Identification of Safer Alternatives to Trichloroethylene (TCE) for Industry Cleaning Applications in Minnesota



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#### I. Introduction

# **Background**

Trichloroethylene (TCE) is used in many facilities located throughout Minnesota. Many of these businesses use TCE as a cleaning or dissolving solvent in fabricated metal products manufacturing and in machine manufacturing. The Toxics Use Reduction Institute (TURI) was contracted by the Minnesota Pollution Control Agency (MPCA), as part of an initiative with the U.S. Environmental Protection Agency (EPA) Region 5 and Minnesota Technical Assistance Program (MnTAP), to help Minnesota companies reduce their use of TCE.

TURI performed the following services:

- Trained Minnesota Pollution Prevention personnel (representatives from MPCA, EPA, MnTAP, and Minnesota companies) on strategies for technical assistance, data collection, sampling, and on-site testing for TCE alternatives assessments.
- A four-hour training was held in Minnesota on June 11, 2019, and covered the following topics:
  - Overview of TURI organization, cleaning background, and TCE alternatives
  - Massachusetts TCE case studies
  - Overview of site visits
  - TURI's CleanerSolutions database and Pollution Prevention Options Analysis System (P2OASys)
    hazard assessment tools
  - Laboratory testing process and implementation

Training presentations were converted into video presentations and written documents in English that are publicly available to view and download on MnTAP's website (<a href="http://www.mntap.umn.edu">http://www.mntap.umn.edu</a>).

Training (for a subset of the training group) also included on-site activities at four companies.

The TURI Laboratory provided the following TCE alternative services for 4 Minnesota sites.

- Test plan development based on criteria and process information provided by the company
- A site visit to visually observe the process and facility space
- Use of Hansen Solubility Parameters in Practice (HSPiP) to identify potential alternatives for certain applications (e.g., solvent carrier)
- Identification of 6 to 10 solvents, solvent blends, and/or commercially available alternative cleaners for performance testing
- Environmental, health, and safety (EHS) assessments of alternative solvents and cleaners compared to TCE using P2OASys (see Appendix A for further details about this tool)
- Performance testing of the 6 to 10 identified alternatives on standard test coupons (typically 2" x 4" flat substrates)
- Remote (via phone and email) review of testing results with MnTAP and company representatives
- Performance testing of the best performing 2 to 4 effective cleaners on parts provided by the company

 A final report with a summary of testing, results, evaluations, and recommendations to assist MnTAP with the on-site pilot testing and implementation of alternatives identified

The process used and results obtained for 3 of the 4 sites are detailed below. Details for the fourth site involve proprietary information and are not included in this report.

# **Assessing the Alternatives**

There are numerous criteria to be considered when identifying and evaluation potential alternatives to TCE. TURI used the following criteria to evaluate the feasibility of alternative solvents, solvent blends, and market-available cleaners:

- Performance and safety criteria. The performance and safety criteria for TCE alternatives were
  provided by each of the Minnesota companies involved in this initiative. The criteria were collected at
  the time of the site visit and through test request form documentation. The criteria were used by TURI
  to determine testing site-specific protocols for chemical classifications (e.g., aqueous, organic solvent)
  and flammability requirements, as well as temperature, time, and method of cleaning (e.g., immersion,
  equipment agitation).
- Human health and environmental criteria. Key human health and environmental criteria for solvents and cleaners as well as their byproducts were considered when identifying and evaluating TCE alternatives. All halogenated solvents were excluded from consideration due to high human health and environmental hazards. Cleaners and the ingredients listed on the SDS were compared to key human health and environmental criteria to determine if they were acceptable alternatives. These criteria are consistent with very high hazard (8 10) P2OASys scores for individual hazard endpoints. Appendix B provides a listing of these criteria.

# II. Facility 1

# **Overview**

Facility 1 used TCE as an industrial solvent. No safer alternatives were identified by TURI. A second effort to identify a cleaning solvent for an alternative process was conducted and a suitable alternative identified that the company can use when they are ready. The detailed performance testing approach and results for Facility 1 are not included in this report due to confidentiality concerns.

# III. Facility 2

#### **Overview**

The TCE reduction project for Facility 2 uses TCE in a vapor degreaser to clean its metal parts. Facility 2 was using approximately 16,000 pounds of TCE per year. In addition to TCE, Facility 2 also uses mineral oils (Petroleum Naphtha 148) and isopropanol (IPA) for spot cleaning of parts.

Facility 2 had already started to research alternatives to replace TCE when MnTAP and TURI representatives conducted a site visit. Facility 2 was interested in exploring modified alcohols, and it was unsure if an aqueous cleaner was an option due to the risk of rusting its substrates and potential inability to clean parts to client specifications.

Two cleaning methods were being considered by Facility 2 to replace its current TCE-based vapor degreasing systems: carbon dioxide (CO<sub>2</sub>) cleaning equipment and vacuum cycling nucleation (VCN). The TURI Lab had just started researching the VCN method with aqueous cleaners and was familiar with the equipment from a previous client. The TURI Lab connected Facility 2 with a VCN vendor to set up testing using alternatives identified by the TURI Lab.

Company 2 cleans 50 to 500 parts at a time in an enclosed vapor degreasing system. Common contaminants found on the parts include metal forming compounds, oils, lubricants, machining fluid, or grease from deep drawing and stamping processes. It is important to Facility 2 for parts to be completely clean of contaminants before parts go through an annealing process or are shipped to a customer.

To identify potential cleaning alternatives, the research team used the human health and environmental criteria developed for TCE alternatives by TURI and MnTAP, along with the following process and safety criteria provided by Facility 2:

#### **Process Criteria:**

- Remove metal forming compounds, oils, lubricants, machining fluid, and grease within 30 minutes
- Parts dry within 0-10 minutes
- Compatible with substrates used for parts and equipment

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# **Approach**

The initial step in the TURI assessment process was a walk-through of both cleaning processes. Using TURI's internal test request form and facility-provided data, TURI and MnTAP representatives walked through both cleaning processes to document contaminants, substrates, current cleaning processes, and methods of evaluating cleanliness. TURI used this information to initially research possible effective and safer cleaners for removing the most stubborn contaminant in use at the facilities. Company 2 sent part samples directly to the TURI Lab. The hardest contaminant for Company 2 to remove was its Aldraw J-2 (Clear) metal forming compound due to its high viscosity compared to its other metal forming compounds. All testing in the lab was performed using Aldraw J-2 as the main contaminant with a maximum clean time of 30 minutes.

