Substitution of trichloroethylene as cleaning solvent in metal processing

This case study aims to illustrate a chemical substitution process. It is based on publicly available information on company’s experience as well as on substance hazards, alternatives to the hazardous substance and regulatory information. The case study is neither complete nor comprehensive in illustrating all substitution options of a substance but rather exemplary.

1. Case description

Trichloroethylene is a colorless, volatile, inflammable solvent, which has a sweet odor and is hazardous to human health.

Synonyms for Trichloroethylene: Acetylene trichloride, Ethinyl trichloride, Trichloroethene, TRI, TRIC, 1-Chloro-2,2-dichloroethylene, 1,1,2-Trichloroethylene, Trilene, Triklone®, Trimar. Industrial abbreviations include trichloroethylene, trichlor, Trike, Tricky and trichloroethylene.

1.1 Hazards of Trichloroethylene (TCE)

Trichloroethylene (CAS number: 79-01-6; EC-number 201-167-4) is classified (harmonised) as a substance that may cause cancer, serious eye and skin irritation and may cause drowsiness or dizziness. It is suspected of causing genetic defects and it is also harmful to aquatic life with long lasting effects.

Additionally, the classification data provided by companies for ECHA in REACH registration process identifies that this substance may cause an allergic skin reaction. Some notifiers also classified it as respiratory sensitiser.

TCE evaporates very quickly and contributes to the formation of ground level ozone (summer smog).

Regulatory status

Trichloroethylene is a so called Substance of Very High Concern (SVHC). It is included in the candidate list for authorization and requires authorization (since April 21 2016) before it can be used (Annex XIV of REACH).

Workplace Regulations/OELs: at EU level an Occupational Exposure Limit (OEL) (8-hour TWA) for TCE is 10 ppm with a Short-Term Exposure Limit (15 min) of 30 ppm.

Restrictions: Consumer uses are prohibited EU-wide, due to the TCE classification as a carcinogen. Because of the use limitations and the authorisation, the number of suppliers of TCE may decrease in the long run.
2 Substitution process

2.1 Substitution incentives

In company „X“, which performs metal processing, the subsequent washing and degreasing of parts, the manufacture process includes the use of trichloroethylene. Since in the manufacture system trichlorethylene has to be periodically replaced, wastes, metal powder containing sludge and oils accumulate and have to be disposed of by the company.

Main reasons for implementing substitution in this company were:

- Authorisation under REACH – it was not clear if authorisation for the specific use will be granted
- Possibility to avoid negative impact for workers and environment (emissions of VOC);
- Possibility to reduce costs for waste management;
- Possibility to unify the products used in deburring and cleaning parts;
- Possibility to reduce the handling of parts between the different stages of the process.

2.2 The substitution project

2.2.1 Identification of alternatives

Among the proposed alternatives there are other chemical substances that have hazardous classification. Main alternative – non chemical aqueous technology, which must be combined with the correct equipment and can be just as effective as solvent cleaning. There are also such technologies as plasma cleaning or dry ice blasting. All these alternatives were evaluated by the environmental expert and purchasing department.
Alternative chemicals

Perchloroethylene
Methylene chloride
n-propylbromide
Hydrofluorocarbons (HFC)

Non chemical alternatives

Aqueous technology
Plasma cleaning
Dry ice blasting

How to move on

As next step, the company decided to make specific requests to their suppliers by writing and with a follow-up call. They enquired if suppliers could provide the alternatives they offer, what is their willingness to cooperate and what is the cost of implementation or/and product.

2.3 Selected alternative and justification

Preliminary assessment of the identified substances, based on their toxicological, ecological and technical performance was made. The results of their screening assessment are shown in the following table.
### LIFE / FIT FOR REACH

<table>
<thead>
<tr>
<th>Substance</th>
<th>Offered</th>
<th>Data source</th>
<th>Acute toxicity</th>
<th>STOT</th>
<th>CMR</th>
<th>Sensitisation</th>
<th>Env hazards</th>
<th>Lack of data</th>
<th>Comment on hazard data</th>
<th>Known limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-propyl bromide (CAS No. 106-94-5)</td>
<td>Yes</td>
<td>ECHA</td>
<td>Skin, Eyes irrit.</td>
<td>SE 3, RE 2</td>
<td>Repr. 2</td>
<td></td>
<td></td>
<td>No</td>
<td></td>
<td>Substance of very high concern (SVHC) and included in the candidate list for authorisation.</td>
</tr>
<tr>
<td>Hydrofluorocarbons</td>
<td>Yes</td>
<td>SDS</td>
<td>Oral, dermal, inhalation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>F-Gas regulations</td>
</tr>
<tr>
<td>Hydrofluoroether</td>
<td>Yes</td>
<td>SDS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>F-Gas regulations</td>
<td></td>
</tr>
</tbody>
</table>

From the gathered information about the hazardousness of proposed alternatives we see that only hydrofluorocarbons and hydrofluoroether could be tested. Other substances have been excluded because of their CMR properties.

