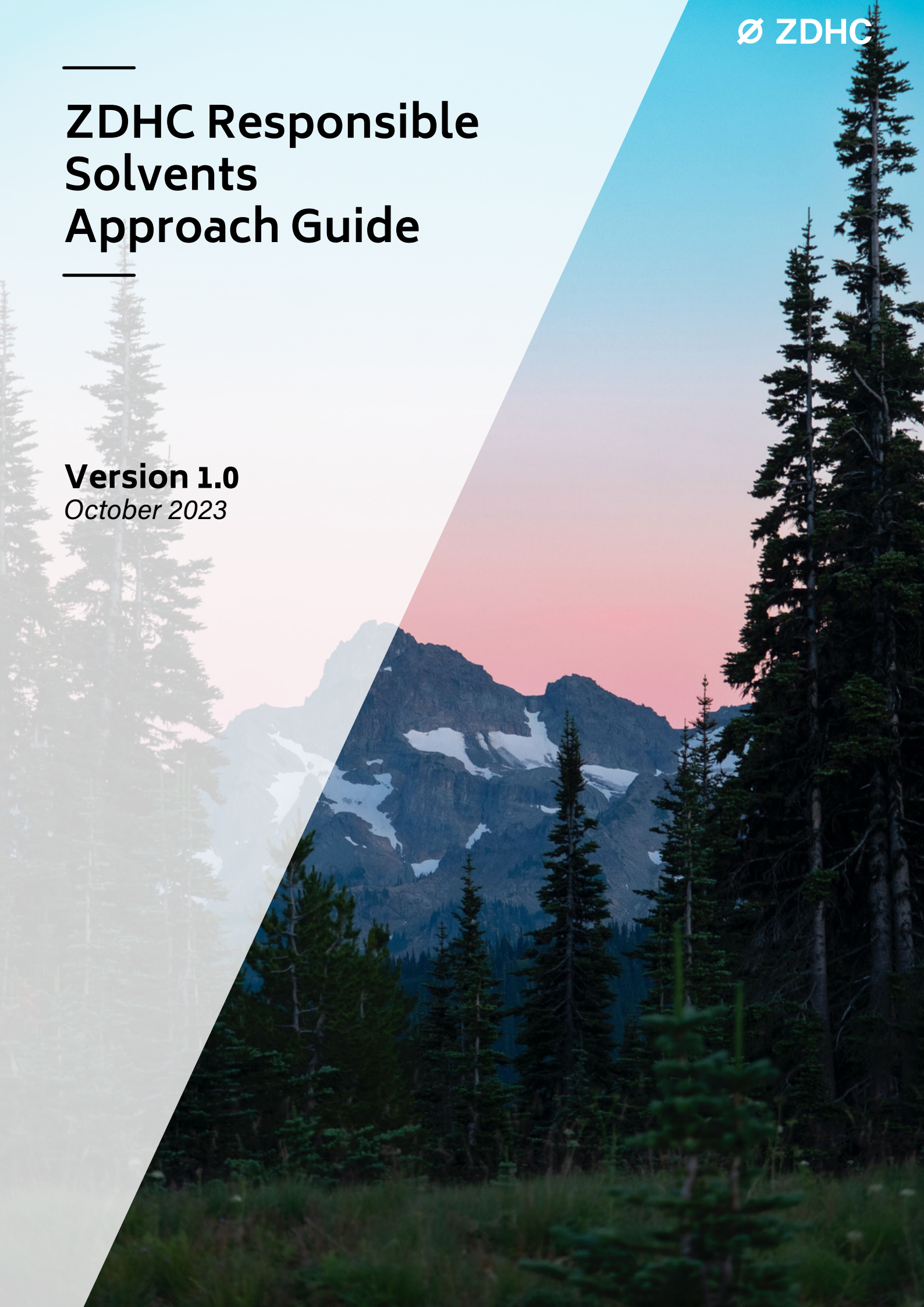

ZDHC Responsible Solvents Approach Guide

Version 1.0
October 2023



NOTES

ZDHC refers to the UN GHS (Globally Harmonized System of Classification and Labelling of Chemicals) as the internationally recognised standard for hazardous material classification and labelling. All the other national and/or regional existing schemes, derived from the implementation of the UN GHS, have to be considered included in the list of the accepted ZDHC standards for this purpose. To simplify the ZDHC Responsible Solvents Approach Guide comprehension, ZDHC uses the UN GHS throughout the document as its reference for hazard statements and pictograms in Safety Data Sheets (SDS) and labels in order to avoid local variables.

Any mentions of innovations and/or innovative practices within this document are provided as examples and shouldn't be construed as the only ones available. Organisations are responsible to conduct their own research into all possible solutions to determine the best one for them.

DISCLAIMERS

The ZDHC Foundation (hereinafter "ZDHC") Responsible Solvents Approach Guide is not intended to replace brand-specific requirements for chemical management, but to be supportive or complimentary to such requirements.

The information in this Responsible Solvents Approach Guide is provided for information only and does not guarantee the following:

- a) Compliance with, or take the place of, legal or regulatory requirements. Examples might include: stricter legal, local or regional regulatory requirements on the use, storage and transport of chemical products; or other requirements relating to the handling and disposal of chemical products, which shall supersede any requirements as set forth in this document.
- b) Compliance with, or conformance to, any national or international environmental or workplace safety requirements, including, but not limited to, relevant regulations and/or standards. Nor do the ZDHC Responsible Solvents Approach Guide replace above-mentioned regulations and/or standards.

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- e) For any results obtained or not obtained from the use of the ZDHC Responsible Solvents Approach Guide.

For the avoidance of doubt this Disclaimer applies to all related documents produced by the ZDHC Group.

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List of Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
APAO	Amorphous Poly Alpha Olefin
BHT	Butylated hydroxytoluene
CAS No.	Chemical Abstracts Service Number
CEN	European Committee for Standardization
CMS	Chemical Management System
CPASL	China Artificial & Synthetic Leather Committee of China Plastics Processing Industry Association
CPME	Cyclopentyl methyl ether
DMAC	N,N-Dimethylacetamide
DMFa	N,N-Dimethylformamide
EC	Emission and Exposure Controls
EHS	Environment, Health and Safety
EVA	Ethylene-vinyl acetate
FID	Flame Ionisation Detectors
FMD	Full Material Disclosures
GCCE	University of York's Green Chemistry Centre of Excellence
GHS	Globally Harmonized System of Classification and Labelling of Chemicals
GVL	Gamma-valerolactone
HAP	Hazardous Air Pollutants
HMA	Hot Melt Adhesives

IREBJAIST	Institute of Resources and Environment, Beijing Academy of Science and Technology
LEDA	Lishui Economic and Technological Development Zone Management Committee
LEV	Local Exhaust Ventilation
MOS	Metal oxide semiconductor
MRSL	Manufacturing Restricted Substance List
NEP	N-Ethyl-2-pyrrolidone
NIOSH	National Institute for Occupational Safety and Health
NMP	N-Methyl-2-pyrrolidone
OECD	Organisation for Economic Co-operation and Development
OEL	Occupational Exposure Limits
PA	Polyamides
PBT	Persistent, Bioaccumulative and Toxic
PID	Photoionisation Detectors
PPE	Personal Protective Equipment
PTE	Potential to Emit
PU	Polyurethane
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
REL	Recommended Exposure Limits
REM	Resource Efficiency Module
RtZ	Roadmap to Zero
SDS	Safety Data Sheet

SOP	Standard Operating Practice
STEL	Short Term Exposure Limit
STOT	Specific Target Organ Toxicity
TEC	Trichloroethylene
TLV	Threshold Limit Value
TBAc	Tertiary butyl acetate
TMO	2,2,5,5-Tetramethyloxolane
TPY	Tons per Year
TVOC	Total Volatile Organic Compounds
TWA	Time-Weighted Average
US EPA	United States Environmental Protection Agency
vPvB	Very Persistent and Very Bioaccumulative
VOC	Volatile Organic Compound

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Introduction

Objective

Organic solvents are used in various processes in the apparel and footwear industries. The ZDHC MRSL V3.1 includes a ban on the intentional use of specific organic and halogenated solvents in textile, leather and footwear production and is therefore a signal to the industry to take appropriate action to shift to safer alternatives.

While ZDHC recognises that these solvents will be termed as ZDHC MRSL non-conformant, the use of these solvents for specific applications in textiles and footwear require proper emission and exposure controls to ensure worker health and safety at facility level and reduce the environmental impact. The halogenated and organic solvents for which these controls should be implemented by a manufacturing facility have been marked as “EC” (Emission and Exposure Controls) in the ZDHC MRSL V3.1.

To support the industry in the transitional phase towards safer alternatives for these solvents, ZDHC has developed the “Responsible Solvents Approach Guide” that intends to:

- Guide facilities on the responsible use of solvents and solvent-based formulations.
- Advise on actions required to shift to safer alternatives and processes (such as highly controlled closed-loop systems) in the textile, leather, and footwear industries, with a focus on the ZDHC MRSL listed solvents.

The intention of this document is to drive positive transformation for a sustainable supply chain and minimise emissions and exposure to workers and the environment through the implementation of best practices.

Scope

The scope of the guide will cover:

- 1) Hazard profiling, toxicological/ecotoxicological information and occupational exposure limits (for VOCs) of ZDHC MRSL listed solvents and information to be interpreted from a Safety Data Sheet (SDS).
- 2) Use patterns in different applications and formulations for textile, leather, footwear, polymers.
- 3) Potential safer alternatives (including water-based solutions).
- 4) Chemical management (safe storage, handling and disposal) best practices including monitoring Volatile Organic Compounds (VOCs) workplace emissions through the calculation of VOCs in the input chemical inventory and using measuring devices to enable the planning of actions to reduce VOCs.
- 5) Training requirements and education of workers and employees handling these solvents/formulations.

Connectivity with other ZDHC guidelines

The ZDHC Responsible Solvents Approach Guide V1.0 is part of a series of guidelines and solutions from ZDHC to drive positive change in the industry towards sustainable chemical management. The document should be read in conjunction with:

- [ZDHC MRSL V3.1](#)
- [ZDHC MRSL Conformance Guidance V2.0](#)
- [ZDHC CMS Framework V1.0](#)
- [ZDHC CMS Technical Industry Guide V1.0](#)

Collaborative process and acknowledgments

The fundamental principle of collaboration at ZDHC was followed in the development of this document. We put out a 'Call to Action' to our ZDHC Signatories and reached out to the former Solvents Focus Group and other relevant industry experts. This resulted in the formation of a team of experts to provide inputs and ideas on the document content. Five focus groups were formed on the five topics listed in the document scope, based on the contribution that each focus group team member could provide from their experience and expertise. The ZDHC Sustainable Chemical Management (SCM) Competence Centre and Roadmap to Zero (RtZ) Delivery teams co-ordinated with these five focus groups from February 2023 through a series of calls, hackathons, e-mails and 1:1 calls to gather and collate inputs on the five topics. A draft document was then prepared by the SCM Competence Centre and reviewed by the Solvents Focus Group team members. The suggestions and comments received from them were incorporated into the draft, which was then sent for review to all ZDHC Signatories and Advisory Groups to receive feedback.

We acknowledge and thank the contribution of the Solvents Focus Group team members and experts for their assistance in the development of this document. For a full list of acknowledgements, please see the end of this document.

List of solvents in ZDHC MRSL V3.1

Table 1 shows the halogenated and organic solvents listed in the ZDHC MRSL V3.1. Formulations containing any of these listed solvents that are above the published formulation limits are non-conformant with the ZDHC MRSL. These solvents are listed in the ZDHC MRSL V3.1 for applicability to textiles, leather and polymers (rubber, foam, adhesives) along with the formulation limit (in mg/kg) for each of the three applicabilities.

The solvents where adequate emission and exposure controls should be implemented by a manufacturing facility have been marked as "EC" (Emission and Exposure Controls). These solvents are highlighted in *blue* in following table:

Two solvents are also listed under the 'Candidate List' which indicates their proposed addition to the next ZDHC MRSL update and encourages the innovation of alternatives.

Table 1: List of ZDHC MRSL solvents^[1]

Sr. No.	Solvent	CAS No.	Supplier Guidance	Formulation Limit
Halogenated solvents				
1	1,2-Dichloroethane	107-06-2	No intentional use	5 mg/kg
2	Benzyl chloride	100-44-7	No intentional use	50 mg/kg and 100 mg/kg for dyes
3	Methylene chloride	75-09-2	No intentional use	5 mg/kg
4	Trichloroethylene	79-01-6	No intentional use	40 mg/kg
5	<i>Tetrachloroethylene</i>	<i>127-18-4</i>	<i>No intentional use / EC (closed-loop solvent scouring)</i>	<i>5 mg/kg</i>
Organic solvents				
1	Benzene	71-43-2	No intentional use	50 mg/kg
2	Cresol (all isomers) o-Cresol m-Cresol p-Cresol	1319-77-3 95-48-7 108-39-4 106-44-5	No intentional use	500 mg/kg for each isomer (1500 mg/kg for all isomers)
3	<i>N,N-Dimethylacetamide (DMAC)</i>	<i>127-19-5</i>	<i>No intentional use / EC (solvent-based PU coating)</i>	<i>1000 mg/kg</i>
4	<i>N,N-Dimethylformamide (DMFa)</i>	<i>68-12-2</i>	<i>No intentional use / EC (solvent-based PU coating)</i>	<i>1000 mg/kg</i>
5	<i>N-Ethyl-2 pyrrolidone (NEP)</i>	<i>2687-91-4</i>	<i>No intentional use / EC (solvent-based PU coating)</i>	<i>1000 mg/kg</i>
6	<i>N-Methyl-2 pyrrolidone (NMP)</i>	<i>872-50-4</i>	<i>No intentional use / EC (solvent-based PU coating)</i>	<i>1000 mg/kg</i>

Table 1: List of ZDHC MRSL solvents^[1]

Sr. No.	Solvent	CAS No.	Supplier Guidance	Formulation Limit
7	<i>Toluene</i>	<i>108-88-3</i>	<i>No intentional use / EC (solvent-based PU coating)</i>	<i>500 mg/kg</i>
8	<i>Xylene (all isomers) o-Xylene m-Xylene p-Xylene</i>	<i>1330-20-7 95-47-6 108-38-3 106-42-3</i>	<i>No intentional use / EC (coating)</i>	<i>500 mg/kg for all isomers</i>
Candidate list				
1	2-Methoxypropanol	1589-47-5	NA	NA
2	Methanol	67-56-1	NA	NA

CHAPTER 1:

Safety and hazard identification of solvents in the ZDHC MRSL V3.1

1.1 Hazard profiling datasets

It is important for suppliers to identify and understand the hazards associated with solvents to ensure proper precautions are taken for their storage, handling and disposal.

