaning is performed in line • Often used at high temperatures (120 to 200°F) • Metal may corrode if part not dried quickly; rust inhibitor may be used with cleaner and rinsewater • Stress corrosion cracking can occur in some polymers
Semi-Aqueous Cleaners	• Some have low vapor pressure and so have low VOC emissions • Terpenes work well at low temperatures, so less heat energy is required • Some types of cleaners allow used solvent to be separated from the aqueous rinse for separate recycling or disposal	• High solvency gives cleaners good ability for removing heavy grease, waxes, and tar • Most semi-aqueous cleaners can be used favorably with metals and most polymers • NMP used as a solvent in paint removers and in cleaners and degreasers	• Rust inhibitors can be included in semi-aqueous formulations • Nonalkaline pH; prevents etching of metals • Low surface tension allows semi-aqueous cleaners to penetrate small spaces • Glycol ethers are very polar solvents that can remove polar and nonpolar contaminants • NMP used when a water-miscible solvent is desired • Esters have good solvent properties for many contaminants and are soluble in most organic compounds	• NMP is a reproductive toxin that is transmitted dermally; handling requires protective gloves • Glycol ethers have been found to increase the rate of miscarriage • Mists of concentrated cleaners (especially terpenes) are highly flammable; hazard is overcome by process design or by using as water emulsions • Limonene-based terpenes emit a strong citrus odor that may be objectionable • Some semi-aqueous cleaners can cause swelling and cracking of polymers and elastomers • Some esters evaporate too slowly to be used without including a rinse and/or dry process • May be aquatic toxins
Petroleum Hydrocarbons	• Produce no wastewater • Recyclable by distillation • High grades have low odor and aromatic hydrocarbon content (low toxicity) • High grades have reduced evaporative loss	• Used in applications where water contact with parts is undesirable • Used on hard-to-clean organic contaminants, including heavy oil and grease, tar, and waxes • Low grades used in automobile repair and related service shops	• No water used, so there is less potential for corrosion of metal parts • Compatible with plastics, most metals, and some elastomers • Low liquid surface tension permits cleaning in small spaces	• Flammable or combustible, some have very low flash points, so process equipment must be designed to mitigate explosion dangers • Slower drying times than chlorinated solvents • The cost of vapor recovery, if implemented, is relatively high
Hydrochlorofluorocarbons (HCFCs)	• Lower emissions of ozone-depleting substances than CFCs • Produce no wastewater	• Used as near drop-in replacements for CFC-113 vapor degreasing • Compatible with most metals and ceramics, and with many polymers • Azeotropes with alcohol used in electronics cleaning	• Short-term solution to choosing an alternative solvent that permits use of existing equipment • No flash point	• Have some ozone depletion potential and global warming potential • Incompatible with acrylic, styrene, and ABS plastic • Users must petition EPA for purchase, per Section 612 of CAAA

(continued)

Table 2. (Continued)

Technology Type	Pollution Prevention Benefits	Reported Application	Operational Benefits	Limitations
Miscellaneous Organic Solvents	• Do not contain halogens, so they do not contribute to ozone depletion • Most are considered biodegradable • Generate no wastewater when used undiluted	• Most are used in small batch operations for spot cleaning	• Alcohols are polar solvents and are good for removing a wide range of inorganic and organic contaminants; soluble in water and may be used to accelerate drying • Ketones have good solvent properties for many polymers and adhesives; they are soluble in water and may be useful for certain rapid drying operations • Vegetable oils are used to remove printing inks and are compatible with most elastomers • Lighter alcohols and ketones have high evaporation rates and therefore dry quickly	• Most evaporate readily and therefore contribute to smog • Alcohols and ketones have low flash points and present a fire hazard • Inhalation of these solvents can present a health hazard • Some have vapor pressures that are too high to be used in standard process equipment • MEK and MIBK are on EPA list of 17 substances targeted for use reduction
Supercritical Fluids (SCFs)	• Nonpolluting when CO_2 is used as the supercritical fluid • Generate no wastewater • Use natural or industrial sources of CO_2, so no net production of carbon	• Remove organic contaminants of moderate molecular weight and low polarity • Precision clean instrument bearings, electromechanical assemblies, direct access storage devices, optical components, polymeric containers, porous metals, ceramics • Low viscosity and high diffusivity permit cleaning in very small cracks and pore spaces	• Compatible with metals, ceramics, and polymers such as Teflon™, high-density polyethylene, epoxies, and polyimides • No solvent residue left on parts • May be very useful for cleaning oxygen equipment • Solvent properties can be altered by adding a cosolvent	• Cosolvents used to improve the solvent power of CO_2 may have a pollution potential • Danger of a pressure vessel explosion or line rupture • Cause swelling in acrylates, styrene polymers, neoprene, polycarbonate, and urethanes • Components sensitive to high pressures and moderate temperatures should not be cleaned by SCF methods • Ineffective in removing inorganic and polar organic contaminants; for example, does not remove fingerprints
Carbon Dioxide Snow	• No polluting emissions released • Replaces CFCs and solvents • Does not generate wastewater • Uses natural or industrial sources of CO_2, so no net production of CO_2 occurs • Carries contaminants away in a stream of inert CO_2	• Cleans critical surfaces on delicate fiber optic equipment • Cleans radioactive-contaminated components • Used in hybrid circuits to remove submicron particles • Used on the largest, most expensive telescopes • Removes submicron particles and light oils from precision assemblies • Removes light fingerprints from silicon wafers and mirrors • Prepares surfaces for surface analysis	• Generates no media waste, thus no media disposal cost • Does not create thermal shock • Is nonflammable and nontoxic • Noncorrosive • Leaves no detectable residue • Can penetrate narrow spaces and nonturbulent areas to dislodge contaminants • Adjustable flake size and intensity • More effective than nitrogen or air blasting • Can clean hybrid circuits without disturbing the bonding wire	• CO_2 must be purified • Requires avoidance of long dwell times • Particulates such as sand may be carried by the gas stream and scratch the surface • Heavier oils may require the addition of chemicals and heat to be completely removed

Table 3. Available Technologies for Alternatives to Chlorinated Solvents for Cleaning and Degreasing: Operational Aspects

Technology Type	Process Complexity	Required Skill Level	Waste Products and Emissions	Cleaner Cost per Gallon	Energy Use	Optional Post-Cleaning Operations	References
Aqueous Cleaners	Medium	Medium	• Skimmed oil; filter-trapped particulates and greases; waste-water and detergent	$6-10; typical dilutions range from 1:3 to 1:9	Medium—temperature control, mechanical control, drying	• Rinsing—Some cleaners may leave a residue; to facilitate removal use DI water and/or alcohol • Drying—May be accelerated by blowing with hot air or rubbing with absorbent material; automated dryers are available	Gavaskar et al., 1992 Monroe et al., 1993 Munie, 1991 Murphy, 1991 Polhamus, 1991 Ross and Morrison, 1988 U.S. EPA, 1991a, b, c Weltman and Evanoff, 1992
Semi-Aqueous Cleaners	Medium	Medium	• Waste terpene containing mostly organic material and aqueous part containing mostly inorganic material; filters trap particulates, grease, and non-emulsified oil	$10-20; typical dilutions range from none to 1:9	Low—mechanical control, drying	• Cleaners may leave residue that is slow to evaporate; water rinse may be required • Drying may be needed if a water rinse is used; rinsing with alcohol will speed drying	Darnall et al., 1976 Hill and Carter, 1993 IPC, 1990 National Toxicology Program, 1990 U.S. EPA, 1991a, b, c U.S. EPA, 1993
Petroleum Hydrocarbons	Low	Medium	• Produce no waste-water when used undiluted. VOCs are emitted; waste solvent incinerated as fuel or recycled by distillation	$1-3 for kerosene and mineral spirits; $7-12 for metal cleaning formulations; up to $30 for some specialty and electronic cleaning formulations; most often used without water	Low—mechanical control, drying	• Parts may be dried by forced air or by some other method	IPC, 1990 U.S. EPA, 1991a, b
Hydrochloro fluorocarbons (HCFCs)	Low	Medium	• Still bottoms; contaminated solvent; HCFCs emitted to air unless closed-loop system is used	$30-35	High—maintain boiling temperature; run primary and possibly secondary condensing systems	• None	Basu et al., 1991 Finegan and Rusch, 1993 Kitamura et al., 1991 U.S. EPA, 1991a, b

(continued)

Table 3. **(Continued)**

Technology Type	Process Complexity	Required Skill Level	Waste Products and Emissions	Cleaner Cost per Gallon	Energy Use	Optional Post-Cleaning Operations	References
Miscellaneous Organic Solvents	Low	Low	• Waste solvents	$2-20	Low—primarily suited for small scale and local cleaning	• Vegetable oil cleaning requires a secondary cleaning step	Burow, 1993 Environmental Program Office, 1991 Hill and Carter, 1993 U.S. EPA, 1991a, b
Supercritical Fluids	High	High	• Contaminants are condensed in a vessel • CO_2 gas may be vented to the atmosphere or purified and reused	Cost of high-purity CO_2 (about 7¢/lb) is insignificant compared to installation cost	Low—Energy is required to operate pumps to perform supercritical cleaning	• Remove part from pressure vessel	Airco Gases, N.D. Gallagher and Krukonis, 1991 Lira, 1988 Salerno, 1990 Schneider, 1978 U.S. EPA, 1991 Woodwell, 1993
Carbon Dioxide Snow	Medium	Medium	• Solid coating residue waste • Airborne particulates • CO_2 gas	Cost of welding grade CO_2 is about 7¢/lb	Medium— • Carbon dioxide liquefier • Refrigeration unit • Compressed gas supply to propel blasting media • Requires current between 8 and 14.5 amps • Requires voltage between 115 and 230 V	• Requires dry air stream or chamber to prevent water condensation while parts are cold	Hoenig, 1990 Layden and Wadlow, 1990 Sherman and Whitlock, 1990 Whitlock, 1989 Zito, 1990

The **Optional Post-Cleaning Operations** column summarizes additional rinsing, drying, or other operations that may be needed following cleaning or degreasing. These are noted to indicate special considerations in the application of the cleaner technology.

The last column in Table 3 lists **References** to publications that will provide further information for each alternative. These references are given in full at the end of the respective available technology sections.

The text further describes the pollution prevention benefits, reported application, operational benefits, and limitations for each technology. Technologies in earlier stages of development are summarized to the extent possible in Section 3, Emerging Technologies.

Aqueous Cleaners

Pollution Prevention Benefits

The primary pollution prevention benefit of aqueous cleaners is that they are non-ozone depleting and may not contain VOCs. Aqueous cleaners that are nonhazardous initially remain so unless they become contaminated with hazardous materials during cleaning operations. In some cases, spent cleaner can be treated to remove contaminants, which may allow them to be discharged to sewers, provided that the effluents meet local discharge requirements.

How Do They Work?

Aqueous cleaners are mixtures of water, detergents, and other additives that promote the removal of organic and inorganic contaminants from hard surfaces. Each component of an aqueous cleaner performs a distinct function and affects the way the contaminant is removed from a substrate.

Surfactants, or "surface action agents," provide detergency by lowering surface and interfacial tensions of the water so that the cleaner can penetrate small spaces better, get below the contaminant, and help lift it from a substrate. Surfactants may be *cationic*, *anionic*, or *nonionic* in nature. These terms refer to the aqueous phase properties of their hydrophilic portions (see below). The anionic and nonionic types most often are used in immersion cleaning; nonionic surfactants have lower foam-producing characteristics and are preferred in applications where agitation is used.

> *Nonionic surfactants are preferred in applications using agitation.*

Surfactants are characterized empirically by their hydrophilic-lipophilic balance (HLB), which describes a relationship between their water-soluble (hydrophilic) and oil-soluble (lipophilic) portions. Oil-soluble surfactants have low HLB values and highly water-soluble surfactants have high HLB values. Typical HLB ranges and applications of surfactants are shown in Table 4.

Table 4. Hydrophilic-Lipophilic Balance Ranges and Applications of Surfactants

HLB Value	Application
3.5 - 6	Water-in-oil emulsifier
7 - 9	Wetting agent
8 - 18	Oil-in-water emulsion
13 - 15	Detergent
15 - 18	Solubilizer

Source: Ross and Morrison, 1988.

In the category of anionic surfactants, sulfosuccinates are commonly used as wetting agents, whereas long-chain sulfonates, fatty alcohol sulfates, and alkali soaps are used as emulsifiers. Among the nonionic surfactants, ethoxylated alkylphenols are used as wetting agents and emulsifiers, while glycol ethers (Cellosolves™) and ethylene oxide condensates of alkylphenols are used as emulsifiers (Ross and Morrison, 1988).

In addition to HLB, Monroe et al. (1993) describe the utility of surfactant chain length ethylene oxide/propylene oxide content, cloud point, and critical micelle concentration in selecting surfactants for aqueous cleaning. Another important surfactant selection factor is emulsion stability, which depends on a complex interaction of properties such as droplet size, interfacial viscosity, repulsion terms, and internal volume (Ross and Morrison, 1988).