The TURI CleanerSolutions database and vendor recommendations were used to identify cleaners currently on the market that meet Company 2's needs. Company 2 was receptive to testing new methods of cleaning, but immersion was the main method of cleaning used when searching the CleanerSolutions database. Environmental, health, and safety considerations were assessed using P2OASys before obtaining samples of the cleaners.

#### **Performance Testing**

The following products were identified as appropriate potential cleaners using the CleanerSolutions database.

Table 1: CleanerSolutions database list of potential cleaning alternatives to replace TCE

Manufacturer	Product	Classification	Concentration %	Temperature (°F)
Gemtek	SC Aircraft and Metal Cleaner Conc.	Alkaline Aqueous	1-2 (10 for harder contaminants)	130
Alconox Inc.	Liquinox	Alkaline Aqueous	1	150-170
ChemFree Corporation	Ozzy Juice SW-3	Neutral Aqueous	100	68 – 160
DOW	Dowanol PnBG	Solvent	100	68
JR Hess	Sta-Sol ESS 160	Solvent (Dibasic Ester)	100	68 – 180
Kyzen	Metalnox 6386	Solvent (Modified Alcohol)	100	68

Initial performance testing was conducted on titanium bead blasted coupons (4" x 4" flat substrates) provided by Company 2 and contaminated with Aldraw J-2. Technical data sheets and expert judgment from previous TURI Lab testing were used to decide what concentration and temperature would be appropriate for testing.

The first round of testing was done with unheated immersion for a 15-minute dwell time to determine how well the cleaners worked at room temperature (68°F) as a baseline. The titanium coupons were weighed before testing, after contaminating, and after being cleaned and air dried at room temperature for 24 hours. The results from this first round of tests are listed in Table 2.

Table 2: Unheated immersion of identified cleaners for baseline testing of products

Product	Concentration %	Average % Removal
Metalnox 6386	100	66.5
Dowanol PnBGE	100	56.6
Liquinox	1	54.7
Sta-Sol ESS 160	100	53.0
Ozzy Juice SW-3	100	52.8
SC Aircraft & Metal Cleaner	1	47.4

Metalnox 6386, Dowanol PnGB, and Liquinox were the most effective at removing the Aldraw J2 soil from titanium coupons using unheated immersion.

Cleaners were used at certain concentrations and elevated temperatures based on vendor recommendations for the contaminant and using expert judgment from previous TURI Lab client projects. The same dwell time (15 minutes) was used for all the products. The titanium coupons with contaminant were weighed before and after being cleaned and air drying for 24 hours at room temperature. The results from the heated immersion tests are provided in Table 3.

Table 3: Heated immersion on bead blasted titanium coupons contaminated with J2

Product	Concentration %	Temperature (°F)	Average % Removal
Dowanol PnBGE	100	100	99.8
Metalnox 6386	100	110	98.6
Sta-Sol ESS 160	100	130	98.4
Liquinox	1	171	95.3
SC Aircraft & Metal Cleaner	1	100	62.4
Ozzy Juice SW-3	100	106	55.1

Sta-Sol ESS 160, Dowanol PnBGE, Metalnox 6386, and Liquinox showed significant improvement with the addition of heat and achieved between 95.3% and 99.8% removal of Aldraw J-2 after a 15-minute dwell time. The SC Aircraft & Metal Cleaner was eliminated from further testing due to residue left on the coupons and poor removal after 15 minutes. Ozzy Juice SW-3 was included for further testing due to previous experience with the cleaner improving with ultrasonics as well as the capability of adding microbes that can prolong the bath life of the cleaner.

The titanium coupons were then tested with heated ultrasonics using a Branson 3800 40Hz tank to investigate how agitation could assist with removal. The results of the ultrasonics testing are listed in Table 4.

Table 4: Heated ultrasonics on bead blasted titanium coupons contaminated with J2

Product	Concentration %	Temperature (°F)	Average % Removal
Dowanol PnBGE	100	100	99.9
St- Sol ESS 160	100	130	99.5
Liquinox	1	171	97.8
Ozzy Juice SW-3	100	106	97.8
Metalnox 6386	100	110	85.6

Compared to heated immersion testing, there was an overall improvement with all the cleaners except Metalnox 6386. The Metalnox 6386 product did not perform as well as previous testing due to the coupons stacking on top of each other after 10 minutes of cleaning, which impacted the overall percent removal. If this stacking did not occur, it was anticipated that Metalnox would have generated a higher average % removal.

After sharing the results with Facility 2, the research team decided to move forward with testing contaminated parts provided by Facility 2. Each cleaner was tested for cleaning on 28 pre-contaminated parts in a basket using heated ultrasonic cleaning. The overall cleanliness of the 28 parts in the basket was determined using a rating scale outlined in Table 5. This method is in accordance with how Facility 2 determines cleanliness.

Table 5: Cleanliness rating key for Facility 2 parts

Rating	Description
1	Contaminant removed completely; no visual contamination on parts
2	Majority of the parts are cleaned; barely any contamination visible on parts
3	Some of the parts are cleaned, but contaminant visible on a lot of the parts
4	Little removal of the contaminant on the parts
5	No removal of the contaminant on the parts

A panel of three TURI lab technicians and/or students rated the cleanliness of the part batches. Table 6 provides a summary of the visual ratings for the cleanliness of parts for heated ultrasonic testing using a Branson 3800 40Hz ultrasonic tank for a 15-minute dwell time.