The following section details the important datasets on hazards that need to be understood for solvents:

1.1.1 Hazard statements or H-Statements

These are listed in Section 2 of a SDS, characterising the whole chemical formulation, and are standardised statements on different kinds of hazards (physical, health, environmental) as outlined in the [GHS document](#).^[2] Each hazard statement has a code with a brief description of the hazard.

The H-Statements are in three series:

- 1) The H-200 series describes physical hazards
(e.g. H-225 — Highly flammable liquid and vapour)
- 2) H-300 series describes health hazards.
(e.g. H304 — May be fatal if swallowed and enters airways)
- 3) H-400 series describes environmental hazards
(e.g. H400 — Very toxic to aquatic life)

1.1.2 Precautionary statements or P-Statements

These are also listed in Section 2 of a SDS. The P-Statements provide information on precautions to be taken for each H-Statement and are grouped into five series:

- 1) P-100 series (General precautions)
- 2) P-200 series (Prevention precautions)
- 3) P-300 series (Response precautions)
- 4) P-400 series (Storage precautions)
- 5) P-500 series (Disposal precautions)

1.1.3 Hazard pictograms

These are images that convey the hazard pictorially. GHS has harmonised hazards into nine pictograms as listed in Table 2. Each pictogram is an image inside a red diamond on a white background. The pictogram is related to the hazard class and category of classification as per the GHS. The hazard pictograms are displayed in Section 2 of the SDS, if applicable. Not every H-Statement is associated with a hazard pictogram.

Table 2: GHS hazard pictograms^[2]






Hazard Pictogram	Symbol Description	Represents/Convey
	EXPLODING BOMB	Explosive, self-reactive, organic peroxides
	FLAME	Flammable, self-reactive, pyrophoric, self-heating, emits flammable gas, organic peroxides
	FLAME OVER CIRCLE	Oxidisers
	GAS CYLINDER	Gases under pressure
	CORROSION	Corrosive to skin and metal parts

Table 2: GHS hazard pictograms^[2]

Hazard Pictogram	Symbol Description	Represents/Convey
	SKULL AND CROSSBONES	Acute toxicity
	EXCLAMATION MARK	Irritant, dermal sensitiser, acute toxicity (harmful), narcotic effects, respiratory tract irritation
	HEALTH HAZARD	Carcinogen, respiratory sensitiser, reproductive toxic, target organ toxic, mutagenicity, aspiration toxicity
	ENVIRONMENT	Environmental hazard

1.1.4 Occupational Exposure Limits (OELs)

OEL indicates the level of admissible exposure, for a length of time (usually eight hours), to a chemical or physical hazard that is not likely to affect the health of a worker. The OELs for chemical substances are established based on the chemical properties of the substance, experimental studies on animals and humans, toxicological and epidemiological data. Different organisations may use different terminology for the OEL. The ACGIH term is the Threshold Limit Value (TLV) while the NIOSH term is the Recommended Exposure Limits (REL). These are expressed in terms of:

- **Time-Weighted Average (TWA):** Is the average concentration of a hazardous substance in the air, averaged over the course of an eight hour workday, or a 40 hour workweek, to which workers are repeatedly exposed.
- **Short Term Exposure Limit (STEL):** Is a 15 minute exposure to the substance that should not be exceeded at any time during the eight hour workday. The STEL is used to account for acute effects of substances that have primarily chronic effects.

Peak exposures of workers should be controlled and should not exceed the STEL limits. If STEL limits are not available, then the exposure should not exceed five times the eight hour TWA. If TWA limits are not available, then the exposure should not exceed one fifth of STEL over eight hours. The unit of measurement for both the Threshold Limit Value — Time-Weighted Average (TLV-TWA) and the Threshold Limit Value — Short Term Exposure Limit (TLV-STEL) is ppm or mg/m³. In all cases, the local regulation for Occupational Exposure Limits, wherever applicable, should be followed.

The OELs are described in Section 8 of a GHS compliant SDS, along with information on required engineering controls and personal protection equipment (PPE).

1.1.5 Physical and chemical properties

For solvents, specific physical and chemical properties are important to identify their Potential to Emit to the air as Volatile Organic Compounds (VOCs) or hazardous air pollutants (HAPs). These properties are also important to plan safe storage conditions.

The list of physical and chemical properties are described in Section 9 of a GHS compliant SDS and the ones relevant to solvents are:

- **Boiling point** — to determine the Potential to Emit as a VOC.
- **Vapour pressure** — to determine the potential for being a VOC.
[A carbon-containing solvent with a boiling point $\leq 250^{\circ}\text{C}$ at standard pressure and a vapour pressure ≥ 0.01 kPa (or 10Pa) at 293.15K is classified as a VOC].
- **Flash point (for liquids)** — to determine safe storage requirements.
[A liquid solvent with a flash point $< 93^{\circ}\text{C}$ is classified as a flammable liquid. Segregation of such solvent containers in the chemical stores with proper fire safeguards is essential].

In addition to the above, information on toxicological and ecotoxicological parameters can be found in Sections 11 and 12 of a GHS compliant SDS.

Information on toxicological effects include acute oral, dermal (in terms of LD50 values) and inhalative toxicity (in terms of LC50 values), skin corrosion, eye/skin damage or irritation, respiratory/skin sensitisation, carcinogenicity, mutagenicity, reprotoxicity, and Specific Target Organ Toxicity (STOT). Ecotoxicological data includes aquatic toxicity (in terms of LC50/EC50 values) and biodegradability/ bioaccumulation potential.

1.2 Hazard profiling of solvents in the ZDHC MRSL V3.1

This section profiles the seven solvents listed as EC in the ZDHC MRSL V3.1 with details on their hazard datasets:

- Hazard statements
- Important precautionary statements
- Occupational Exposure Limit (OEL)
- Physical and chemical properties

Considerations are also detailed for emission and exposure control of each solvent based on their hazard profiles.

1.2.1 Tetrachloroethylene (CAS No. 127-18-4)



Hazard statements

- **Aquatic Chronic, Category 2: H411** — Toxic to aquatic life with long lasting effects.
- **Carcinogenic, Category 2: H351** — Suspected of causing cancer.
- **Eye Irritant, Category 2: H319** — Causes serious eye irritation.
- **Skin Irritant, Category 2: H315** — Causes skin irritation.
- **Skin Sensitiser, Category 1: H317** — May cause an allergic skin reaction.
- **STOT Single Exposure, Category 3: H335** — May cause irritation of the upper respiratory tract.

Important precautionary statements

- **P280** — Wear protective gloves/face protection/protective clothing/respiratory protection/protective footwear.
- **P302+P352** — IF ON SKIN: Wash with plenty of water.
- **P305+P351+P338** — IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

OELs

- **TLV-TWA (8 hours)** — 138 mg/m³
- **TLV-STEL** — 257 mg/m³

Physical and chemical properties

- Vapour pressure at 20°C is 1106 Pa and boiling point at atm pressure is 121°C.
- Tetrachloroethylene is classified as a VOC and can impact worker health and safety unless proper respiratory precautions are put in place.

i Considerations for emission and exposure control for tetrachloroethylene

Tetrachloroethylene is banned from intentional use in the ZDHC MRSL V3.1 and should be replaced with a safer alternative as it is suspected to be carcinogenic. If unintentionally discharged into wastewater, it can have long-term damaging effects on aquatic life. Exposure to tetrachloroethylene can cause eye irritation, skin sensitisation and respiratory irritation. Therefore, tetrachloroethylene should be used in a closed-loop system with proper engineering controls. If this is not possible, proper PPE should be given to workers handling the solvent.

1.2.2 N,N-Dimethylacetamide (DMAC) (CAS No. 127-19-5)



Hazard statements

- **Acute Toxicity, Category 4: H312+H332** — Harmful if in contact with skin or if inhaled.
- **Reprotoxic, Category 1B: H360D** — May damage an unborn child.

Important precautionary statements

- **P261** — Avoid breathing dust/fume/gas/mist/vapours/spray.
- **P280** — Wear protective gloves/face protection/protective clothing/respiratory protection/protective footwear.
- **P304+P340** — IF INHALED: Remove the person to fresh air and keep at rest in a position comfortable for breathing.

OELs:

- **TLV-TWA (8 hours)** — 36 mg/m³
- **TLV-STEL** — 72 mg/m³

Physical and chemical properties

- Vapour pressure at 20°C is 204 Pa and boiling point at atm pressure is 166°C.
- DMAC is classified as a VOC and can impact worker health and safety unless proper respiratory precautions are put in place.

i Considerations for emission and exposure control for DMAC

DMAC is banned from intentional use in the ZDHC MRSL V3.1 and should be replaced with a safer alternative as it is a reprotoxic chemical. It can also be harmful to workers when exposed to vapours. Therefore, DMAC should be used in a closed-loop system with proper engineering controls or if this is not possible, proper face masks should be given to workers handling the solvent.

1.2.3 N,N-Dimethylformamide (DMFa) (CAS No. 68-12-2)



Hazard statements

- **Acute Toxicity, Category 4: H312+H332** — Harmful if in contact with skin or if inhaled.
- **Eye Irritant, Category 2: H319** — Causes serious eye irritation.
- **Flammable. Liquid. Category 3: H226** — Flammable liquid and vapour.
- **Reprotoxic, Category 1B: H360D** — May damage an unborn child.

Important precautionary statements

- **P210** — Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
- **P280** — Wear protective gloves/face protection/protective clothes/eye goggles.
- **P370+P378** — In case of fire: Use ABC powder extinguisher to extinguish.

OELs

- **TLV-TWA (8 hours)** — 15 mg/m³
- **TLV-STEL** — 30 mg/m³

Physical and chemical properties

- Vapour pressure at 20°C is 332 Pa and boiling point at atm pressure is 153°C.
- Flash point = 58°C.
- DMFa is classified as a VOC and can impact worker health and safety unless proper respiratory precautions are put in place.

i Considerations for emission and exposure control for DMFa

DMFa is banned from intentional use in the ZDHC MRSL V3.1 and should be replaced with a safer alternative as it is a reprotoxic chemical. It can also be harmful to workers exposed to it in terms of its toxicity and serious eye irritation. Therefore, the use of DMFa should be done with proper engineering controls and protective equipment given to workers handling the solvent. Due to its low flash point, it is classified as a flammable liquid and should be stored separately with all fire safety precautions, avoiding direct exposure to sunlight and where the maximum temperature of the storage area does not exceed 30°C. Water should not be used as an extinguishing media, only foam or CO₂ type fire extinguishers should be used.

1.2.4 N-Ethyl-2-pyrrolidone (NEP) (CAS No. 2687-91-4)



Hazard statements

- **Eye Damage, Category 1: H318** — Causes serious eye damage.
- **Reprotoxic, Category 1B: H360Df** — May damage an unborn child. Suspected of damaging fertility.

Important precautionary statements

- **P280** — Wear face protection/eye goggles/protective clothing.
- **P305+P351+P338** — IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

OELs

- **TLV- TWA (8 hours)** — 23 mg/m³
- **TLV — STEL** — 46 mg/m³

Physical and chemical properties

- Vapour pressure at 20°C is 36 Pa and boiling point at atm pressure is 202°C.
- NEP is classified as a VOC and can impact worker health and safety unless proper respiratory precautions are put in place.

i Considerations for emission and exposure control for NEP

NEP is banned from intentional use in the ZDHC MRSL V3.1 and should be replaced with a safer alternative as it is a reprotoxic chemical. It can also be harmful to the eyes of workers exposed to it. Therefore the use of NEP requires correct protective equipment to be given to workers handling the solvent.

1.2.5 N-Methyl-2-pyrrolidone (NMP) (CAS No. 872-50-4)



Hazard statements

- **Skin irritant, Category 2: H -315** — Causes skin irritation.
- **Eye Irritant, Category 2: H319** — Causes serious eye irritation.
- **Reprotoxic, Category 1B: H360D** — May damage an unborn child.
- **STOT Single Exposure, Category 3: H335** — May cause respiratory irritation.

Important precautionary statements

- **P280** — Wear protective gloves/face protection/protective clothing/respiratory protection.
- **P305+P351+P338** — IF IN EYES: Rinse cautiously with water for several minutes.
- **P304+P340** — IF INHALED: Remove the person to fresh air and keep at rest in a position comfortable for breathing.

OELs

- **TLV-TWA (8 hours)** — 40 mg/m³
- **TLV-STEEL** — 80 mg/m³

Physical and chemical properties

- Vapour pressure at 20°C is 35 Pa and boiling point at atm pressure is 202°C.
- NMP is classified as a VOC and can impact worker health and safety unless proper respiratory precautions are put in place.

i Considerations for emission and exposure control for NMP

NMP is banned from intentional use in the ZDHC MRSL V3.1 and should be replaced with a safer alternative as it is a reprotoxic chemical. It can also be harmful to the eyes of workers exposed to it and cause respiratory irritation. Therefore the use of NMP requires correct protective equipment to be given to workers handling the solvent.

