# Alternatives to Halogenated Solvents Used in Surface Cleaning





#### **ACKNOWLEDGMENTS**

This report was prepared by Hayley Hudson of the
Toxics Use Reduction Institute, with assistance from Jason Marshall,
Joy Onasch, Liz Harriman, Pam Eliason, Stacie Caldwell, Alicia McCarthy,
and Karen Angelo. Special thanks go to Saskia van Bergen of the
Washington Department of Ecology and Laura Babcock of the Minnesota
Technical Assistance Program for providing technical review.

OCTOBER 2021



#### **Toxics Use Reduction Institute**

University of Massachusetts Lowell | The Offices at Boott Mills West 126 John Street, Suite 14, Lowell, MA 01852-1152 (978) 934-3275 | www.turi.org

	Acronyms, Abbreviations, and Symbols	iv
I.	Setting the Context	1
II.	Using this Guide	2
III.	Halogenated Solvents in Cleaning Applications	3
	Chemistries	3
	Environmental, Health and Safety Comparative Assessment	5
	Performance	6
	Financial Considerations	6
	Regulatory Implications	6
IV.	Alternative Surface Cleaning Chemistries	8
	About the Alternatives	8
	Characteristics of Alternative Chemistries	12
V.	Equipment and Processes for Surface Cleaning	15
	Vapor Degreasing	15
	Vacuum Degreasing	15
	Vacuum Cycling Nucleation	15
	Ultrasonic Cleaning	16
	Spray Cleaning	16
	Pressure Washing	16
	Immersion	16
	Manual Wiping	16
VI.	Identifying Alternatives to Halogenated Solvents in Surface Cleaning	17
	Identifying and Assessing Performance of Alternatives	17
	CleanerSolutions	17
	CleanerSolutions Database Background	18
VII.	Tools to Compare the Relative Hazard of Alternatives	19
	Pollution Prevention Options Analysis System (P2OASys)	19
	Additional Research	21
VIII.	Next Steps	23
	Pilot Testing Alternatives	23
	Gathering Information Needed to Promote Adoption	24
	Fndnotes	25

### **Tables**

Table 1	Primary Health Hazards Associated with Halogenated Solvents	5
Table 2	Relative Hazard Rating Associated with Halogenated Solvents	6
Table 3	Primary Regulations for Halogenated Solvent Users	7
Table 4	Modified Alcohol Substituted for PCE (Umicore)	12
Table 5	Powdered Detergent Mixture Replaces TCE (Morgan)	13
Table 6	Alkaline Aqueous Cleaner Substituted for nPB (CD Aero)	13
Table 7	EPI Suite Key Environmental Factors	2
Table 8	Massachusetts Facilities That Successfully Switched to Safer Alternatives	22

## ACRONYMS, ABBREVIATIONS, AND SYMBOLS

**ACGIH** American Conference of Governmental Industrial Hygienist

**ATSDR** Agency for Toxics Substances and Disease Registry

**BCF** Bioconcentration factor

CAA Clean Air Act

**DCM** Methylene Chloride

EHS Environmental Health and Safety
EPA Environmental Protection Agency

**EPCRA** Emergency Planning and Community Right-to-Know Act

**GHS** Globally Harmonizing System

HAP Hazardous Air PollutantHCFC Hydrochlorofluorocarbon

**HFC** Hydrofluorocarbon **HFE** Hydrofluoroether

IARC International Agency for Research on Cancer

IDLH Immediately Dangerous to Life and Health

MA Massachusetts

**NIOSH** National Institute for Occupational Safety and Health

NTP National Toxicology Program

**OSHA** Occupational Safety and Health Administration

OTA Office of Technical Assistance

**P2** Pollution Prevention

**P20ASys** Pollution Prevention Options Assessment System

**PCE** Perchloroethylene

**REACH** Registration, Evaluation, Authorization and Restriction of Chemicals

**SDS** Safety Data Sheet

**SVHC** Substances of Very High Concern

TCE Trichloroethylene

transDCE 1,2 Trans dichloroethylene
 TRI Toxic Release Inventory
 TUR Toxic Use Reduction
 TURA Toxics Use Reduction Act
 TURI Toxics Use Reduction Institute

**US** United States

VCN Vacuum Cycling Nucleation
VOC Volatile Organic Compound

### SETTING THE CONTEXT

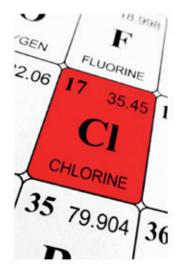
alogenated solvents have historically been used for a wide variety of industrial surface cleaning needs in numerous industry sectors. These solvents are easy to use, relatively inexpensive, and very effective in removing a wide range of contaminants from various surface materials and configurations. These are typically relatively simple molecules that contain halogens—chlorine (CI), fluorine (F), bromine (Br), or iodine (I).

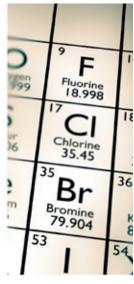
As a category, however, these solvents present concerns for the environment as well as human health and safety. Hazards noted for some of these halogenated chemicals include damage to the central nervous system, reproductive and developmental toxicity, carcinogenicity and negative respiratory effects. Most halogenated solvents are persistent in air and/or sediment, are ozone-depleting chemicals and/or contribute to the generation of greenhouse gases. Due to these concerns, stricter regulations have been enforced, leading many halogenated solvent users to investigate possible alternatives. Without sufficient information, replacing halogenated solvents can lead to regrettable substitution for cleaning applications.

As a category, halogenated solvents present concerns for the environment as well as human health and safety.

This report, developed by the Massachusetts Toxics Use Reduction Institute (TURI), provides information about a suite of safer alternative chemistries and equipment that can be used to replace halogenated solvents in surface cleaning applications.









his guide has been developed to assist manufacturing facilities in identifying feasible safer alternatives to halogenated solvents used in specific surface cleaning applications. Because facilities use solvents for a wide variety of applications, on a variety of surfaces and geometries of metal, ceramic and plastic parts, a single document cannot address every specific application. This guide has therefore been developed to help manufacturers:

- · Identify potential options for their specific applications
- Learn how to evaluate these alternatives
- Determine key information needed from equipment and product vendors to assist in identifying appropriate alternatives

This guide is organized according to these key steps:

- Identifying the hazards associated with the most commonly used halogenated solvents for industrial parts cleaning
- 2. Identifying potential alternatives (both chemistries and equipment) for your specific application
- 3. Assessing the alternatives
- 4. Identifying the next steps necessary to successfully adopt safer surface cleaning processes

The steps included in this guide fit within a larger toxics use reduction planning process, and the user is reminded that the first essential step is to assess your current cleaning operations and requirements, as outlined below. Ultimately, the process you use and the choices you make depend upon the very specific conditions associated with your unique operations.

### ASSESSING THE EXISTING CLEANING PROCESS

#### WHAT IS BEING CLEANED AND WHEN?

Lay out the process and identify the material and size of parts, the points in the process where cleaning is taking place, and impacts on the process, such as time needed to clean. How frequently and at what points in the process it is needed?

#### WHAT ARE THE CONTAMINANTS?

It is necessary to identify all contaminants introduced and whether they are vital to the process. Can difficult-to-remove contaminants be avoided or substituted with those that are easier to remove?

#### WHO IS APPLYING THE CONTAMINANT?

Some may be applied in-house, while others may be introduced with parts from a supplier. If a supplier is introducing contaminants, can you work with that supplier to reduce the contaminant level?

#### WHY DOES IT NEED TO BE CLEANED?

Consider why cleaning is being performed. Can any extra cleaning steps be eliminated?

### WHAT LEVEL OF CLEANLINESS IS REQUIRED?

Certain industries must adhere to specific standards, while others may have their own in-house requirements that specify a certain level. Can you change the cleanliness standard to reduce the use of cleaning chemicals without significantly impacting downstream processes?



# HALOGENATED SOLVENTS IN CLEANING APPLICATIONS

his section of the report provides information on the most widely used halogenated solvents in Massachusetts industries. The information presented provides important context for comparison with the fourteen classes of alternatives explored in subsequent sections of the report.

#### **Chemistries**

Halogenated solvents have been used extensively in Massachusetts for years and continue to be used today, despite the environmental health and safety concerns associated with them. The following sections present a high-level overview of traditional halogenated solvents used in surface cleaning, in no specific order.