Table 6: Heated ultrasonics for 15 minutes on titanium parts contaminated with J2

Product	Concentration %	Temperature	Panel Ratings			Cleanliness
Product	Concentration %	(°F)	Α	В	С	Average Rating
Metalnox 6386	100	110	1	1	1.5	1
Dowanol PnBGE	100	100	2	2	1.5	2
Sta-Sol ESS 160	100	130	2	2	1.5	2
Ozzy Juice SW-3	100	106	3	4	2.5	3
Liquinox	1	171	5	5	5	5

Liquinox did not perform as well on the complex parts as compared to the flat coupons. Ozzy Juice SW-3 also did not perform as well on the parts and had inconsistent removal of the J2 contaminant in the corners of the part. The three top performing cleaners were Dowanol PnBGE, Metalnox 6386, and Sta-Sol ESS 160. Facility 2 asked for a final test to review the air-dry time at room temperature (68°F) of those three cleaners. TCE normally dries parts immediately due to rapid solvent evaporation, and Facility 2 needed to determine if it would need to add a drying step for the alternative cleaners. An ideal dry time would be immediate, but a dry time of five to ten minutes was considered acceptable by Facility 2.

Metalnox 6386 dried completely within ten minutes after cleaning. This cleaner satisfied Facility 2's drying time requirement.

Dowanol PnBGE was completely dry at 100 minutes, and Sta-Sol ESS 160 took 120 minutes to completely dry. A drying process step, heated or unheated, would be required to reduce the drying time for these two products. Therefore, both of these cleaners did not meet the drying process criteria.

TURI did not conduct any testing with the purity of the cleaner over time with multiple cleaning runs using Company 2's parts or contaminates. The alcohol purity and all other future testing would need to be performed on-site at Facility 2, as it was outside of the scope of this project.

#### **Environmental, Health, & Safety Evaluation**

A P2OASys evaluation was conducted comparing the original solvent (TCE) with the top three performing cleaners. As before, dimethyl glutarate as a single solvent was added to the overall EHS assessment to show the difference between the solvent itself and Sta-Sol ESS 160. The comparison is provided in Table 7.

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Table 7: P2OASys evaluation of TCE compared to the alternatives identified by the TURI Lab

	Original Solvent		Alternativ	e Cleaners	
Category	Trichloroethylene	Dowanol PnBGE	Metalnox M6386	Dimethyl Glutate	Sta-Sol ESS 160
Acute Human Effects	8	8	8	2	6
Chronic Human Effects	9	3	2	2	6
Ecological Hazards	8	2	4	3	8
Environmental Fate & Transport	9	4	5	8	10
Atmospheric Hazard	6	2	2	2	2
Physical Properties	10	6	8	5	5
Process Factors	7	8	4	4	5
Life Cycle Factors	10	4	4	3	6

### Summary

Table 8 provides a summary of whether or not the cleaning alternatives evaluated met the human health and environmental criteria listed in Appendix B, as well as the process and safety criteria provided by Facility 2. Consideration of the layout of the facility cleaning area and available equipment determined if cleaners met process criteria.

Table 8: Summary of environmental, human health, process, and safety criteria for Facility 2

	Appendix	( B Criteria	Facility 2 Criteria		
Name	Human Health	Environmental	Current Process: Vapor Degreasing	Proposed Process: VCN	
TCE	No	No	Yes	Yes	
Downanol PnGBE	Yes	Yes	No	No	
Metalnox 6386	Yes	Yes	No	Yes	
Dimethyl glutarate	Yes	No	No	No	
Sta-Sol ESS 160	No	No	No	No	

As mentioned previously, Sta-Sol ESS 160 is more hazardous than simple dimethyl glutarate. Metalnox 6386 has a very high P2OASys hazard rating in acute human health due to eye and skin irritation. However, Facility 2 would be using all potential alternatives in an enclosed system, which reduces the risks of the high hazard endpoints during operation.

Alternatives available for Facility 2 to move forward with include Dowanol PnBGE, Metalnox 6386, or Sta-Sol ESS 160. Dowanol PnBGE and Sta-Sol ESS 160 would require the addition of a drying step. As the TURI Lab was finalizing testing of parts, Facility 2 was working with vendors to test VCN processes using Metalnox 6386 as its preferred cleaner.

# IV. Facility 3

#### **Overview**

Facility 3 cleans batches of 1,500 to 3,000 parts in a 20- to 30-gallon TCE-based vapor degreaser. Precision cleaning of tubing used microscopes and white glove tests to determine cleanliness.

To identify potential cleaning alternatives, the human health and environmental criteria listed in Appendix B was used along with the following process and safety criteria provided by Facility 3:

#### **Process Criteria:**

- Remove oils, machining-fluid, lubricants, grease, buffing compounds, and coatings 30 minutes
- Parts dry within 0-10 minutes
- Compatible with substrates used for parts and equipment

# **Approach**

The initial step in the TURI assessment process was a walk-through of both cleaning processes. Using TURI's internal test request form and facility-provided data, TURI and MnTAP representatives walked through both cleaning processes to document contaminants, substrates, current cleaning processes, and methods of evaluating cleanliness. TURI used this information to initially research possible effective and safer cleaners for removing the most stubborn contaminant in use at the facilities.

### **Performance Testing**

Performance testing for Facility 3 was conducted as outlined for Facility 2 to identify suitable alternative solvents with similar results.

Facility 3 sent parts with contamination for cleaning to Vacuum Processing Systems, a VCN equipment manufacturer, to test its solvent cleaning equipment. The TURI Lab did not receive any parts or equipment from Facility 3.

# IV. Facility 4

# **Overview**

Facility 4 builds parts for metal enclosures, and the facility utilizes TCE to remove vanishing oil (WD40), lubricants, greases, and dirt from cold rolled and galvanized steel parts. The cleaning process utilizes a TCE-based vapor degreaser with a flooding spray to clean parts within 8 to 16 minutes. Many of its parts are large and complex in shape. Part sizes can be up to 3'x 3' and can include piano hinge parts and tight overlapping seams.

A potential future change to Facility 4's process is to install a powder coating paint line with integrated cleaning, which could help eliminate the use of TCE-based vapor degreaser. Most of Facility 4's product is cold rolled steel, but the proportion of galvanized steel may increase in the future. Facility 4 had two priorities while trying to eliminate TCE from its process:

- 1. Find an interim cleaner to clean parts and eliminate TCE. The facility was using Tergo Metal Cleaner, a DCE-based product, as a temporary replacement.
- 2. For the long term, identify a safer cleaner that can be used in a powder coating paint line with integrated cleaning for immersion or spray applications.