1.2.6 Toluene (CAS No. 108-88-3)



Hazard statements

- **Aspiration Toxic, Category 1: H304** — May be fatal if swallowed and enters the airways.
- **Flammable Liquid, Category 2: H225** — Highly flammable liquid and vapour.
- **Reprotoxic, Category 2: H361d** — Suspected of damaging an unborn child.
- **Skin Irritant, Category 2: H315** — Causes skin irritation.
- **STOT Repeated Exposure, Category 2: H373** — May cause damage to organs through prolonged or repeated exposure.
- **STOT Single Exposure, Category 3: H336** — May cause drowsiness or dizziness.
- **Aquatic Chronic Category 3: H412** — Harmful to aquatic life with long lasting effects.

Important precautionary statements

- **P210** — Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
- **P280** — Wear protective gloves/face protection/protective clothing/respiratory protection.
- **P302+P352** — IF ON SKIN: Wash with plenty of water.
- **P304+P340** — IF INHALED: Remove the person to fresh air and keep at rest in a position comfortable for breathing.
- **P370+P378** — In case of fire: Use ABC powder extinguisher to extinguish.

OELs

- **TLV- TWA (8 hours)** — 192 mg/m³
- **TLV — STEL** — 384 mg/m³

Physical and chemical properties

- Vapour pressure at 20°C is 2980 Pa and boiling point at atm pressure is 111°C.
- Toluene is classified as a VOC and can impact worker health and safety unless proper respiratory precautions are put in place.
- Flash point = 4°C, indicating it to be a highly flammable liquid requiring special precautions for storage.

i Considerations for emission and exposure control for toluene

Toluene is banned from intentional use in the ZDHC MRSL V3.1 and should be replaced with a safer alternative as it is suspected to be reprotoxic, an aspiration toxic chemical and a Specific Target Organ Toxic substance. It can also be fatal if swallowed or inhaled. Therefore, the use of toluene requires correct protective equipment to be given to workers handling the solvent. Being a highly flammable liquid, it should be stored separately in a cool, dry place with all fire safety precautions in place. ABC powder fire extinguishers should be installed at the storage place. It is also an environmental hazard in terms of aquatic toxicity and should be disposed of in a responsible manner.

1.2.7 Xylene

(CAS No. 1330-20-7) —
all isomers



Hazard statements

- **Acute Toxic, Category 4: H312+H332** — Harmful if in contact with skin or if inhaled.
- **Aquatic Chronic 3: H412** — Harmful to aquatic life with long lasting effects.
- **Aspirational. Toxicity, Category 1: H304** — May be fatal if swallowed and enters the airways.
- **Eye Irritant, Category 2: H319** — Causes serious eye irritation.
- **Flammable Liquid, Category 3: H226** — Flammable liquid and vapour.
- **Skin Irritant, Category 2: H315** — Causes skin irritation.
- **STOT Repeated Exposure, Category 2: H373** — May cause damage to organs through prolonged or repeated exposure (oral).
- **STOT Single Exposure, Category 3: H335** — May cause respiratory irritation.

Important precautionary statements

- **P210** — Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
- **P280** — Wear protective gloves/face protection/protective clothing/respiratory protection.
- **P302+P352** — IF ON SKIN: Wash with plenty of water.
- **P304+P340** — IF INHALED: Remove the person to fresh air and keep at rest in a position comfortable for breathing.
- **P305+P351+P338** — IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

OELs

- **TLV-TWA (8 hours)** — 221 mg/m³
- **TLV — STEL** — 442 mg/m³

Physical and chemical properties

- Vapour pressure at 20°C is 748 Pa and boiling point at atm pressure is 131°C.
- Xylene is classified as a VOC and can impact worker health and safety unless proper respiratory precautions are put in place.
- Flash point = 25°C, indicating it to be a highly flammable liquid requiring special precautions for storage.

i Considerations for emission and exposure control for xylene

Xylene and its isomers are banned from intentional use in the ZDHC MRSL V3.1 and should be replaced with a safer alternative. It is an aspiration toxic chemical, as well as a Specific Target Organ Toxic substance through oral exposure. It can be fatal if swallowed or inhaled. Therefore, the use of xylene requires correct protective equipment to be given to workers handling the solvent. Being a highly flammable liquid, it should be stored separately in a cool, dry place with all fire safety precautions in place. ABC powder fire extinguishers should be installed at the storage place.

1.3 Important Sections in a Safety Data Sheet (SDS) to gather information on hazard datasets

A Safety Data Sheet (SDS) is an important document for a formulator to communicate hazards and precautions about a chemical formulation or substance. As a best practice, every formulator must share an updated SDS with the formulation user, that conveys all information regarding any of the below international standards:

- Globally Harmonised System of Classification and Labelling (GHS)
- EC 1907/2006 (REACH)
- EU 2020/878
- ISO 11014:2009
- ANSI Standard Z400.1-2004
- JIS Z 7250:2005 (Part 1)

Under GHS guidelines, hazards are divided into three TYPES: Physical, Health and Environmental. Each hazard type is further subdivided into hazard CLASSES and each class is further divided into hazard CATEGORIES ranging from Category 1: Severe hazards to Category 5: Least severity. Each hazard category is assigned specific H-Statements, corresponding P-Statements and a pictogram to depict the hazard symbolically, if applicable.

There are 16 sections that are mandatory within an SDS:

- 1) Identification of the substance/mixture and the company
- 2) Hazards identification
- 3) Composition/information on ingredients
- 4) First aid measures
- 5) Fire fighting measures
- 6) Accidental release measures
- 7) Handling and storage
- 8) Exposure controls/ personal protection

- 9) Physical and chemical properties
- 10) Stability and reactivity
- 11) Toxicological information
- 12) Ecological information
- 13) Disposal considerations
- 14) Transport information
- 15) Regulatory information
- 16) Other information

A textile or footwear manufacturer should read the following sections carefully to interpret the hazards and plan precautions for safe handling, storage and disposal of the chemicals used in the facility, especially for solvents.

Section 1: Gives information about the chemical manufacturer, phone number, email address and contact name, which are useful in the case of an accident or the need for further information.

Section 2: Gives information about the hazard classification of the chemical through the H-Statements and pictograms. It also lists out the generic P-Statements in terms of storage and handling, linked to the hazard classification.

Section 3: Where a chemical product is a formulation/mixture and not a pure substance Section 3 of an SDS provides information on hazardous ingredients in this formulation/mixture, the percentage of each ingredient used and the hazard(s) associated with each ingredient.

Section 4: Details the requirements for first aid, as per the routes of exposure. If any special medical treatment is described for a chemical accident, it should be available in the facility.

Section 5: Provides details for flammable solvents. It is important to note not only the suitable but also the unsuitable extinguishing media. The relevant fire safety precautions should be available at the storage place.

Section 7: Advises precautions required for safe storage of the chemical. In case the chemical is flammable, it should be stored separately in a dedicated area where all fire safety precautions are in place and limited access is given to workers. Incompatible chemicals, mentioned in this section, should not be stored together.

Section 8: Outlines the Occupational Exposure Limits (OELs), that should be monitored in the workplace to ensure that exposure limits are not exceeded, as well as detailing PPE requirements and specifications. A facility should follow these specific PPE instructions to ensure that the correct equipment is provided and used by workers. If specific engineering controls are mentioned in this section, facilities should implement these to ensure worker health and safety.

Section 9: Details Physical and chemical properties, especially providing information on boiling point, flash point and vapour pressure for solvents to calculate the potential to emit as a VOC.

Sections 11 and 12: Provide further information on toxicological and ecotoxicological properties of the formulation or substance.

Section 13: Outlines generic disposal and treatment methods (specific disposal containers, methods and precautions for incineration or landfill). These should be followed for disposal of unused chemical waste and containers.

A SDS should be prepared by a trained expert, with well documented training records, including any revisionary training. The SDS must be issued in the official language of the country where the product is placed on the market.

Formulators should revise their SDS without delay on the following occasions:

- Any change has been made in the product or formulation that may affect the earlier hazard classification.
- New information is available which may affect the risk management measures (storage, handling, disposal).
- New information is available on hazard classification.
- An authorisation has been granted under Annex XIV for that particular substance under EU REACH Article 31(9).
- Any restriction has been imposed under Annex XVII on a substance or mixture under EU REACH Article 31(9).

In case the Competent Authority in a country has a specified time limit within which information in the SDS should be revised, then the formulator needs to revise as per the local law. (Under GHS, Competent Authority is defined as any national body or authority designated or otherwise recognised as such, in connection with implementation of GHS.)

CHAPTER 2:

Use patterns in different applications and formulations for textile, leather, footwear, polymers

Solvents can be used as such in on-site manufacturing processes in footwear, fibres and synthetic coated fabric (coated fabric with leather like aspects) and as ingredients in formulations for specific applications such as cleaning, degreasing, inks, coatings, adhesives, glues, lacquers and thinners.

The use patterns of the solvents marked as 'EC' in the ZDHC MRSL V3.1 in different applications and formulations for textiles, leather, footwear, polymers are listed in Table 3 below.

Table 3: Use pattern summary

Sr. No.	Solvent	CAS No.	Manufacturing Processes	Ingredients in Formulations
Halogenated solvents				
1	Tetrachloroethylene	127-18-4	<ul style="list-style-type: none"> Solvent scouring Coatings Dry cleaning Spot cleaning 	<ul style="list-style-type: none"> Printing inks Paints Adhesives Cleaning solvents
Organic solvents				
2	N,N-Dimethylacetamide (DMAC)	127-19-5	<ul style="list-style-type: none"> Solvent in acrylic fibre Solvent in PU elastane yarns Solvent in meta-aramid fibres 	<ul style="list-style-type: none"> Adhesives PU based polymer dispersions for printing and coating

Table 3: Use pattern summary

Sr. No.	Solvent	CAS No.	Manufacturing Processes	Ingredients in Formulations
3	N,N-Dimethylformamide (DMFa)	68-12-2	<ul style="list-style-type: none"> PU elastomers PU dispersions for synthetic coated fabric PU soles As a solvent in non-woven fabrics Acrylic fibres spinning (as a substitute of DMAC) Solvent for PU-based coating on fabric 	<ul style="list-style-type: none"> Solvent-based PU resin Solvent-based TPU Coatings PU based polymer dispersions for printing and coating Adhesives Degreasing products Cleaning solvent Printing inks Carrier for inks & dyes Booster in PVC & VAM co-polymers Surfactants & fluorescent whitening agents (FWAs)
4	N-Ethyl-2 pyrrolidone (NEP)	2687-91-4	<ul style="list-style-type: none"> Coating Water-based PU 	<ul style="list-style-type: none"> PU based polymer dispersions for printing and coating
5	N-Methyl-2 pyrrolidone (NMP)	872-50-4	<ul style="list-style-type: none"> Water-based PU Resins Coating 	<ul style="list-style-type: none"> Paint stripping agent PU based polymer dispersions for printing and coating
6	Toluene	108-88-3	<ul style="list-style-type: none"> Solvent in leather finishing Cleaning agent for utilities Solvent in synthetic coated fabric manufacture in washing Solvent for PU/acrylic coating on fabrics Coating 	<ul style="list-style-type: none"> Glue and adhesives Yellow glue Cleaning agent Solvent-based primer Printing inks Polymer dispersions for printing and coating Polystyrene based resins Lacquers Thinners
7	Xylene (all isomers)	1330-20-7	<ul style="list-style-type: none"> Solvent in leather finishing Cleaning agent for utilities Solvent in synthetic coated fabric manufacture in washing 	<ul style="list-style-type: none"> Adhesives Polymer dispersions for printing and coating Polystyrene based resins Lacquers Thinners Printing inks Oil extractants Cleaning agents Solvent in finishing agents

Safer alternatives

3.1 Approaches to finding safer alternatives to solvents

Choosing a substance that is least regulated is not a guarantee that it is safer or that its hazard properties are fully understood. It is a challenge to identify a solvent alternative that can be substituted with minimal adjustments to the process. Substituting solvents with similar chemical structures, but with similar hazard properties, can lead to regrettable substitutes.

For example, The inclusion of trichloroethylene (TCE) on REACH's Authorisation List resulted in the substitution of TCE with tetrachloroethylene (perc). Research has indicated that perc is a suspected carcinogen and aquatic toxicant and therefore not likely to result in adequate risk reduction.^[3] Therefore, a full evaluation of a chemical's potential hazards to human and ecological health should be undertaken to avoid such a regrettable substitution.

While the focus is to select the least hazardous option, it is important to balance these decisions with other impact metrics. To the greatest extent possible, selection of safer alternatives should be balanced against other sustainability attributes like circularity, climate impacts, equity, and social justice. Worker's health and safety as well as ecological concerns should be paramount.

To avoid regrettable substitutes, substances should be verified against rigorous hazard criteria. Apart from GHS classification, there are many transparent hazard methodologies available to assist in the identification of safer solvent alternatives. For example, the US EPA Design for the Environment Alternatives Assessment Criteria for Hazard Evaluation is a publicly available methodology.^[4]

Conducting an alternatives assessment will help to fully understand the broader implications of these decisions in combination with exposure considerations, changes in performance, cost effectiveness, etc.^[5]

3.1.1 OECD Minimum Safer Criteria for decision-making

In 2021, the OECD published guidance on Key Considerations for the Identification and Selection of Safer Chemical Alternatives.^[6] This guidance established a broad agreement on the approach and selection criteria for safer chemical alternatives. It states that the minimum decision-making threshold, when selecting a candidate alternative, should NOT be high concern for:^[2]

- Carcinogenicity
- Germ cell mutagenicity
- Reproductive/developmental toxicity
- PBT
- vPvB

It is important to note that this is the minimum threshold for selection, and depending on the context of the analysis and the substance that is targeted for substitution, additional criteria should be considered.

The OECD guidance (2021) suggests two steps to assess substances as potentially safer alternatives:

- 1) Screen out chemicals included on authoritative lists that have known hazard concerns.
- 2) Conduct a comparative hazard assessment that incorporates, at a minimum, a broad set of human health, ecological and physical hazards.^[6]

This approach goes beyond the assessment requirements for most SDS disclosures, which typically only disclose classifiable hazards for components present above certain amounts in a product. It also encompasses the assessment of endpoints without specific GHS criteria such as endocrine activity/disruption, neurotoxicity and persistence accompanied with bioaccumulation or mobility and toxicity.