#### **Trichloroethylene (TCE)**

TCE (CAS #79-01-6) is a chlorinated solvent that has been produced commercially since the 1920s. Its earliest uses were as an anesthetic, a stain remover in dry cleaning, a metal parts degreaser, and an ingredient in adhesives and paints. Its main use today is as an intermediary chemical in making other chemicals, but it is still used as an industrial degreaser. TCE is volatile and evaporates quickly into the air during cleaning operations. The solvent can break down into phosgene, a known lung irritant. Precipitation carries airborne TCE to the ground. When in the soil, TCE may filter into surface and drinking water supplies, potentially resulting in widespread contamination. TCE can persist in soil and groundwater, with a half-life of up to 10 months. TCE has been classified as Group 1 (carcinogenic to humans) by the International Agency for Research on Cancer (IARC) and is associated with many other health hazards. Exposure to TCE can result in damage to the central nervous system, liver, kidneys, respiratory and reproductive systems. TCE

also has genotoxic and immunotoxic potential, and some studies indicate that it may be a teratogen.<sup>2</sup> According to EPA's 2020 Final Risk Evaluation for TCE, there is unreasonable risk to consumers, occupational non-users, workers, and bystanders for 52 out of 54 conditions of use.<sup>3</sup>

### Methylene Chloride (also known as Dichloromethane or DCM)

Methylene chloride (CAS #75-09-2) is a widely used component in paint and coating removal products and other surface cleaners. The three major categories of use are industrial (e.g., in a permanent stationary technical installation), professional (e.g., by a tradesman), and consumer (e.g., by a homeowner for do-it-yourself activities). Methylene chloride is highly volatile, and the primary route of exposure is inhalation. Methylene chloride evaporates readily and once released in the air persists with a half-life of 57 to 127 days.4 Exposure may cause damage to the skin, eyes, liver, and the central nervous system. Numerous occupational and consumer deaths during paint stripping operations have resulted from acute methylene chloride poisoning, with 56 reported accidental exposure deaths linked to methylene chloride since 1980. IARC classifies methylene chloride as Group 2A (probably carcinogenic to humans).5

#### Perchloroethylene (PCE or perc)

Able to dissolve most organic materials, perchloroethylene (CAS #127-18-4) has been widely used as a dry-cleaning agent, metal degreaser, and a chemical intermediate. The major use of PCE nationally is as a raw material in the manufacture of fluorinated gases, such as hydrofluorocarbons (HFCs), used as refrigerants. PCE evaporates quickly but degrades slowly in the air with a half-life of approximately 100 days. PCE can also break down into several other

hazardous chemicals such as trichloroethylene, vinyl chloride, and dichloroethylene. Exposure to PCE may damage the nervous system, kidneys, liver, reproductive system, and may be harmful to a developing fetus. IARC classifies perchloroethylene as Group 2A (probably carcinogenic to humans).7

#### N-Propyl Bromide (nPB)

N-propyl bromide (CAS #106-94-5), or 1-bromopropane, is a non-flammable, organic solvent with a strong odor. It is used to remove solder flux, wax, oil and grease from electronics parts, metals and other materials. In addition, nPB is used as a solvent in adhesive formulations. N-propyl bromide is a volatile liquid with a high vapor pressure that evaporates quickly in the air. It is persistent in air, with a half-life of approximately two weeks.8 In 2007 the US EPA approved use of n-propyl bromide as an alternative to ozone-depleting substances for cleaning under certain conditions. Since that time, research has confirmed that nPB is reasonably anticipated to cause cancer in humans and can cause other chronic health effects such as reproductive and neurotoxicity. IARC classifies nPB as Group 2B (possibly carcinogenic to humans).9

#### 1, 2 Trans Dichloroethylene (transDCE)

1-2 Trans dichloroethylene (CAS #156-60-5) is a regulated VOC and a highly flammable, colorless liquid with a sharp, harsh odor. It is now widely used in cleaning formulations. The solvent has a high vapor pressure, evaporating rapidly into the air and persistent in air with a half-life of 5 to 12 days. 10 Most transDCE in the soil surface or bodies of water will evaporate into air. In addition, transDCE can travel through soil or dissolve in water in the soil, potentially contaminating groundwater. When in groundwater, it takes about 13 to 48 weeks to break down. While expected to have lower human toxicity than some other halogenated solvents, transDCE affects the central nervous system and there is evidence of immunotoxicity. Acute exposure can cause central nervous system depression and chronic exposure can cause liver, circulatory, immune system and central nervous system damage. The primary route of exposure for trans-DCE is inhalation, and breathing high concentrations can result in nauseous, drowsiness, and even death.11 The longterm toxicity of transDCE is not well known and there have been few studies conducted on its health effects.

#### **Hydrofluoroethers (HFE)**

Hydrofluoroethers (HFEs) are clear, colorless liquids that have very little odor. As another replacement for ozone depleting chemicals, HFEs were thought to offer safety and performance properties similar to CFCs, HFCs, and HCFCs, but with a preferable environmental profile.<sup>12</sup>



These substances are non-flammable and have lower global warming potentials than HFCs and HCFCs. However there is increasing evidence documenting HFEs breaking down in the environment to hazardous per- and polyfluoroalkyl substances (PFAS) that persist in the environment.13 These solvents are under review in Europe for persistence and bioaccumulative impacts based on specific physicochemical properties that have raised concern.<sup>14</sup> Currently, the most widely used HFE solvents for cleaning applications include HFE-7100 (CAS #163702-08-7 and #163702-07-6); HFE-7200 (#163702-05-4 and #163702-06-5); and HFE-7500 (#297730-93-9). HFE-7200 will be used as the representative substance for the evaluation in the next sections. Although skin and eye irritation are known hazards for some of these HFEs, these are relatively new solvents and additional toxicity tests, including carcinogenicity, have not been reported.

#### **Hydrofluorocarbons (HFC)**

Hydrofluorocarbons (HFCs) are primarily used for cooling and refrigeration but are also found in some cleaning solvent blends. HFC-4310mee (CAS #138495-42-8) is a commonly found HFC in precision cleaners today. Certain chemicals within this class of compounds were viewed by the industry and scientific community as acceptable alternatives to ozone-depleting chlorofluorocarbons (CFCs), 1,1,1 trichloroethane (TCA) and hydrochlorofluorocarbons (HCFCs) on a long-term basis. Because the HFCs contain no chlorine, they do not directly affect stratospheric ozone. However, this class of compounds are potent greenhouse gases and have high global warming potentials. As a result, many restrictions on their use are in place and will be becoming more stringent.

**Table 1: Primary Health Hazards Associated with Halogenated Solvents** 

Product	Acute Hazards	Chronic Hazards	Cancer Designations
Trichloroethylene CAS #79-01-6	Headache, dizziness, and sleepiness     Coma and death     Skin irritation     Nervous system, liver, respiratory system, kidneys, blood, immune system, and body weight	Decreased libido, sperm quality, and reproductive hormone levels in men     Kidney, liver, and blood cancer     Mutagen     Scleroderma	NTP: Known to be a human carcinogen  IARC: Group 1 (carcinogenic to humans)  EPA: Carcinogenic to humans by all routes of exposure
Methylene Chloride CAS #75-09-2	Burning and redness of the skin     Eye irritation     Unconsciousness and death	<ul> <li>Central nervous system depression</li> <li>Liver and kidney damage</li> <li>Reproductive and developmental effects</li> </ul>	NTP: reasonably anticipated to be a human carcinogen     IARC: Group 2A (probably carcinogenic to humans)
Perchloroethylene CAS #127-18-4	<ul> <li>Irritating to the skin, eyes, and respiratory system</li> <li>Dizziness, confusion, headache, nausea</li> </ul>	Kidney and liver damage     Reproductive toxin     Central nervous system     effects	<ul> <li>IARC: Group 2A (probably carcinogenic to humans)</li> <li>ACGIH: A3 (confirmed animal carcinogen)</li> </ul>
n-Propyl bromide CAS #106-94-5	Headache, nausea     Decreased sensation in fingers and toes     Drunk like feeling     Eyes, nose, throat or lung irritation	Weakness, loss of feeling     Damage to kidneys, liver     Limit ability to resist infection     Impair ability to get pregnant     Hematological effects     Immunosuppression	NTP: Reasonably anticipated to be a human carcinogen IARC: Group 2B (possibly carcinogenic to humans) ACGIH: A3 (confirmed animal carcinogen) with unknown relevance to humans
1-2 Trans dichloroethylene CAS #156-60-5	Central nervous system depression	Immunotoxicant     Neurotoxicant	No data
Hydrofluoroethers CAS #163702-05-4	Mild skin and eye irritation	No data	No data
Hydrofluorocarbons CAS #138495-42-8	Mild skin and eye irritation	No data	No data

#### **Environmental, Health and Safety Comparative Assessment**

Table 1 summarizes the human health effects associated with the halogenated solvents described above.