For identifying and evaluating potential alternatives, the research team used EHS criteria previously developed by TURI and MnTAP along with the following process criteria provided by Facility 4:

- Remove vanishing oil from substrate within 30 minutes
- Be compatible with substrates used for equipment and parts

### **Approach**

The initial step in the TURI assessment process was a walk-through of Facility 4 by a MnTAP representative. Using TURI's internal test request form and company-provided data, the most common contaminants, substrates, and cleaning methods were documented, and samples were scheduled to be sent to the TURI Lab. TURI used this information to initially research possible effective and safer cleaning alternatives.

TURI's CleanerSolutions database was used to identify cleaners that could potentially satisfy Facility 4 requirements. Two cleaning applications were considered when searching for alternatives:

- 1. Immersion cleaning:
  - a. Dipping parts into the tank with potential agitation if needed.
  - b. Could be used in a vapor degreaser without using the vapor function. Discussions with the equipment vendor would be needed to verify feasibility.
- 2. Spray Application: May need a low foam cleaner as part of a spray application on a paint coating equipment line.

The 10 products listed in Table 9 were identified as potential cleaners for Facility 4 using the CleanerSolutions database. The vendor-recommended cleaner concentration percentages and operating temperatures are also listed in Table 9.

Table 9: Potential cleaning alternatives to replace TCE for Facility 4

Manufacturer	Product	Туре	Concentration	Temperature (°F)
International Products Corps	Micro 90	Alkaline Aqueous	1-2%	68-150
Brulin Holding Company	Aquavantage 1400	Alkaline Aqueous	5-30%	130-180 (Typically used at 140-150)
Alconox Inc.	Liquinox	Alkaline Aqueous	1%	150-170
Mirachem Corporation	Mirachem 500	Alkaline Aqueous	20%	105-140
Gemtek	SC Aircraft & Metal	Alkaline Aqueous	2.5-50%	68-110
Gemtek	SC 1000	Alkaline Aqueous	20%	Dependent on Use
J.R. Hess & Co. Inc.	Sta-Sol ESS 160	Solvent (Dibasic Ester)	100%	68-180
United Laboratories International	Smart Solve 605	Solvent (Biobased)	100%	68-150
Kyzen Corporation	Metalnox 6386	Modified Alcohol	100%	68
Alconox	Alconox	Powder Detergent	2g/200ml	150-170

### **Performance Testing**

Initial performance testing was conducted using unheated immersion for a 15-minute dwell time on cold rolled steel coupons contaminated with vanishing oil. The results for the six initial cleaners selected are provided in Table 10.

Table 10: Unheated immersion for 15 minutes on cold rolled steel coupons contaminated with vanishing oil

Product	Туре	Concentration	Average % Removal
Liquinox	Alkaline Aqueous	1%	87.3
SC 1000	Alkaline Aqueous	20%	75.6
Aquavantage 1400	Alkaline Aqueous	5%	71.9
Alconox	Powder Detergent	2g/200ml	66.3
Micro 90	Alkaline Aqueous	2%	62.1
Sta-Sol ESS 160	Ester, Organic	100%	46.0

The next performance test conducted used heated immersion for a 15-minute dwell time on the same type of coupon (cold rolled steel coupons contaminated with vanishing oil). All cleaners were heated to 125°F. The results for the six cleaners tested are provided in Table 11.

Table 11: Heated immersion for 15 minutes on cold rolled steel coupons contaminated with vanishing oil

Product	Classification	Concentration %	Temperature (°F)	Average % Removal
Micro 90	Alkaline Aqueous	2%		206
Alconox	Powder Detergent	2g/200ml		193
SC 1000	Alkaline Aqueous	20%	125	140
Liquinox	Alkaline Aqueous	1%	125	127
Aquavantage 1400	Alkaline Aqueous	5%		113
Sta-Sol ESS 160	Ester, Organic	100%		107

Although the results of the unheated immersion tests seemed promising, all of the cleaners removed over 100% of the vanishing oil, meaning that some substrate was removed along with the contaminant. All six of the cleaners left some cleaner residue, caused discoloration of the substrate, and/or visibly damaged the surface of the cold rolled steel coupons. Vendor technical data sheets were reviewed again, but all manufacturers either stated that their cleaners were potentially compatible with cold rolled steel or they had no substrate testing information available.

Since many of the initial cleaners had poor results with heated immersion, TURI used the CleanerSolutions database to identify four additional cleaners (Smart Solve 605, Metalnox 6386, Mirachem 500, and SC Aircraft and Metal Cleaner). These cleaners were then tested using heated and unheated immersion for a 15-minute dwell time on the same type of coupon (cold rolled steel coupons contaminated with vanishing oil). The vendors were contacted to verify substrate compatibility to the best of their knowledge. Technical data sheets and expert judgment from previous testing were used to decide what concentration and temperature would be appropriate for testing. Due to project time constraints, only Smart Solve 605 was tested at both the heated and unheated condition. The cleaners are listed from highest to lowest average removal percentage. The results are shown in Table 12.

Table 12: Unheated and heated immersion on cold rolled steel coupons contaminated with vanishing oil

Product	Classification	Concentration %	Temperature (°F)	Average % Removal
Mirachem 500	Alkaline Aqueous	20	110	100.0
Smart Solve 605	Biobased	100	100	93.3
Metalnox 6386	Modified Alcohol	100	68	92.9
SC Aircraft & Metal Cleaner	Alkaline Aqueous	20	130	78.5
Smart Solve 605	Biobased	100	68	63.7

The next step was performing ultrasonic testing, using a Branson 3800 40Hz tank, on piano hinge parts provided by Facility 4. This testing was designed to check if cleaners could clean in between the small spaces within the hinge. The parts were initially cleaned by Facility 4 in its TCE cleaning process to provide the TURI Lab with clean parts as a baseline for comparison. Gravimetric data was not collected because the piano hinges were too long for TURI Lab scales to accurately measure. Instead, contact angle measurements and white glove tests were used to assess the cleaning results for the alternative cleaners.