> *Emulsifiers disperse contaminants in water.*

Oil-in-water emulsifiers cause water-immiscible contaminants, such as oil or grease, to become dispersed in the water. This kind of emulsification can be accomplished by surfactants with moderate to high HLB values. Many kinds of surfactants are used as emulsifiers in aqueous cleaners; however, users should be aware that some are hazardous and should note OSHA or NIOSH exposure limits on the Material Safety Data Sheet (MSDS) provided with the product. Examples of hazardous components found in some aqueous cleaners are 2-butoxyethanol (or ethylene glycol butyl ether; CAS#111-76-2), 2-ethoxyethanol (or ethylene glycol ethyl ether; CAS#110-80-5), and dipropylene glycol methyl ether (CAS#34590-94-8). Oil-in-water emulsifiers are most useful when a small amount of contaminant is present so that the cleaner does not become "loaded" too quickly. Oil-in-water emulsifiers are undesirable in situations where a large amount of oil is to be removed. In cleaning situations where the oil content is high, a better methodology is to rely on the oil's natural immiscibility with water and allow *separation* to occur so that the lighter fractions can be skimmed off the top and the heavier fractions can be removed by filtration. The volume of waste generated is greatly reduced using this kind of phase separation technique, and the lifetime of the cleaner is thereby extended.

Deflocculants assist in dispersion.

Chemicals added to help maintain the dispersion of contaminant particles in the cleaning medium are known as **deflocculants**. Deflocculants may be anionic or nonionic surfactants, or they may be inorganic salts such alkali phosphates. Because many emulsions remain stable only at elevated temperatures and under alkaline conditions, separation of the oily fraction from the aqueous cleaner often can be induced in emulsion-type aqueous cleaners by lowering the temperature and, sometimes, by acidifying the bath. Individual manufacturers can provide information on their specific oil separation techniques.

Saponifiers form soaps.

Saponifiers are compounds that react chemically with oils containing fatty acids to form soaps. Vegetable oils and animal fats (triglycerides) are examples of substances that can be saponified by alkalis. It is common for some contaminants in a particular kind of "soil" to be saponifiable, whereas others are not. For example, thickeners added to a base oil to form grease may be saponifiable, whereas the base oil may not. Nevertheless, the grease is more readily removed by this kind of chemical action. Coupled with saponifiers, surfactants can act as wetting agents to help remove contaminants from the surface.

The organic amines comprise an important class of saponifiers. Organic amines can react with many common hydrocarbon contaminants, including the saponifiable portion of solder flux rosin (Munie, 1991). However, users should be aware that the organic amines are hazardous and also should note OSHA or NIOSH exposure limits on the MSDS provided with the product. Examples of organic amines found in some aqueous cleaners are ethanolamine (CAS#141-43-5), diethanolamine (CAS#111-42-2), and triethanolamine (CAS#102-71-6). The organic amines range in volatility according to molecular weight and will volatilize (evaporate) over time when the cleaner is used at high temperatures. As the loss of these compounds will affect cleaning performance, the cleaner may require maintenance to restore its chemical balance.

Aqueous cleaners tend toward mild to high alkalinity.

Alkalinity is a property of aqueous media which describes its ability to neutralize acid. Alkalinity is not a factor of pH alone but also is a measure of a solution's ability to *buffer* itself against acid. Buffering capacity provides stability, so that the chemical environment of the cleaner is not subject to abrupt pH and other chemical changes. Alkalinity also promotes detergency. Aqueous cleaners range in alkalinity from mild alkaline (pH 8 to 10) to high alkaline (pH 12 and higher). Mild alkaline conditions prevent etching of most metals, which have solubility minima in the range of pH 8 to 11. Two important cases where mild alkaline cleaners should be used are aluminum and magnesium, which are readily etched above pH 11. Mild alkalinity often is maintained by soluble silicates, carbonates, borates, and citrates.

In some cases, high alkalinity is desired to remove metal oxides and hydroxides from a surface to provide a fresh surface. Highly alkaline (caustic) cleaners are used to prepare metal surfaces prior to plating. Typically, very high pH (>12) is achieved by adding strong bases such as sodium hydroxide (lye) or potassium hydroxide. Highly alkaline cleaners often are used to remove heavy grease and oil from corrosion-resistant steels. The hydroxide ions attack the saponifiable part (e.g., the thickeners) of the grease and oil.

Sequestering agents assist cleaning in hard water. Other additives enhance cleaning performance in various ways.

Sequestering agents prevent the mineral content of hard waters (mostly waters rendered hard by calcium and magnesium ions) from forming insoluble products with the cleaner. The use of sequestering agents permits the cleaner to attack only the contaminant and ensures that lower cleaner concentrations are needed. Common chelating agents, such as sodium EDTA, NTA, and ODA, typically are used to sequester cations. In all aqueous cleaners, the alkalis, deflocculants, and sequestering agents are referred to as **builders**. Other additives may be included to enhance overall cleaning performance, for example, **anti-foaming agents** and **corrosion inhibitors**. Corrosion inhibitors work either by *passivating* the surface through adsorption of a molecular species onto it that will react with oxygen before the metal can oxidize, or by forming a protective *barrier* over the surface that excludes oxygen.

Operating Features

Aqueous cleaning and degreasing can be performed for a wide variety of applications, including those that once were considered the domain of vapor degreasing or cold solvent cleaning. However, some ferrous metals may exhibit flash rusting in aqueous environments; therefore, such parts should be tested prior to full-scale use.

The cleaner chosen depends both on contaminant type and the type of process equipment to be used.

Many kinds of aqueous cleaning products are available. Thus, some investigation is required to find cleaners that are most effective against the contaminants typically encountered and to find cleaners that give the best performance with the process equipment that will be used. Whereas solvents depend largely on their ability to dissolve organic contaminants on a molecular level, aqueous cleaners utilize a combination of physical and chemical properties to remove macroscopic amounts of organic contaminants from a substrate. Aqueous cleaning is more effective at higher temperatures, and normally is performed above 120°F using suitable immersion, spray, or ultrasonic washing equipment. For this reason, good engineering practices and process controls tend to be more important in aqueous cleaning than in traditional solvent cleaning to achieve optimum and consistent results.

When switching from solvent cleaning to aqueous cleaning, users must be aware that parts usually need to be rinsed and will remain wet for some time unless action is taken to speed up the drying process. Three common methods for drying parts are *evaporation*, *displacement*, and *mechanical removal* (Polhamus, 1991).

Techniques exist to speed up evaporation.

Evaporation of rinsewater under ambient conditions is slow, depends on temperature and humidity, and creates an opportunity for dust to settle onto the part. A heat lamp can speed the process but is dependent on orientation and still exposes the parts to air contact. Parts can be dried in small batches in a vacuum oven. Evaporation is improved by the technique of *hot air recirculation*, in which heated air is recirculated within a large chamber; makeup air is continuously introduced to replenish moist air which is slowly exhausted. Another method, called *evaporative drying*, passes dry air or inert gas (to lessen the tendency for oxidation) through a chamber to provide laminar flow past the wet parts.

Displacement uses water or oil to peel off water.

Displacement methods include capillary or slow-pull drying. With this method, a hot part is extracted slowly from equally hot deionized water. The surface tension of the water in effect peels the water off the part; whatever water is left readily vaporizes. Another displacement technique, common to metalworking, uses oil to displace water from the part. The oil also acts as a rust inhibitor by forming a protective barrier between the part surface and the air. However, if the cleaning objective is to produce a residue-free surface, this latter option would be inappropriate.

Mechanical removal includes blowing and spinning techniques.

Mechanical removal techniques also are commonly used. *Air knives* blow water off the part with high-pressure air. *Centrifugal drying* spins the water off. Aqueous cleaners are available in the form of concentrated liquids and as powders. The concentrated liquids cost between $6 and $10 per gallon, when purchased in drum-size quantities. They are diluted 1:3 to 1:10 with water for most applications. The cost of powders is equivalent when prepared to the same final concentrations.

The cleaner's longevity also must be considered when evaluating cost. Filtering to remove particulates and skimming to remove oil will extend a cleaner's lifetime. Other benefits of these actions include more uniform cleaning performance and reduced disposal costs, because the oily wastes collected can be disposed of separately.

Technologies exist for separating the contaminants removed by aqueous cleaners from the wastewater to lower disposal costs.

Waste disposal costs can be kept low by discharging the bulk of the used cleaner to a sewer. In choosing an aqueous cleaner, it must be determined whether rinsewater can be discharged to a local sewer. If municipal or other restrictions are in effect, the cost of performing all required pretreatments must be considered and included in estimates of an operating budget. It is necessary to treat the cleaner prior to disposal, if dissolved metals can be precipitated or absorbed onto a substrate using a number of developed technologies. Suspended solids can be removed by small-pore filters (10 µm or less). Emulsified oil can be separated from the aqueous cleaner by means of coalescing equipment or advanced membrane ultrafiltration techniques.

Cleaning system equipment manufacturers should be consulted to determine the best approach.

Application

Aqueous cleaners have been used for a long time by metal finishers, and new products are continually being developed for an expanding market. Primary detergents are used to process buffed metals at temperatures of at least 120°F. Alkaline detergent cleaners are used to remove light oils and residues (including solvents or other types of cleaners) left by manufacturing processes, shop dirt, and light scale. Alkaline cleaners are used at elevated temperatures, ranging from 120 to 200°F (Murphy, 1991). Field evaluations of aqueous cleaners are available from U.S. EPA's Waste Reduction Innovative Technology Evaluation (WRITE) Program. For example, see Gavaskar et al. (1992). Weltman and Evanoff (1992) discuss performance, materials compatibility, and regeneration of aqueous cleaners.

Benefits

The ability of aqueous cleaners to remove most contaminants has been demonstrated in numerous tests. Aqueous cleaners are capable of removing inorganic contaminants, particulates, and films. They also exhibit considerable flexibility in application because their performance is strongly affected by formulation, dilution, and temperature. The formulation that gives the best results can be found through some investigation, and the user can select the dilution factor and temperature that give the best results.

Limitations

Health and Safety. Health risks associated with aqueous cleaners are relatively low. However, as noted earlier, some aqueous cleaners contain organic substances that may be hazardous. Because aqueous cleaners are nonflammable, there is no risk of fire. Material Safety Data Sheets (MSDSs) for individual products should be consulted before use.

Compatibility with Materials. Metal corrosion may occur if parts cannot be dried quickly enough. A rust inhibitor may be used along with the cleaner to help prevent rust. Stress corrosion cracking can occur in some polymers as a result of contact with alkaline solutions. Consult with cleaner manufacturers to obtain recommended formulations and procedures.

Water Tolerance. The most important factor in aqueous cleaning is whether the product and/or process can tolerate water. Compatibility of the product/process with water must be carefully investigated.

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Semi-Aqueous Cleaners

Pollution Prevention Benefits

The primary pollution prevention benefit of semi-aqueous cleaners is that they are non-ozone-depleting. However, they may be partly or completely composed of VOCs. In addition, their use commands substantially more concern about aquatic toxicity and human exposure than does the use of aqueous cleaners. Most semi-aqueous cleaners are reported to be biodegradable. One benefit of semi-aqueous cleaners is that distillation and membrane filtration technologies are being developed that will permit recycling and reuse of the products.

How Do They Work?

Semi-aqueous cleaners comprise a group of cleaning solutions that are composed of natural or synthetic organic solvents, surfactants, corrosion inhibitors, and other additives. The term *semi-aqueous* refers to the use of water in some part of the cleaning process, such as washing, rinsing, or both. Semi-aqueous cleaners are designed to be used in process equipment much like that used with aqueous cleaners. The commonly used semi-aqueous cleaners include water-immiscible types (terpenes, high-molecular-weight esters, petroleum hydrocarbons, and glycol ethers) and water-miscible types (low-molecular-weight alcohols, ketones, esters, and organic amines). Petroleum hydrocarbons are the next Available Technology to be discussed in this *Guide*. Alcohols and ketones are discussed in Available Technologies under Miscellaneous Organic Solvents. One water-miscible solvent, *N*-methyl-2-pyrrolidone (NMP), commonly is used for large-scale cleaning and paint removing and so is included in this discussion of semi-aqueous cleaners.

Terpenes, derived from citrus oils, frequently are used in semi-aqueous cleaners.

Terpenes are natural hydrocarbons used in semi-aqueous cleaners. There are many kinds of terpenes. Among them, *d*-limonene and α- and β-pinene are listed most frequently in commercial semi-aqueous cleaners. Terpene alcohols and para-menthadienes also are used. Terpenes are derived from plant sources such as citrus (orange, grapefruit, and lemon) and pine oils. Although terpenes are not miscible in water, they do form emulsions with water that are stabilized by surfactants and other additives.

Terpenes may be diluted for use on less difficult contaminants.

In cleaning applications, terpenes may be used undiluted or diluted with water. Dilution reduces cleaning performance but, on the other hand, decreases usage, reduces expense, and lowers vapor pressure which decreases vapor emissions. Diluted terpene semi-aqueous cleaners may produce acceptable results with less difficult contaminants.

Terpenes have relatively low flash points (about 115 to 120°F) and so it is unsafe practice to heat them above about 90°F, except when used in an inert atmosphere or when diluted to a safe concentration with water as recommended by the product manufacturer. Some commercial formulations of terpene-based cleaners and degreasers contain higher-molecular-weight hydrocarbons which lower the volatility of the terpene-hydrocarbon mixture and increase the flash point.

Low-molecular-weight esters are soluble in water.

Esters have good solvent properties for many contaminants and are soluble in most organic compounds. High-molecular-weight esters have limited solubility in water, whereas low-molecular-weight esters are soluble in water. The types of high-molecular-weight esters most often used in cleaning and degreasing include aliphatic mono-esters (primarily alkyl acetates) and dibasic acid esters. Dibasic acid esters are made by reacting alcohols, such as methyl-, ethyl-, propyl-, or butyl alcohol, with dicarboxilic acids, such as glutaric acid, adipic acid, and succinic acid. High-molecular-weight esters may be used either cold or heated to improve cleaning performance.