3.1.2 Functional substitution to eliminate the need for a solvent entirely

The incorporation of functional substitution into the evaluation and decision-making process can help compare alternatives on a broader range instead of a narrower chemical-to-chemical comparison. Functional substitution considers potential substitutes based on the desired function rather than the properties of a chemical. As a result, changes to the process, product, or the service are considered.^[7] This may result in transitioning to processes that eliminate the need for hazardous substances altogether. This has already been successfully demonstrated in synthetic coated fabric for water-based polyurethane dispersion technologies eliminating the need for DMFa.^[8] Details on DMFa phase-out are provided in Chapter 6 of this document.

3.1.3 Products from ZDHC Gateway conformant to ZDHC MRSL V3.1

Conformance of a formulation to the ZDHC MRSL is an indication of worker and consumer safety. ZDHC has approved third-party certifiers for conformance of chemical formulations to the ZDHC MRSL V3.1. The ZDHC Gateway contains a database of ZDHC MRSL conformant commercial chemical formulations that can be used by the textile, leather and footwear value chain. Suppliers can check their input chemical inventory with the ZDHC Gateway database to confirm MRSL conformant chemistry.

Alternatively, suppliers can search on the ZDHC Gateway to find safer alternatives. The steps to be followed by a supplier to find alternatives in the ZDHC Gateway are:

- 1) Log in to the supplier's ZDHC Gateway account.
- 2) Click on "Browse by Substrate"
- 3) Choose the appropriate substrate (Leather, Synthetic, Textile, Adhesives, Foams, Rubber).
- 4) Choose the use category within the substrate.
- 5) This will lead to the next page on the ZDHC Gateway where you can choose the applicable use type from the drop down options.

- 6) A list of all formulations certified for ZDHC MRSL V3.1 at appropriate ZDHC MRSL conformance levels will be displayed for the use type chosen. A supplier can then review the appropriate chemical formulation and contact the respective chemical manufacturer.

Shown below in Figure 1 and Figure 2 is a snapshot of "Textile" as the chosen substrate and "Textile Finishing Auxiliaries" as the use category:

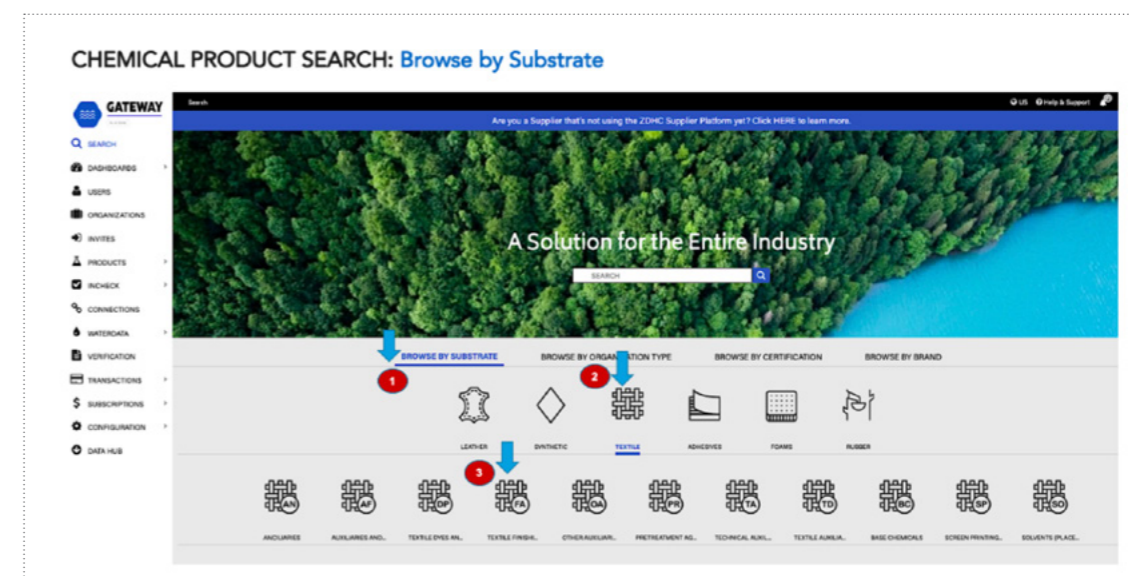


Figure 1: Chemical product search on ZDHC Gateway (Browse by substrate) — Part I

Within this use category, the below snapshot demonstrates the different use types and the list of formulations displayed:

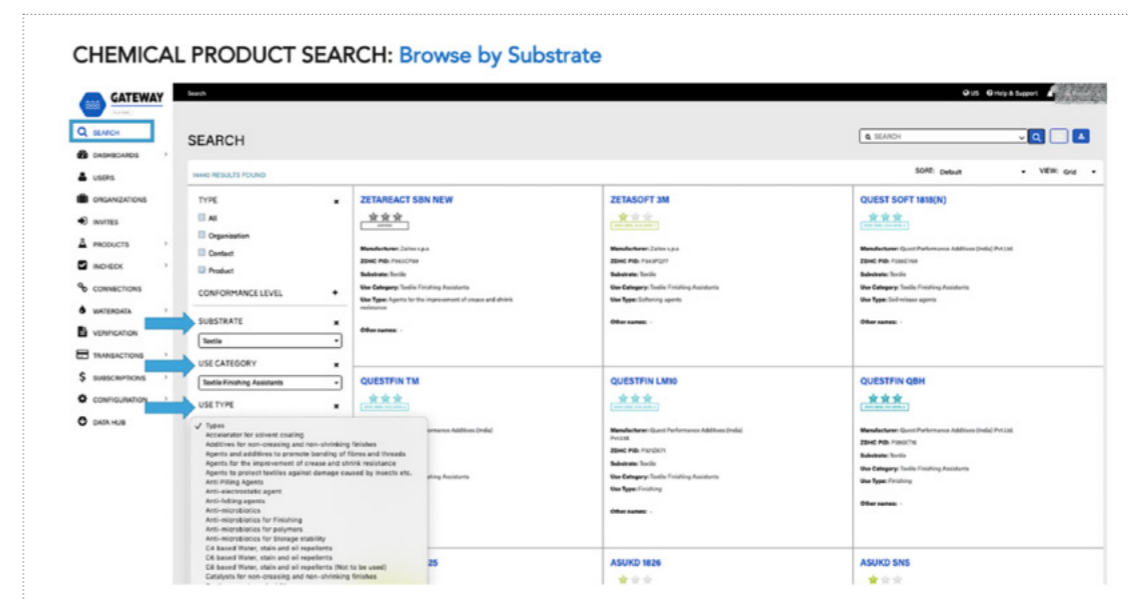


Figure 2: Chemical product search on ZDHC Gateway (Browse by substrate) — Part II

3.1.4 Resources for finding safer solvents

There are various tools and resources available that can help to identify safer alternatives to those solvents currently listed in the ZDHC MRSL V3.1. Table 4 lists out these resources. This is not an exhaustive list and other tools, or combinations of tools, may be needed to make informed substitution decisions.

Table 4: Tools and resources for finding and assessing safer solvents

Type	Name	Features
Based on chemical properties	Hansen Solubility Parameters ^[9]	<ul style="list-style-type: none"> Hansen Solubility Parameters are important properties that can be used to identify candidate solvents based on the "like dissolves like" principle by considering dispersion (δ_D), polarity (δ_P), and hydrogen bonding (δ_H) parameters. Comparing these parameters can help find effective combinations of solvents, including ones that were not ideal on their own. Stand-alone software is available for a fee.
Positive chemicals list	US EPA's Safer Chemical Ingredients List ^[10]	<ul style="list-style-type: none"> Features 100 solvents that currently meet standard criteria and are recognised as best in class for their functional use. Chemicals are marked to signify the level of confidence in the underlying assessment (green or half-green) or whether substances have some associated hazards (yellow triangle) but still represent a safer option when compared to conventional counterparts.
Solvent specific guidance	GlaxoSmithKline's Solvent Sustainability Guide ^[11]	<ul style="list-style-type: none"> Incorporates assessment of common solvents against multiple criteria metrics like human health, environmental impact, waste, flammability, reactivity, lifecycle, and regulatory restriction.

Table 4: Tools and resources for finding and assessing safer solvents

Type	Name	Features
Frameworks & Approaches	NRC's A Framework to Guide Selection of Chemical Alternatives ^[12]	<ul style="list-style-type: none"> The seminal guidance for a chemical alternatives assessment, akin to the "Red Book" for risk assessment. Covers how to assess chemicals in the context of their human health and ecological hazards, exposures, cost, performance, and life cycle impacts^[7].
	Interstate Clearinghouse Alternatives Assessment Guide (V1.1) ^[13]	<ul style="list-style-type: none"> Offers a flexible approach to conducting chemical alternatives assessments that can be tailored to meet the needs of various organisations. Incorporates different levels of guidance, ranging from simple to complex, for various modules such as hazard, performance, cost & availability, exposure assessment, material management, social impact, and life cycle.
Free web-based tools	CleanerSolutions Database (TURI) ^[14]	<ul style="list-style-type: none"> Helps users find products, replace solvents, and evaluate product safety for various products used for surface cleaning.
	Pollution Prevention Options Analysis System – P2OASYS (TURI) ^[15]	<ul style="list-style-type: none"> Assists users in organising, comparing, and evaluating relevant chemicals and process data to better identify and adopt safer alternatives.
	Prio (KEMI) ^[16]	<ul style="list-style-type: none"> Allows users to upload an inventory of chemicals, search for available hazards and environmental information, prioritise the substances of concern, and conduct substitution.
	MarketPlace ^[17]	<ul style="list-style-type: none"> Allows users to find commercially available, safer alternatives.

3.1.5 Potential chemical and process substitutes for ZDHC MRSL listed solvents

There are available potential chemicals that can be used as substitutes to the listed ZDHC MRSL V3.1 solvents with proper emission and exposure controls. Table 5 lists out these potential substitutes.

Processes to eliminate the use of solvents can also be implemented as alternatives. Table 6 gives examples of such processes.

Table 5: Potential chemical substitutes for specific functions

Sr. No.	Candidate Alternative	Function	DMFa / DMAC	NMP / NEP	Tetrachloro-ethylene
1	Cyclohexane & propan-2-o ^[18]	Textile washing and cleaning			✓
2	Isoalkanes C11-15 & 3,5,7-Trimethyldecane ^[19]	Textile washing and cleaning			✓
3	KJCMFA-100 ^[20]	PAI, PI, nylon, and PUR synthesis	✓	✓	
4	Methyl 408 and Ethyl 408 ^[21]	Cleaning (textile connection unclear)		✓	✓
5	High flash point hydrocarbons (DF-2000™, EcoSolv [®] ^{[22][23]}	Dry cleaning			✓

Table 5: Potential chemical substitutes for specific functions

Sr. No.	Candidate Alternative	Function	DMFa / DMAC	NMP / NEP	Tetrachloro-ethylene
6	Dihydrolevoglucosenone (Cyrene™) ^[8]	Polyurethane synthetic coated fabric	✓		
7	Dimethyl isosorbide ^[8]		✓		
8	Gamma-valerolactone ^[8]		✓		
9	Cyclopentyl methyl ether (cPME) ^[8]		✓		
10	Glycofuro (THFP) ^[8]		✓		
11	Propylene carbonate ^[8]		✓		
12	Dimethyl glutarate ^[8]		✓		
13	Solketal ^[24]	Polymer dissolution	✓	✓	
14	Dimethyl sulfoxide (DMSO) ^[24]	Polymer dissolution	✓	✓	

Table 6: Potential process alternatives

Target Solvent	Function	Alternative Process
DMFa	Synthetic coated fabric	Water-based, solvent-free polyurethane dispersions ^[8]
Tetrachloro ethylene	Dry cleaning	Carbon dioxide cleaning (liquid or supercritical), Wet cleaning with aqueous detergents & conditioners ^[25]
Various	Surface cleaning	Aqueous vacuum degreasing, Aqueous vacuum cycling nucleation, Ultrasonic cleaning, Spray cleaning, Pressure washing, Immersion

3.2 Safer alternatives to solvent-based formulations in footwear production

3.2.1 Hot Melt Adhesives (HMA)

HMAs are safer alternatives for solvent-based adhesives used in bonding shoe soles and shoe uppers as their Potential to Emit is significantly reduced compared to current technologies. They are made of thermoplastic elastomers such as ethylene-vinyl acetate (EVA), amorphous poly alpha olefin (APAO), ethylene-methyl acrylate, ethylene n-butyl acrylate, styrene block copolymers and polyamides (PA). Some tackifiers such as hydrogenated rosin, rosin esters and terpene derivatives, are also incorporated in the HMA. The hot melt glue has low VOC emissions, quick curing and wide surface bonding properties. It is suitable for continuous production and convenient for storage and transportation. In developed countries, hot melt glue (including hot melt pressure sensitive glue) has accounted for more than 20% of the total synthetic adhesive. Hot melt can also be applied in several ways, including through nozzles, extrusion, melt blowing, spiral spraying, screen printing and slot die coating. HMAs can also be disposed of without any special precautions.

3.2.2 List of safer chemicals that can be used in footwear manufacturing

The list of safer chemicals that can be used in the footwear manufacturing processes with proper emission and exposure controls is given in the Table 7 below. These solvents are listed on the U.S. EPA's Safer Chemical Ingredients List (except ethyl acetate which can be used as safer replacement for toluene in PU/acrylic coating), meaning they meet the Safer Choice Criteria for Solvents. However, additional research and development will be needed to determine if they will be appropriate for every manufacturing situation.