Contact angles were recorded by TURI using an FTA200 dynamic contact angle analyzer. The FTA200 accuracy has a contact angle deviation of less than 1 degree and a standard deviation for surface tensions of less than 0.5 mN/m.

Contact angle measurements were first taken by TURI on the TCE-cleaned parts provided by Facility 4. These measurements were used as the baseline of cleanliness for the piano hinge parts. The parts were then contaminated with oil, and contact angle measurements were taken for some contaminated parts. When the contaminant (oil) was added to the surface of the part, the contact angle measurements were lower. Contaminated parts for cold rolled steel had an average contact angle measurement of 56°. The parts were then cleaned in the TURI Lab using heated and unheated ultrasonics for 15 minutes and air dried with a heat gun for five minutes before final contact angles were taken. Effectiveness of the cleaners was determined by:

- Contact angle measurement: The contact angle for parts cleaned with the alternative cleaner, and parts
  cleaned with TCE were measured. The cleaning process was considered effective if the parts cleaned
  with the alternative cleaner contact angle was equal or greater than the contact angle of the TCE
  cleaned parts.
- 2) White glove test: This test evaluated whether any oil was visible when a white glove was wiped on the clean surface, including rounded areas. If the glove had no visible oil on the glove, then the cleaner was given a "Passed" rating. Parts that transferred visible oil onto the glove when wiped were given a "Failed" rating.

Table 13 shows the results for each product tested. The cleaners are listed in order of change in contact angle.

Table 13: Ultrasonic cleaning for 15 minutes on cold rolled steel piano hinges

Product	Concentration %	Temperature (°F)	TCE Cleaned Part Contact Angle°	Cleaned Part Contact Angle°	Change in Contact Angle	White Glove Test	Rusting/ Residue
Mirachem 500	20	110	59	79	20	Passed	No Rusting/ No Residue
Smart Solve 605	100	100	75	79	4	Failed	Flash Rusting/ No Residue
Metalnox 6386	100	68	64	66	2	Passed	No Rusting/ No Residue
SC Aircraft & Metal Cleaner	20	130	55	46	-9	Failed	No Rusting/ Residue

Smart Solve 605 flash rusted immediately after placing the part in the cleaner; neither the TURI Lab nor the vendor could explain why this happened. Mirachem 500 and Metalnox 6386 were the most effective cleaners on the piano hinges, because they passed the white glove test and had a higher contact angle than the TCE cleaned parts. SC Aircraft & Metal Cleaner had the worst performance, with a lower contact angle than the TCE cleaned parts and a failed white-glove test.

Mirachem 500 was tested again, using the same testing parameters but on the galvanized steel piano hinge parts, to see if the aqueous cleaner's contact angle would be closer to the TCE-cleaned part. Results are listed in Table 14.

Table 14: Ultrasonic cleaning for 15 minutes of galvanized steel piano hinges

Product	Concentration %	Temperature (°F)	TCE Cleaned Part Contact Angle°	Cleaned Part Contact Angle°	White Glove Test
Mirachem 500	20%	110	58	64	Passed

Mirachem 500 was effective cleaning the galvanized piano hinges, because it passed the white glove test and had a higher contact angle than the TCE-cleaned parts.

#### **Environmental, Health, and Safety Evaluation**

A P2OASys evaluation was conducted comparing the original solvent (TCE) with the Tergo Metal Cleaning Fluid (Facility 4's temporary cleaning product) and two identified potential alternatives. The comparison is listed in Table 15. The Tergo Metal Cleaning Fluid contains DCE, which is currently the subject of a risk evaluation by EPA under the TSCA. Appendix C provides further information about DCE.

Table 15: P2OASys evaluation of TCE, Tergo metal cleaning fluid, and identified alternatives

Catagoni	Original Cleaning Fluid Solvent		CleanerSolutions Database Alternatives	
Category	TCE	Tergo Metal Cleaning Fluid	Mirachem 500	Metalnox 6386
Acute Human Effects	8	7	5	8
Chronic Human Effects	9	4	2	2
Ecological Hazards	8	6	6	4
Environmental Fate & Transport	9	9	2	5
Atmospheric Hazard	6	4	5	2
Physical Properties	10	8	6	8
Process Factors	7	6	5	4
Life Cycle Factors	10	9	6	4

### Summary

Table 16 provides a summary of whether or not the cleaning alternatives evaluated met the human health and environmental criteria listed in Appendix B, as well as the process and safety criteria provided by Facility 4. Consideration of the layout of the facility cleaning area and available equipment determined if cleaners met process criteria.

Table 16: Summary of environmental, human health, process, and safety criteria for Facility 4

	Appendi	x B Criteria	Company 3 Criteria		
Name	Human Health	Environmental	Current Process (Vapor Degreasing)	Proposed Process (Integrated Cleaning, Immersion/Spray Applications)	
TCE	No	No	Yes	Yes <sup>1</sup>	
Tergo Metal Cleaning Fluid	Yes	No	Yes	Yes <sup>1</sup>	
Mirachem 500	Yes	Yes	No	Yes	
Metalnox 6386	Yes	Yes	No	Yes <sup>1</sup>	

<sup>&</sup>lt;sup>1</sup> Enclosed immersion system only.

The P2OASys assessment of Mirachem 500 is based on concentrate and not a 20% dilution; the hazards would be reduced with a 20% dilution during operation, which was shown in TURI tests to be an effective concentration. Metalnox 6386 did not meet the human health criteria because of eye and skin irritation risks; the very high P2OASys score in physical properties is due to its flammability and being a combustible liquid.

Mirachem 500 with heated immersion at 20% concentration is the primary alternative for Facility 4's proposed cleaning process as a long-term aqueous cleaning solution. This product can be recycled through an ultra-filtering process. The Mirachem 500 vendor lists the product for use in low- and high-pressure spray applications that could potentially meet the needs of Facility 4's future powder coating line cleaning process. Facility 4 will need to have discussions with the cleaner supplier and equipment vendors about operating conditions and verifying performance with in-house testing of the alternatives.

If Facility 4 replaces its vapor degreaser in the future with a new piece of equipment that is not attached to its powder coating line, then the Metalnox 6386 product might be a potential alternative product to consider, if the new equipment is an enclosed system that would reduce Metalnox's physical hazards.