The relative hazards of these halogenated solvents can be summarized using TURI's P2OASys tool. TURI developed P2OASys (Pollution Prevention Options Analysis System) to help companies determine whether the toxics use reduction (TUR) options they are considering improve upon their existing process when looking at environmental, health and safety endpoints. By using P2OASys, safer options can be

By using P2OASys, safer options can be identified which can help companies avoid unforeseen environmental. worker or public health impacts.

identified which can help companies avoid unforeseen environmental, worker or public health impacts. P2OASys is designed to allow the user to compare chemical and product substitutions as well as process changes that have been identified as potential alternatives to the current use of, in this case, halogenated solvents.

In P2OASys, potential hazards posed by current and alternative processes identified during the TUR planning process are compared using data endpoints for eight main categories that encompass chemical, physical, environmental, and occupational hazards as well as process and life cycle factors. Using both quantitative data and qualitative input, the tool can rate each category based on endpoints that correlate with values, key phrases, Globally Harmonized System (GHS) classifications, and other government agency designations.

For this study, TURI used P2OASys to compare the environmental health and safety of halogenated solvents and their alternatives. Process and life cycle factors are specific to the application and may vary for each facility, so they

Category	Trichloroethylene	Methylene Chloride	Perchloro- ethylene	N-propyl bromide	1,2 trans dichloro- ethylene	Hydrofluro- ethers	Hydrofluoro- carbons
Acute Human Effects	VH	VH	VH	Н	Н	M	М
Chronic Human Effects	VH	VH	VH	VH	н	L	L
Ecological Hazards	VH	L	VH	VH	М	Н	Н
Environmental Fate & Transport	VH	Н	Н	н	VH	VH	VH
Atmospheric Hazard	Н	Н	Н	Н	L	М	Н
Physical Properties	VH	VH	VH	VH	VH	Н	Н

**Table 2: Relative Hazard Rating Associated with Halogenated Solvents** 

were not included in this assessment. Table 2 presents the relative hazard rating for each endpoint category for each of the halogenated solvents. The evaluation of TCE, PCE, DCM, nPB, and transDCE were based on the specific chemical. The evaluation for HFEs and HFCs were based on the representative substance and corresponding CAS number listed in the descriptions above.

■ Medium
■ High
■ Very High

All the halogenated solvents reviewed in this report are irritating to the skin, eyes, and respiratory system, and they are all hazardous for the environment. As shown in Table 1, the primary concern with TCE, perc, DCM and nPB is the potential to cause cancer in humans and animals. TCE, DCM and nPB are also reproductive and developmental toxicants. In addition, TCE, nPB, and transDCE are volatile organic compounds and contribute to ground-level ozone.

Some of the solvents that were first thought to be suitable replacements for many of the earlier solvents that posed ozone depleting potential and global warming hazards have been shown to pose new environmental hazards. For instance, HFEs have the potential to break down into PFAS chemicals that are highly persistent in the environment. HFCs are potent greenhouses gases with have high global warming potentials. There are reasons for concern regarding ecological and aquatic toxicity for all halogenated solvents.

#### **Performance**

Low

Halogenated solvents are known for their high performance in surface cleaning operations as they are able to dissolve most contaminants and are compatible with a variety of substrates. Many industries are still using these solvents because they dry quickly and leave no residue, which eliminates the need for an additional drying or rinsing step. This is especially important for cleaning delicate parts with hard-to-reach blind holes and crevices that could rust or corrode if not dried completely. Most halogenated solvents

have a low surface tension, are nonflammable, and can be recycled.

#### **Financial Considerations**

It is important to recognize that a decision to use a halogenated solvent in a surface cleaning process is influenced by more than just the unit cost of the chemistry or associated equipment. There are a variety of other cost factors that influence the final cost of using a certain option. These other factors include:

- Regulatory fees associated with use, storage, emissions and waste management
- Reporting requirements
- Ancillary process equipment and appropriate control measures
- Personal protective equipment
- Worker training and monitoring
- Waste management, transportation and disposal
- Construction, engineering and architectural planning
- Electrical, water, or plumbing changes
- System delivery and setup
- · Insurance; potential liability costs

#### Regulatory Implications

Halogenated solvent users must adhere to a variety of strict guidelines and regulations at the federal and state level based on usage, type of equipment, how the chemical is used and the overall specific process. In Massachusetts, TCE, DCM, PCE, and nPB are listed as Higher Hazard Substances under the Toxics Use Reduction Act (TURA). They are also listed as Hazardous Air Pollutants (HAPs) under the US EPA Clean Air Act (CAA) and are on California's Proposition 65 list. TransDCE and most HFCs are listed chemicals under TURA. HFEs are not currently listed under TURA, but would be included in the proposed PFAS category.

TCE, nPB, and transDCE are subject to reporting under EPA's EPCRA Toxic Release Inventory (TRI) and are VOCs, which may require users to comply with varying regulations. HFCs are under increasing scrutiny for their global warming potential, and new regulations are being put into place as

a result of the Kigali Amendment to the Montreal Protocol. In Europe, DCM is restricted under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulation. TCE and nPB are listed as Substances of Very High Concern (SVHC) under REACH.

Table 3: Primary Regulations for Halogenated Solvent Users<sup>a</sup>

Regulation	Trichloroethylene	Methylene Chloride	Perchloro- ethylene	N-propyl bromide	1,2 trans dichloro- ethylene	Hydrofluro- ethers	Hydrofluoro- carbons
MA DEP							
TURA	Listed, HHS	Listed, HHS	Listed, HHS	Listed, HHS	Listed	Proposed <sup>a</sup>	Some Listed
US EPA							
НАР	X	X	X	Xp	_	_	_
voc	X	_	_	X	Х	_	_
GHG/GWP	_	Low	_	_	_	Х	Х
EPCRA-TRI	Х	Х	Х	Х	Х	_	Some Listed
OTHER STATES							
California	Prop 65	Prop 65	Prop 65	Prop 65	_	_	_

a This information is not to be use for compliance purposes.

b HFEs are not currently listed under TURA but would be included in the proposed PFAS category.



# ALTERNATIVE SURFACE CLEANING CHEMISTRIES

#### **About the Alternatives**

he categories of potentially safer alternatives to halogenated solvents assessed in this report are technically and economically feasible options that have demonstrated high performance in the surface cleaning industry. For many of these categories there are a wide range of products that are currently available on the market. This report will describe each alternative category and provide resources and instructions on how to find a product that fits a user's specific needs.

The two main alternative categories and their subcategories assessed are listed below. Note that there are overlaps between some of the categories, and a particular alternative may have characteristics or ingredients that could fit into more than one.

- · Aqueous Cleaners
  - Acidic aqueous
  - Alkaline aqueous
  - Neutral aqueous
  - Caustic
  - Enzymatic-microbial
  - Powdered detergent

The categories of potentially safer alternatives to halogenated solvents assessed in this report are technically and economically feasible options that have demonstrated high performance in the surface cleaning industry.

- Solvents
  - Biobased solvents
  - Terpenes
  - Esters
  - Alcohols
  - Glycol ethers
  - Ketones
  - Petroleum distillates
  - Volatile methyl siloxane
  - Semi-aqueous solvents containing biobased solvents, terpenes or esters

#### **Aqueous Cleaners**

Aqueous cleaners have been used for decades to meet the needs of the surface cleaning industries. There are numerous aqueous products on the market that are suitable replacements for halogenated solvents in specific applications. Aqueous cleaning uses water and additives such as mineral acids, builders, corrosion inhibitors, detergents, chelating and sequestering agents, emulsifiers, and surfactants to improve cleaning.

The hazards of products in this broad category will vary depending on the concentration as well as the surfactants and additives used. Aqueous cleaners are nonflammable, but may contain additives with some level of VOCs. However, these cleaners may pose environmental hazards and risks to aquatic life, particularly as concentrates. Many aqueous cleaners can be further categorized as acidic, alkaline, neutral, caustic, enzymatic-microbial, and powdered detergents.

#### Acidic Aqueous

Acidic aqueous chemistries are cleaners that have a pH less than six. Acidic cleaning is routinely used to remove scale, rust, and oxides from metals. Due to the acidity of these cleaners, they tend to have acute skin and eye hazards

associated with them. As there are many variations of acidic aqueous cleaners on the market, some pose greater risks than others. Formulations based on hydrofluoric or chromic

acid, in particular, have high levels of concern. <sup>15</sup> Some cleaners can be harmful to the respiratory system and may cause breathing difficulties if inhaled.

#### SYNVENTIVE SAVES TIME AND MONEY WITH A SWITCH TO AN ALKALINE AQUEOUS CLEANER

Synventive Molding Solutions of Peabody, MA, is one of the world's leading manufacturers of hot runner systems for the plastics injection molding industry. Synventive used nPB in a vapor degreaser at their facility to clean oils, lubricants, and greases from copper and steel parts. The TURI lab identified an alternative cleaning method for Synventive that not only decreases the potential human health hazard but also saves time and money. Synventive replaced nPB with an alkaline aqueous cleaner in an ultrasonics tank for heat pipe cell cleaning to replace its vapor degreasing process. The implementation of this new aqueous cleaner and equipment significantly improves workplace health and safety, reduces environmental impact, eliminates the need to report under TURA and reduces operating costs. Learn more in the online Synventive presentation.