Among the low-molecular-weight esters, (L_+) ethyl lactate is reported to have good cleaning, health, and safety properties (Hill and Carter, 1993). Ethyl lactate is an ethyl ester of (L_+) lactic acid. It is a VOC, with moderate flash point (126°F). Additional information on ethyl lactate is given in the Available Technology section, "Miscellaneous Organic Solvents." Other esters that currently are being studied for cleaning and degreasing solvents are the small cyclic esters such as ethylene carbonate and propylene carbonate.

Glycol ethers have good solvent properties but are a health risk.

Glycol ethers also have good solvent properties for common contaminants. They form emulsions with water that can be separated for recycling. Health concerns relating to the use of both the ethyl- and propyl- series glycol ethers are now being examined in the wake of reports that they cause an increased rate of miscarriage among women.

NMP has solvent properties, is miscible with water and other compounds, and can be used cold or heated.

***N*-methyl-2-pyrrolidone,** or **NMP**, has been used in the chemical and petrochemical industries as a solvent for extraction and as a formulating agent for coatings, paint removers, and cleaners. NMP has high solvency for a number of contaminants. It normally is used undiluted, but it can be mixed with water. NMP is completely miscible with water and organic compounds such as esters, ethers, alcohols, ketones, aromatic and chlorinated hydrocarbons, and vegetable oils. NMP can be used cold or heated because of its high flash point (about 199°F).

Operating Features

Semi-aqueous cleaners are designed to be water-rinsable or non-water-rinsable. After washing in a water-rinsable type, cleaned parts may be rinsed in water to remove residue. If a non-water-rinsable type is used, cleaned parts may be rinsed in alcohol, such as isopropyl alcohol, or other organic solvent, or the residue may be allowed to remain on the parts. If rinsing is the desired option, it is common practice to rinse in a secondary tank to capture dragout cleaner.

Several technologies allow semi-aqueous cleaners to be separated from the wastewater to be recycled or discharged for treatment.

If the semi-aqueous cleaner is diluted with water to form an emulsion, the cleaner can be coalesced into its aqueous and nonaqueous components by gravity separation or by advanced membrane separation techniques. These techniques permit used cleaner to be recycled back into the wash tank or discharged for treatment and disposal. Vacuum distillation can be used to purify single-component solvents. Reclaimed rinsewater also can be reused or discharged.

Proper use of these cleaners is required to reap their full pollution prevention benefits. Good engineering design is essential so that air emissions can be kept low. For example:

- The cleaning bath should be operated at the minimum temperature where acceptable cleaning performance is obtained.
- Low-vapor-pressure cleaning agents should be used.
- Dragout should be minimized by the use of air knives.
- The air exhaust rate should be maintained at a minimum level.

Knowing the flash point is important when heating semi-aqueous cleaners.

Terpene semi-aqueous cleaners normally are used at ambient temperature or heated to no higher than 90°F. However, many high-molecular-weight esters have flash points in excess of 200°F. Also, the glycol ethers generally have flash points above 200°F and can be heated for improved solvency.

NMP has been used for removing cured paint and hence is a substitute for methylene chloride. NMP is better suited for immersion tanks than other application methods, because elevated temperatures are required to enhance its chemical activity. Usually, NMP immersion cleaning or paint removing is done at 155°F in an open tank, or up to 180°F if a mineral oil seal is present.

Semi-aqueous cleaners are effective on heavy grease, tar, and waxes, and can penetrate small crevices.

In general, the semi-aqueous cleaners have excellent solvency for a number of difficult contaminants, such as heavy grease, tar, and waxes. The cleaners have low surface tension, which decreases their contact angles and allows them to penetrate small spaces such as crevices, blind holes, and below-surface-mounted electronic components.

As with aqueous cleaners, rinsing is necessary to avoid leaving a residue on the cleaned parts. If water rinsing is performed, the parts must be dried. The methods of drying cited for aqueous cleaners apply here as well. If rinsing is done by a volatile organic solvent, such as isopropyl alcohol, then drying will be accelerated.

Semi-aqueous cleaners are widely available. Terpenes, esters, and glycol ethers are typically priced from $10 to $20 per gallon, when purchased in drum-size quantities. The cost of NMP is higher, about $25 to $30 per gallon, when purchased by the drum.

More waste streams must be managed with semi-aqueous cleaners than with either solvent cleaning or aqueous cleaning. Each waste stream can increase costs.

Application

Semi-aqueous hydrocarbon cleaners first gained acceptance in the metal cleaning industry, where they were known as *emulsion cleaners*. Semi-aqueous cleaners currently are gaining wider appeal in all types of industries where parts are cleaned, such as metal fabrication, electronics, and precision parts manufacturing. The performance of some of these cleaners has been validated in government tests, for example, the Phase 2 Standards for Electronic Components issued by The Institute for Interconnecting and Packaging Electronic Circuits (IPC, 1990).

Benefits

Semi-aqueous cleaners may have certain advantages over aqueous cleaners; for example, semi-aqueous cleaners

- May be more aggressive in removing heavy organic contaminants.
- May have lower corrosion potential with water-sensitive metals.
- Penetrate small spaces more easily because they have lower surface tensions.

Limitations

Health and Safety. Mists of concentrated semi-aqueous cleaners can be ignited at room temperature. Terpenes are a special concern because they have the flash points as low as 115°F. The low flash point restricts safe operating temperatures to no more than 90°F in some cases . Washing equipment should be designed to avoid creating mists, such as by spraying or agitating below the fluid surface or by using ultrasonic action. Also, equipment used with low-flash point cleaners should have overtemperature protection.

Health effects of semi-aqueous cleaners require further research.

The health effects associated with using semi-aqueous cleaners have not been fully explored. Limited testing of *d*-limonene has yielded positive carcinogenicity results in male rats (National Toxicology Program, 1990). Also, the terpenes in general, and *d*-limonene in particular, are highly photochemically reactive (Darnall et al., 1976), so it is desirable to minimize losses. Another concern with terpenes is that their strong odors may become objectionable to workers, thus requiring additional ventilation in areas where they are used.

The reproductive health problems associated with glycol ethers are a cause for serious concern. Whether glycol ethers can be used safely will have to be established by further testing. U.S. EPA's Office of Pollution Prevention and Toxics (OPPT) recently published a report stating that NMP could present a significant risk of reproductive and developmental harm to humans (U.S. EPA, 1993). The route of entry is dermal, so it is believed that protective gloves may be sufficient in preventing harmful exposure. OPPT is currently working with NMP product manufacturers to resolve the issues of worker health and safety.

Although semi-aqueous cleaners are biodegradable, the capacity of treatment facilities to treat wastewater must be understood. For example, the residence time of a waste stream in older industrial wastewater treatment facilities may be too short to effect complete degradation. In such cases, an add-on treatment system should be considered. An industrial plant may consider purchasing a batch-type or continuous-flow fixed-film or other type biological reactor to process rinsewater from semi-aqueous cleaning. This kind of add-on treatment system may be essential if wastewater otherwise would be discharged directly to a publicly owned treatment works (POTW).

Semi-aqueous cleaners do not corrode most metals or plastics. Use on some rubbers and plastics is not recommended.

Compatibility with Materials. Semi-aqueous cleaners are noncorrosive to most metals and generally are safe to use with most plastics. Terpenes generally are not recommended for cleaning polystyrene, PVC, polycarbonate, low-density polyethylene, and polymethylpentene; nor are they compatible with the elastomers natural rubber, silicone, and neoprene. NMP dissolves or degrades ABS, Kynar™, Lexan™, and PVC and it causes swelling in Buna-N, Neoprene, and Viton™. Glycol ethers seem to degrade polystyrene and cause swelling in the elastomers Buna-N and silicone rubber.

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Petroleum Hydrocarbons

Pollution Prevention Benefits

The primary pollution prevention benefits of petroleum hydrocarbon solvents are that they produce no wastewater and they are recyclable by distillation. Paraffinic grades have very low odor and aromatic content and low evaporative loss rates. However, planned recovery of VOCs is an important part of pollution prevention if these solvents are to be used.

How Do They Work?

Petroleum hydrocarbons are available in two grades, the basic *petroleum distillates* and the specialty grade of synthetic *paraffinic hydrocarbons*. Products of the petroleum distillate grade include mineral spirits, kerosene, white spirits, naphtha, Stoddard Solvent, and PD-680 (military designation; types I, II, and III). These are technologically less advanced, as they contain components that have a broad range of boiling points and may include trace amounts of benzene derivatives and other aromatics. Petroleum distillates were available many years before chlorinated solvents attained their popularity.

More recently, improved separation and synthesis techniques have led to the production of the specialty grade of paraffinic hydrocarbons. Paraffins are straight-chain, branched, or cyclic alkanes; they are aliphatic as opposed to aromatic (i.e., derived from benzene and naphthalene). The number of carbons in the paraffin solvent typically ranges from 10 to 14. Compared to petroleum distillates, the paraffinic hydrocarbons have very low aromatic content, narrower boiling ranges, and higher solvency, and they are more expensive.

> *Nonpetroleum additives often are used to raise the flash point of petroleum hydrocarbons.*

Hydrocarbon solvents work by dissolving organic soils. Some solvents that have flash points as low as 105°F must be used at ambient temperature to avoid a fire hazard. Many high-grade hydrocarbon solvents have flash points above 140°F. Higher flash points are achieved using higher-molecular-weight compounds. Some formulations contain nonpetroleum additives such as high-molecular-weight esters to improve solvency and raise the flash point.

When the cleaning lifetime of a hydrocarbon solvent expires, the entire bath must be replaced. Used hydrocarbon solvents commonly are blended with other fuels and incinerated in cement kilns.

Petroleum hydrocarbons typically are used when water contact with the parts is undesirable. Cleaning with petroleum distillates lends itself to simple, inexpensive, one-step cleaning in situations where a high level of cleanliness is not essential.

Operating Features

Petroleum hydrocarbons have high solvencies for many "hard-to-clean" organic soils, including heavy oil and grease, tar, and waxes. In addition, they have low liquid surface tensions (~22 to 28 dynes/cm), which allows them to penetrate and clean small spaces.

Mineral spirits cost around $3 per gallon, and paraffinic hydrocarbons for metal cleaning cost from $7 to $10 per gallon, when purchased in drum-size quantities. Specialty-grade paraffinic hydrocarbons for electronic cleaning may cost up to $30 per gallon.

Because hydrocarbon cleaners have slower drying times than chlorinated solvents, parts may be dried by forced air or by oven drying. Restrictions on VOC emissions may apply in some areas. If so, the cost of vapor recovery also must be considered when evaluating the cost of using these solvents.

Application

Petroleum distillates have had a long history of use, particularly in automobile repair and related service areas. Specialty-grade paraffinic hydrocarbons have become widely available only recently, but are reported to be used for a broad range of metal cleaning and electronics defluxing purposes. They currently are undergoing rapid development for specialized cleaning operations. The performance of some of these solvents has been validated in government tests, for example, the Phase 2 Standards for Electronic Components issued by The Institute for Interconnecting and Packaging Electronic Circuits (IPC, 1990).

Benefits

No water is used with hydrocarbon cleaners, so there is no potential for water corrosion or for water to become trapped in cavities. Some precision cleaning operations are most effective with hydrocarbon cleaners.

Limitations

Health and Safety. Petroleum hydrocarbons are flammable or combustible, and some have very low flash points, as low as 105°F. Process equipment, including drying ovens, must be designed to mitigate explosion dangers. The toxicity level of hydrocarbon solvents is considered low: 8-hour PELs for Stoddard solvent and VM & P naphthas are 100 ppm and 400 ppm, respectively. Values for synthetic petroleum hydrocarbons have not been determined yet, but they are expected to be higher than the values for petroleum distillates. Products with high flash points evaporate more slowly than low-flash point solvents.

Residues may remain on the parts long after they are cleaned. Petroleum distillates contain compounds with different molecular weights, and hence a range of evaporation rates. In addition, some specialty solvents are blends of paraffinic hydrocarbons and other organic solvents. In either case, the less volatile components may be left on the parts after the bulk liquid has evaporated. Furthermore, contaminated solvents will tend to leave a residue, so they should be replaced when slow drying or residue becomes a problem. If residues are unacceptable, a second level of cleaning may be needed. Follow-up cleaning may include rinsing in a clean or more volatile organic solvent or aqueous cleaning.

Hydrocarbons are VOCs, and hence they are photochemical smog producers. Restrictions against their use may be realized in the future. Businesses choosing this alternative must consider the expenses of possible requirements for recovering VOCs from exhaust equipment.

Compatibility with Materials. Hydrocarbon cleaners are compatible with most metals and plastics, and with some elastomers.

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Hydrochlorofluorocarbons (HCFCs)

Pollution Prevention Benefits

Hydrochlorofluorocarbons, or HCFCs, were developed to lower emissions of ozone-depleting substances that are used in cleaning, foam-blowing agents, and refrigerants. Although HCFCs accomplish the goal of reducing emissions, they have some Ozone Depletion Potential—about 0.15 for HCFC-141b and 0.033 for HCFC-225cb—relative to CFC-113, which is 1.0. Therefore, HCFC-141b depletes ozone at a rate about 6 or 7 times less than that of CFC-113, but about equal to that of TCA (see Table 5). The ozone depletion rate for HCFC-225cb is about 30 times lower than that of CFC-113.

How Do They Work?

HCFCs are designed to be near replacements to CFC-113 for vapor degreasing. However, the properties of the HCFCs differ somewhat from those of CFC-113, so that vapor degreasing equipment that was designed for CFC-113 would have to be retrofitted to accommodate HCFCs.