# Appendix A: About P2OASys

# **Pollution Prevention Options Analysis System (P20ASys)**

The primary goal of alternatives assessment for chemicals of concern is to reduce risks to humans and the environment by identifying safer choices. In the mid-1990s, TURI developed the Pollution Prevention Options Analysis System (P2OASys) tool to help companies systematically determine whether the toxics use reduction options being considered may have unforeseen negative environmental, worker, or public health impacts. The intended use of the P2OASys tool is to provide a methodical way to assess toxics use reduction process changes. Ideally, the tool will help shed light on environmental, worker, and public health concerns that currently exist or that may arise during a change of manufacturing process(es). The tool is only intended to provide the user with a safety assessment, one of the pieces of the three-legged alternatives assessment process (technical and financial being the other two legs). By providing a systematic, critical-thinking process about the potential hazards posed by current and alternative processes, better informed decisions can be made and regrettable substitutions can be prevented. This document, partnered with an instructional video, will inform the reader how to use the on-line tool (<a href="https://p2oasys.turi.org">https://p2oasys.turi.org</a>) to help guide them to possible alternatives for given parameters.

#### How it works

The score is meant to give the user a way to compare a current process with possible substitutes. The values are not meant to provide the user with a number that would provide a definitive "this is good" or "this is bad" answer. The scores need to be considered in a "How does this compare with that?" mindset. Figure 5 shows the main homepage of the tool.

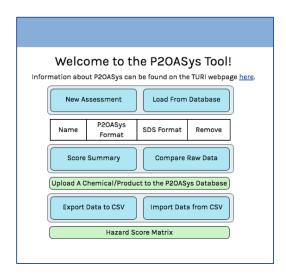


Figure 5: Home page of the P2OASys Tool

The first step in the EHS assessment is to collect as much data on the chemical/product as possible. The more information available, the more robust the assessment can become. Common resources to collect would be safety data sheets (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 accurate information is utilized. From the main menu, a user would select "New Assessment" and be directed to the screen pictured below in Figure 6 where you can enter the chemical or product identity information to add it to your active

session. The product will now show up on the main page where you can choose to enter your data in the P2OASys format or SDS format.

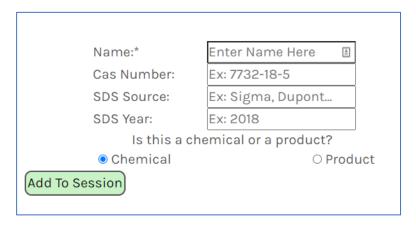


Figure 6: New Assessment page of the P2OASys Tool

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, psychological, and environmental hazards, each of which can be expanded to an overall 150 subcategories. Figure 7 is an example of the subcategories in one of the main categories (acute human effects).

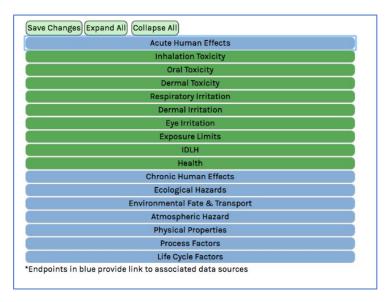


Figure 7: P2OASys eight main categories with Acute Human Effects expanded to view the related subcategories

Using both quantitative and qualitative data input, the tool has been set up to rate each category based on endpoints that correlate with values, key phrases, Global Harmonizing System (GHS) classifications, and other government agencies' designations.

Within each category, there are subcategories that can be populated. Each of these subcategories have several options. For subcategories that have multiple options, the most hazardous criterion is used to provide the

subcategory score. In each of the eight categories, P2OASys calculates the average of the two most hazardous values for the various subcategories to give a numerical rating for that overall category. To obtain a category score, the user must therefore fill in data or information for all subcategories possible.

The tool does not require every criterion, subcategory, or category to be assessed in order to create an assessment. However, the more data that can be entered into each of the subcategories, the better the overall profile of the process will be.

To complete the EHS review, the user will need to enter some end points for the chemical/process based on his/her professional judgment. Process and life cycle endpoints are typically case specific and should be part of the judgment assessment. After a level of acceptable data points has been entered and a summary score is generated, the user must then review the values and compare to other products. A further assessment should check for data gaps and go back to fill in if possible, to ensure best comparison of all evaluated options. Then with acceptable data collection complete, the individual category values can be assessed and looked at to identify products that are of low, medium, high, or very high concern.

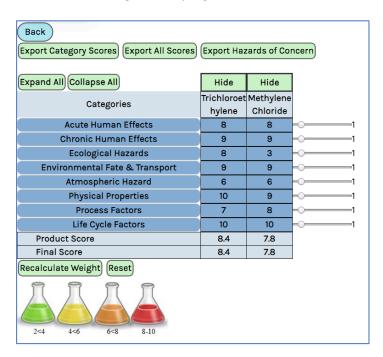


Figure 8: Score Summary of a P2OASys Evaluation of Two Chemicals

P2OASys allows the user to review the information and compare data in many different ways. When you are finished your assessment, from the main screen you can a generate "Score Summary," pictured in Figure 8 above, and you can see final scores and the overall score of each of the main category. Figure 9 is the key used by the main category, subcategory, and final scores.

Color	Level of Hazard	Score Range
	Low (L)	2 < 4
	Medium (M)	4 < 6
	High (H)	6 < 8
	Very High (vH)	8 - 10

Figure 9: Key for P2OASys scores and how the levels are defined in assessments

If your current product or process has a worse score (i.e., a higher overall P2OASys score) than the alternative, this is a good indication that further plans to investigate adoption of the alternative should be considered.

It is important to note that P2OASys does not include economical comparisons or performance criteria. These considerations are necessary for a thorough assessment of alternatives. For projects focused on surface cleaning, the TURI Lab can assist with performance testing.

