

**DETOX Program
Hazardous Substances Fact Sheet**

**Chlorinated Solvents & Volatile
Organic Compounds (VOCs)**

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1 Background

Volatile organic compounds (VOCs) are liquids, which evaporate quickly but continuously at room temperature and are released as gases into the surrounding air if not kept in a closed container. VOCs are used in the apparel and the shoe industry as solvents in paints and glues, paint thinners, dry-cleaning agents, cleaning agents and shoe primers. They are also formed as by-products of chemical reactions (e.g. formaldehyde) and occur as unreacted monomers (e.g. styrene) or contaminants (e.g. PAH). These sources contribute to the overall release of VOCs and lead to exposure as workers and consumers inhale them with the surrounding air (indoor air pollution). VOCs may have both short- as well as long-term adverse health effects. Amongst the most harmful VOCs are many **chlorinated solvents**, which merit special focus as the most important subgroup of VOCs, important both application-wise as well as risk-wise.

VOCs are main ingredients in many chemical preparations used in textiles and shoes production.¹ Other VOCs are formed as chemical by-products or remain in plastics as unreacted monomers. Further VOCs and SVOCs (semi-volatile organic compounds) occur as contaminants (e.g. nitrosamines and PAH). Although these VOCs and SVOCs are not intentionally used, they still need to be addressed due to their high significance from a health- and safety perspective.

Chlorinated Solvents are still being used in many industrial processes, including as solvent during the production of dyestuffs and pigments, for printing inks (ink-jet), for de-greasing operations or as cleaning agents for printing screens and printing tables for spot-removal on ready-made products or as foaming agents for PU foams. While their use normally happens on purpose, there is a risk that this information is lost within the supply-chain, for example between the synthesis and the formulation of the printing paste.

- Dyeing auxiliaries, e.g. carrier systems that improve the dyeability of polyester which typically contain solvents (0 % - 10 %) and active substances such as alkylphthalimides, benzoic acid esters /-ethers including benzyl chloride as impurity, chlorobenzenes and -toluenes, diphenyl, phthalates, aromatic hydrocarbons including toluene and benzene.
- Adhesives are of high importance in shoe production. Typical solvents used there are²: Toluene (including benzene as an impurity), acetone, ethyl acetate, benzene, butanone, methyl acetate, dichloromethane, cyclohexane, ethanol, methanol, 4-methylpentan-2-on, 1,1,1-trichlorethane, tetrahydrofuran, xylene, N,N-Dimethylformamide (DMF), heptane, butyl acetate.
- Solvents for dry cleaning and spot removal² include perchloroethylene, trichloroethylene and further chlorinated hydrocarbons such as dichloromethane, carbon tetrachloride ethanol but also terpenes such as d-limonene and even acetic acid ester.
- Other important applications are: Solvent based coatings (e.g. based on polyurethane (PU)), finishing chemicals, hydrophobic/oleophobic agents such as repellents.³

¹ USGS (undated): Volatile Organic Compounds (VOCs), [<http://toxics.usgs.gov/definitions/vocs.html>], (Creation date: undated; access at: 17.07.18).

² AFIRM (undated): Chemical Guidance Document.

³ Cai, Ronggang/ Glinel, Karine/ De Smet, David/ Vanneste, Myriam/ Mannu, Nicolas/ Kartheuser, Benoît/ Nysten, Bernard/ Jonas, Alain M. (2018): Environmentally friendly Super-Water-Repellent Fabrics prepared from water-based suspensions; ACS Applied Materials & Interfaces, 10 (18), p. 15346-15351, <https://pubs.acs.org/doi/10.1021/acsami.8b02707>

2 Definition

Volatile organic compounds used in textile industry include Formaldehyde, Styrene, Toluene, Benzene and others as well as the subgroup of chlorinated solvents. Chlorinated solvents which are used in textile industry include substances such as trichloroethylene (TCE), CAS no: 79-01-6 and per-chloro-ethylene (PCE), CAS no: 127-18-4.

Chlorinated solvents can be clustered in three sub-groups:

- **Chlorinated Methanes** (tetrachloromethane, chloroform, dichloromethane etc.)
- **Chlorinated Ethanes** (1,1,1-trichloroethane etc.)
- **Chlorinated Ethenes** (perchloroethylene, 1,1-dichloroethylene, chloroethylene etc.)