Table 5. Physical Properties[a] of CFC-113 and HCFCs

Compound	CFC-113	HCFC-141b	HCFC-225ca	HCFC-225cb
Molecular Weight	187.38	116.95	202.94	202.94
Boiling Point (°C)	47.6	31.7	51.1	56.1
Freezing Point (°C)	-35	-103	-112	-116
Liquid Density (cm^3)	1.57	1.24	1.55	1.56
Liquid Viscosity (cps)	0.68	N/A	0.58	0.60
Liquid Surface Tension (dyne/cm)	17.3	19.3	15.8	16.7
Heat of Vaporization (cal/g)	34	51	33	33
Kauri-Butanol Value	31	56	34	30
Flash Point	None	None	None	None
Relative Evaporation Rate (Ether=100)	123	120	101	84
Azeotropic Composition with Alcohol (wt%)				
Methanol	93.6/6.4	96.0/3.9[b]	94.7/5.3	93.3/6.7
Boiling Point (°C)	39	29.4	45.5	47.2
Ethanol	96.2/3.8	No data	97.3/2.7	95.6/4.4
Boiling Point (°C)	44.5		50.0	53.8
ODP	0.8	0.15	0.025	0.033

[a] Property measurements at 25°C.

[b] 0.1% Nitromethane added.

Sources: Basu et al., 1991; Kitamura et al., 1991.

Two basic chemistries of HCFCs are being used for vapor degreasing: HCFC-141b (CCl_2FCH_3) which is in the ethane series, and HCFC-225 which is in the propane series. Actually, HCFC-225 is a mixture of isomers HCFC-225ca ($CF_3CF_2CHCl_2$) and 225cb ($CClF_2CF_2CHClF$). The physical properties of these HCFCs are compared to the properties of CFC-113 in Table 5. The table shows that the boiling temperature of HCFC-141b is lower than that of CFC-113. However, the heat of vaporization of HCFC-141b is greater, so that the evaporation rates for both compounds are similar. The table also shows that the boiling temperatures of HCFC-225ca and -cb are higher than that of CFC-113, and that all three compounds have similar heats of vaporization. The surface tension, density, and Kauri-Butanol values of the HCFCs are comparable to those of CFC-113, which indicates that similar cleaning performance is expected.

Both HCFC-141b and 225ca, -cb can be used in pure form or as azeotropes with methanol; HCFC-225ca, -cb also can be used in azeotrope form with ethanol. Azeotropes are liquid mixtures that produce a vapor of the same chemical composition. Boiling temperatures for azeotropes are compared with boiling temperatures for CFC-113 in Table 5. Alcohols provide improved solvency for ionic and polar contaminants, such as solder flux. Nitromethane sometimes is added in small amounts to stabilize the alcohol component.

Operating Features

It is important to realize that HCFCs are being developed for interim use only. The London Amendments to the Montreal Protocol call for a ban of HCFCs between 2020 and 2040. The main reason for choosing this technology is to enable an existing CFC-113 vapor degreasing system to continue in use until a long-term alternative is found. The long-term alternative could be a completely enclosed vapor degreaser or a non-HCFC technology discussed in this *Guide*.

HCFC-141b currently costs approximately $3.00 to $3.50/lb, or about $30.00 to $35.00/gallon. Because production of HCFC-225 mixtures is under development, prices were not available.

Application

HCFCs had no commercial solvent use prior to passage of the Clean Air Act Amendments (CAAA) of 1990. HCFCs now are used in vapor degreasers for the same applications as CFC-113. HCFCs have similar performance characteristics to CFC-113. However, like the CFCs, the HCFCs will be phased out of use. It is unknown at this time whether regulations will permit use of HCFCs until at least the year 2020, as expected.

Benefits

HCFCs provide a short-term solution to choosing an alternative solvent and allow use of existing equipment.

Limitations

Health and Safety. Because HCFCs have lower boiling points than CFC-113, HCFC solvent vapors may be lost too quickly in older degreasers, and these vapors may be a health risk. Some emission control features may have to be added, such as extending freeboard height, adding secondary condensers, or completely enclosing the system (*Guide to Cleaner Technologies: Cleaning and Degreasing Process Changes*, 1993).

Toxicity testing of HCFC has been ongoing by the industry consortium — Program for Alternative Fluorocarbon Toxicity Testing (PAFT). Results of their findings were recently reported (Finegan and Rusch, 1993) and are summarized below.

The toxicology program studied the effects of HCFC-141b on rats, showing that, at an exposure level of 20,000 ppm, an increase in cholesterol, reduced fertility, and reduced body weight were the predominate effects. No effects were seen with pup viability or survival.

Metabolism studies showed that HCFC-141b has a low activity rate and can be metabolized to 11-dichloro-1-fluoroethanol. HCFC-141b in the gas phase was active in the CHO cell chromosome aberration assay up to exposure levels of 10% but inactive in all the other assays.

The chronic inhalation toxicity study at exposure levels of up to 20,000 ppm found no effects on survival, hematology, clinical observations, serum chemistries, urinalysis, or organ weights. An increased incidence of benign Leydig cell tumors and related hyperplasia in male rats in the mid- and high-level exposure groups did not result in any life shortening effects, as survival rates were excellent in all groups.

The program showed HCFC-225ca to have slight liver effects at 650 ppm, whereas all levels of exposure (50, 500, 5,000 ppm) in the 4-week inhalation study showed hepatotoxic effects and peroxisome induction. At the 500 and 5,000 ppm levels there was indication of cytochrome P450 induction. A 14-day comparative effect study in rats, hamsters, and guinea pigs run at 5, 50, and 500 ppm showed minimal effects in rodents at 5 ppm, consisting of hepatotoxicity, induction of peroxisome, and cytochrome P450 activity. Guinea pigs showed minimal effects at 500 ppm.

A marmoset study at an exposure level of 1,000 ppm is showing similar signs of peroxisome induction, marked reduction in triglycerides, a reduction in cholesterol, and discolored livers. The cause of the one death is unknown. HCFC-225ca was not active in the chromosome aberration assay.

The same program conducted on HCFC-225cb using levels 10 times higher than those for the HCFC-225ca study showed results, for the most part, parallel to those for HCFC-225ca. The no-adverse-effect level was 500 ppm for rodents and 5,000 ppm for guinea pigs. Pharmacokinetics work indicated a blood half-life of 11 minutes.

The marmoset study indicates a mild reduction in triglycerides at its exposure level of 5,000 ppm but so far no evidence of peroxisome induction or induction of cytochrome P450. The genetics program and results are similar to those for HCFC-225ca.

HCFCs have no flash point and are nonflammable. Like TCA, however, HCFC-141b will burn if the oxygen content is sufficiently high.

Compatibility with Materials. HCFC cleaners are compatible with most metals and ceramics and with many polymers. They are incompatible with acrylic, styrene, and ABS plastic.

HCFCs probably have been developed to their full extent. Except for HCFC-141b and HCFC-225, all other HCFCs that are suitable as cleaning and degreasing solvents have turned out to be toxic.

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Miscellaneous Organic Solvents

Pollution Prevention Benefits

The miscellaneous organic solvents do not contain halogens; therefore, they do not contribute to ozone depletion. However, all of these compounds are VOCs and evaporate readily, thereby contributing to smog formation. The solvents discussed in this section normally are used in small quantities for niche applications.

How Do They Work?

This group covers a wide range of solvents that may be beneficial as a replacement technology, particularly on a small scale, such as bench-top or spot cleaning. Types of miscellaneous organic solvents that are commonly used are shown in Table 6.

Both alcohols and ketones are useful in certain drying operations.

Alcohols are polar solvents and have good solubility for a wide range of inorganic and organic soils. The lighter alcohols are soluble in water and may be useful in drying operations.

Ketones have good solvent properties for many polymers and adhesives. Lighter ketones, such as acetone, are soluble in water and may be useful for certain rapid drying operations. Heavier ketones, such as acetophenone, are nearly insoluble in water. Ketones generally evaporate completely without leaving a residue. Some ketones such as methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK) once were widely used. However, they now are considered HAPs and thus are not favorable solvent substitutes.

Esters and ethers also have good solvent properties. Low-molecular-weight compounds dry readily without leaving a residue.

Table 6. Properties of Miscellaneous Organic Solvents

Compound	Molecular Weight	Boiling Point (°C)	Melting Point (°C)	Density g/cm^3	Solubility in Water
Alcohols					
ethanol	46.07	78.5	-117	0.789	Soluble
n-propanol	60.11	97.4	-127	0.803	Soluble
isopropanol	60.11	82.4	-90	0.786	Soluble
n-butyl alcohol	74.12	117	-89	0.81	9%
furfuryl alcohol	98.10	171	-14	1.130	Soluble
benzyl alcohol	108.15	205.3	-15	1.042	4%
cyclohexanol	100.2	161	25	0.96	4%
Ketones					
acetone	58.08	56.2	-95	0.790	Soluble
acetophenone	120.16	202.6	20.5	1.028	Slight
Esters					
n-butyl acetate	116.16	125	-77	0.883	<1%
(L)ethyl lactate	118.13	154	NA	1.031	Soluble
Ether					
anisole	108.15	155	-37.5	0.996	Insoluble
Linear Methyl Siloxanes					
2-Si chain	162	100	-68	0.76	Insoluble
3-Si chain	236	149	-86	0.82	Insoluble
4-Si chain	310	192	-76	0.85	Insoluble
Vegetable Oils					
peanut oil	—	443 (ignition temperature)	-5	0.917 to 0.921	Insoluble
soybean oil	—	445 (ignition temperature)	-10	0.916 to 0.922	Insoluble

A new class of organic solvents are the volatile methyl siloxanes. Their molecular structure is either linear or cyclic. The linear type, which was recently introduced commercially (Burow, 1993), has the general formula $(CH_3)_3SiO\text{–}[SiO(CH_3)_2]_n\text{–}Si(CH_3)_3$, where $0 \leq n \leq 4$. Thus, $n=0$ corresponds to a 2-Si-unit chain, $n=1$ corresponds to a 3-Si-unit chain, and so on. The linear methyl siloxanes are nonpolar and are most effective in removing nonpolar and nonionic contaminants. The most volatile methyl siloxane ($n=0$) can function as a drying agent.

Vegetable oils are finding use in removing printing inks. They also seem to be compatible with elastomers (Environmental Program Office, City of Irvine, 1991). Vegetable oils contain triglycerides of fatty acids, typically oleic, linoleic, linolenic, palmitic, and stearic fatty acids. Unsaponifiable matter usually is low (<1%).

Operating Features

These cleaners, which are commercially available, probably will find their greatest use in small batch operations, rather than as substitute solvents in large-scale processes.

Approximate costs when solvents are purchased in bulk quantities are as follows:

- isopropyl alcohol $ 0.50/lb or $3.30/gal
- *n*-propyl alcohol $ 0.70/lb or $4.70/gal
- acetone $ 0.50/lb or $3.30/gal.

Application

Most of these cleaners have been used for a long time as general-purpose solvents and their solvent properties are well known. They are most often used cold in a small immersion tank, with mild agitation or ultrasonics. In addition, fully enclosed spray washers are available for alcohol cleaning.

Benefits

Most of these solvents are well developed and some have been used as cleaners for a century or more. Many of them have reached their full potential for development. The lighter alcohols and ketones have high evaporation rates and, therefore, fast drying times. The more volatile solvents are best suited for spot cleaning, where rapid evaporation is desired.

Ethyl and isopropyl alcohols are commonly used in spot cleaning and touch-up applications. Because they are slightly polar, they tend to be good, general-purpose solvents for nonpolar hydrocarbons, polar organic compounds, and even ionic compounds. Ethyl and isopropyl alcohols are fully miscible in water.

Benzyl alcohol is a solvent for gelatin, casein (when heated), cellulose acetate, and shellac (Budavari, 1989), and is used as a general paint softener (when heated). The good solvent properties of benzyl alcohol can be enhanced by heating; its flash point is 101°C, or 213°F (closed cup). Mixtures composed of 90% benzyl alcohol and 10% benzoic acid also are used for solvent cleaning applications. Pure benzyl alcohol is 4% soluble in water, but is miscible in lighter alcohols and with ether.

Furfuryl alcohol forms a miscible, but unstable solution in water. It is used as a general cleaning solvent and paint softener. Furfuryl alcohol is soluble in water and is miscible in lighter alcohols and in ether. The solvent properties of furfuryl alcohol can be enhanced by moderate heating; its flash point is 75°C, or 167°F (closed cup).

N-butyl alcohol is a solvent for fats, waxes, resins, shellac, varnish, and gums. It is 9% soluble in water at 25°C, but forms an azeotrope with water (63% *n*-butyl alcohol/37% water) that boils at 92°C. *N*-butyl alcohol is miscible in lighter alcohols, ether, and many other organic substances.

N-butyl acetate is a solvent used in lacquer production. It is less than 1% soluble in water at 25°C. The solvent activity of *n*-butyl acetate is enhanced by mixing with *n*-butyl alcohol. A mixture of 80% *n*-butyl acetate and 20% *n*-butyl alcohol is used to dissolve oil, fats, waxes, metallic resinates, and many synthetic resins such as vinyl, polystyrene, and acrylates. Also, the mixture dissolves less highly polymerized alkyd resins and shellac.

Ethyl lactate is another ester that has useful solvent properties. The use of ethyl lactate is relatively new to cleaning and degreasing. Recently, it has been shown to have good solubility for skin oils, cutting fluids, coolants, mold release compounds, and marking inks (Hill and Carter, 1993). Ethyl lactate has a flash point of 47°C, or 117°F (closed cup).