Similar to performing the assessment, you can expand each category to see the score for each endpoint within that category. The side bars next to each category allow for the user to add more weight to a category if that is of particular concern to the user. From this page the user can also choose to export this information into an excel spreadsheet in various ways:

- 1. The 8 category scores and final score (shown above)
- 2. All scores for each endpoint of data gap
- 3. Hazards of concern (endpoints that received an 8 or higher)

It is important to remember that the information the user gets in the excel spreadsheet from the "Score Summary" screen is just the scores. If you want to see what information you put in to drive that score you must go back to the main screen and select "Compare Raw Data." From here the user can expand all categories and view the specific information that was entered. This information can also be saved by selecting "Export Data Comparison" and the user can have all the raw data saved for his/her own use or to review at a later date.

Assessments made using P2OASys can vary from one person to the next for the same process or chemical, based on the technical expertise of the assessor. But to help make the process easier to start an assessment, the TURI staff are populating the database with common solvents. P2OASys scores for these chemicals can be downloaded to an active P2OASys session.

### **Load from Database**

In addition to the user being able to perform a personalized assessment, Figure 10 shows the page where the user can load chemicals/products from the database. P2OASys evaluations of various products have been conducted and reviewed by TURI staff for accuracy. If the user is not finished with an evaluation, he/she can also export the data collected and save the excel file to a personal device. The user can then reload the unfinished assessment back into the database to continue editing and completing a final assessment.

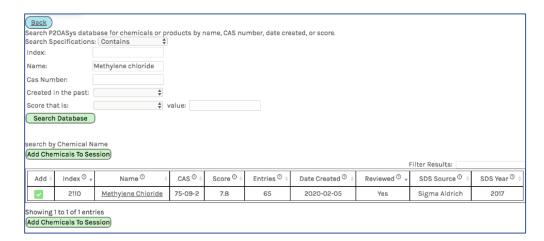


Figure 10: P2OASys database page

# **Appendix B: Human Health and Environmental Criteria**

Key environmental and human health criteria for solvents and cleaners as well as their byproducts were considered when identifying and evaluating TCE alternatives. Cleaners and the ingredients listed on the SDS were compared to the following key environmental and human health criteria to determine if they were acceptable alternatives. The criteria are consistent with very high hazard (8-10) P2OASys scores for individual hazard endpoints.

- 1. The following human health endpoint values were considered not acceptable:
  - a) Acute toxicity
    - Inhalation GHS Category 1 and 2
      - LC50 ≤500 ppm; gas/vapor ≤10mg/l
    - Skin GHS Category 1 and 2; H310 Fatal in contact with skin; H311 Toxic in contact with skin; H312 - Harmful in contact with skin
      - LC50 ≤1000 mg/kg
  - b) Carcinogenicity
    - GHS Category 1, 1A, 1B; H350 May cause cancer (state route of exposure if it is conclusively
      proven that no other routes of exposure cause the hazard)
    - GHS Category 2; H351 Suspected of causing cancer (state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard)
    - IARC Category 1, 2A/2B
    - EPA Class A-C
    - OSHA Category 1 and 2
    - ACGIH Category A1 and A2
    - Listed on the Prop 65 List
  - c) Mutagenicity/Teratogenicity
    - GHS Category 1A and 1B; H340 May cause genetic defects (state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard)
    - GHS Category 2; H341 Suspected of causing genetic defects (state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard)
  - d) Reproductive/ Developmental Toxicity
    - GHS Category 1A and 1B; H360 May damage fertility or the unborn child (state specific effect if known) (state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard)
    - GHS Category 2; H361 Suspected of damaging fertility or the unborn child (state specific effect if known)(state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard); H362 - May cause harm to breast-fed children (No related GHS category)
    - Listed on the following
      - ChemSec SIN List
      - Prop 65 List

- e) Endocrine disruption
  - Listed on the following:
    - ChemSec SIN List
    - The Endocrine Disruption Exchange (TEDX) List
    - European Union List of Endocrine Disruptors List
- f) Sensitization
  - Respiratory
    - GHS Category 1; H334 May cause allergy or asthma symptoms or breathing difficulties if inhaled
    - Listed on the Association of Occupational and Environmental Clinics (AOEC) List
  - Skin
    - GHS Category 1A and 1B; H317 May cause an allergic skin reaction
- g) Neurotoxicity and Target Organ Systemic Toxicity (TOST)
  - Specific Target Organ Toxicity (STOT)
    - Single Exposure
      - i. GHS Category 1; H370 Causes damage to organs (or state all organs affected, if known) (state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard)
      - ii. GHS Category 2; H371 May cause damage to organs (or state all organs affected, if known) (state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard); GHS Category 2
  - Repeated Exposure
    - GHS Category 1
      - i. H372 Causes damage to organs (state all organs affected, if known)
        through prolonged or repeated exposure (state route of exposure if it is
        conclusively proven that no other routes of exposure cause the hazard)
    - GHS Category 2
      - i. H373 May cause damage to organs (state all organs affected, if known) through prolonged or repeated exposure (state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard)
- h) Listed on the Grandjean Neurotoxin List
- 2. The following environmental endpoint values were considered not acceptable:
  - I. Aquatic toxicity
    - a) Acute and Chronic GHS Category 1-2; H400, H401, H410 and H411
      - H400 –Very toxic to aquatic life (acute)
      - H401 Toxic to aquatic life (acute)
      - H410 Very toxic to aquatic life with long lasting effects (chronic)
      - H411 Toxic to aquatic life with long lasting effects (chronic)
    - b) U.S. Environmental Protection Agency for EPI Suite
      - Acute ≤ 1mg/l LC50 & EC50

- Chronic ≤ 0.01 mg/l ECx or NOAEC
- II. Persistence
  - a) U.S. Environmental Protection Agency for EPI Suite
    - Water half-life, days ≥ 60
    - Air half-life, days ≥ 5
    - Soil half-life, days ≥ 180
    - 28-day Study: % Breakdown Dissolved Organic Carbon ≥ 55
      - % Based on O2 or CO2 ≥ 45
    - Biochemical Oxygen Command (BOD) ≥ 500
- III. Bioaccumulation
  - a) U.S. Environmental Protection Agency for EPI Suite
    - Log Know/Pow ≥ 6
    - Bioconcentration Factor (BCF) ≥ 5000 I/kg
- IV. Atmospheric hazards
  - a) Greenhouse gas
    - Global Warming Potential (GWP) Relative to CO2 ≥ 1000
    - Listed on the following:
      - Center for Climate and Energy Solutions
      - Green House Gas Protocol List
  - b) Ozone depletion
    - Listed on the EPA Ozone Depleting Substances List
  - c) Acid Rain Formation
    - Product may form SO2 or NOx upon combustion
    - Contains SO2 or NOx
  - d) Air Pollutant
    - Listed on the National Emission Standards for Hazardous Air Pollutants (NESHAP)