#### ASSABET ELIMINATES HARMFUL AEROSOL PRODUCTS. AND MOVES TO BIOBASED **SYSTEMS**

The Assabet Valley Technical High School Auto Tech Program previously used a parts washing station and aerosol products that contained toxic chemicals in their classrooms. To create a safer and healthier learning environment, they purchased three biobased enzymatic parts washing systems, eliminating the washing station and greatly reducing the use of the aerosol products. The new system and degreasing solution are safer and effective. The new parts washing system includes a particulate trap that catches the large particles washed off the car parts. The degreasing solution contains microbes that break down the oils and greases washed off the car parts. The solution is pH neutral, non-flammable and contains biodegradable detergents and emulsifiers. For more information, please see the full case study and video.

#### Alkaline Aqueous

Alkaline aqueous cleaning chemistries have a pH greater than eight and less than twelve. They are common solutions in aqueous cleaning. Alkaline aqueous cleaners are generally low-hazard cleaners. Human health hazards associated with these cleaners tend to be more acute and do not result in long-term effects. Alkaline aqueous products may be harmful if ingested and may be irritating if they get in the eyes or on skin.

#### **Neutral Aqueous**

Neutral aqueous cleaners are mixtures of water and other chemical compounds with a pH between six and eight. Neutral and alkaline aqueous solutions are the most commonly used aqueous solutions. Neutral aqueous cleaners have very few hazards associated with them and are nonirritating. Most cleaners are not corrosive, not flammable, and may have a slight or minor odor.

#### Caustic

Caustic cleaning chemistries are highly alkaline (pH greater than twelve) and usually contain sodium hydroxide or potassium hydroxide. These cleaners are effective at removing oils and greases from hard surfaces such as steel, stainless steel, and cast iron. However, high caustic concentrations are usually not suitable for use on aluminum, brass, copper and other soft alloys. Caustic cleaners are highly corrosive and cause severe chemical burns to the skin and eyes. Eye exposure to caustic cleaners may cause permanent eye damage and even blindness.

#### Enzymatic-Microbial

Enzymatic-microbial cleaners contain blends of naturally occurring, nonpathogenic microbes. The cleaning solution cleans the desired part, and the microbes break down and digest the hazardous grease, lubricating oils, and any other contaminants that were removed from soiled parts. Enzymaticmicrobial cleaners are a growing class of chemistries on the market. They are neutral cleaners, typically with slight or minor skin and eye irritation concerns.

#### Powdered Detergent

Powdered detergents are solids that, when mixed with water, form aqueous cleaners. As powders, they do not have a pH listed. When they get mixed with water to make a solution, the pH is typically in the neutral, alkaline, or caustic ranges. In addition to any hazards of the aqueous cleaner liquid, the dry powdered detergents may be harmful if ingested

or if dust is inhaled. Exposure can also lead to skin and eye irritation.

#### **Solvents**

Solvents are liquid cleaners that work by dissolving contaminants on a surface and breaking them down into smaller particles. Solvents are typically fast acting and do not need extended preparation or drying time after cleaning. Solvents are very volatile and evaporate quickly, creating air quality concerns in the workplace. Most non-halogenated organic solvents are also flammable or combustible liquids and may pose environmental hazards and risks to aquatic life.

Solvents represent a large and diverse category of cleaners and vary greatly in level of hazard. When aqueous cleaning is not feasible or practicable, solvents may be required. There are many alternative solvent-based products available that can provide the needed performance with significantly improved environmental health and safety profiles compared to halogenated solvents. This category includes biobased cleaners, terpenes, esters, alcohols, petroleum distillates, volatile methyl siloxanes, and semi-aqueous. It is important to note that there is overlap within the categories and also that some aqueous cleaners may also contain organic solvents.

#### **Biobased Solvents**

Biobased cleaning chemistries are composed largely or wholly of biological products, forestry materials, or renew-

# MORGAN ELIMINATES TCE AND NOW USES A SAFER POWDERED DETERGENT

Morgan Advanced Materials of New Bedford, MA. manufactures ceramic feedthroughs for medical and aerospace markets. The facility used trichloroethylene (TCE) for several tasks, including wax removal after ceramic grinding. Morgan sought a cleaner that would effectively remove two types of wax used in their process. TURI identified several safer alternatives to be effective in the lab that consisted of both liquid and powdered detergents. Morgan independently identified a powdered detergent mixture used by a sister facility that provided the necessary performance. Morgan eliminated the use of TCE, thereby enhancing the health and safety of its workers, eliminating TURA reporting, and reducing costs. Additional details can be found in the video and case study.

able domestic agricultural materials (including plant, animal, and marine materials), as opposed to non-renewable materials such as petroleum. Biobased ingredients are less likely to be harmful to aquatic life or persist in the environment. Most biobased cleaners are expected to be biodegradable and are not corrosive. They are often included in neutral pH aqueous cleaners. Biobased solvents can also fit under any of the other categories or be used as a feedstock to generate other types of solvents.

#### **Terpenes**

Terpenes are a subset of the biobased solvent category that are usually derived from natural sources such as pine trees or citrus fruit. They generally have strong characteristic odors. Specific terpenes used in cleaning are  $\alpha$ -pinene, d-limonene, and turpentine, which is a mixture of terpenes. Terpenes are often VOCs and may be irritating to skin, eyes, and the respiratory system. Many products in this category can be highly flammable liquids.

#### **Esters**

A variety of monobasic and dibasic esters are used alone or in semi-aqueous and co-solvent blends. They are particularly effective in removal of waxes, pitches, coatings, and other hard-to-remove mixed soils. Esters have relatively strong odors and high boiling points. Esters with an acetic acid base are called acetates and are commonly used in solvents and cleaners due to their ability to dissolve oils and various greases. Most ester cleaning chemistries have relatively low hazards.

#### Alcohols

Alcohol cleaners can be used in many different cleaning applications, from simply removing dirt from work surfaces to cleaning away oils and lubricants from electronic components. Commonly used alcohols in cleaning include methanol, ethanol, and isopropanol (IPA). In addition, alcohols are often mixed with other chemicals to increase their effectiveness. Recently there has been an increasing interest in what are advertised as "modified alcohols," and there are a variety of products like this currently on the market. Many of these products contain glycol ethers mixed with alcohols. Alcohols and glycol ethers together create versatile cleaners as they can be used in water-based formulations due to their high degree of water compatibility. Alcohol cleaners may have a high evaporation rate, are flammable and may be VOCs. They also may be harmful if swallowed and may cause breathing difficulties if inhaled. Alcohols and modified alcohol cleaners may cause mild skin and eye irritation.

#### **Glycol Ethers**

Glycol ethers represent a large family of chemicals, and not all present the same hazards. Glycol ethers are separated into two groups of chemicals; the ethylene series (E-series) and the propylene series (P-series). Testing of propylene glycol-based ethers have shown that they are less toxic than the ethylene series. 16 For example, the ethylene glycol ethers, 2-methoxyethanol (2ME) and 2-ethoxyethanol (2EE), have the potential to cause embryo toxicity and other reproductive effects in male and females.<sup>17</sup> It is important to avoid glycol ethers from the E-series as they are not considered as safer alternatives. Substances from the P-series are commonly used in formulations with alcohols to create specialty-modified alcohol cleaners as discussed above.

#### Ketones

Ketones represent a large class of chemicals that can be used to clean to clean a variety of contaminants, including greases, paints, permanent marker, and adhesives. Acetone, the simplest of ketones, is one of the most commonly used substances as a replacement for halogenated solvents, because it is exempt from VOC regulations and is lower in toxicity. Hazards vary greatly in this large group; low molecular weight ketones, such as methyl ethyl ketone (MEK) and acetone, are flammable and highly volatile. Primary health hazards consist of skin, eye, and respiratory irritation. However, long-term exposure to some ketones can result in narcotic and adverse effects to the central nervous system.

#### Petroleum Distillates

Petroleum distillate cleaning chemistries consist of hydrocarbon solvents produced from crude oil. These solvents include mineral spirits, kerosene, white spirits, naphtha, and Stoddard solvent. Petroleum distillate chemistries were widely used before chlorinated solvents, and many industries have returned to petroleum distillates due to the hazards and regulatory impacts associated with using halogenated solvents. Many cleaners in this category are flammable or combustible liquids. Petroleum distillate chemistries are VOCs and may contain small amounts of other more hazardous solvents, such as benzene, that may be carcinogenic or mutagenic. Exposure can result in acute health effects such as skin, eye, and respiratory irritation. Long-term exposure can lead to dermatitis.