Most of these solvents are rather stable and do not tend to react with the chemical that they solubilize, which renders them very suitable for this purpose.

3 Legal Aspects

There is comprehensive international legislation on the limitation of VOCs exposure/inhalation at work places and their emissions into the environment. The EU has also an overarching air quality directive, and EU wide limits for ambient air are fixed in order to improve air quality. Key elements of EU Air Quality Directives 2008/50/EC are⁴:

- EU limit values are legally binding concentration thresholds that must not be exceeded;
- Target values - are to be attained where possible by taking all necessary measures not entailing disproportionate costs – which is calculated comparing the cost of abatement technique with societal cost measured in DALYs⁵;
- Exposure reduction obligation concentrations are to be reduced by a given percent by 2018–2020.

In particular, the Air Quality Directives 2008/50/EC and 2004/107/EC set legally binding limits for ground-level concentrations of outdoor air pollutants.

Suppliers of the REWE Group must assure that they produce in full accordance with the legal requirements of the country where the production takes place, and the legal provisions of the European Union regarding final products. In Europe VOCs are regulated for consumer exposure and for industry within the individual permits of the plants that have to follow Best Available Technique (BAT) as specified in the EUs Best Available Technique Reference Document (Bref)⁶, that is currently being revised. This document lists many valid pollution abatement techniques applied in the textile industry.

⁴ EU Air Quality Directive, EU Official Journal 2008/50/EC (2008): <https://eur-lex.europa.eu/eli/dir/2008/50/oj>

⁵ WHO (undated): Disability Adjusted Life Years, [http://www.who.int/healthinfo/global_burden_disease/metrics_daly/en/], (Creation date: undated; access date: 18.07.18).

⁶ European Commission, H. Schönberger: Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques for the Textiles Industry, Sevilla July 2003 , updated expected 2020. http://eippcb.jrc.ec.europa.eu/reference/BREF/txt_bref_0703.pdf

4 Hazardous Properties and Exposure

Long-term exposure to some VOCs, in particular to some halogenated solvents may result in the development of particular cancers. Furthermore, some *halogenated solvents* can be toxic to aquatic organisms and - above certain exposure levels - may even cause long-term adverse effects in the aquatic environment.

4.1 Hazardous Properties

The ability of VOCs to cause health effects varies greatly depending on the chemical and there is a broad range of short- and long-term adverse health effects documented. Many VOCs are human carcinogens⁷. Exposure to VOCs may result in acute reactions of the upper respiratory tract and eye irritation, rhinitis, nasal congestion, rash, pruritus (itch), headache, nausea, loss of coordination, vomiting and acute asthma attacks.⁸

VOCs may cause chronic damage to the liver, kidneys, and central nervous system (CNS), allergic skin reaction and dyspnoea (difficulty in breathing). Respiratory, allergic or immune disorders of infants or children have been associated with man-made VOCs. The extent and nature of the health effect depends on many factors, including the level of exposure and time-span of exposure.⁹

VOCs are important with regard to the creation of smog: Some VOCs can react with nitrogen oxides (NOX) or with ozone in the atmosphere and form new oxidation products and secondary aerosols, which may cause sensory irritation symptoms.⁹ The emissions of volatile organic compounds (VOCs) in the atmosphere contribute to the formation of the tropospheric ozone (ozone in the lower atmosphere). Large quantities of this ozone can damage vegetation, forests and crops. Sensitive people may suffer irritation of the throat and eyes, as well as respiratory difficulties.¹⁰

VOCs are mainly an issue of indoor air pollution and exhaust gas emissions. But also waste water from chemical factories often contains high amounts of VOCs and must be controlled.