After consultation with specialists from Environmental Protection Agency it was clarified that an additional registration in databases is needed for users of hydrofluorocarbons and hydrofluoroether. It was also stated that from the environmental point of view, the use of substances that are involved in ozone depletion is not the best solution.

From the financial perspective all of the proposed chemicals were more expensive 1-50%. Installation of plasma cleaning technology would cost 150 000 Eur, installation of dry ice blasting would cost 85 000 Eur, installation of aqueous technology would cost about 80 000 Eur.

After evaluation of all alternatives, a non-chemical alternative - aqueous technology was chosen for implementation.
2.4 Implementation

Implementation plan

Process evaluation when water based cleaning machine is used:

Although fresh aqueous cleaning solutions are usually classified as non-hazardous, they may accumulate enough contaminants during the cleaning process such as metal powder or oil and grease. As a result, it could be classified as hazardous waste when disposed. Chemical analysis should be performed to determine the spent aqueous cleaning solution waste classification. Spent solutions are typically treated in an on-site wastewater treatment system or shipped off site for disposal.

It must be taken into account that in some cases aqueous systems have the disadvantage of much higher energy demand. For example if dry parts are required, and due to the non-universal material compatibility (combined cleaning of different materials is restricted).

State of play

The company’s substitution action included the installation of a cleaning machine at the exit of each deburring device. The machines use a water-based, non-toxic cleaning agent (96% de-ionized water). This product can be used as a cleaner and as a lubricant/coolant in deburring processes. This eliminates the use of cooling oils in deburring.

The new cleaning machines use a system to separate cutting and deburring fluids from metal powder originating in the deburring process. This extends the lifetime of the cleaning product considerably, which is recycled after cleaning to be used as a deburring lubricant.

2.5 Communication of substitution

It was decided in company not to make specific communication of substitution as the qualities of the end product remained unchanged and customers would not be affected by the changes.
2.6 Costs and savings

It was also made evaluation of costs

<table>
<thead>
<tr>
<th></th>
<th>Process with TCE</th>
<th>Aqueous process</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Balance on material</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trichloroethylene consumption</td>
<td>9,600 Kg/year</td>
<td>0 Kg/year</td>
</tr>
<tr>
<td>Coolant consumption</td>
<td>6,500 Kg/year</td>
<td>0 Kg/year</td>
</tr>
<tr>
<td>Consumption of new cleaning compound</td>
<td>0 l/year</td>
<td>700l/year</td>
</tr>
<tr>
<td><strong>Economic balance</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trichloroethylene consumption</td>
<td>6,058 €/year</td>
<td>0 €/year</td>
</tr>
<tr>
<td>Coolant consumption</td>
<td>7,813 €/year</td>
<td>0 €/year</td>
</tr>
<tr>
<td>Disposal of Trichloroethylene</td>
<td>4,788 €/year</td>
<td>0 €/year</td>
</tr>
<tr>
<td>Disposal of Trichloroethylene sludge</td>
<td>847 €/year</td>
<td>0 €/year</td>
</tr>
<tr>
<td>Consumption of new cleaning compound</td>
<td>0 €/year</td>
<td>3,142 €/year</td>
</tr>
<tr>
<td><strong>Total savings</strong></td>
<td></td>
<td>16,364 €/year</td>
</tr>
<tr>
<td><strong>Investment</strong></td>
<td></td>
<td>79,383 €/year</td>
</tr>
<tr>
<td><strong>Return on assets</strong></td>
<td></td>
<td>4,85 years</td>
</tr>
</tbody>
</table>

2.7 Evaluation

Investment costs pay off after 5 years and workers safety is significantly improved.

If treated in WWTP, it is wastewater and the metal and grease contaminations should be removed (and disposed of).
3 References