#### **Volatile Methyl Siloxanes**

Volatile methyl siloxanes (VMS) are high-purity solvents that are linear or cyclic siloxanes. They perform best on nonpolar soils such as mineral and silicone oils. VMS are typically used in metal vapor degreasing and defluxing applications and are compatible with most materials. Their low surface

#### UMICORE ELIMINATES THE **USE OF PCE BY CHANGING OUT THEIR EQUIPMENT AND CHEMISTRIES**

Umicore Electrical Materials of Attleboro, MA, manufactures clad metals, tapes, buttons, absorber rods, and brazing materials for the electronics industry. Umicore had been using a vacuum degreaser that held 2,000 pounds of perchloroethylene. Working with the manufacturer, Umicore was able to extend the changeout from 12 to 18 months, resulting in a 2,000-pound reduction in perc over three years. However, EHS staff at the facility wanted to eliminate the use of perc entirely. Working with its equipment and chemical vendors, Umicore identified and purchased a new vacuum degreaser to be used with a new, modified alcohol-based cleaning solvent blend. The facility expects to save money in cleaning chemicals over a three-year period. The new, more energy-efficient degreaser is expected to deliver additional energy cost savings. For additional details, refer to the case study.

tension and viscosity allows for fast wetting of parts, and the high evaporation rate ensures that parts dry quickly. There are very few VMS products on the market, as these solvents evaporate readily and are associated with high flammability and low flash points which increase hazards in the workplace. VMS cleaners are not ozone-depleting chemicals but have aquatic toxicity concerns. The cyclic siloxanes, in particular, pose concerns for persistence and bioaccumulation.

#### Semi-Aqueous Cleaners

Semi-aqueous cleaners are emulsified mixtures of water and solvents. Biobased solvents, terpenes, and esters are among the solvents used in semi-aqueous cleaners. Semiaqueous cleaning also includes processes where parts are first cleaned in a solvent, then rinsed in water. Most semiaqueous solutions leave a residue that can be removed with a water rinse. Sometimes the film is left on the part as a protective coating. Semi-aqueous chemistries have a wide range of capabilities and can be recycled using filtration technologies. They are effective at cleaning hard-to-remove soils and their low surface tension allows the solution to penetrate into blind holes and crevices. The solvents in semi-aqueous cleaners are usually VOCs such as glycol ethers, esters, or hydrocarbons. These solvents are also often flammable prior to mixing.

#### **Characteristics of Alternative Chemistries**

#### **Environmental Health and Safety**

The alternative chemistries described are found in a wide range of products at varying concentrations, yielding differing comparative environmental health and safety profiles. Based on the wide variety in formulation makeup for products associated with each of the many categories of alternative chemistry discussed, it is important that the user understand how to use hazard comparison tools like the previously described Pollution Prevention Options Analysis System (P2OASys) tool to compare options. Use of this tool to conduct EHS comparisons with a current solvent is described in a subsequent section of this report.

#### Performance

Halogenated solvents are known for their versatility, so it is important to consider how many surfaces and contaminants the alternatives are effective at cleaning. Alternative categories included in this assessment exhibit improved environmental health and safety profiles and demonstrate high performance on numerous substrates and soils based on testing performed in the TURI lab. This performance data has been collected since the mid-1990s and is accessible in the CleanerSolutions database. Section VI of this report describes how users can take advantage of the performance data found in Cleaner-Solutions as a starting point for identifying which of the safer alternative chemistries presented may meet their specific performance needs.

#### **Relative Costs**

In comparing alternative cleaners or cleaning processes, costs and savings to consider include the cost of the cleaning product, equipment, process changes, utilities, waste disposal, training, maintenance, and regulatory compliance. There are other benefits that may not be easily quantified, but are equally important, including improved worker health and safety, business reputation and the risk of spills and accidents.

TURI has assisted many Massachusetts manufacturing facilities in their conversion from a halogenated solvent to a safer alternative. Through that process, TURI has collected financial information as examples of costs and savings associated with changing cleaning solutions and equipment. The following three examples show the financial benefit for the facilities. The costs of research and performance testing are not included in these case studies due to the availability of TURA resources.

Alternative categories included in this assessment exhibit improved environmental health and safety profiles and demonstrate high performance on numerous substrates and soils based on testing performed in the TURI lab.

**Table 4: Modified Alcohol Substituted for PCE (Umicore)** 

Table 4. Modified Alcohol Substituted for PCE (Offlicore)							
Cost category	Capital investment	Annual cost: old system (PCE)	Annual cost: new system (modified alcohol)	Annual savings	Other business factors		
Equipment	\$250,000	_	_				
Training	\$7,280	_	_				
Repairs	_	\$15,000	\$0 for the first few years	\$15,000			
Solvent/cleaner	_	\$4,851	\$2,736	\$2,115			
Stabilizer (to maintain acidity)	_	\$2,410	_	\$2,410			
Booster	_	_	If used, \$41	(\$41)			
Waste disposal costs	_	\$2,200	\$110	\$2,090			
Electricity					Approx. 50% reduction		
Totals	\$257,280	\$24,461	\$2,887	\$21,574			

The annual savings from the modified alcohol system are expected to be \$21,574. With a capital investment of \$257,280, this results in a payback period of about 12 years. As the unit is expected to last well over 20 years, this is a worthwhile investment. While this calculation does not

factor in eventual repair costs, it does factor in the use of 80 gallons of the new cleaner per year, and the facility is certain they will use less than that per year. Also, the facility estimates that the new system uses 50% less electricity than the PCE system, which is an additional source of savings.

**Table 5: Powdered Detergent Mixture Replaces TCE (Morgan)** 

Cost category	Capital investment	Annual cost: old system (TCE)	Annual cost: new system (borax mixture)	Annual savings
Equipment	\$79,642ª	_	_	
Training	\$2,000	_	_	
Chemistry	-	\$6,105	\$500	\$5,605
Waste disposal	_	\$1,300	_	\$1,300
TURA fees	-	\$6,825	_	\$6,825
Labor—cleaning time	-	\$20,800	\$2,080	\$18,720
Totals	\$81,642	\$35,030	\$2,580	\$32,450

a The equipment cost was \$109,642, offset by a \$30,000 TURI grant.

Ongoing annual savings from the borax system are expected to be approximately \$30,000. Using the full cost of the new ultrasonic cleaner, Morgan will see a return on investment in

a little over three and a half years, or a little over two and a half years factoring in a grant received from TURI.

**Table 6: Alkaline Aqueous Cleaner Substituted for nPB (CD Aero)** 

Cost category	Capital investment	Annual cost: old system (nPB)	Annual cost: new system (JenFab/ Aquaease)	Annual savings	Other business factors
Equipment	\$260,000				
Cleaning solution	_	\$15,000	\$15,000		
Electricity	_	\$56,500	\$35,500	\$21,000	
Steam	_	\$25,500	\$11,249	\$14,251	
Water	_	\$0	\$1,000	(\$1,000)	
Impregnation oil disposal	_	\$600	\$600	\$0	
TURA fees	_	\$1,200	\$0	\$1,200	
Maintenance	_	\$11,000	\$0	\$11,000	
Available floor space					Increased
Worker health concerns					Reduced
Totals	\$260,000	\$109,800	\$63,349	\$46,451	

In addition to over \$46,000 in annual savings due to the changes in operating costs, the facility has had to conduct minimal training and has seen an increased throughput of 68% and a 30% reduction in maintenance labor. At a capital cost of \$260,000 the facility will see a payback on their investment in just over 5.5 years. That payback period is reduced to just over 4 years considering the additional savings of \$16,000 per year due to added manufacturing space gained by removing the old, large equipment. The

It is always important to review the EHS aspects of a cleaner first, because some cleaners may have minor ingredients that could be hazardous even in small amounts. facility also has seen the benefits of not having to worry about a carbon absorption system in the new unit, and the workers are very happy with it as it is easy and safer to use.

#### **Regulatory Implications**

In most cases, switching to any of the alternatives discussed in this report will alleviate the regulatory burden that comes with using a halogenated solvent. The alternative categories do not contain major ingredients that are listed as HAPs under EPA's CAA or that are listed under TURA or TRI. They also do not contain ingredients known to have ozone-depleting or high global warming potential. It is always important to review the EHS aspects of a cleaner first, because some cleaners may have minor ingredients that could be hazardous even in small amounts, such as nonylphenol ethoxylate surfactants or ethylene glycol ethers. Some of the solvent-based alternatives may also have ingredients that are VOCs or flammable, potentially requiring users to comply with certain regulations or industry standards. Each facility should revisit all applicable regulations when considering alternatives.