Example of a VOC and chlorinated solvent: **Toluene** (CAS 108-88-3)¹¹

Example: Toluene is commonly used in adhesives and may be found in fabric or leather coatings, fabric inks, synthetic leather and as an impurity in polystyrene-based resins used for button production. Toluene is suspected to cause cancer and it shows reproductive toxicity. Due to Regulation (EC) No 1272/2008 it is classified as¹²:

- H225 - Flammable liquid (Category 2);
- H 315 Skin irritation (Category 2);
- H361d Reproductive toxicity (Category 2);
- H336 Specific target organ toxicity/single exposure (Category 3), Central nervous system;

⁷ UBA (2018): Volatile Organic Compounds (VOC), [https://www.umweltbundesamt.de/en/topics/health/environmental-impact-on-people/chemical-substances/volatile-organic-compounds-voc#textpart-1], (Creation date: 19.03.2018; retrieval date: 24.08.18).

⁸ Michigan Network for Children's Environmental Health (undated): Respiratory Health and Asthma: Mold, VOCs, and Cleaning Products, [http://wiki.mnceh.org/index.php/Respiratory_Health_and_Asthma:_Mold,_VOCs,_and_Cleaning_Products], (Creation date: undated; access date: 19.07.18).

⁹ Muthu, S. S (2014): Roadmap to Sustainable Textiles and Clothing, Hong Kong, 2014.

¹⁰ European Commission (2010): Summaries of European Legislation 2010, Reducing the emissions of volatile organic compounds (VOCs), [http://europa.eu/legislation_summaries/environment/air_pollution/l28029b_en.htm], (Creation date: 02.09.10; access date: 17.07.18).

¹¹ ZDHC (undated): Factsheet Toluene, [https://www.roadmaptozero.com/fileadmin/layout/media/downloads/en/Toluene.pdf], (Creation date: undated; access date: 24.07.18).

¹² Sigma Aldrich (2018): MSDS Toluene, [http://www.sigmaaldrich.com/MSDS/MSDS/DisplayMSDSPage.do?country=DE&language=EN-generic&productNumber=244511&brand=SIAL&PageToGoToURL=http%3A%2F%2Fwww.sigmaaldrich.com%2Fcatalog%2Fsearch%3Fterm%3D108-88-3%26interface%3DCAS%2520No.%26N%3D0%2B%26mode%3Dpartialmax%26lang%3Dde%26region%3DDE%26focus%3Dproduct], (Creation date: 22.03.18; access date: 19.07.18).

- H373 Specific target organ toxicity/repeated exposure (Category 2);
- H304 Aspiration hazard (Category 1).

Example of a chlorinated solvent: **Perchloroethylene** (PCE) is widely used in dry-cleaning, in water-proofing agents (also for maintenance) and in stain-removers and cleaners.

- Exposure of humans to PCE happens mostly through the breathing of contaminated air (workplace) and through accidental ingestion, including via breast-milk. Consumers are mainly affected via dry-cleaned textiles.
- Adverse health effects are cancers such as lung cancer and cancers of colon-rectum and bladder cancer. PCE is reasonably anticipated carcinogen, which means that it was proven to cause tumors in mice and it has the potential to cause the above cancers in humans, especially with higher exposure.
- Further adverse effects include damage to the central nervous system, nausea, vomiting, unconsciousness, difficulty to walk or speak, respiratory depression as well as spontaneous deaths, as could be observed in rats.
- Prolonged exposure may lead to skin irritation, menstrual problems and spontaneous abortions, dizziness, headache as well as liver- and kidney damage.

4.2 Exposure

Workers

Exposure can occur in the various formulating and production facilities that use chemical preparations based on VOCs. Workers may be exposed during handling chemical preparations where they can get in contact with processing liquids, waste water or treated products, when carrying out maintenance, sampling, testing, or other procedures that may even lead to ingestion. This may be limited by the use of adequate personal protection equipment and special practices and measures in places where chlorinated solvents are handled.

Environment

VOCs are mainly an issue of indoor air pollution and exhaust gas emissions (e.g. in printing). But also waste water from chemical factories can contain high amounts of VOCs. VOCs are ground water contaminants of concern because of very large environmental releases, human toxicity, and a tendency for some compounds to persist in and migrate with ground water to drinking water.¹³ This is a problem as many VOCs degrade only slowly, particularly some of the chlorinated solvents, and are rather persistent, too.