Table 7: Potential list of chemicals that can be used in footwear manufacturing processes with proper emission and exposure controls

Sr. No.	CAS No.	Substance
1	110-98-5	1,1'-Oxidipropan- 2-ol
2	6920-22-5	Hexane-1,2 diol
3	107-88-0	Butane-1,3-diol
4	504-63-2	Propane-1,3-diol
5	629-11-8	Hexane-1,6-diol
6	100-79-8	2,2-dimethyl-1,3-dioxolane-4-methanol
7	56539-66-3	3- methoxy-3-methylbutane-1-ol
8	1117-86-8	Caprylyl glycol
9	143-28-2	(Z)-octadec-9-enol
10	25265-71-8	Oxydipropanol
11	24800-44-0	Tripropylene glycol
12	112-60-7	Tetraethylene glycol
13	1569-01-3	1-propoxypropan-2-ol
14	107-41-5	2 methylpentane-2,4-diol
15	102-76-1	Glycerol triacetate
16	110-27-0	Isopropyl myristate
17	123-95-5	Butyl stearate
18	763-69-9	Ethyl 3-ethoxypropionate
19	108-32-7	Propylene carbonate
20	1119-40-0	Dimethyl glutarate
21	627-93-0	Dimethyl adipate
22	106-65-0	Dimethyl succinate
23	97-64-3	Ethyl lactate

Table 7: Potential list of chemicals that can be used in footwear manufacturing processes with proper emission and exposure controls

Sr. No.	CAS No.	Substance
24	14035-94-0	Dimethyl methylglutarate
25	55934-93-5	Tripropylene glycol n butyl ether
26	108-32-7	Propylene carbonate
27	8001-79-4	Castor oil
28	56-81-5	Glycerol
29	8042-47-5	White mineral oil, petroleum (residual content of benzene in the complex oil-derived substances should be below 0.1%)
30	9004-74-4	Polyethylene glycol monomethyl ether
31	141-78-6	Ethyl acetate

3.3 Recent developments in safer alternatives to solvents

- 3-methoxy-N,N-dimethylpropanamide (C₆H₁₃NO₂) can dissolve a variety of substances with different polar characteristics. It is a highly-amphiphilic amide solvent and does not show reproductive toxicity. It is a colourless liquid with a flash point of 99°C and boiling point of 215°C.^[26]
- Gamma-valerolactone (GVL) is an excellent solvent which, today, can be made of sustainable materials. Toxicity tests with aquatic plants, bacteria, invertebrates, and a vertebrate cell line indicated a low acute toxicity of GVL towards aquatic organisms. Additionally, GVL is shown to be readily biodegradable, which further strengthens its potential as a safer solvent. Its vapour pressure is remarkably low, even at higher temperatures (3.5 kPa at 80°C), thereby not qualifying as a VOC.
- Cyclopentyl methyl ether (CPME) is a safer solvent, non-mutagenic, and non-reprotoxic.^[27]

- Glycofurol is a clear, colourless liquid solvent that can dissolve water-insoluble compounds.
- Cyrene™ (dihydrolevoglucosenone) is a new, safer, bio-based potential alternative to DMFa and NMP, which was first developed by the Circa Group in partnership with Professor James Clark, PhD, at the University of York's Green Chemistry Centre of Excellence (GCCE). Cyrene™ is synthesised in a two-step process from renewable cellulose waste, via a manufacturing process that is almost energy neutral and releases water to the environment. Although this green solvent possesses similar physical properties to dipolar aprotic organic solvents, rigorous safety tests demonstrate that it has very low toxicity. Cyrene is a powerful solvent that easily dissolves many polymeric materials and, on the other hand, it can be simply removed by washing with water.^[28]
- TMO (2,2,5,5-tetramethyloxolane) is a non-peroxide forming ether solvent that can replace common hydrocarbon solvents such as toluene. TMO demonstrates the ability to produce radical-initiated polymers of high molecular weight for use as pressure-sensitive adhesives.^[29]
- Tertiary butyl acetate (TBAC) is a non-HAP and non-VOC alternative to toluene and xylene used in adhesives, but may have slightly inferior performance across a wide range of solvent-based applications.^[30]

Individual facilities should use a phase-out step or internal research and development for using alternative solvents in place of the solvents marked with EC in the ZDHC MRSL V3.1.

CHAPTER 4:

Chemical management best practices

The ZDHC MRSL V3.1 mentions the need for emission and exposure controls when using the listed solvents. This necessitates the implementation of best practices for chemical management that covers purchasing policy, chemical inventory list, identifying hazards and planning precautions for safe storage, handling and disposal of solvents and ensuring worker health & safety.

This chapter details the chemical management practices that should be implemented by suppliers at their facility to properly manage the non-MRSL conformant solvents, in case these have to be used.

The [ZDHC CMS Technical Industry Guide V1.0](#) published by ZDHC in March 2021 gives an overview of the requirements of a chemical management system in the form of nine chapters. Suppliers are expected to reference and read this document when implementing chemical management practices for responsible solvents usage. Special attention should be given to Chapter 4 (Health and Safety) and Chapter 6 (Storage and Handling).

When implementing the ZDHC CMS as per the above guidelines, the following specific considerations should be taken into account for management of solvents and solvent-based formulations.

4.1 Precautions for storage of solvents

Solvents and solvent-based formulations need to be kept confined and with a high-degree of protection. In general, these chemical containers should be:

- 1) Kept at room temperature and away from direct sunlight (or as instructed by the chemical vendor).
- 2) Kept tightly closed.

- 3) A working exhaust line should be installed within confined storage spaces, in order to remove any gas accumulation.
- 4) The exhaust gas should also be treated before dissipation into the atmosphere (refer to Section 4.3).
- 5) Incompatible chemicals (such as oxidisers, corrosive and toxic chemicals) should not be stored along with these solvents. Reference should be made to understand the details on incompatible materials given in Section 10 (Stability and Reactivity).
- 6) Cross-ventilation should be provided in the storage space.
- 7) Solvents identified as flammable should be segregated and stored with all requisite fire safety precautions. Foam spray, CO₂ or ABC type fire extinguishers should be installed. Water should never be used to extinguish a fire caused by solvents. Fire alarm systems (sound and light) which are distinct from other alarms and notification systems must be installed. It is also recommended to have explosion-proof lights and proper grounding devices.

4.1.1 Large scale storage in cabinets.^[31]

- Cabinets storing a large capacity of solvent (greater than 250L) should be installed on the ground level with direct street or ground floor access.
- Unless the wall is constructed of concrete/masonry, these large capacity cabinets should not be installed closer than three metres away from a common wall (walls shared between two rooms).
- The concrete/masonry walls should measure three metres either side of the cabinet, and reach the ceiling height or three metres tall (whichever is lowest).
- The cabinets should not be close to residential or worker accommodation buildings or schools and hospitals.
- In case of storage cabinets for flammable solvents, the local regulatory norms should be followed. The following parameters are recommended:
 - The roof, floor, doors and cabinet walls must be made of double walled sheet steel with a minimum of a 40mm air gap between the walls.
 - Doors should be self-closing, close-fitting and automatically hold shut with catches at two or more points.

- Cabinet shelves must be perforated to allow air flow.
- All gaps around the doors of the cabinet should be sealed to prevent fire and heat radiation from spreading.
- All cabinet components must be made of materials that can withstand, without melting, temperatures below 850°C.
- Each storage cabinet containing flammable solvents must be marked with “No smoking” signage and no ignition sources must be allowed nearby.

4.1.2 Outdoor Storage

Cabinets stored outside, storing flammable solvents in capacities larger than 850L should be stored in a floor space of 250m². This reduces the risk of incidents such as chemical spillages or fire.

Other key requirements for outdoor storage include:

- Larger spill containment capacity.
- Provision of natural ventilation away from the facility area.
- Heavy duty construction.
- Provision of emergency decontamination equipment.

4.1.3 Secondary containment

A manufacturing facility should as best practice ensure that secondary containment is available for liquid chemicals stored in tanks, drums, and temporary containers (where applicable) to ensure that unintended spillages or releases are contained or localised. The secondary containment should always be in good condition, without cracks or gaps. At a minimum, the capacity of the secondary containment should be 110% of the volume of the largest primary container stored in a cluster.

As shown in the Figure 3, if two containers with volumes 20L each and two containers with volume 120L each are stored with one 300L volume container, then the secondary containment capacity for this storage cluster should be calculated as 330L (=110% of

the largest volume container), irrespective of whether the 300L container is partially filled at the time of storage.

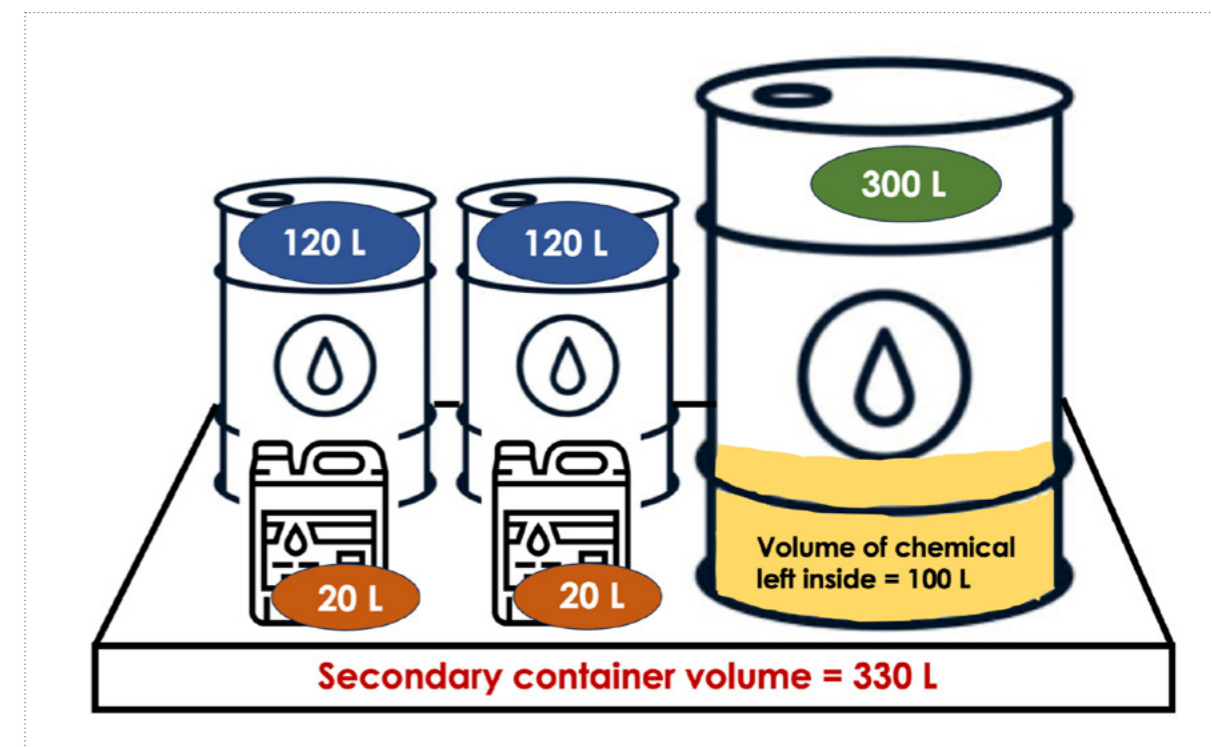


Figure 3: Secondary storage capacity calculation (Photo Courtesy: Decathlon)

The secondary containment must meet applicable local legal requirements based on chemical volume and container sizes.

4.2 Precautions during handling of solvents

Solvents can be corrosive to the skin and can cause serious eye damage. Therefore workers should be trained to handle the chemical containers properly to prevent chemical incidents.

Solvent handling covers all types of use and transportation. Well defined handling practices help to prevent the risk of personal injury and economic implications.

The following requirements are recommended for proper handling of solvents and solvent-based formulations:

- Workers should be trained on and use all relevant PPE when handling solvent containers. The quality of PPE used should be as stipulated in the SDS Section 8 for handling the solvents and should be regularly checked for wear and tear.
- Clear communication of hazards must be available, including appropriate signage informing of potential hazards. Workers who handle these chemicals must have appropriate training about the hazard symbols (GHS pictograms) or other means of communication adopted by the facility.
- The SDS should be kept and available in the chemical use and storage area.
- Development of a standard operating practice (SOP) with complete information on handling chemicals in the safest possible way, preferably in the local/official language. The SOP may also be translated into additional languages commonly used by workers at the site.
- Emergency response measures such as an eye wash station and a body shower should be installed for chemical incidents of splashes or contact.
 - An eye wash station should be preferably installed within 10 metres of the store, but no closer than two metres.
 - A body shower station must also be located within 10 metres, but not closer than two metres for cabinets storing more than 2000L of flammable solvents.
- First aid boxes should be installed in the stores and near high risk production areas. A certain number of personnel should be trained in first aid and their names and contact details should be displayed prominently in the production area, along with the contact details of the chemical spill response team and EHS leader. At least one of the trained personnel should be included in each shift. Details of ambulance services and the nearest hospital emergency hotline number should also be prominently displayed.
- During actual usage it is extremely important to isolate the solvent from the exposed areas of workers. Installing and using isolating curtains, closed systems for using the solvents, continuous vacuum/exhaust systems etc. are some of the engineering controls that can be employed.
- It is also recommended to have continuous monitoring of the work environment to know the real-time status of the VOC/solvent concentration in the work environment.

- Weekly/daily corrective and preventive maintenance (as per the company policies) must be done strictly to check, locate and fix any leakages at the production shop floor.

4.2.1 Personal Protective Equipment (PPE)

PPE is the last barrier between a human and chemical exposure and should be used for protection from incidents that may occur despite appropriate management control systems and operational procedures. At a minimum, each organisation shall:

- Identify the types of PPE needed in the facility. Where possible, select PPE types which may cover all possible chemical uses appropriately. Ensure that chemicals are also segregated based on the type of PPE required to handle them. This segregation will help educate workers so they can understand immediately the appropriate PPE to be used for each chemical.
- Create a SOP to identify and use appropriate PPE. The right PPE can be determined based on the SDS, regulations, standards, specific tasks, required performance of PPE, and other special requirements. Many PPE manufacturers also have information on how to identify the most appropriate PPE.
- Ensure that PPE is always available to employees working in areas where a potential exposure has been identified.
- PPE should be stored in a proper area and a designated person should be in charge of PPE management. This person is also responsible for PPE distribution, frequency of changing the PPE and choosing the PPE suppliers.
- Provide training on PPE usage to all workers working with chemicals.