Acetone is a solvent for fats, oils, waxes, resins, rubber, some plastics, lacquers, varnishes, and rubber cements. It is completely miscible in water and in most organic solvents. Acetophenone is only slightly soluble in water, but is miscible in alcohol, ether, and other organic substances.

Limited information is available on the use of anisole as a cleaning solvent. Use of a mixture of equal parts of anisole and ethanol with 10% sodium ethoxide has been reported for cleaning and paint removal. Anisole is used primarily in perfumery and in organic syntheses. Anisole is insoluble in water, but is soluble in alcohol and ether. Toxicity test data show its LD_{50} (orally in rats) to be 3700 mg/kg (Budavari, 1989).

Volatile methyl siloxanes have been found to remove contaminants in precision metal working, optics, and electronics processing (Burow, 1993). They remove cutting fluids, greases, and silicone fluids. They have low odor and evaporate in the range of butyl acetate, without leaving a residue. They can be used in cleaning equipment designed for use with isopropyl alcohol.

Limitations

Limitations of some of these cleaners is that some have vapor pressures that are too high to be used in standard process equipment, whereas others evaporate too slowly to be used without including a rinse and/or dry process.

Health and Safety. Most of the organic solvents mentioned in Table 6 have low flash points and present a fire hazard. Inhalation of these solvents can present a health hazard. It is not known whether the more volatile solvents will be able to meet VOC emission restrictions in highly regulated areas of the country. Users should consult MSDS literature for safe handling practices.

The lighter alcohols, such as ethanol and propanol, have flash points below room temperature so they are potential fire hazards unless precautions are taken to mitigate the possibility of igniting their vapors. *N*-butyl alcohol has a flash point of 36 to 38°C or 97 to 100°F (closed cup), which is considered flammable.

N-butyl alcohol may cause irritation of mucous membranes, dermatitis, headache, dizziness, and drowsiness (Budavari, 1989). Furfuryl alcohol is relatively toxic (OSHA permissible exposure limit is 40 mg/m^3). Also, furfuryl alcohol is an irritant to eyes and skin; exposure to its vapor should be avoided.

N-butyl acetate is irritating to eyes and skin and it may cause conjunctivitis. Also, it is a narcotic in high concentrations (Budavari, 1989). *N*-butyl acetate has a flash point of 22°C, or 72°F (closed cup), so it is a potential fire hazard unless precautions are taken to prevent igniting its vapor.

Acetone is quite volatile, evaporates quickly, and is a highly flammable liquid. Its flash point is -18°C, or 0°F (closed cup) making it a fire safety hazard unless strict fire prevention measures are taken. Acetophenone has a flash point of 105°C or 221°F (closed cup).

Inhalation of acetone may cause headache, fatigue, excitement, bronchial irritation, and in large amounts, narcosis (Budavari, 1989). Prolonged breathing of acetone may cause erythema.

The flash points of the volatile methyl siloxanes are in the flammable and combustible ranges: -1°C (30°F) for n=0, 34°C (94°F) for n=1, and 57°C (135°F) for n=2 compounds.

The volatile methyl siloxanes are reported to have low oral and dermal toxicities, and are non-irritating to the skin and respiratory tract (Burow, 1993). They are mild eye irritants.

Compatibility with Materials. In general, solvents are safe to use with most metals, but some can cause swelling and cracking of polymers and elastomers. Ketones also are incompatible with many structural polymers. Esters, on the other hand, seem compatible with most polymers.

Ethyl lactate hydrolyzes to form lactic acid upon exposure to water, including contact with moist air. The acidity could have a negative impact on cleaning metal parts. In one set of tests, a sample of lactic acid aged 6 months at room temperature without nitrogen purge showed 0.10% acidity by titration (Hill and Carter, 1993). Therefore, precautions are needed to minimize the contact of lactic acid with moist air.

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Supercritical Fluids

Pollution Prevention Benefits

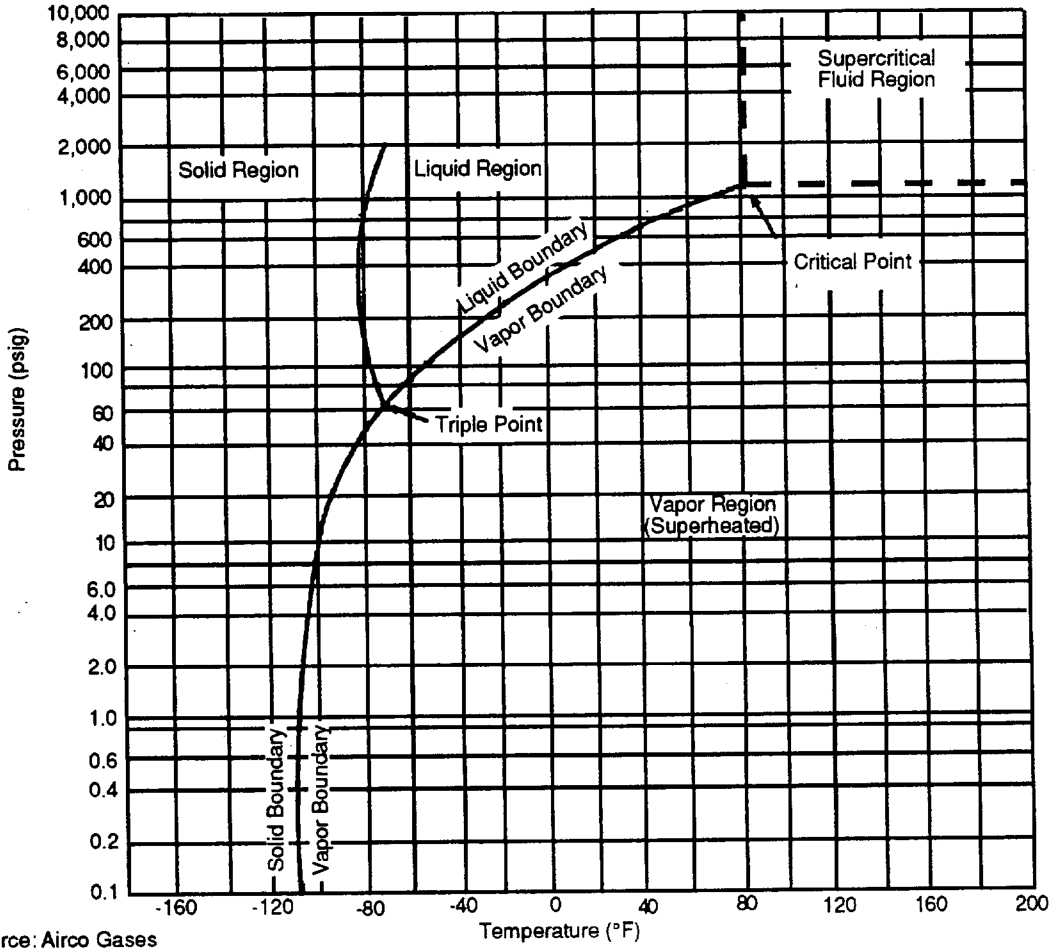
The main advantage of using carbon dioxide (CO_2) as a supercritical fluid (SCF) is that CO_2 is nonpolluting. CO_2 is derived from the atmosphere and is not created for use as a solvent. Furthermore, the small quantity of CO_2 released would have an insignificant effect on global warming. On the other hand, cosolvents, which may be used to improve the solvent power of CO_2, may have pollution potential and should be investigated before use. Energy is required to operate the pumps and temperature control equipment that are needed in supercritical cleaning equipment.

How Do They Work?

CO_2 compressed above its critical pressure (73.7 bars, or 1077 psi) becomes a critical fluid, and if also heated above its critical temperature (31.1°C, or 88.0°F), it becomes a supercritical fluid. Typically, however, the term *supercritical* (SC) is applied to any region in phase space that is above either the critical temperature (T_c) or the critical pressure (P_c). Critical and supercritical fluids are excellent solvents for dissolving many medium-molecular-weight, nonpolar or slightly polar organic compounds.

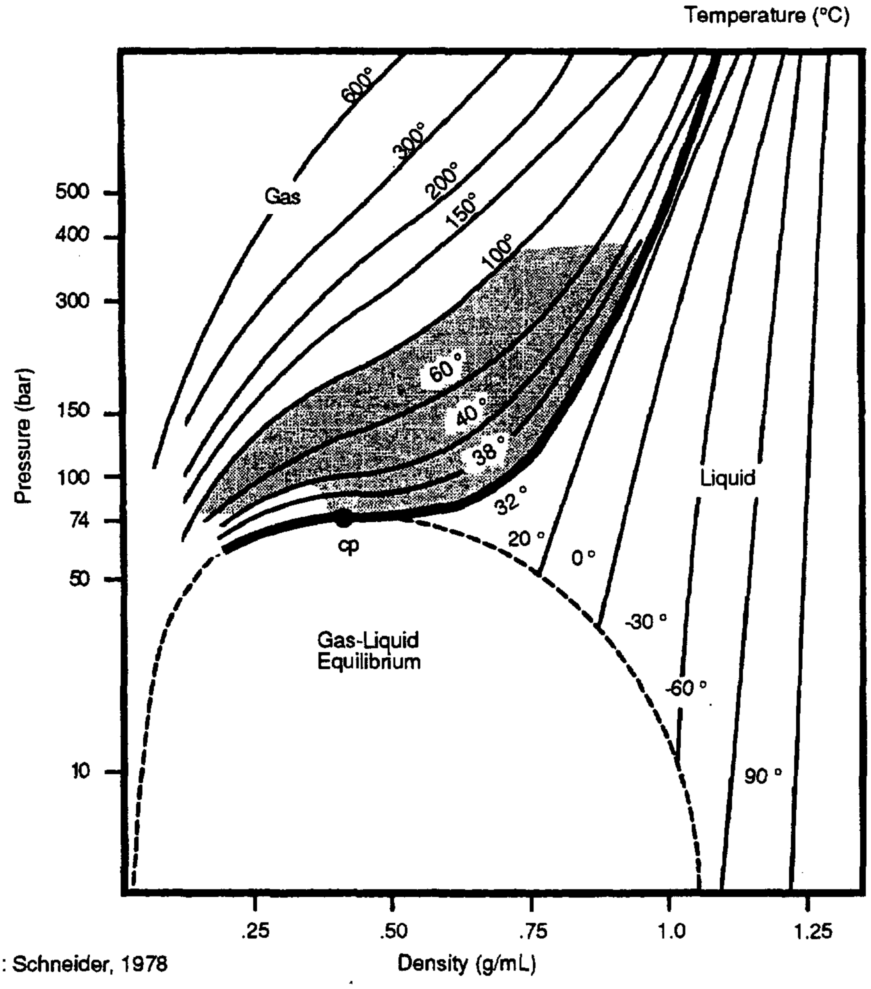
SCFs have more solvent power the denser they are.

Figure 1 is a phase diagram for CO_2 that shows its stable phase boundaries, including the supercritical region. The solvent power of supercritical fluids increases as the density of the fluid increases. The density of SC CO_2 can be made nearly liquid-like at moderate pressures. The shaded region in Figure 2 shows the pressure-temperature (*P-T*) region that is most useful for cleaning. Fluid densities range from approximately 0.2 to 0.8 g/cm^3. Figure 2 shows how the fluid density may be varied to achieve a broad range of solvating ability. It may be said that supercritical fluids can be "tailored" to achieve a desired solvent capability.



Source: Airco Gases

Figure 1. Phase diagram for pure CO_2.



Source: Schneider, 1978

Figure 2. Pressure-density diagram for pure CO_2; temperature in °C; cp = critical point.

Other factors that affect the cleaning abilities of SCFs are their gas-like low viscosity and high diffusivity, which enable them to penetrate into small confined spaces, such as cracks and blind holes. In the *P-T* region of interest (shaded area in Figure 2) viscosities are about twice those of the gas at atmospheric pressure and at the same temperature, whereas diffusivities are about 30 times smaller (Lira, 1988). However once CO_2 molecules have solvated contaminant molecules, the kinematic properties of the fluid may change, especially near the SCF/contaminant interface. With this change, the solvated contaminant species may be difficult to remove. In practice, some sort of mixing mechanism or flow control usually is built into the extraction vessel.

A typical SCF cleaning system consists of the following components:

- CO_2 source (compressed gas cylinder)
- Chiller to condense CO_2 gas to liquid
- Pressure pump to elevate CO_2 liquid pressure
- Hot water bath to elevate line temperature to that of the cleaning chamber
- Cleaning chamber where parts are cleaned
- Pressure reduction valve at fluid exit port
- Separator vessel to collect contaminants
- Air flow meter to monitor CO_2 usage.

Supercritical CO_2 dissolves and carries away soluble contaminants.

Samples to be cleaned are placed in the cleaning chamber, which also is called an *extraction vessel* or *autoclave*. The process is started by drawing CO_2 from the gas cylinder, then pressurizing and heating the CO_2 to the same *P-T* conditions as in the extraction vessel. Heat tape may be wound around all critical fluid transfer lines, and temperatures should be monitored at various points by thermocouples. SC CO_2 flows through the cleaning chamber where it dissolves and carries away soluble substances. After extraction, the

CO_2 and dissolved contaminants pass through a pressure reduction valve where pressure is dropped below P_c, and then they enter the separator vessel. As CO_2 returns to the gaseous state, its solvent power decreases substantially and contaminants drop out of solution and remain in the separator vessel. The CO_2 continues to flow out of the separator vessel through a flow meter and to the atmosphere.

As a rule of thumb, to achieve good solvency at moderate temperature, the fluid pressure should be 2 or more times the critical pressure of the fluid. Typical operating conditions for SCF cleaning equipment are listed in Table 7.