Some chlorinated solvents are even toxic to aquatic organisms. All chlorinated solvents tend to cause severe long-term pollution as unfortunately they do penetrate deeply into the aquifer: Due to their high densities (greater than 1 g/cm³) and low water-solubility, they tend to form a separate layer underneath the water-layer, from where they dissolve slowly (due to their low water-solubility) and oftentimes back up unobserved into the ground-water.¹⁴

¹³ Department of Health Minnesota (n.a.): VOCs: Volatile Organic Chemicals in Private Drinking Water Wells, [<http://www.health.state.mn.us/divs/eh/hazardous/topics/vocs.html>], (Creation date: n.a.; retrieval date: 24.08.18); EPA (n.a.): Volatile Organic Compounds' Impact on Indoor Air Quality, [<https://www.epa.gov/indoor-air-quality-iaq/volatile-organic-compounds-impact-indoor-air-quality>], (Creation date: n.a.; retrieval date: 24.08.18).

¹⁴ US EPA (2014): Chlorinated solvent impact and remediation strategies for the dry cleaning industry, Lamar University, [https://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.highlight/abstract/5869], (Creation date: 08.2014; access date: 24.07.18).

Consumers

There are many different household consumer products that contribute to overall level of VOC indoor air pollution including detergents, floor care products, furniture and household fabrics, paint, personal care products and scenting products. VOCs from consumer products may contribute on average to 10-20 % of total VOCs in different indoor environments.

5 Alternative and Substitute Substances

The uses of chlorinated solvents are manifold, and for the use as solvent, it is likely that other less hazardous solvents can serve as alternatives. As alternatives, solvents that may be selected should not be chlorinated and should not present the same risks include flammable solvents such as isopropyl alcohols, other mineral spirits and combustible solvents such as terpenes, DBE, NMP and Alkyl Acetates.¹⁵ Any alternatives used as substitutes for hazardous substances must be free of hazardous properties to avoid regrettable substitution.

VOCs may not be fully replaceable in textiles and shoes industry. In order to minimize environmental and health effects and to use resources efficiently, the use of best available technology (BAT¹⁶) in textile industry is a standard requirement (e.g. use of closed systems). Highly hazardous VOCs that are listed by REWE Groups MRSL must be replaced. Alternatives for many VOCs are available. For toluene, alternatives may be for instance¹¹:

- A blend of cyclohexane and acetone;
- Methylcyclohexane-based adhesives may be used as substitutes;
- Water-based adhesives require upfront costs to achieve higher drying temperatures; but they use far fewer hazardous chemical ingredients.

Other examples for possible safer or greener alternatives¹⁷ are¹⁸:

Acetic acid, tetrahydrofuran, dimethyl ether, acetophenone, diethylene glycol, glycerol, benzyl benzoate, dimethyl sulfoxide (DMSO), hexane, tert-butanol, dimethyl ether, methanol, diethylene glycol, ethyl acetate, polyglycol E 200, dibutyl ether, ethylene glycol, propylene glycol.

For further information, the Chemsec Textile Guide offers access to a list of hazardous and safer surfactants and should be taken into account when a chemical inventory is prepared¹⁹.

¹⁵ Ph.D Wolf, Katy/ Yazdani, Azita/ Yates, Pamela (1991): Chlorinated Solvents: Will the Alternatives be Safer?, Journal of the Air & Waste Management Association, 41:8, p.1055-1061, <https://doi.org/10.1080/10473289.1991.10466899>.

¹⁶ Schönberger, H./ Schäfer, T. (2003): Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques for the Textiles Industry, Umweltbundesamt, [<https://www.umweltbundesamt.de/publikationen/beste-verfuegbare-techniken-in-anlagen>], (Creation date: 03.2003; access date: 24.07.18).

¹⁷ Ash, M./ Ash, I. (1996): The index of solvents, an international guide to 1700 products by trade name, chemical, application, and manufacturer, Brookfield, 1996.

¹⁸ Please note, that this cannot be seen as any endorsement or recommendation by REWE and cannot replace own in-depth assessment.

¹⁹ ChemSec (undated): Textiles come with a toxic footprint, [<http://textileguide.chemsec.org/find/textiles-come-with-a-toxic-footprint/>], (Creation date: undated; access date: 24.07.18).