A general PPE selection rule can be read from ZDHC CMS Technical Industry Guide V1.0, Section 4.1.2. The use of basic PPE with the appropriate CE marking in compliance with Regulation (EU) 2016/425 is advised as a preventive precaution. Reference should be made to Section 8 of a GHS compliant SDS to know more details on which PPE is applicable and their required specifications. Table 8 below gives a summary of the PPE requirements when handling the solvents listed in the ZDHC MRSL V3.1.

Table 8: Selection of PPE for solvent usage

PPE for	Tetrachloro ethylene	DMAC	DMFa	NEP	NMP	Toluene	Xylene
Respiratory protection							
Description	Filter mask for gases and vapours	Filter mask for gases and vapours	Filter mask for gases and vapours	Filter mask for gases and vapours	Filter mask for gases and vapours	Filter mask for gases and vapours	Filter mask for gases and vapours
Labelling	CE CAT-III	CE CAT-III	CE CAT-III	CE CAT-III	CE CAT-III	CE CAT-III	CE CAT-III
CEN standard	EN 405:2002+A1:2010	EN 405:2002+A1:2010	EN 405:2002+A1:2010	EN 405:2002+A1:2010	EN 405:2002+A1:2010	EN 405:2002+A1:2010	EN 405:2002+A1:2010
Hands protection							
Description	Chemical protective gloves (Material: linear low-density polyethylene (LLDPE), Breakthrough time: > 480 min, Thickness: 0.062 mm)	Non-disposable chemical protective gloves	Chemical protective gloves (Material: linear low-density polyethylene (LLDPE), Breakthrough time: > 480 min, Thickness: 0.062 mm)	Non-disposable chemical protective gloves	Chemical protective gloves (Material: linear low-density polyethylene (LLDPE), Breakthrough time: > 480 min, Thickness: 0.062 mm)	Chemical protective gloves (Material: linear low-density polyethylene (LLDPE), Breakthrough time: > 480 min, Thickness: 0.062 mm)	Chemical protective gloves (Material: linear low-density polyethylene (LLDPE), Breakthrough time: > 480 min, Thickness: 0.062 mm)
Labelling	CE CAT-III	CE CAT-III	CE CAT-III	CE CAT-III	CE CAT-III	CE CAT-III	CE CAT-III
CEN standard	EN ISO 21420:2020	EN ISO 374-1:2016+A1:2018 EN 16523-1:2015+A1:2018 EN ISO 21420:2020	EN ISO 21420:2020	EN ISO 374-1:2016+A1:2018 EN 16523-1:2015+A1:2018 EN ISO 21420:2020	EN ISO 21420:2020	EN ISO 21420:2020	EN ISO 21420:2020
Eye and face protection							
Description	Face shield	Face shield	Face shield	Face shield	Face shield	Face shield	Face shield
Labelling	CE CAT-II	CE CAT-II	CE CAT-II	CE CAT-II	CE CAT-II	CE CAT-II	CE CAT-II
CEN standard	EN 166:2002 EN 167:2002 EN 168:2002 EN ISO 4007:2018	EN 166:2002 EN 167:2002 EN 168:2002 EN ISO 4007:2018	EN 166:2002 EN 167:2002 EN 168:2002 EN ISO 4007:2018	EN 166:2002 EN 167:2002 EN 168:2002 EN ISO 4007:2018	EN 166:2002 EN 167:2002 EN 168:2002 EN ISO 4007:2018	EN 166:2002 EN 167:2002 EN 168:2002 EN ISO 4007:2018	EN 166:2002 EN 167:2002 EN 168:2002 EN ISO 4007:2018

Table 8: Selection of PPE for solvent usage

PPE for	Tetrachloro ethylene	DMAC	DMFa	NEP	NMP	Toluene	Xylene
Body protection							
Description	Disposable clothing for protection against chemical risks	Disposable clothing for protection against chemical risks	Disposable clothing for protection against chemical risks, with antistatic and fireproof properties	Disposable clothing for protection against chemical risks	Disposable clothing for protection against chemical risks	Disposable clothing for protection against chemical risks, with antistatic and fireproof properties	Disposable clothing for protection against chemical risks, with antistatic and fireproof properties
Labelling	CE CAT-III	CE CAT-III	CE CAT-III	CE CAT-III	CE CAT-III	CE CAT-III	CE CAT-III
CEN standard	EN 13034:2005+A1:2009 EN 168:2002 EN ISO 13982- 1:2004/ A1:2010 EN ISO 6529:2013 EN ISO 6530:2005 EN 464:1994	EN 13034:2005+A1:2009 EN 168:2002 EN ISO 13982- 1:2004/ A1:2010 EN ISO 6529:2013 EN ISO 6530:2005 EN 464:1994	EN 1149-1,2,3 EN 13034:2005+A1:2009 EN ISO 13982- 1:2004/A1:2010 EN ISO 6529:2013 EN ISO 6530:2005 EN ISO 13688:2013 EN 464:1994	EN 1149-1,2,3 EN 13034:2005+A1:2009 EN ISO 13982- 1:2004/A1:2010 EN ISO 6529:2013 EN ISO 6530:2005 EN ISO 13688:2013 EN 464:1994	EN 13034:2005+A1:2009 EN 168:2002 EN ISO 13982- 1:2004/A1:2010 EN ISO 6529:2013 EN ISO 6530:2005 EN 464:1994	EN 1149-1,2,3 EN 13034:2005+A1:2009 EN ISO 13982- 1:2004/A1:2010 EN ISO 6529:2013 EN ISO 6530:2005 EN ISO 13688:2013 EN 464:1994	EN 1149-1,2,3 EN 13034:2005+A1:2009 EN ISO 13982- 1:2004/ A1:2010 EN ISO 6529:2013 EN ISO 6530:2005 EN ISO 13688:2013 EN 464:1994
Foot protection							
Description	Safety footwear for protection against chemical risk	Safety footwear for protection against chemical risk	Safety footwear for protection against chemical risk, with antistatic and heat resistant properties	Safety footwear for protection against chemical risk	Safety footwear for protection against chemical risk	Safety footwear for protection against chemical risk, with antistatic and heat resistant properties	Safety footwear for protection against chemical risk, with antistatic and heat resistant properties
Labelling	CE CAT-III	CE CAT-III	CE CAT-III	CE CAT-III	CE CAT-III	CE CAT-III	CE CAT-III
CEN standard	EN ISO 20345:2011 EN 13832-1:2019	EN ISO 20345:2011 EN 13832-1:2019	EN ISO 13287:2020 EN ISO 20345:2011 EN 13832-1:2019	EN ISO 20345:2011 EN 13832-1:2019	EN ISO 20345:2011 EN 13832-1:2019	EN ISO 13287:2020 EN ISO 20345:2011 EN 13832-1:2019	EN ISO 13287:2020 EN ISO 20345:2011 EN 13832-1:2019

4.2.2 Engineering and manufacturing controls

Workers can be exposed to solvents during work either from leakages or from evaporation losses. Therefore, manufacturing and engineering controls are required to minimise the exposure of workers and reduce environmental contamination.

Some recommended engineering controls include:

- Using automated dispensing, handling, collecting and discharging systems.
- Separating the solvent and workers by enclosing or isolating the task, and using local exhaust ventilation (LEV) to minimise the vapour concentration in a worker's breathing zone. Use of appropriate PPE for inhalation should be done by the workers in this isolated work area (refer to Figure 4 and Figure 5).
- LEVs can include:
 - Capture hoods and duct systems to remove solvent vapours.
 - Increasing supply of fresh air to the isolated work area.
(The emphasis should be placed on the collection effect of the exhaust gas while following the local norms for fugitive emission of VOCs.)
- Enclosure of the process in a dedicated work area with zero exposure of the worker (refer to Figure 6).
- Regular maintenance and inspection of equipment and pipelines to prevent leaks, along with prompt repair for any leak detections.

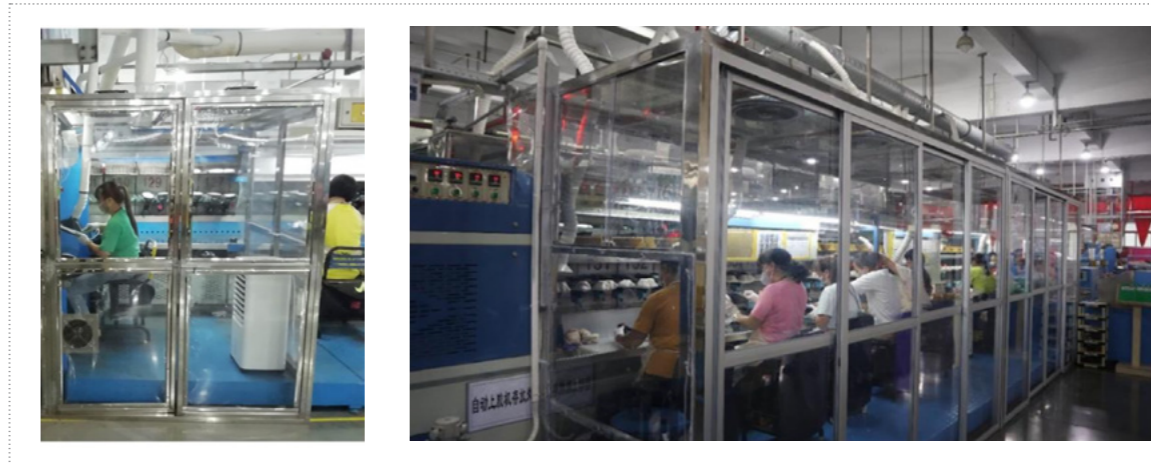


Figure 4: Isolating the task by Local Exhaust Ventilation
(Photo Courtesy: Nike, Inc.)

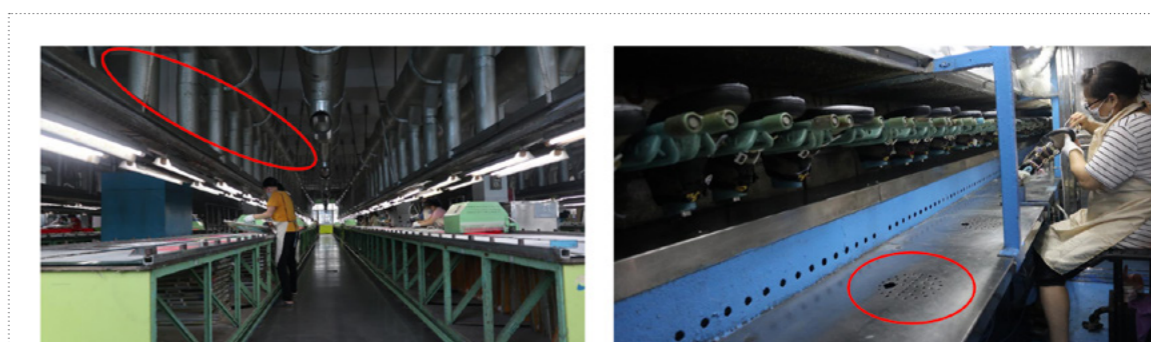


Figure 5: Local exhaust ventilation and use of local fume arm
(Photo Courtesy: Nike, Inc.)

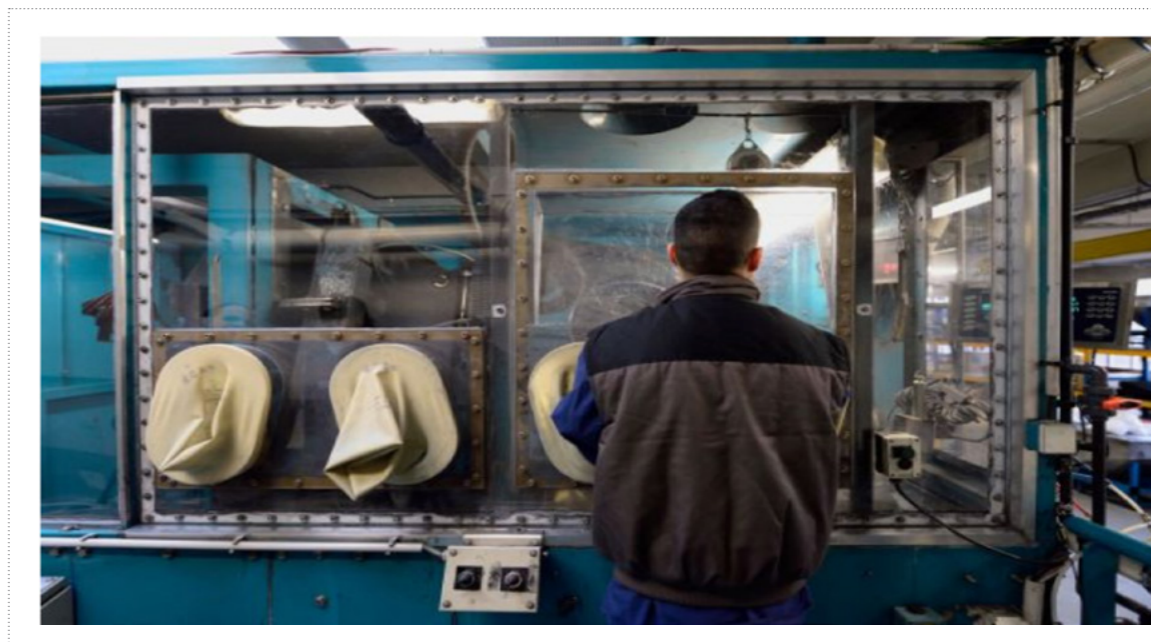


Figure 6: Enclosure of the process in the dedicated work area
(Photo Courtesy from INRS)

4.2.3 VOC emissions monitoring

Monitoring of Volatile Organic Compounds (VOCs) in the workplace and the ambient air helps to check and control emissions through completing corrective actions. In many countries VOC emissions measurement is also required by regulatory bodies and facilities must comply with these local regulatory norms and national standards.