Table 7. Typical Operating Conditions for Supercritical CO_2 Cleaning

Parameter	Scientific Units	Engineering Units
Pressure (gauge)	100-300 bars	1,450-4,350 psi
Temperature	40-85°C	100-185°F
SC CO_2 Density	0.5-0.8 g/cm³	30-50 lb/ft³
SC CO_2 Flow Rate	1-5 kg/hr	2-11 lb/hr
Time	0.5-3 hours	0.5-3 hours

Operating Features

SCF cleaning exploits the marked improvement of the solvent power of CO_2 or other substances after they undergo a phase transition from a gas or liquid phase to become supercritical fluids. Supercritical CO_2 has been used very successfully to remove organic soils of moderate molecular weight and low polarity. Supercritical CO_2 does not give good results for soils that are ionic or polar in nature, such as fingerprints.

SCF cleaning is most useful for precision cleaning operations.

SCF cleaning is probably best reserved for removing small amounts of soil from parts that require a high degree of cleanliness. For example, precision cleaning operations have been performed successfully on the following devices: gyroscope parts, accelerometers, thermal switches, nuclear valve seals, electromechanical assemblies, polymeric containers, optical components, porous metals, and ceramics (Gallagher and Krukonis, 1991; Woodwell, 1993). The cleaning technology is available commercially.

Capital costs for installing SCF equipment are high, at least $100K for small-capacity equipment. The cost of the autoclave increases considerably with size. Small vessels may be only 1 liter in volume and are relatively inexpensive. Large vessels—30 liters, for example—are many times more expensive for the same pressure rating. If large parts are to be cleaned, it may be more cost effective to purchase lower-pressure-rated equipment and operate the SCF system for longer times at lower pressure. The expense of supplying CO_2 to the system, however, is quite small, about 7 cents per pound.

Application

Supercritical fluids have been used in organic chemical analysis equipment and in the food and flavor industries. SCFs have been used to clean and degrease precision parts in the defense industry since the mid-1980s.

Supercritical fluids have been used to remove machine coolants on aluminum and stainless steel substrates (Salerno, 1990). The cleaning process, performed at 35°C, 138 bars for 15 to 30 minutes, yielded a residual 0.65% of the coolants on the substrates. The solubility of the coolants ranged from about 1 to 5% under these conditions.

Benefits

Low viscosity and high diffusivity permit SCFs to clean within very small cracks and pore spaces. The solvent power of SCFs is pressure-dependent, making it possible to extract different soils selectively and precipitate them into collection vessels for analysis.

Limitations

Health and Safety. The only major safety concern is the danger of a pressure vessel or line rupture. However, the pressures used in SCF cleaning are well within the strength limits of most standard autoclave equipment.

Compatibility with Materials. SCFs are compatible with metals, ceramics, and polymers such as Teflon™, high-density polyethylene, epoxies, and polyimides. SCFs cause swelling in acrylates, styrene polymers, neoprene, polycarbonate, and urethanes (Gallagher and Krukonis, 1991). Components that are sensitive to high pressures and temperatures should not be cleaned by SCF methods. Process developments in the future probably will make SCF cleaning more aggressive toward removing cross-linked polymeric materials and displacing particulates.

Cleaning Efficacy. The major deficiencies of SCF cleaning are that SCFs are not effective in removing inorganic and polar organic soils, nor do they remove loose scale or other particulates. For these reasons, the soil must be well characterized to ensure its solubility in SCF before an investment is made in this technology.

It also is not known whether the process can remove a complex mixture of contaminants. Therefore, a detailed analysis of the contaminants must be done before the likelihood of success can be determined.

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Carbon Dioxide Snow

Pollution Prevention Benefits

Chilled CO_2 is a nontoxic, inert gas that replaces solvent use to eliminate ozone-depleting substances. Because the CO_2 is recycled, there is no need for disposal, nor is any wastewater produced. It generates no hazardous emissions.

How Does It Work?

Gaseous or liquid CO_2 is drawn from a room-temperature gas cylinder or high-pressure dewar and expanded through a nozzle to produce fine CO_2 particles and CO_2 gas. These particles are dry ice *snowflakes* and are propelled by the gas stream.

The CO_2 gas or liquid is expanded through a special nozzle to form a jet. For example, when liquid CO_2 at 750 psi is throttled through a nozzle and expanded into a volume at 1 atm pressure, it undergoes a phase change to the solid state. The shape and size of the snowflakes depend on the configuration of the nozzle and the conditions in which the flake formed in the gas stream. The snowflakes can be individual crystals or collective groupings of crystallites.

Cleaning action is performed when the snow particles impact a contaminated surface, dislodge adherent contaminant particles, and carry them away in the gas stream. The process is effective in removing very small (submicron) particles, where fluid drag normally restricts the performance of liquid phase cleaning. The CO_2 snow cleaning process also is believed to attach hydrocarbon film by dissolving hydrocarbon molecules in a temporal liquid CO_2 phase at the film-substrate interface (Whitlock, 1989). The dissolved film is then carried away by subsequent flow of snow and gas.

Operating Features

A complete system includes a CO_2 purifier, a pneumatic actuated head, and a microprocessor-based timing circuit. Several models of manual spray booths are available that provide a nitrogen-purged, heated, and monitored environment for CO_2 spraying that cost $10K to $15K. One commercial purifier is available in a 17 x 14 x 24 1/2 inch stainless steel cabinet. It weighs 135 lb and requires an energy supply of 6 A, 115 VAC, and 60 Hz.

Another commercially available purifier is capable of purifying CO_2 to a water content of less than 20 ppb by weight. In laboratory analyses of CO_2 before and after purification, the hydrocarbon content of 1800 ppb by weight was reduced to 3 ppb hydrocarbon; CO_2 with 140 ppb by weight halocarbons was purified to 1 ppb wt halocarbons. The purifier works on a 25% duty cycle, allowing use for 1 minute to every 3 minutes of recovery time. The snow gun consumes 0.6 lb of CO_2 per minute when used continuously.

If the dust or dirt particles removed by CO_2 snow cleaning are a hazard, they can be collected by an electrically charged curtain (Hoenig, 1990).

Application

CO_2 snow gently removes particles smaller than 10 microns in diameter down to 0.1 micron that are difficult to remove using high-velocity liquid nitrogen. It is used to remove light oils and fingerprints from mirrors, lenses, and other delicate surfaces, and from precision assemblies, without scratching the surface.

Uses of CO_2 snow range from hybrid circuitry to the optics industry.

CO_2 snow can clean hybrid circuitry and integrated circuits without disturbing the bonding wires. This unique ability cannot be duplicated by any other cleaning mechanism. In the disc drive industry, CO_2 snow is used to remove particles from discs without damage to the operation (Hoenig, 1990).

The process is used to remove paste fluxes in soldering. If the grease cannot be removed with CO_2 snow alone, a combination of CO_2 snow and ethyl alcohol is effective, followed by CO_2 snow alone to remove the impurities from the alcohol (Hoenig, 1990).

CO_2 is used to remove hydrocarbons and silicone grease stains from silicon wafers. Wafers artificially contaminated with a finger print, a nose print, and a thin silicone grease film were found to have surface hydrocarbon levels 25 to 30% lower after CO_2 snow cleaning than the original wafer surfaces (Sherman and Whitlock, 1990).

CO_2 snow cleaning is extremely effective.

Layden and Wadlow (1990) report a reduction of zinc orthosilicate concentration on a silicon wafer of more than 99.9% after cleaning by high-velocity CO_2 snow. Whitlock (1989) reports removal of greater than 99.9% for particles ranging from 0.1 to 0.5 micron diameter.

In the field of optics, CO_2 snow is used to clean the light-scattering particles and debris from the mirrors of the world's largest and most expensive telescopes.

CO_2 snow also is used to clean surfaces exposed to contaminants in air prior to surface analysis. The process was found to work better than solvents to clean vacuum components. Because the aerosol could penetrate narrow spaces, no disassembly was required, greatly shortening the time required for cleaning. Furthermore, CO_2 cleaning is effective on some plastic parts that cannot be cleaned by solvents (Layden and Wadlow, 1990).

Benefits

Some of the major beneficial aspects of CO_2 snow include

- CO_2 snow performs ultrapure cleaning of light oils down to submicron size on the most delicate, sensitive materials ranging from bonding wires to precision mirrors in telescopes.
- The CO_2 snow crystals generated by the snow gun are extremely gentle.
- The CO_2 snowflakes are adjustable to a wide range of size and intensity.
- The process does not create thermal shock, is nonflammable and nontoxic, and causes no apparent chemical reactions.
- Cleaning by CO_2 snow is noncorrosive and leaves no residue.
- CO_2 snow does not crack glass or other ceramics.
- No media separation system is needed, nor is there a media disposal cost.
- CO_2 snow can penetrate the nonturbulent area to dislodge contaminants and can be used on components without disassembly that otherwise must be disassembled because the aerosol penetrates narrow spaces.

Limitations

Potential hazards and limitations of CO_2 snow include

- Heavier oils, alone or mixed with light oils, may require chemical precleaning and/or heating to be completely removed.
- The CO_2 must be purified because of its tendency to dissolve contaminants from the walls of tanks in which it is stored. Purification equipment adds expense to the CO_2 snow cleaning system.
- When surfaces are excessively chilled by long dwell times, airborne impurities may condense and settle on the clean surface (Zito, 1990).
- CO_2 snow has low Mohs hardness and will not scratch most metals and glasses. However, hard particulates such as sand that may be present on a surface potentially could cause scratching when they are carried by the gas stream.

References

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SECTION 3
EMERGING TECHNOLOGIES

How to Use The Summary Tables

Two emerging alternatives to chlorinated solvents for cleaning and degreasing are evaluated in this section:

- Catalytic wet oxidation cleaning
- Absorbent media cleaning.

Tables 8 and 9 summarize descriptive and operational aspects of these technologies. The tables contain evaluations or annotations describing each emerging cleaner technology and give a compact indication of the range of technologies that may be applicable to specific situations. Readers are invited to refer to the summary tables throughout this discussion to compare and contrast technologies.

Descriptive Aspects

Table 8 describes each emerging cleaner technology. It lists the **Pollution Prevention Benefits, Application, Benefits,** and **Limitations** of each emerging cleaner technology.

Operational Aspects

Table 9 shows the key operating characteristics for the emerging technologies. The technical qualitative rankings are estimated based on the descriptions and data in the literature.

The summary tables will help identify possible candidate cleaner technologies.

In Table 8, **Process Complexity** is qualitatively ranked as "high," "medium," or "low" based on such factors as the number of process steps involved and the number of material transfers needed. **Process Complexity** is an indication of how easily the technology can be integrated into existing plant operations. A large number of process steps or input chemicals, or multiple operations with complex sequencing, are examples of characteristics that would lead to a high complexity rating.

The **Required Skill Level** of equipment operators also is ranked as "high," "medium," or "low." **Required Skill Level** is an indication of the level of sophistication and training required by staff to operate the new technology. A technology that requires the operator to adjust critical parameters would be rated as having a high skill requirement. In some cases, the operator may be insulated from the process by complex control equipment. In such cases, the operator skill level is low, but the maintenance skill level is high.

Table 9 also lists the **Waste Products and Emissions** from the emerging cleaner technologies. It indicates tradeoffs in potential pollutants, the waste reduction potential of each, and compatibility with existing waste recycling or treatment operations at the plant.

Use the information in the text, from the references, and from industry and trade groups to get more detail on the best candidates.

The **Capital Cost** column provides a preliminary measure of process economics. It is a qualitative estimate of the initial cost impact of the engineering, procurement, and installation of the process and support equipment compared to continuing to use chlorinated solvents. Due to the diversity of cost data and the wide variation in plant needs and conditions, it is not possible to give specific cost comparisons. Cost analysis must be plant-specific to adequately address factors such as the type and age of existing equipment, space availability, throughput, product type, customer specifications, and cost of capital. Where possible, sources of cost data are referenced in the discussions of each cleaner technology.

The **Energy Use** column provides data on energy use for a specific technology.

Operations Needed After Cleaning summarizes additional inspection, hand cleaning, or other operations that may be needed after use of the clean alternative solvent. These are noted to indicate special

Table 8. Emerging Technologies for Alternatives to Chlorinated Solvents for Cleaning and Degreasing: Descriptive Aspects

Technology Type	Pollution Prevention Benefits	Application	Benefits	Limitations
Catalytic Wet Oxidation Cleaning	• Only CO_2 and water produced	• Oxidizable organic soils	• Can be used to clean wet parts	• May damage/corrode some substrates
Absorbent Media Cleaning	• No water involved in cleaning • Replaces solvents • Media biodegradable and/or can be recycled	• Degrease low alloy steel prior to heat treatment • Clean fingerprints from mylar • Sop up oil • Degrease aluminum and other sensitive parts	• Wipes are made of recyclable, potentially reclaimable materials • Wipes can be incinerated • Starch applicators can be reused indefinitely • Sewered starch is useful as a feedstock for municipal processing plants • Spent wipers and starch have BTU value	• Plant air or a shop vacuum needed in most cases • Not useful on complex surfaces or detailed parts

Table 9. Emerging Technologies for Alternatives to Chlorinated Solvents for Cleaning and Degreasing: Operational Aspects

Technology Type	Process Complexity	Required Skill Level	Waste Products and Emissions	Capital Cost	Energy Use	Operations Needed After Cleaning	References
Catalytic Wet Oxidation Cleaning	Medium	Medium	CO_2, water	No commercial system to date	• Low	• Drying to remove water	Dhooge, 1990
Absorbent Media Cleaning	Low	Low	Spent media	Low material cost and low operating cost	• Low for air filtration or vacuum system	• Sweeping or vacuuming may be required	Doscher, 1991 Doscher et al., 1990

considerations in the application of the cleaner technology.