# EQUIPMENT AND PROCESSES FOR SURFACE CLEANING

urface cleaning can be accomplished with various equipment and processes, depending on the application. Common cleaning processes include simple immersion as well as the use of ultrasonic machines to provide agitation on a small scale. The many different types of equipment vary in cost and scale. Some of these processes can be used in conjunction with each other or can be scaled up depending on a facility's needs and size of operation. This is an important piece of the puzzle for halogenated solvent users to consider when finding an alternative, as some existing equipment may be able to be used or modified to work with alternative chemistries. Vapor degreasing is the only piece of equipment that is limited to solvent use; the others can be used with aqueous or safer solvent products. The equipment below includes that used for halogenated solvents as well as solvent or aqueous/ semi-aqueous alternatives.

Identifying appropriate equipment is an important piece of the puzzle for halogenated solvent users to consider when finding an alternative.

#### **Vapor Degreasing**

Vapor degreasing is a favored technology in surface cleaning and is used with solvents only. Vapor degreasing provides

Identifying appropriate equipment is an important piece of the puzzle for halogenated solvent users to consider when finding an alternative. the ability to quickly remove soils and reach into complex parts with small nooks and crevices. Parts are typically loaded into a basket and lowered into the degreaser above the liquid to where parts only encounter the vapor. The vapor then condenses on the parts dissolving any contaminants. Vapor degreasers rely on cooling blankets and covers to limit emissions.

#### **Vacuum Degreasing**

Vacuum degreasing cleans inside a sealed unit, allowing for a low-emission work environment. This type of equipment allows the user to select from multiple cycle programs and process options to match the needs of parts or products. Vacuum degreasing can be conducted with a wider variety of cleaners, including solvents or aqueous cleaners. The solvent or aqueous solutions can be almost fully recovered and reused.

#### **Vacuum Cycling Nucleation**

Vacuum cycling nucleation (VCN) is a process that is accomplished by applying a vacuum to an enclosed chamber containing a part submerged in a liquid. Reducing the pressure below the vapor pressure of the liquid results in the formation of vapor bubbles at the solid part's surface. The growing vapor forces liquid away from the part creating fluid agitation throughout the part. This allows for the cleaner to penetrate small crevices and carry all particles and soils to the bulk fluid. This equipment can be used with solvents or aqueous products and offers significantly more time-efficient cleaning cycles. Hazards to workers are minimal as the system is completely enclosed. The risk of exposure to the cleaning product of choice would only be when refilling the system. The VCN system also has built-in recycling, using much less product than conventional cleaning methods.

#### **Ultrasonic Cleaning**

Ultrasonic cleaning uses high-intensity sound waves and frequencies to activate a liquid and enhance the performance or ability to clean hard-to-remove contaminants or intricate parts. This process may not be ideal for delicate parts as the vibrations may damage components. Higher frequencies can be used that are less damaging to delicate parts; however, this is often less effective in cleaning. Ultrasonic cleaning can be hazardous to the operator, as the cavitation can penetrate the skin. Hearing protection may also be required when ultrasonic cleaning because the sound generated by the vibrations in the tank can be a nuisance for workers.

#### **Spray Cleaning**

Spray cleaning can be either a conveyor system or a batch/booth system. Spray cleaning has the potential to limit worker exposure as the system is completely enclosed and fully automated. This type of system also provides an opportunity to reduce costs on cleaners, labor, and overspray waste as the automated spray system can target specific areas that need to be cleaned.

#### **Pressure Washing**

Pressure washing requires the use of high-pressure water or cleaner spray to remove contaminants from a surface. The main hazard of using a pressure washing system is that the high pressure can easily cut through skin and cause serious injuries, resulting in severe nerve damage and even the

# LYTRON SAVES MONEY AND IMPROVES WORKING CONDITIONS BY MOVING AWAY FROM TCE

Lytron Inc. of Woburn, MA, manufactures thermal management and liquid cooling systems used in a variety of industrial applications. Lytron wanted to eliminate use of TCE in its operations due to health and safety concerns. They were able to replace their aging vapor degreasing system with a closed loop VCN system that used an alternative cleaning solvent. The VCN system reclaims 99.9% of the cleaner during the drying process. Lytron was able to reduce costs associated with their current cleaning process, improve efficiency and reduce health risks to their employees. See the Lyton video for more information.



possibility of amputation. If not used in an enclosed system, the use of a pressure washer also creates a dangerous work environment as the ground and surrounding workspace will become wet, putting the operator at risks for slips, trips, and falls.

#### **Immersion**

Heated and unheated immersion can be conducted using a variety of different tanks or baths depending on the size of the product the user is trying to clean. The product is immersed in the cleaning product for a desired amount of time and the cleaner does all the work. Hazards associated with this cleaning process involve inserting and removing parts. In this process, it is especially important to consider if your cleaner will evaporate into the air and create exposure concerns.

#### **Manual Wiping**

Manual wiping is typically used in applications where a product cannot be fully immersed in a cleaner or when only spot cleaning is needed. The user can spray the cleaner on the desired location and then wipe the surface, or spray directly on to the cloth or rag and then wipe the soiled part. Depending on the cleaner, this process can be hazardous for the worker as they will be working directly with the cleaner. Considerable training and/or operator certification may be required. Cleaning or disposal of used wipes would have to be considered as part of a company's waste management program.



# IDENTIFYING ALTERNATIVES TO HALOGENATED SOLVENTS IN SURFACE CLEANING

### Identifying and Assessing Performance of Alternatives

search for safer alternatives in cleaning applications must look at the uses of chemicals of concern and the availability of safer, technically feasible, and affordable alternatives. To ensure a product will work, a systematic evaluation process needs to be used. In the TURI lab, the substitution of a new cleaning product for halogenated solvents is performed in a six-step process that increases the likelihood of selecting safer and effective alternatives for cleaning applications. Note that this is often an iterative process, requiring re-evaluation of options after initial or subsequent rounds of testing. In addition, initial testing is often performed with test coupons and soils, with subsequent testing on a company's soiled parts. The six evaluation steps are:

- 1. Existing process assessment
- 2. Potential alternative product identification
- 3. Chemistry evaluation
- 4. Mechanical agitation
- 5. Lab testing
- 6. Field piloting

In the TURI lab, the substitution of a new cleaning product for halogenated solvents is performed in a six-step process that increases the likelihood of selecting safer and effective alternatives for cleaning applications.



#### **CleanerSolutions**

The TURI lab process is tailored to the specific end user's needs. All of the performance data and testing information that has been collected over the years is stored and publicly available in the CleanerSolutions database. The data found in TURI's CleanerSolutions database includes numerous results of alternative chemistries and information related to performance, safety, and vendor recommendations. The results are drawn from many years of testing, so some products may no longer be available.

Additional information on a product can be accessed by clicking on a specific product name from the populated list. This links to vendor-supplied information, which includes recommended substrates, equipment, and safety data sheets or technical data sheets (SDSs/TDSs). The lab has evaluated many but not all of the products for performance. If available, the laboratory testing along with TURI's safety evaluation can also be accessed from the individual Product Information pages.

#### **CleanerSolutions Database Background**

Since 1993, the TURI lab has been evaluating the effectiveness of different cleaning chemistries and equipment for a variety of surfaces and contaminants. The lab's goal is to assist in the search for safer cleaning processes by identifying, developing and promoting safer alternatives to hazardous solvents. The lab created the Cleaner Solutions database to provide access to the results of the more than 25 years of performance testing it has conducted. This publicly available database links performance evaluations to specific testing parameters and environmental assessments performed at the lab.

#### **How it Works**

Cleaner Solutions provides two main sources of information that are useful when identifying and assessing options: TURI lab-tested results and vendor-supplied information. The first section yields search results based on TURI lab testing for specific client situations. The Vendor section allows users to search and browse information supplied by over 100 product vendors. Vendor information may not have been independently tested/validated by the TURI lab.

#### Find a Product

Using the online user search interface, possible alternatives can be identified by matching specific process needs (Contaminant, Substrate, Equipment) from the *Find a Product* tab. Watch this video for guidance on finding a cleaner.

#### Replace a Solvent

In addition to the basic search for alternatives, the Cleaner-Solutions.org site was designed to provide other avenues for looking for alternative solvents. Using the same simple click and select methodology, the *Replace a Solvent search* allows the end user to investigate options based on tested

alternative chemistries for specific solvent cleaners. The user can choose a solvent from the menu bar and add in the contaminant, substrate, and equipment to provide a listing of possible products that have previously been tested for replacing the selected solvent. From this list, the lab would select a handful of alternatives to verify applicability through lab testing on specific soils and other operating conditions (time, temperature, agitation). Watch this training video for guidance on replacing a solvent.