VOC emissions monitoring does not mean occupational exposure measurement. The latter must be done by a third-party service provider who is a qualified occupational hygienist.

The monitoring and recording of VOC emissions in indoor workplaces and the ambient air can be carried out using portable measuring devices or fixed measuring devices.

To monitor VOCs in a facility, it is important to identify different risk areas where VOCs may be released in the facility. Typically, the risk areas include places where:

- Formulations containing solvents come in contact with heat.
- Places where there is less air circulation.
- Places confined by design.
- Places where raw materials/articles are stored for extended periods of time.
- Hot and cold zone intersections.

Please note that these are only guidelines and when sites install VOC analysers they will need an expert visit, opinion and a detailed analysis of on-site conditions. Facilities should preferably get help from experts.

4.2.3.1 VOC monitoring in formulations

A chemical inventory is important to understand the potential impact of chemicals that contribute to occupational exposure and air emissions. Therefore, a facility should first document all the formulations used in the [ZDHC Chemical Inventory List \(CIL\) template](#), with details on substance name, CAS number(s) and hazard classification for each formulation. Once the CIL is prepared, it is important to identify the list of VOCs in the formulations.

For an ingredient in a formulation to be classified as a VOC, the following criteria in Table 9 must be met.

Table 9: Criteria for formulation to be classified as VOC

Required VOC Classification	
1	Contains carbon
2	Vapour pressure $\geq 0.01\text{kPa}$ ($\sim 0.075\text{ mm Hg}$) at 293.15K
3	Boiling point $\leq 250^\circ\text{C}$ at standard pressure of 101.3kPa

To identify the VOCs in an input chemical formulation, refer to Section 3 of a GHS compliant SDS and check the above VOC criteria for the CAS numbers of the listed ingredients. Note the concentration of the identified VOC ingredient used in the formulation (as a %) from this section of the SDS and its total consumption per year (in kgs).

Then, the Potential to Emit (PTE) of the VOC from that formulation can be calculated as per the below formula:

Potential to Emit of VOC (kgs)* = Max concentration of the substance(s) classified as VOC (%) in the formulation X Annual usage of the formulation (kgs)

For example, if a formulation (A) in the CIL contains toluene (CAS number 108-88-3) at a concentration of 15% and the annual usage of formulation (A) is 400 kgs, then Potential to Emit (PTE) for toluene = 15% x 400 = 60 kgs

The PTE for all VOCs from the input chemical inventory should be added together to arrive at the total PTE value in tons per year (TPY) at the facility.

* assuming 100% of the VOC is emitted

If the PTE for VOCs exceeds five tons per year (TPY), an emissions calculation and/or testing should be completed to prove proper management of these pollutants.**

① As a best practice, a supplier should aim to reduce the VOC usage in input chemical formulations through a step-by-step approach to phase out and substitute VOC-containing formulations with safer alternatives. An action plan for this should be established and implemented with a timeline.

4.2.3.2 VOC monitoring at the workplace

In a textile, leather or footwear manufacturing facility, there are many risk areas for VOC emissions such as the chemical warehouse, coating, finishing, adhesive application, print screen etching and preparation, printing, lacquering, liming & swelling, tanning, etc. In addition to reduction in VOC usage through substitution of VOC-based formulations, it is important that the VOC emissions at such high-risk areas in the facility are monitored and engineering and abatement controls are put in place to reduce the harm to workers and surrounding communities.

The VOC monitoring at the workplace can be achieved through two types of instruments:

- 1) Hand-held/portable detectors
- 2) Fixed detection systems

These instruments use different types of detectors such as photoionisation detectors (PID), flame ionisation detectors (FID) and metal oxide semiconductor (MOS) sensors. When using PID, it is important to make the correct selection of the lamp and apply the corrective factor wherever relevant to get accurate results.

Some detectors come with alarms built into each sensor, which can alert nearby personnel of any toxic VOC levels immediately.

** ZDHC will publish the Air Emissions Guidelines V1.0 in 2024 where a list of VOCs will be provided as an appendix. Suppliers are recommended to refer to this document when it is published. Also, the evaluation of PTE for Total VOC is planned to be monitored through the Resource Efficiency Module (REM) on the ZDHC Supplier Platform.

4.2.3.2.1 Handheld/portable detectors

Handheld/portable detectors are specifically useful, where the monitoring is needed on a regular basis or at places that are difficult to physically access. Sometimes leakages can get diluted on contact with the environment and need to be detected by such devices. Portable detectors can detect a wide range of substances and come in different shapes and sizes, as depicted in Figure 7 and 8. They have a good detection range that can record measurements over several hours. Some advanced instruments with a computer connection are also available. Drager pumps can also be used for automatic air sampling to measure specific substances as an inexpensive alternative to PIDs. However, Drager pumps cannot indicate if there are other substances in the air sample and can be used for a one-time measurement only.



Figure 7: Portable PID detector and Drager Pump (Photo Courtesy: Decathlon)



Figure 8: Handheld DMFa detection system (Photo courtesy Lishui Heli New Material, Lishui, China)

4.2.3.2.2 Fixed detectors

These detectors are bulkier compared to handheld detectors and are meant to be installed at a fixed location as shown in Figure 9 and 10. They are used to monitor VOC levels continuously at a fixed interval of time and at a specific site. Due to the inherent fixed position and sampling, the data obtained by such instruments is used to check/monitor the VOC content in the work environment over a period of time, get an average value and monitor any incidents or process non-conformity for VOC emissions. Some of the fixed detectors can be set to detect a specific VOC, while some other advanced instruments come with an in-built alarm system, which notifies the surrounding areas, if the total VOC (TVOC) or set value is exceeded.



Figure 9: Fixed VOC detector
(Photo courtesy: <https://oizom.com/product/AQBot-industrial-voc-gas-monitor/>)



Figure 10: Continuous VOC monitoring system
(Photo courtesy: Hefei Ketian Waterborne Science and Technology Co. Ltd.)

The choice of detector depends upon the application and final use. Therefore, the individual site will need to decide what type of instrument is to be used for their work area.

VOC sensors work more efficiently if the alarm system can be specifically programmed for each process or risk area. By setting stringent detection parameters, plant personnel can obtain more accurate results and avoid false alarms.^[32] Depending on the type of VOCs present and the area in which the monitor is placed, targeted or mixed measurements can be taken. Targeted measurements are more efficiently recorded if a specific VOC is being released, and the exact emission parameters are known. Mixed VOC measurements are better utilised in open-air environments where various VOCs are being detected.

4.2.4 Corrective action for non-conformities

As per the hierarchy of controls (refer to Figure 11), the most effective action to control VOCs is to eliminate or substitute the usage of VOC-based formulations or use water-based technologies. This should be done by calculating the PTE as detailed in Section 4.2.3.1 and create an action plan to phase out the problematic solvent-based formulations.

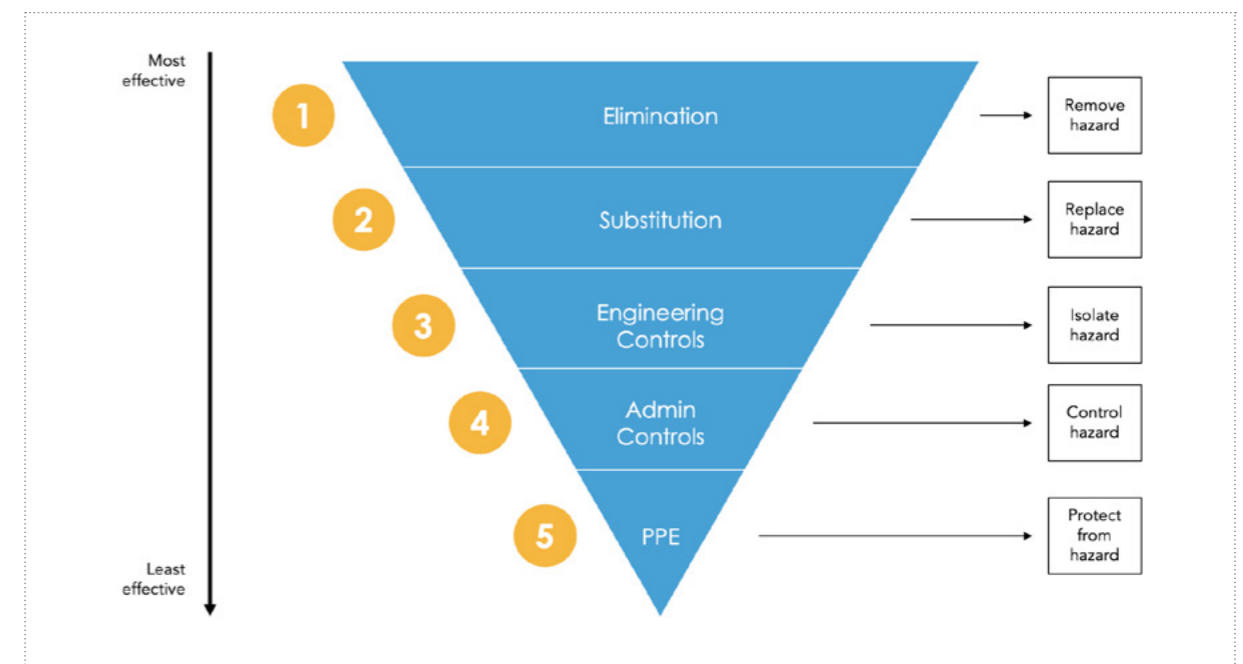


Figure 11: Hierarchy of controls^[33]

In cases where the elimination or substitution is not immediately possible, proper engineering controls, as detailed in Section 4.2.2, should be implemented to reduce worker exposure and control VOC emissions at the workplace. The last option should

be to provide proper PPE and ensure the usage of PPE at all times by the workers in the affected area through appropriate PPE management SOP.

Along with VOC monitoring in the workplace, the facility should also measure occupational air exposure through a third-party accredited laboratory at least once a year. Based on the data from the chemical risk assessment, a sampling strategy should be set up by a qualified occupational hygienist who should define the areas, sampling time, materials choice, chemicals and workers to be tested. The principle of similar exposure groups should be used to reduce the number of measurements: these are groups of workers performing the same tasks under the same conditions and therefore having the same exposure profile for the substances concerned.

The determination of “short-term” exposure is made over a period of 15 minutes and is compared with the Short Term Exposure Limit (STEL), whereas the comparison with the 8 hour Time Weighted Average (TWA) is made on the basis of longer measurements ideally equal to the duration of the workstation.

The test report should contain: Risk analysis of chemicals used at the supplier site, protocol of measurement, results and a conclusion.

4.3 Disposal controls and downstream processes (waste management)

VOCs that are collected through local exhaust ventilation or other engineering controls need to be treated before they are released to the environment.

It must be noted that the exhaust gases collected from all point sources should be properly treated before being released into the environment. This pretreatment is to ensure that the VOCs collected from the point source are not dissipated into the atmosphere, which avoids further increase of VOCs concentration in the atmosphere. ZDHC recommends that such exhaust gas treatment systems are installed at a facility in order to treat the VOCs (these can be clubbed with other air purification/treatment systems) before the release into the environment. This is in addition to the local norms required for removal of HAP emitted from discharging techniques such as electrostatic discharging etc.^[34]

Exhaust gases containing VOCs are expected to go through a proper channel of scrubbing these solvents in gaseous phases. They can then pass through (commercially available) thermal oxidisers in order to oxidise solvents into corresponding oxides.

Adsorption for exhaust gases through activated carbon is also possible, as long as it shows sufficient efficiency. Catalytic burning of VOCs as an abatement system can also be installed before releasing the exhaust gases into the atmosphere.

Solvents that are used in a process may become waste after their usage and can impact the environment if they are disposed of through uncontrolled disposal pathways. Usually, such solvent waste that cannot be recovered is incinerated.

Instead of allowing this solvent waste to be incinerated, it is financially and environmentally beneficial to either recover and recycle the solvent waste on-site or reuse it in a different process on-site or for some other industry.

Possible methods of recycling of solvents are suggested below in Table 10.

Table 10: Recommended recycling methods for waste solvents

Name of the Solvent	Boiling point (°C)	Suggested Recycling Process
Tetrachloroethylene	121.1	Simple distillation
N,N-Dimethylacetamide (DMAC)	165	Fractional distillation/azeotropic distillation
N,N-Dimethylformamide (DMFa)	153	Fractional distillation/azeotropic distillation
N-Ethyl-2 pyrrolidone (NEP)	212.5	Fractional distillation/azeotropic distillation
N-Methyl-2 pyrrolidone (NMP)	202-204	Fractional distillation/azeotropic distillation
Toluene	110	Simple distillation/ azeotropic distillation
Xylene (all isomers) o-Xylene m-Xylene p-Xylene	138-145	Simple distillation/ azeotropic distillation

Training and education

Training and education of staff, workers and management is important for managing solvents in a responsible manner. This avoids accidents, leads to improved productivity and optimises efficiency. It is the responsibility of the facility management to ensure that all workers are properly trained in the usage and handling of hazardous chemicals, including solvents, which motivates them in their work and guarantees their health and safety.

Each manufacturing facility should have in-house personnel trained in chemical management practices. Preferably, these personnel will have undergone training in chemical management modules through the ZDHC Academy. Wherever required, the facility management should encourage external training sessions from experts.