The last column in Table 9 cites **References** to publications that will provide further information for each emerging technology. The citations are given as full references at the end of the respective Emerging Technology sections.

The text further describes pollution prevention benefits, application, product benefits, and limitations known for each technology. More highly developed technologies are summarized in Section 2, **Available Technologies**.

Catalytic Wet Oxidation Cleaning

> *Catalytic wet oxidation consumes little energy.*

Catalytic wet oxidation is a proposed method for chemically oxidizing, or "burning," organic contaminants within an aqueous medium. Oxygen-rich air pumped into an aqueous solution can be used to gasify organics that adhere to a substrate, thereby converting them to more easily degradable chemical intermediates. The concept was developed for the destruction of organic wastes (Dhooge, 1990), but may be applicable to substrate cleaning as well. In principle, the final waste products are CO_2 and water. The process consumes little energy.

Oxidation in the presence of water is the source of the term *wet oxidation*. This technology can be used to treat waste streams high in organic matter. Wet oxidation works most effectively on materials that contain substantial amounts of water and cannot be easily combusted under conventional burning conditions.

A catalyst—typically iron (III)/iron (II) salts that dissolve in solution—and one of several homogeneous (aqueous phase) cocatalysts are used to increase the rate of the wet oxidation reaction. Typical cocatalysts could be chosen from the platinum (IV), ruthenium (III), rhodium (III), nickel (II), cobalt (II), palladium (II), or vanadium (V) complex.

The process works by forming water-soluble intermediates as organic materials are broken down into smaller molecular species. Sometimes polymerization occurs, as in the formation of gums in petroleum oils. High temperatures (250 to 300°C) may be required to obtain nearly complete conversion of organic matter with the wet oxidation technology.

Reference

Dhooge, P. M. 1990. *Method for Treating Organic Waste Material and an Oxidation Catalyst/Cocatalyst Composition Useful Therefor.* U.S. Patent No. 4,925,540. May 15.

Absorbent Media Cleaning

Absorbent media can be used to remove grease and oil in situations where aqueous or semi-aqueous treatments cannot be used, as in degreasing water-sensitive materials or where lack of floor space makes rinsing impractical. Two types of absorbent media have been introduced to replace VOC-exempt solvents. The first involves wiping with oil-absorbent wipers containing polypropylene fibers. The second makes use of a variety of particulate absorbents, such as natural silicates, wheat starch, and dry cellulose pulp (Doscher, 1991).

The effectiveness of wipers depends on the surface size and viscosity of the grease or oil. Cheesecloth and specially produced wipers of fine texture have been used to remove fingerprints from mylar. Wipers of larger fiber dimension and rougher surface texture are used to sop up oil used during shop equipment maintenance and are effective on large, exposed surfaces. As part complexity increases and part size decreases, wipers containing thinner, finer fibers are required.

> *Absorbent media cleaners now are made of recycled materials.*

The new generation of wipers are made of recycled materials such as polypropylene. Because the fibers are not woven or coated, excess lint or shedding may occur. To combat this problem, a ventilation system should be designed to capture fugitive dusts. Spent wipers should be disposed of by recycling, incinerating, or landfilling, provided that they were not used to absorb toxic materials. Recycling is seen as the most desirable option, but in lieu of a cost-effective method for removing oil and grease from the fibers, incinerating or landfilling the wipers are the only currently available options. Because polypropylene has high BTU value, incineration may be the better alternative.

> *Loose, particulate absorbents are made of natural materials.*

Loose, particulate absorbents are reported to be even more effective than wipers for removing grease and oil because of their greater surface area and better impingement. They may also have a greater affinity for oil (Doscher, 1991). The term *particulate absorbent* comprises such materials as siliceous materials and organic cellulose-based materials. The three commonly used siliceous materials, talc, kaolin, and diatomaceous earth, visibly scratch aluminum surfaces and are unacceptable unless abrasive surface preparation is required. Of the organic absorbents tested, wheat starch performed best in terms of ease of use and results (Doscher, 1991).

Starch waste can be used in various ways, so that waste handling requirements are minimal.

Starch cleaning involves dipping a foam-backed nylon bristle paint pad in the loose starch and using standard wipe techniques. The process waste, i.e., the oil-soaked starch aggregate, is vacuumed or swept away and can be sewered in many cases, depending on the toxicology and wastewater characteristics of the oil. When sewered, the starch itself is useful as a feedstock for municipal processing plants. If the process grease or oil cannot be sewered, the process waste has BTU value for incineration. The nylon bristle pad can be reused many times. Thus, the waste volume and handling requirements for starch are minimal.

In a test to compare cleaning of sesame oil with the solvent MEK to starch cleaning of the same oil, starch applied in one wiping cycle (5 up-and-down scrubs) got the panels 99% clean. Using fresh MEK in three successive wipings, replacing the wiper each time, achieved 96% clean panels (Doscher, 1991).

Starch cleaning has been shown to be more effective than cleaning with the solvent MEK.

Absorbent cleaning has in the past been regarded as a "last resort" substitution method. With starch, however, the material cost; shop time; and safety, health, and environmental considerations outweigh the disadvantages for cleaning flat, exposed surfaces. A dust collection unit or vacuum table must be provided to prevent excess material from becoming airborne. When the surface is not too complex and dust collection is feasible, starch cleaning is a process improvement. The effectiveness of starch in a fluidized bed dry-cleaning system is described by Doscher and others (1990).

References

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SECTION 4
POLLUTION PREVENTION STRATEGY

The main federal environmental regulations influencing the application of new cleaning technologies are the Clean Air Act Amendments (CAAA), the Resource Conservation and Recovery Act (RCRA), the Right to Know provisions of the Superfund Amendment and Reauthorization Act (SARA), and the emphasis on eliminating pollution at the source in the Pollution Prevention Act of 1990. Solvent cleaners also increase the potential workplace exposures to volatile organic compounds (VOCs) regulated under the Occupational Safety and Health Act (OSHA). There are a wide variety of state and local limits on VOC, hazardous, and aqueous wastes that also are of concern.

RCRA regulations make processes that generate significant solvent waste streams unattractive.

The requirements for cradle-to-grave management for solvent waste established by RCRA create several incentives to seek solvent-free alternatives. Disposal of RCRA wastes (including solvent waste) is costly and carries continued liability. RCRA also requires the waste generator to maintain a waste minimization program. Converting all possible plant applications to a cleaning technology that eliminates or reduces solvent use helps to demonstrate an effort to minimize hazardous waste.

Hazardous solvent emissions have to be reported under Title III of SARA.

Since 1988, manufacturing facilities have been reporting emissions of more than 300 chemicals or chemical categories. The reporting requirements are established under Title III of SARA. The toxic chemical release reporting usually is referred to as the Toxics Release Inventory (TRI). The reporting rule requires annual data on direct releases to all environmental media.

Facilities meeting the following conditions must file TRI data:

- A Standard Industrial Classification (SIC) code in the range of 20 to 39
- 10 or more employees
- Manufacture or processing of more than 25,000 pounds or use of more than 10,000 pounds of a chemical on the TRI list.

The reporting requirements were expanded to include data on recycling as required by the Pollution Prevention Act. The effort required to track and report chemical usage as required by these legislations is significant. For plants that exceed the reporting threshold, reducing chemical use below the threshold eliminates the requirement to prepare a report for the chemical. Commonly used cleaning solvents—1,1,1-trichloroethane (TCA), trichloroethylene (TCE), methylene chloride (METH), and perchloroethylene (PERC)—also are TRI chemicals. Therefore, reducing or eliminating the use of any such solvent will eliminate the need to complete a TRI reporting form for that solvent.

Many solvents used in cleaning processes are part of a list of 17 priority toxic chemicals in the 33/50 Program targeted for early reduction.

The EPA also encourages the voluntary reduction of 17 priority toxic chemicals identified in the 33/50 Program for early pollutant reductions (U.S. EPA, 1991, 1992). Several cleaning solvents are on the list of priority toxic chemicals identified by the EPA Administrator for early reduction in the 33/50 Program. Switching from conventional solvent cleaning to a cleaner technology will assist in meeting the reduction goal.

OSHA regulations for solvent air emissions in the workplace are becoming increasingly stringent.

Another consideration is that the organic solvents used in cleaning may result in sufficient vapor concentrations to cause concern for workers in the area. The National Institute for Occupational Safety and Health (NIOSH) recommends that occupational exposure to carcinogens be limited to the lowest feasible concentration. OSHA regulations for workplace emissions are also becoming increasingly stringent.

Title III of the CAAA requires adoption of Maximum Achievable Control Technologies (MACT) for control of 189 hazardous air pollutants (HAPs). Cleaning processes using solvents are considered major sources of HAPs and are subject to MACT standards. Vapor degreasing is the single largest use for solvents, followed by dry cleaning (clothes cleaning) and cold cleaning (liquid solvent cleaning). Based on 1987 U.S. EPA estimates, approximately 25,000 to 35,000 batch vapor degreasers and 2,000 to 3,000 continuous cleaners were used in the United States.

The Pollution Prevention Act establishes source reduction as the preferred method for pollutant management.

The Pollution Prevention Act establishes pollution prevention as the preferred method for pollutant management. The processes described in this document provide promising alternatives to conventional processes for potential users, i.e., the metal-finishing, dry-cleaning, electronics, and any other industry that uses cleaning processes. Under programs such as the U.S. EPA's 33/50 Program, industries are encouraged to reduce pollutants voluntarily in anticipation of future regulations, which are expected to become increasingly stringent. The CAAA of 1990 allows the U.S. EPA to grant a 6-year compliance extension on the MACT compliance date to any existing source of air toxics that reduces emissions voluntarily by 90% (95% for particulates) below 1987 levels before January 1, 1994.

MACT standards will be issued by the U.S. EPA for new and existing sources, using the best controlled similar sources as a measure. MACT can include control equipment, process changes, material substitutions, equipment design modifications, work practices, or operational practices. All sources in a source category or subcategory will have to implement MACT. Unless the owner of the source is eligible for the 6-year extension (for 90% reduction), all industrial sources are expected to be in compliance within 3 years of promulgation of the MACT standards. A 5-year compliance extension also may be granted for prior installation of Best Available Control Technology (BACT) or Lowest Achievable Emissions Rate (LAER).

Under CAAA, MACT standards can be expected for halogenated solvent cleaners.

Under Title III of the CAAA, the U.S. EPA on July 16, 1992 (*Federal Register*, 1992) added halogenated solvent cleaners as an area source category. Thus, halogenated solvent cleaners are considered a major source category emitting at least 10 tons/year of any one air toxic or 25 tons/year of any combination of air toxics. Therefore, MACT standards can be expected to be promulgated for these cleaners. Vapor degreasing constitutes the single largest use of solvents in the United States, and therefore is an important area targeted for pollution prevention.

References

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U.S. Environmental Protection Agency. 1992. *EPA's 33/50 Program Second Progress Report.* TS-792A, Office of Pollution Prevention and Toxics. February.

SECTION 5
CLEANER TECHNOLOGY TRANSFER CONSIDERATIONS

Since the 1970s it has been realized that some chlorofluorocarbons (CFCs) undergo chemical changes in the upper atmosphere that subsequently lead to the destruction of the ozone layer. The world community has since sought to eliminate production and use of CFCs. According to the Montreal Protocol, agreements were made to restrict the production and use of ozone-depleting chemicals. The Montreal Protocol and later amendments led to changes in the U.S. Clean Air Act, which was amended by President Bush on November 15, 1990. The Clean Air Act Amendments (CAAA) established a time frame to eliminate all fully halogenated CFCs, certain chlorinated hydrocarbons, and hydrochlorofluorocarbons (HCFCs).

Class I ozone layer-depleting substances must be phased out by 1996.

In November 1992, the participating countries voted to advance the deadline for phasing out ozone layer-depleting substances (OLDS Class I) to January 1, 1996. The OLDS Class I list includes CFCs and halons, among which are CFC-113 and TCA, which are the substances most important to cleaning. The expected ban on Class II OLDS, which includes the HCFCs, is between 2020 and 2040 or earlier, as stipulated by the London Amendments to the Montreal Protocol.

New aqueous and semi-aqueous washers are more efficient compared to conventional aqueous cleaning processes.

Some users may want to retain vapor degreasing rather than convert to aqueous or semi-aqueous cleaning. Industries have been reluctant to eliminate vapor degreasing completely because of its advantage with certain types of parts or simply because of tradition and ease of operation. Some users in this group may consider completely enclosed vapor degreasing (see *Guide to Cleaner Technologies: Cleaning and Degreasing Process Changes*) or HCFC vapor degreasing solvents (see Available Technologies) as a temporary solution. Because perfect "drop-in" replacements do not exist, some process modification will be needed to obtain results that are similar to those achievable with the former vapor degreasing process. In addition, users who want to purchase HCFC solvents for major use areas, such as vapor degreasing in electronics and metal finishing industries, must petition EPA, per Section 612 of the CAAA.

If users are ready to switch to a liquid cleaning approach, many options already are available. Aqueous, semi-aqueous, and solvent cleaning technologies have advanced in recent years in terms of both the type of cleaning chemicals used and the type of equipment used. (See the discussion of cleaning equipment in *Guide to Cleaner Technologies: Cleaning and Degreasing Process Changes*).