#### **Compare Products**

In addition to being able to open up more details on a specific product from the list, the tool provides the end user with a way to compare up to three products side-by-side. This feature provides a simple way to compare products, as the window summarizes vendor-suggested usage, safety evaluations (as determined by use of TURI's P2OASys tool), and performance. P2OASys will be discussed in more detail in the following section, but the embedded safety (P2OASys) evaluation provides a sense of the relative environmental health and safety profile of a product or chemical.

#### **Browse Client Types**

The site also allows the user to browse past lab tests by general industry sector and provides a summary of the various performance testing projects. An end user could use the Browse Client Types page to quickly identify other projects from a specific industry type, filtering out many of the unrelated testing results. Clicking on the Client, Project and Trial #'s will allow you to do further research into the specific operating conditions of the listed results.

Another option allows you to search by inputting characteristics of the parts to be cleaned. Watch this video for guidance on the safety search, browsing clients search and parts search.



# TOOLS TO COMPARE THE RELATIVE HAZARD OF ALTERNATIVES

#### Pollution Prevention Options Analysis System (P2OASys)

he primary goal for finding alternatives to chemicals of concern is to reduce risks to humans and the environment by using less hazardous chemicals. TURI developed P2OASys to compare alternatives and to determine whether the options being considered may have negative environmental, worker, or public health impacts. The objective is to shed light on

environmental, worker, and public health concerns that currently exist or that may arise during a change of manufacturing process(es). By providing a systematic way of comparing the potential hazards posed by current and alternative processes, better informed decisions can be made, and regrettable substitutions can be avoided.

This document provides background on how the online P2OASys tool is used to compare the relative hazards associated with possible alternatives.



The primary goal for finding alternatives to chemicals of concern is to reduce risks to humans and the environment by using less hazardous chemicals.

#### **How it Works**

The P2OASys safety evaluation is used to compare a current process or chemical with possible substitutes. Numeric values range from 2 (lower hazard) to 10 (higher hazard) and represent an approximate evaluation of relative hazard based on the data considered by the individual completing the evaluation. The values are only designed for comparison within an individual project, not as a singular value assigned to a chemical or product.

The first step in the Environmental Health and Safety (EHS) assessment is to collect as many data points on the chemical or product as possible. The more information available, the more robust the assessment. Resources include SDSs and technical data sheets from vendors. During the evaluation process, checking the date of the SDS and determining if a newer version exists is an important step to ensure that up-to-date information is used. However, the quality of SDSs is quite variable, and there are many other resources for information on chemicals (described below in the "Additional Research" section) that can be used to help fill any gaps in critical data.

P2OASys uses eight primary categories of EHS endpoints and process and lifecycle factors, each of which expand into several subcategories. Many of the data points are found on an SDS, but many other resources are used as well. SDSs are often incomplete and may contain inaccuracies. Some endpoints require significant professional judgement, such as process and life cycle factors. Once an acceptable level of information has been entered, the alternatives can be compared. While an initial assessment can be made using only data found on an SDS, the data should be checked for gaps to ensure the most complete comparison of options possible.

#### **Reviewing the Information**

P2OASys allows the user to review and compare information about chemicals and products in many different ways. When the assessment is finished, from the main screen an evaluation summary is generated and overall evaluations for each main category are shown. Each category can be expanded to see the evaluation for each endpoint within that category. The side bars next to each category allow a category to be weighted if that is of particular concern. From this page all this information can be exported into an CSV file.

It is important to remember that the information in the spreadsheet coming from the "Compare Summary" screen is just the numerical scores. In order to see the information that produced the evaluations, the user must go back to the main screen and select "View Raw Data." From here, all categories can be expanded with specific information that was entered along with references.



#### **Load from Database**

P2OASys evaluations of various products have been conducted by TURI staff for specific projects. These stored assessments can be viewed to see details behind chemical or product assessments, or they may be used as a starting point for a user to create their own assessment. Note that users always need to review the assessment to ensure that information is sufficient and applicable to their particular conditions.

#### **Additional Research**

For some chemicals, researching additional resources may be warranted to verify information on the SDS, or when there is no information on the SDS. TURI's Environmental Health and Safety Resource Libguide is a valuable resource that provides links to numerous databases and online resources organized by hazard. In addition, TURI has Tools and Methods listed on their website that may be useful when conducting alternatives assessments. A few other helpful sites that may provide hard to find data include:

- Immediately Dangerous to Life or Health (IDLH)
- Integrated Risk Information System (IRIS) Assessments
- Association of Occupational and Environmental Clinics (AOEC), which indicates likely asthma or sensitivity concerns
- The Endocrine Disruption Exchange (TEDX List—archived site no longer being updated)
- · Chemsec SIN List
- Initial List of Hazardous Air Pollutants with Modifications (HAP)
- Chemical Hazard and Alternatives Toolbox (ChemHat) a tool designed for workers to provide information on current restrictions and concerns associated with a chemical
- Washington State Department of Ecology—Tools and Resources for Assessing Chemicals and their Alternatives
- Pharos Chemical and Material Library
- PubChem
- OECD Substitution and Alternatives Assessment Toolbox



For experienced users, EPA's EPI Suite can be used to assess several key environmental factors for specific chemicals. Calculated values from EPA's EPI Suite software can provide key information, summarized in the Table 7.

#### **Industry Sector Examples**

Halogenated solvent users in specific sectors can learn about other companies' experiences in making the switch to safer alternatives. This information, in the form of case studies, demonstrations, in-person trainings, webinars, or published articles, can be very helpful in making the decision to implement a change.

Companies in the same or similar industry sectors often use many of the same operations. Therefore, resources are often available to provide more information to help with making the decision to implement a change. The table below summarizes selected examples of Massachusetts companies that successfully switched to safer alternatives.

**Table 7: EPI Suite Key Environmental Factors** 

Environmental Factor	Description					
Log Kow	Log Octanol-water partition coefficient; relative solubility of a chemical					
Vapor Pressure	Likelihood of a chemical to volatilize into the ambient environment					
Biodegradability	Probability of rapid aerobic and anaerobic biodegradation of an organic compound					
Bioconcentration factor	Potential to bioconcentrate in lipids (fatty tissue) of organisms					
Persistence	Half-life for air, water, and soil					
Quantitative Structure Activity Relationships	Predict the aquatic toxicity of chemicals based on their similarity of structure to chemicals for which the aquatic toxicity has been previously measured (LC 50 fish; EC 50 Algae; ChV Fish; ChV Algae)					

**Table 8: Massachusetts Facilities That Successfully Switched to Safer Alternatives** 

Organization	Industry Sector	Toxic Replaced	Safer Alternative	Annual Reduction	More details
Morgan Advanced Materials, New Bedford	Porcelain electrical supplies	TCE	New equipment that uses Borax, baking soda and water	3,300 lbs.	Video and Case Study
Umicore Electrical Materials, Attleboro	Electrical materials	PCE	New vapor degreaser that uses a modified alcohol-based cleaner Metalnox M6386	2,000 lbs.	Case Study
Lytron, Inc., Woburn	Metals manufacturing	TCE	New vacuum cycling nucleation system that uses transDCE	6,000 lbs.	Video
CD Aero, New Bedford	Capacitor manufacturer	nPB	New equipment Alkaline aqueous cleaner Aquaease PL	5,600 lbs.	Video Case Study
Synventive, Peabody	Hot runner system manufacturer	nPB	Aqueous with ultrasonics Buckeye Immersion Cleaner	2,778 lbs.	Continuing Education Presentation
Bird Precision, Waltham	Precision glass jewels	TCE	Dimethyl glutarate with heat drying oven	2,468 lbs.	
Inner-Tite Corporation, Holden	Manufacture metal anti-left devices	TCE	New vacuum vapor degreaser with an alkaline aqueous cleaner	2,675 lbs.	Case Study
S.E. Shires, Holliston	Brass instruments	TCE DCM	Ultrasonic aqueous system and rinse tank; Alcohol lacquer strip and rinse	3,600 lbs. 300 lbs.	Case Study
Shawmut Corporation, West Bridgewater	Coated and laminated materials	TCE	Hot-melt adhesive process	15,500 lbs.	Case Study
V.H. Blackinton & Co. Incorporated, North Attleboro	Metal finishing	TCE	Aqueous cleaning system	30,000 lbs.	Case Study

Vendors and other technical service providers, such as the TURI lab, the TURI Industry and Business Program and the Massachusetts Office of Technical Assistance, periodically offer hands-on training workshops for companies to demonstrate successful implementation of safer alternatives for their cleaning needs. Consultants and other state and federal pollution prevention programs can also help companies make this switch.