# Appendix C: Trans-dichloroethylene (DCE) and Hydrofluoroether (HFE) Advisory

# Toxics Use Reduction Program Advisory Revised 2019

### trans-1,2-Dichloroethylene, CAS 156-60-5

(synonyms: trans DCE, trans-1,2-dichloroethene, 1,2-DCE)

The <u>Toxics Use Reduction Program</u> cautions companies that certain alternatives to trichloroethylene (TCE), perchloroethylene (perc) and n-propyl bromide (nPB) also present significant hazards to human health and/or the environment. *Trans*-1,2-dichloroethylene is one such alternative. While it is recognized as a potentially effective alternative, either alone or in solvent blends, it is listed on the TURA list of toxic or hazardous substances (see the table below). It is, therefore, reportable if more than 10,000 pounds are "otherwise used" in one calendar year. *Trans*-DCE is not considered a preferable alternative to TCE, perc, nPB or other hazardous solvents.

Trans-DCE has a high vapor pressure (336 mm Hg @ 25°C), has a low boiling point (48.5°C), is a flammable liquid (flash point 2°C), and is a regulated VOC. While having lower human toxicity than some other halogenated solvents, trans-DCE is an immune system toxicant and a neurotoxin. Acute exposure can cause central nervous system depression and chronic exposure can cause liver, circulatory, immune system and central nervous system damage.

Trans-DCE is often used in blends with fluoroalkanes or hydrofluoroethers (HFEs) (e.g., Fluosolv™ CX, Vertrel™ SDG, and Opteon™ Sion). This expands the range of cleaning power of HFEs, while the HFEs lower the flammability of the mixture. The HFEs have lower human toxicity than trans-DCE and are not flammable, but do contribute to global warming, break down into very persistent and toxic PFAS chemicals, and are more expensive than many solvents.

Identifying safer drop-in substitutes for TCE, perc, nPB and other halogenated solvents is challenging. Staff at the <u>Toxics Use Reduction Institute (TURI)</u> and the <u>Massachusetts Office of Technical Assistance and Technology</u> (OTA) would be happy to work with your company to investigate safer alternatives for your specific needs.

#### TURA Listing Breakdown by CAS

<i>trans-</i> 1,2- Dichloroethylene	CAS 156-60-5	TURA listed
<i>cis</i> -1,2- Dichloroethylene	CAS 156-59-2	reportable as part of TURA C1-C4 Halogenated Hydrocarbons and Halocarbons Not Otherwise Listed category ("C1-C4 Halogenated NOL")
cis- and trans- mixture	CAS 540-59-0	TURA listed

Note: The *cis* isomer of DCE is not commonly used in commercial cleaning solvents; it is provided here for information only.

# Appendix D: Hansen Solubility Parameter (HSP) Theory

The HSP theory can be used to predict which solvents will be able to dissolve target solutes, and is an efficient method to rapidly identify safer and effective alternatives to toxic solvents used in a variety of products. A solute is the substance being dissolved, and a solvent is the substance that dissolves it. Both substances (solute and solvent) must have similar Hansen Solubility Parameters to dissolve the solute. The HSP approach is based on three distinctive forms of inter-molecular force:

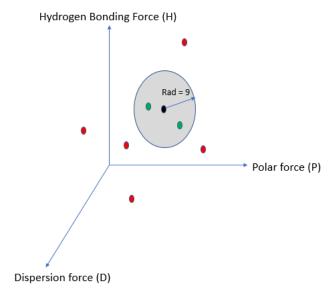
- 1) Dispersion forces (D): All atoms are surrounded by electron "clouds." The electron cloud is, on average, evenly distributed around the atom. At a given instant, however, the electron distribution may be uneven. This temporary polarization results in attractive interactions with nearby atoms.
- 2) Polar forces (P): Dipole moments are created when atoms of the same molecule have different electronegativities.
- 3) Hydrogen bond forces (H): This force exists between hydrogen atoms and other atoms present in adjacent molecules.

These three forces or parameters are used to describe solvent and solute interactions. Each parameter can be used as an axis in three-dimensional solubility space. Instead of the common X, Y, and Z axis, the three-dimensional solubility space will have a Dispersion Force (D) axis, a Polar Force (P) axis, and a Hydrogen Bonding Force (H) axis. Each solvent can be represented as a point in three-dimensional solubility space, and each solute can be represented as a sphere in three-dimensional solubility space.

HSP values are based on the principle that "like dissolves like," meaning that the closer the solute and solvent are in three-dimensional solubility space, the greater the likelihood that the solvent will be effective. If the solvent is located inside the sphere of solubility, then it will dissolve the polymer. If the solvent is located outside the sphere of solubility, then it will NOT dissolve the polymer. The distance between HSP points in solubility space is calculated as follows:

Distance = 
$$[4 (D_1-D_2)^2 + (P_1-P_2)^2 + (H_1-H_2)^2]^{1/2}$$

As shown below, the three axes are for the polar force, hydrogen bonding force, and dispersion force. The black dot represents the center point for the sphere of solubility. The green dots represent solvents that are inside the polymer solubility sphere and will dissolve the coating. The red dots represent solvents that are outside the polymer solubility sphere and will NOT dissolve the coating.



Solvents and Sphere of Solubility in Hansen Solubility Parameter 3D Space

In general, the lower the HSP distance between the solvent and the solute, the better the solubility performance. The lower the HSP distance between solvent and the center of the solute (coating) solubility sphere, the faster the coating dissolves.

# **About the Toxics Use Reduction Institute**

The Toxics Use Reduction Institute (TURI) at the University of Massachusetts Lowell provides resources and tools to help Massachusetts businesses and communities make the Commonwealth a safer and more sustainable 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 economic competitiveness of Massachusetts businesses. Learn more at www.turi.org.



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