Databases can assist users in choosing a new cleaning technology.

Reluctance to switch over to a new cleaning technology may stem from concern over cleaning performance, as well as from uncertainty in choosing an alternative from the large number of cleaning technologies and products now available. Users may be intimidated by the list of options and wonder how to begin selecting an alternative. Although trade journals provide technical literature on alternative cleaning technologies, the subject may not be presented in a systematic form that facilitates making detailed comparisons among all the different attributes. To assist in making knowledgeable decisions, several online and offline computer databases are available that provide information searching in various ways. These databases are discussed in the following paragraphs: The Alternative Technologies Transfer Information Clearinghouse (ATTIC), the Pollution Prevention Information Exchange System (PIES), the Solvent Alternatives Guide (SAGE), the Solvent Alternative Utilization Handbook, and the NCMS Solvent Database.

ATTIC is a four-in-one network.

The **ATTIC** network is maintained by the Technical Support Branch of EPA's Risk Reduction Engineering

Laboratory (RREL). This network has four online databases that can be searched by external users.

- The ATTIC database contains abstracts and bibliographic citations to technical reports, bulletins, and other publications produced by EPA, other federal and state agencies, and industry dealing with technologies for treatment of hazardous wastes. Performance and cost data, quality assurance information, and a contact name and phone number are given for the technologies.
- The Risk Reduction Engineering Laboratory (RREL) Treatability Database provides information about contaminants physiochemical properties, environmental data, treatment technologies, contaminant concentration, media or matrix, performance, and quality assurance.
- The Technical Assistance Directory lists experts from government, universities, and consulting firms who can provide guidance on technical issues or policy questions.
- A Calendar of Events list provides information on conferences, seminars, and workshops on treatment of hazardous wastes. International as well as U.S. events are covered.

There is no charge for the ATTIC service. It is available via modem over standard telephone lines. The phone number for the ATTIC modem contact is (301) 670-3808 (300-2400 baud), and the modem settings are no parity, 8 data bits, 1 stop bit, and full duplex. The user's manual also is available from EPA.

PIES links to several databases.

PIES is a bulletin board system that links to several databases and provides messaging capabilities and forums on various topics related to pollution prevention. Through its link to the United Nation's International Cleaner Production Information Clearinghouse, it provides a communication link with international users. PIES is part of the Pollution Prevention Information Center (PPIC), which is supported by EPA's Office of Environmental Engineering and Technology Demonstration and Office of Pollution Prevention and Toxics. PIES contains information about the following topics:

- Current events and recent publications relating to pollution prevention
- Summaries of federal, state, and corporate pollution prevention programs
- Case studies and general publications.

Searches can be performed by keywords related to specific contaminants, pollution prevention technologies, or industries. The phone number for dial-up access is (703) 506-1025; qualified state and local officials can obtain a toll-free number by calling the PPIC at (703) 821-4800. Modem settings are 2400 baud, no parity, 8 data bits, 1 stop bit, and full duplex.

SAGE ranks alternatives.

SAGE has a question-and-answer format that lets the user input basic cleaning parameters about the parts to be cleaned and about the desired process outcome (Monroe and Hill, 1993). The user-provided information is then applied, internally, to the SAGE database, which derives recommendations for chemical and process alternatives. Based on the information given, the alternatives are assigned a relative score that allows them to be compared. A brief summary of each recommendation can be presented on the screen. Other information, such as a representative MSDS and case studies, also is included.

SAGE is available through the Control Technology Center (CTC) of the U.S. EPA Air and Energy Engineering Research Laboratory (AEERL). A system operator at the CTC can be reached by calling (919) 541-0800. The SAGE software can be transferred on an electronic bulletin board system in a file named SAGE.ZIP. The bulletin board can be reached at (919) 541-5742 (9600 baud, no parity, 8 data bits, 1 stop bit).

An online Solvent Utilization Handbook assists solvent users.

The U.S. Department of Energy (DOE) has supported a solvent alternative utilization study through the Idaho National Engineering Laboratory. As a result, a program was established to develop an online electronic **Solvent Utilization Handbook**. The handbook helps users accomplish the following tasks:

- Identify solvents that are not restricted for use at DOE Defense Programs, U.S. Department of Defense (DoD) facilities, and private business.
- Evaluate their cleaning performance needs.
- Identify potential problems, such as corrosivity, flammability (flash point), and hazardous material content (OSHA and NIOSH exposure limits).
- Evaluate potential concerns for air emissions.
- Decide whether solvent recovery and recycling are feasible.
- Determine whether the solvents are biodegradable.

The information provided in this database is based on results of actual experiments that included 16 different contaminants on 26 metal alloys. The database is accessible through Internet or by using a telephone modem. Further information can be obtained from the Idaho National Engineering Laboratory by calling (208) 526-7834.

The electronic Solvent Database is fully searchable.

The National Center for Manufacturing Sciences (NCMS) is developing an electronic **Solvent Database** that provides information on environmental fate, health and safety data, regulatory status, chemical and physical properties, and product suppliers. The database includes more than 320 pure solvents and trade name mixtures. A relational search capability enables users to identify potential alternative solvents by specifying search criteria. For example, solvent alternatives can be selected by minimum flash point or by a particular regulatory issue. Product performance data are not included in the current version.

The NCMS Solvent Database will be a stand-alone application that runs on the DOS platform. It will be distributed on floppy disks. The cost of the software has not been released. For further information contact Mike Wixom, Project Manager, Environmentally Conscious Manufacturing, NCMS; telephone (313) 995-4910.

Because there is no universal definition of "clean," process developers must adopt their own criteria for judging cleanliness using methods that meet their individual needs. Underestimating the level of cleanliness required for a particular application may lead to a loss of product performance or quality, while overestimating may cause time, energy, and materials to be wasted. As a working definition, "clean" usually is the level of cleanliness required for any of the following to occur:

- Mechanical devices function according to design specifications
- Electronic or electrical devices perform reliably over their expected service lifetimes
- Organic coatings adhere properly to a substrate
- Product finish meets performance and appearance criteria.

Characteristics of the parts to be cleaned must be taken into account when choosing a cleaner technology.

Before selecting an alternative solvent, process developers must consider the following aspects about the parts to be cleaned:

- Material composition—is the part sensitive to water or solvents?
- Coating type—will the coating become damaged?—should it be removed?
- Part size—a concern for cleaning equipment configuration
- Part shape—complex shape may require engineering modifications to ensure thorough cleaning and drying
- Value of the part—determines how much investment should be made in an alternative process
- Stability of the part—will an aggressive cleaning process damage the part?
- Type of contaminants present—potential for aqueous, semi-aqueous, or other types of cleaning
- Rate of production—determines speed and capacity of the alternative process
- Postcleaning steps—how clean must the part be?—must it be dry immediately?

Process changes may influence one's decision in choosing an alternative cleaning process.

In addition, considerations must be made for process changes that do not directly impact the cleaning process:

- Operational costs—cleaner/solvent; particulate filters, heating, ultrasonics, tap water, water deionization, drying, and other energy costs
- Investment costs—cost of the cleaning unit; accessories; electrical, water, steam, and drainage connections
- Labor requirements—regular labor compared to current requirements, special training
- Hazardous material usage—fire protection, air ventilation, waste collection and shipment
- Waste stream handling—used solvent, skimmed oil/grease, solvent vapor emission/capturing, wastewater pretreatment
- Process sensitivity—cleaner/solvent testing/maintenance, requirement to add chemicals to restore balance, filter changes.

A multiple-attribute evaluation can be done to assist in selecting a cleaner technology.

An approach to selecting a cleaning system that will perform the necessary cleaning functions and one that can be supported by industry is to conduct a multiple-attribute evaluation based on the attributes listed above. The evaluation should compare attributes of the current cleaning system (the baseline) with those of alternative technologies. A simple numerical scheme can be easily developed. For example, scores between 1 and 10 would be assigned to each attribute and their sum would then rank the technology. The highest scoring technology would be the best alternative. If the score should fall below that of the baseline, then the need to change technologies should be reevaluated. The attributes can be weighted evenly or they can be weighted to emphasize issues of particular concern. For example, if removal of an adhesive is a critical concern, then a cleaner that is capable of attaining this goal should be prioritized. As another example, if a plant has no industrial wastewater treatment facility and must discharge wastewater directly to a POTW, then a process that either does not produce wastewater, or one that could produce wastewater that meets the discharge criteria of the POTW would be an important attribute which should be weighted accordingly. This methodology can include quantitative and qualitative attributes, both of which are important in making process engineering and waste minimization decisions.

Pilot testing of the new technology can be done to evaluate its effectiveness.

In addition to querying electronic databases and reading technical literature, it is a good idea to consult with industry partners who face similar choices and may have had to make critical decisions. Another approach is to discuss the possibility of testing a cleaning system on site or at a vendor's location. Many vendors have test units at their manufacturing locations, where typical parts can be cleaned to evaluate the effectiveness of the technology.

Vendors can help in the selection process.

When evaluating the effectiveness of a new cleaning technology, the user often must evaluate how clean the part is after washing. Evaluating the cleanliness of the workpiece can involve anything from simple visual observation to sophisticated surface analysis depending on the requirements of the application. For example, many metal finishing industries use a relatively simple test called the water-break test to evaluate a clean surface. The test involves dipping the cleaned workpiece or a cleaned test panel into a beaker of water and pulling it out. If the water film forms a continuous layer on the workpiece surface that can be sustained for about a minute, the surface is considered clean enough for further product finishing steps such as electroplating. Evaluating the cleanliness of an irregularly shaped part with crevices or blind holes may be more difficult.

Alternative cleaning technologies have enough flexibility to overcome many performance problems.

If cleaning effectiveness of an alternative cleaning system should fall below expectations, equipment vendors or contractors often can bring about improvements by making design or process modifications. For example, in spray cleaning, changing the angle of the spray nozzles can sometimes improve the cleaning effectiveness dramatically. Parts holders also can be custom designed for a particular application to maximize cleaning performance. Similarly, optimization of process parameters can improve performance. Process parameters include bath temperature, run time, solution filtration, and the chemical balance of the cleaner or solvent.

If aqueous cleaning seems like a desirable option, then keep the following features and limitations in mind:

- Aqueous cleaning is more effective at higher temperatures, and normally is performed above 120°F using suitable immersion, spray, or ultrasonic washing equipment. For this reason, good engineering practices and process controls tend to be more important in aqueous cleaning than in traditional solvent cleaning to achieve optimum and consistent results.
- In cleaning situations where the oil content is high, a useful methodology is to rely on the oil's natural immiscibility in water and allow *separation* to occur so that the lighter fractions can be skimmed off the top and the heavier fractions can be removed by filtration. The volume of waste generated is greatly reduced using this kind of phase separation technique, and the lifetime of the cleaner is thereby extended.
- An important factor in choosing aqueous cleaning is whether the product and/or process can tolerate water. Compatibility of the product/ process with water must be carefully investigated. For example, some ferrous metals may exhibit flash rusting in aqueous environments; therefore, such parts should be tested prior to full-scale use.

Similarly, if semi-aqueous and solvent alternatives seem desirable, then consider the following features and limitations:

- Semi-aqueous cleaners may be more aggressive in removing heavy organic contaminants.
- They may have lower corrosion potential with water-sensitive metals.
- Semi-aqueous cleaners penetrate small spaces more easily than aqueous cleaners because they have lower surface tensions.
- No water is used with hydrocarbon cleaners, so there is no potential for water corrosion or for water to become trapped in cavities.
- One benefit of semi-aqueous cleaners and hydrocarbon solvents is that distillation and membrane filtration technologies are being developed that will permit recycling and reuse of the products.

- A wide range of organic solvents is available that may be beneficial as a replacement technology, particularly on a small scale, such as bench-top or spot cleaning.
- Most semi-aqueous cleaners are reported to be biodegradable.
- One must be more concerned about aquatic toxicity and human exposure than one is with the use of aqueous cleaners.

Finally, advanced technologies such as supercritical CO_2 and CO_2 snow cleaning may be suitable in niche applications. In addition, the emerging technologies discussed in Section 3, and those yet to be developed, may find a role in alternative cleaning methods.

Reference

Monroe, K. R., and E. A. Hill. 1993. "SAGE (Solvent Alternatives Guide): Computer Assisted Guidance for Solvent Replacement." In: *Proceedings of the 1993 International CFC and Halon Alternatives Conference*. The Alliance for Responsible CFC Policy, Washington, D.C. pp. 431-439.

SECTION 6
INFORMATION SOURCES

Table 10 shows the trade associations and the technology areas they cover. Readers are invited to contact these trade associations and request their assistance in identifying one or more companies that could provide the desired technological capabilities.

Table 10. Trade Associations and Technology Areas

Trade Association or Technology Group	Technology Areas Covered	Contact
Association for Finishing Processes of the Society of Manufacturing Engineers	Industrial finishing operations	P.O. Box 930 One SME Drive Dearborn, MI 48121 (313) 271-1500
Industry Cooperative for Ozone Layer Protection (ICOLP)	Alternative substances for ozone layer protection	1440 New York Avenue, NW Suite 300 Washington, D.C. 20005 (202) 737-1419
Institute for Interconnecting and Packaging Electronic Circuits (IPC)	Electronic assemblies, defluxing operations	7380 North Lincoln Avenue Lincolnwood, IL 60646 (708) 677-2850
National Association of Metal Finishers	Industrial finishing operations	111 East Wacker Drive Chicago, IL 60601 (312) 644-6610
Society of Automotive Engineers	Process engineering and finishing operations	400 Commonwealth Drive Warrendale, PA 15096 (412) 776-4841

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