#### **Research into Solvent Blends**

TURI has demonstrated that blends of safer solvents can help achieve required performance results for applications for which a one-to-one drop-in replacement has proven elusive. If you have not been able to identify a safer solvent solution based on the information in this guide, contact TURI for assistance in determining if a solvent blend might be viable for your application. View this video for more on how TURI can help companies find safer solvents.



alogenated solvent users seeking safer alternatives should always consider key environmental and human health criteria initially, and then apply performance and financial criteria unique to their facility to determine the best alternative for their specific process. The next steps described in this section are crucial in ensuring the successful adoption of an alternative cleaning process.

#### **Pilot Testing Alternatives**

Once safer alternatives to halogenated alternatives have been identified and evaluated in a laboratory setting (such as by the TURI lab), the next step is to conduct on-site feasibility testing of the alternative. Often a vendor can loan companies small-scale equipment to evaluate the identified products on-site. The facility can then set up and run batch

cleaning tests using parts that come directly off the production line.

In addition to the equipment, it is beneficial to have other key members of the project present during on-site testing, including those from: production and maintenance, EHS, cleaning and equipment vendors, as well as a P2 technical assistance professional. These experts can improve opportunities for success by providing operator training, a critical component in switching to an alternative, as well as real-time troubleshooting support. For example, TURI works in conjunction with the Massachusetts Office of Technical Assistance, which provides free on-site technical assistance for Massachusetts firms. Companies in other states may have access to similar pollution prevention assistance organizations. EPA created an interactive map to find EPA regional contact information and state/local P2 technical assistance resources.



Implementing a safer alternative often results in unforeseen benefits that become especially valuable when reporting progress around toxics use reduction efforts.

### **Gathering Information Needed** to Promote Adoption

The overall goal of this Guide is to support companies in making informed decisions on substitutions, including insight into potential trade-offs when making the switch, and to provide resources, tools, and information to assist in identifying, evaluating, and adopting a safer and technically feasible alternative. In summary, the key information crucial in promoting adoption includes:

- Evaluation of your current cleaning process
- Environmental health and safety comparison
- · Performance testing results
- Cost analysis
- Regulatory Implications

In addition, it should be noted that this is frequently an iterative process, requiring multiple rounds of laboratory testing, piloting, assessing additional alternatives, and fine-tuning of the process.

There are many considerations in the decision to adopt a safer alternative. Being able to identify those considerations and quantify or describe the impact, where possible, may increase your chances of adoption. For example:

- Increase in productivity and efficiency
- · Improved public image and reputation
- Improved supply chain and consumer response
- Stakeholder and customer relation improvement

- · Decreased regulatory burden and reporting requirements
- · Sustainability benefits
- Energy or water use savings
- Improved employee satisfaction and overall psychosocial health
- · Consideration of employee training needs
- Impact on emergency preparedness plans, equipment, and training

In addition, other industry sector case studies and success stories will provide valuable insight into the benefits and challenges of a particular switch, and may help management be more comfortable with the change.

Once an alternative process has been selected and implemented, it is important to continually evaluate and measure many of these metrics listed above, beyond just cost savings. Implementing a safer alternative often results in unforeseen benefits that become especially valuable when reporting progress around toxics use reduction efforts.

#### FOR MORE INFORMATION

For more information on how the TURI lab can assist you in identifying viable safer alternatives to halogenated solvents, visit https://www.turi.org/Our\_Work/Cleaning\_Laboratory

For more information on additional research support from TURI, visit https://www.turi.org/Our\_Work/Research

For information on how the Massachusetts Office of Technical Assistance and Technology can assist you, visit https://www.mass.gov/orgs/office-oftechnical-assistance-and-technology-ota

#### **ENDNOTES**

- 1 International Agency for Research on Cancer (IARC), (2014) IARC Monograph for Trichloroethylene, Tetrachloroethylene, and Some Other Chlorinated Agents, Volume 106, pages 35-189
- 2 Agency for Toxic Substances and Disease Registry (ATSDR), (2019), Toxicological Profile for Trichloroethylene
- 3 U.S. EPA (2020) Final Risk Evaluation for Trichloroethylene; EPA Document #740R18008 https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/final-risk-evaluation-trichloroethylene
- 4 Agency for Toxic Substance and Disease Registry (ATSDR), (2000) ATSDR Toxicological Profile for Methylene Chloride
- 5 International Agency for Research on Cancer (IARC), (2017) IARC Monograph for Some Chemicals Used as Solvents and in Polymer Manufacturing, Volume 110, Dichloromethane, pages 177-243
- 6 Agency for Toxic Substance and Disease Registry (ATSDR), (2019) ATSDR Toxicological Profile for Tetrachloroethylene
- 7 International Agency for Research on Cancer (IARC), (2014) IARC Monograph Trichloroethylene, Tetrachloroethylene, and Some Other Chlorinated Agents, Volume 106, pages 219-350
- 8 United States Environmental Protection Agency (2017) Scope of the Risk Evaluation for 1-Bromopropane CASRN:106-94-5, EPA Document # EPA-740-R1-7009, Office of Chemical Safety and Pollution Prevention
- 9 International Agency for Research on Cancer (IARC), (2018) IARC Monograph, Some Industrial Chemicals, Volume 115, pages 37-67
- 10 U.S. EPA. IRIS Toxicological Review of Cis-& Trans-1,2-Dichloroethylene (Final Report). U.S. Environmental Protection Agency, Washington, DC, EPA/635/R-09/006F, 2010.
- 11 U.S. EPA. Final Scope of the Risk Evaluation for trans-1,2-dichloroethylene. U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention (OCSPP), Office of Pollution Prevention and Toxics (OPPT), Washington, DC, EPA/740/R-20/007, 2020
- 12 Kanegsberg, B., and E. Kanegsberg, eds. *Handbook for critical cleaning; applications, processes, and controls, 2d ed.* (2011) Boca Raton: CRC Press
- 13 Organization for Economic Cooperation and Development (OECD). (2015) Working Towards a Global Emission Inventory of PFASS: Focus on PFCAS Status Quo and the Way Forward. OECD Environment, Health and Safety Publications Series on Risk Management No. 30
- 14 Justification Document for the Selection of a CoRAP Substance. Group Name: Hydrofluoroethers. March 3, 2019. https://echa.europa.eu/documents/10162/7a3d5e0b-5f63-c235-80d5-8a5da0a428f3
- 15 Reeb-Whitaker CK, Eckert CM, Anderson NJ, Bonauto DK. Occupational Hydrofluoric Acid Injury from Car and Truck Washing--Washington State, 2001-2013. MMWR Morb Mortal Wkly Rep. 2015 Aug 21; 64(32):874-7. doi: 10.15585/mmwr. mm6432a4. PMID: 26292206; PMCID: PMC5779585.
- 16 High Production Volume Chemicals, OECD. Propylene Glycol Ethers https://hpvchemicals.oecd.org/UI/handler.axd?id=039c70c4-cbb8-4820-b8be-c0f1754bc2e8
- 17 The National Insitute for Occupational Safety and Health (NIOSH) Current Intelligence Bulletin 39: Glycol Ethers 2-Methoxyethanol and 2-Ethoxyethanol. DHHS (NIOSH) Publication Number 83-112. Accessed 7/14/21: https://www.cdc.gov/niosh/docs/83-112/default.html
- 18 Marshall, J., Wilcox, H. In Search of the Silver Bullet: Assessment of Alternatives For Trichloroethylene in Cleaning Operations (2015) Green Research, Developments, and Programs, Nova Science Publishing, Inc.

# Guide to Finding Safer Alternatives to Halogenated Solvents Used in Surface Cleaning Applications



The Toxics Use Reduction Institute (TURI) at UMass Lowell provides the resources and tools to help Massachusetts companies and communities make the Commonwealth a safer place to live and work. Established by the state's Toxics Use Reduction Act of 1989, TURI provides research, training, technical support, laboratory services and grant programs to reduce the use of toxic chemicals while enhancing the conomic competitiveness of Massachusetts businesses. Learn more at <a href="http://www.turi.org">http://www.turi.org</a> or contact info@turi.org, 978-934-3275.

#### TURA AGENCIES —

The Massachusetts Department of Environmental Protection (MassDEP) certifies Toxics Use Reduction (TUR) Planners, receives and reviews toxics use reports submitted by companies, provides guidance, takes enforcement actions, and collects chemical use data and makes it available to the public.

The **Office of Technical Assistance and Technology (OTA)** is a non-regulatory agency within the Executive Office of Energy and Environmental Affairs that provides free, confidential, on-site technical and compliance consultations to Massachusetts businesses and institutions.

The **Toxics Use Reduction Institute (TURI)** provides education, training, and grants for Massachusetts industry and communities; sponsors research and demonstration sites on safer materials and technologies; and provides laboratory and library services and policy analyses.