A training plan (refer to Figure 12) should be formulated by the facility to cover the following:

- 1) Identification of training needs
- 2) Identification of target groups (existing and new workers/staff/management)
- 3) Decide on training topics
- 4) Define training objectives and learning outcomes
- 5) Select training methods and identify resources needed
- 6) Set up a training timetable (agenda, venue, duration, frequency)
- 7) Establish evaluation methods and follow-up on training results/refresher training
- 8) Establish documentation of training records

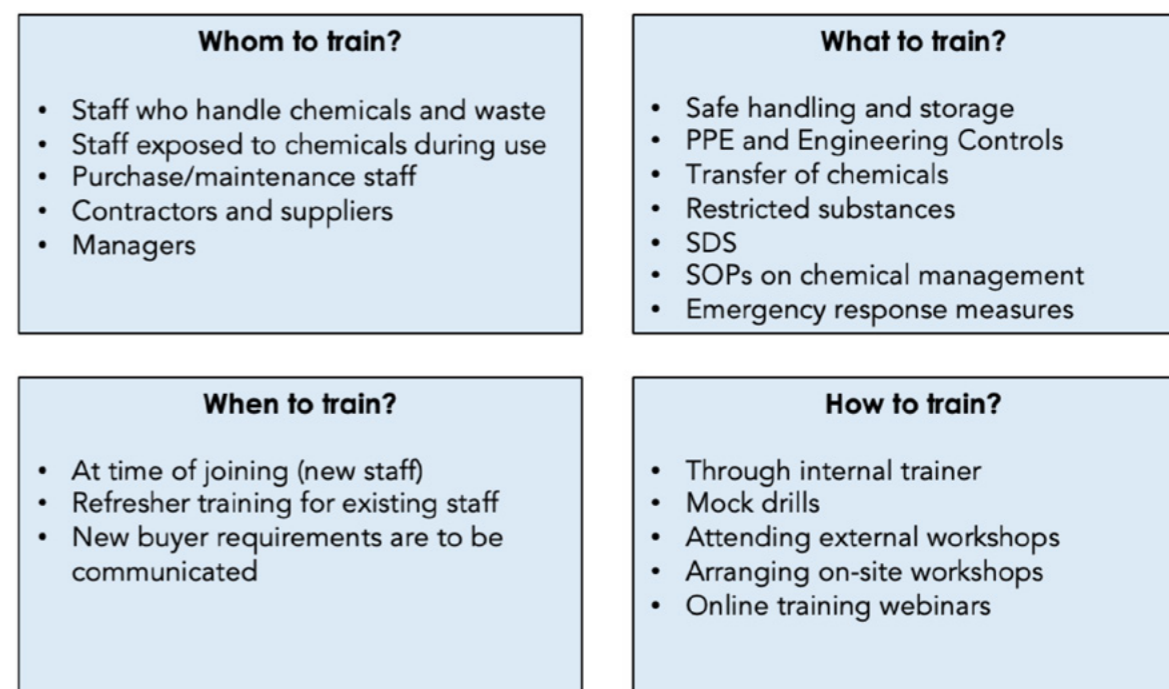


Figure 12: Training plan^[33]

5.1 Whom to train and what to train?

Based on the identification of training needs, the following is recommended to be included (refer to Table 11) in the training plan.

Table 11: Recommended training plan

Target Group	Expected Training
Workers (New recruits)	Company safety policies
	PPE usage
	GHS hazard pictograms and labelling
	Chemical spillage containment
	Emergency response measures
	Fire safety measures
	Safe chemical handling practices and general housekeeping

Table 11: Recommended training plan

Target Group	Expected Training
Workers (regular) - refresher course	PPE usage
	Chemical spillage containment
	Emergency response measures
	Safe chemical handling practices and general housekeeping
Staff (Supervisor/Manager)	Internal audit processes for CMS
	Mass balance of solvent usage
	Hazard identification and planning of safe storage and handling precautions
	Applicable local laws on chemical management and emission norms
Management	Policy making on responsible management of solvents
	Designing phase out plan for solvents

5.2 How to train and when to train?

Training programmes should:

- Cover all workers at the manufacturing facility, including contractors and subcontractors, as appropriate.
- Be conducted by competent persons.
- Provide
 - Information in languages easily understood by all workers.
 - Practical and theoretical training before commencement of duties.
 - Refresher training at appropriate intervals, or further to significant changes in risk levels for workers or in their functions.

- Include participants' feedback and evaluation of their comprehension and retention of the training with a view to the continuous improvement of the training.
- Be reviewed periodically by a health and safety committee, where it exists, or by the management in consultation with workers or their representatives, and modified as necessary.
- Be documented and recorded.

The training should be conducted by experts. These can be in-house personnel who are qualified and trained to impart the education and have the skills and experience to conduct such training. Wherever required, the help of external expert agencies can be employed.

The training should be conducted:

- As soon as a new recruit joins the facility.
- When a change in process, chemicals, technology or machinery is introduced.
- As refresher training, based on needs/risk assessment.
- At least once in a year for all employees and management.
- In cases where the desired outcome of the training is not achieved.
- When any adverse incidents have happened.

The form and the content of training should be devised and implemented in consultation with workers and their representatives. Training should be in accordance with the needs identified.

Training should be provided to all workers at no cost to them and should take place during paid working hours. Training should not cause any worker discrimination.

Employers should ensure that training and information requirements and procedures are kept under review, as part of the assessment review and documentation.

Industry examples of solvent management

The vision of ZDHC is a world in which better chemistry leads to the protection of life, land, air and water. ZDHC drives the textile, leather and footwear industry towards sustainable chemical management through a focus on eliminating hazardous substances in the manufacturing process. Halogenated and organic solvents have been included in the ZDHC MRSL V3.1 to push the industry towards water-based and other safer solutions.

Described below are two examples of solvent management that can be adopted by the industry in the journey to reduce impacts on human health and environment:

- 1) Phase out of DMFa in the manufacture of polyurethane dispersions and footwear.
- 2) Closed-loop solvent scouring using tetrachloroethylene with proper controls.

The examples provided in this document are just a few examples of the innovations possible within the industry. A supplier should conduct their own research into all possible solutions to determine the best one for their organisation.

6.1 Example 1: DMFa phase-out in polyurethane manufacturing

By placing DMFa on the ZDHC MRSL V3.1 list, ZDHC bans the intentional use of DMFa in textile and footwear manufacturing. This is a culmination of the DMFa Phase-Out Project that was initiated by ZDHC in 2016 in collaboration with some of our Signatory Brands, chemical companies and PU and synthetic coated fabric manufacturers and associations in China. This project focussed on the functional use with the biggest impact in the value chain, which was manufacture of synthetic coated fabric and PU coatings and dispersions. The full success story is worth reading on our [website](#).

6.1.1 Background

The production of solvent-borne synthetic coated fabric and PU coatings includes several processes in which solvents like DMFa are used. PU elastomers offer high levels of elasticity, tensile strength, elongation, and shock-absorbing abilities when making footwear. Solvent-borne PU is widely used as a coating due to its special properties like the microporous structure, air and water vapour permeability or water repellency.

DMFa plays an important role because it is a well-functioning solvent for the PU production process, it does not readily evaporate from solutions due to its high boiling point, and it is highly miscible with water.

6.1.2 Process of making solvent based PU

PU is prepared mostly in a two-part process consisting of a coagulation and a transfer coating process. DMFa is employed as a solvent or as a medium of reaction as explained in the sections below.

6.1.2.1 Polymerisation step

For the coating of textiles, a liquid form of solvent-borne PU is required, which is produced by the reaction of polyols and poly isocyanates, often using DMFa as a reaction solvent. The reaction product is a PU suspension, which is a mixture of DMFa and PU threads with a solid PU content of about 30-35%.

6.1.2.2 Manufacturing of synthetic coated fabric and PU coatings

DMFa is used as a processing solvent in the coagulation (wet process) for the production of synthetic coated fabric and PU coatings.

Before the coagulation takes place, the textile substrate is coated by knife or dip coating with a PU suspension, which has been diluted with DMFa to achieve a 7-16% solid content.

The PU coated textile goes through a water bath, which contains 5-40% DMFa. In this bath, the coagulation process takes place. During this process, water can permeate into the DMFa solution while DMFa merges from the substrate into water. This causes the PU threads to coagulate and form a porous film. After the coagulation process, the textile substrate passes through several bathing cycles to wash out residual DMFa and is then dried to form the final base layer (coagulate).

In parallel to this base layer production, a skin layer is produced by applying a solvent-borne PU paste to a release paper through a coating and drying process. To achieve the final synthetic coated fabric, the base and skin layer are bonded through lamination. This process describes only one possibility to produce PU coatings or synthetic coated fabric (refer to Figure 13).

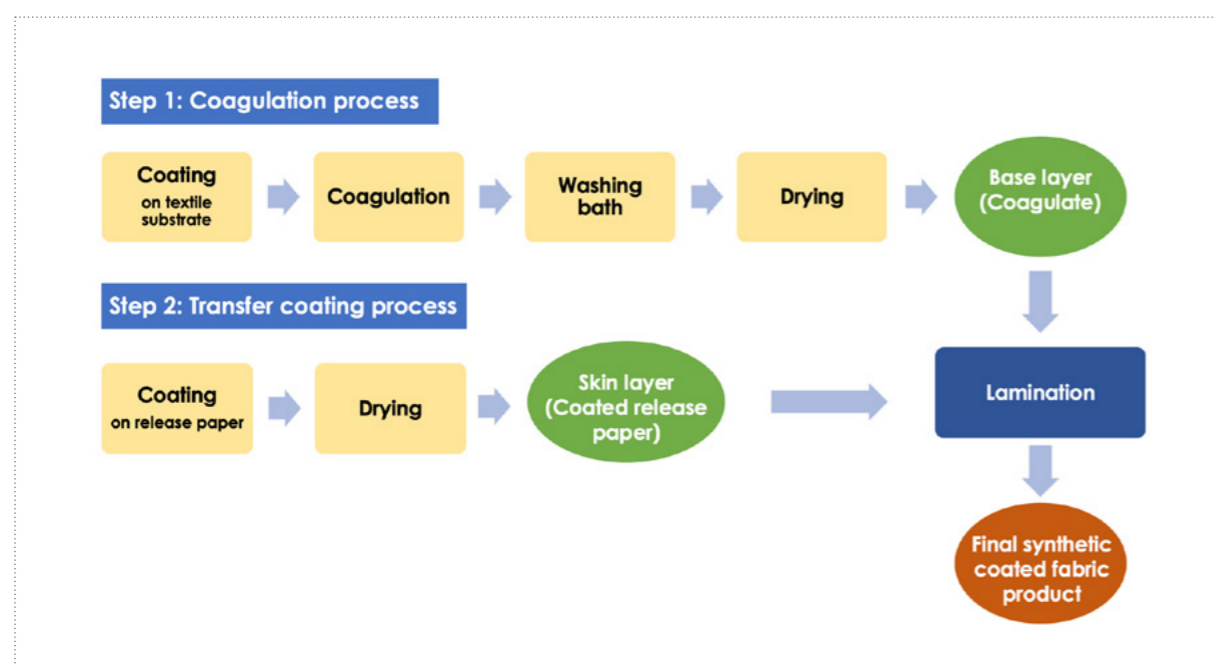


Figure 13: Production processes for synthetic coated fabric

6.1.3 Safer substitutes available to eliminate use of DMFa

As part of the DMFa Phase-Out Project, several chemical companies have developed safer alternatives that completely eliminate the need to use DMFa in the above two application processes. These are water-borne alternative technologies that use fewer, or no, solvents or new generation polymer chemistry that does not use any solvent in the polymerisation process. These alternatives also show a reduction in water and

energy use, but may require additional investments in mixing and dosing equipment as well as modification of the dry process line.

There are chemical manufacturers who provide DMFa-free solutions for synthetic coated fabric manufacturing at scale. For example: BASF (Haptex), Covestro (InSquin), Huntsman, Everlight Chemical Corporation, Nicca Chemicals, Hefei Ketian, Stahl, TFL. Suppliers are advised to connect with their chemical vendors to check the availability of DMFa-free solutions.

These technologies are already being adopted commercially and are known to be scalable. Some challenges that need attention in the implementation of these technologies are: cross-contamination of DMFa between DMFa-free and DMFa-based processes conducted within the same site as well as cost, quality and investment issues. ZDHC understands that such a technology shift requires time and expects from suppliers an aggressive approach to phase-out the usage of DMFa in synthetic coated fabric production.

6.2 Example 2: Use of tetrachloroethylene in solvent scouring application

Closed-loop solvent scouring with tight emission and exposure controls is another example of use of solvents in the industry. Solvent scouring eliminates the use of water in the process and is very effective in removing all stains and spots on the textile substrate, which can otherwise create problems in subsequent processing stages.

The scouring operation is carried out with tetrachloroethylene as an organic solvent in a closed-circuit with more than 99% of the solvent recovered and reused.

Each solvent scouring plant consists of:

- 1) Fabric treatment unit: where the fabric enters and is washed with pure tetrachloroethylene in a countercurrent flow. The solvent evaporates on a special dryer and contains the removed oils from the fabric.

2) Recovery units:

- Distillation: for recovering almost all the tetrachloroethylene used in the process (more than 99%) and re-using it on the machine. The distillation residue, consisting of the non-distilled solvent-saturated oils extracted from the fabric, is removed from the cycle as waste product called ‘chlorinated emulsions’ that must be disposed off according to the country regulation (for example as EWC code 13.01.04 in the EU)
- Activated carbon filter: The cleansed fabric is treated with an air jet at 130°C to strip the residual tetrachloroethylene from the fabric. The tetrachloroethylene-laden air is treated in activated carbon towers after cooling and condensation. The dried fabric then passes to the cooling stage by means of a cold air current that strips off the last residual tetrachloroethylene on the fabric, the same air after passing through the condenser passes to the activated carbon section.

At many facilities, activated carbon sections are washed in steam baths. The discharge of the associated condensate constitutes the water effluent from the machine (intermediate discharge). This discharge should be pretreated before being sent to the equalisation tank in the effluent treatment plant.

In a new development from Lafer, the contaminated water is sent to a Contact Water Recovery System and re-used as steam in specific devices, resulting in no discharge of water.^[35] This steam is used to feed the parts of the plant in which there is already presence of tetrachloroethylene such as active carbon filter system (regeneration phase) or distillation unit (final phase sludge extraction). It should be confirmed that no traces of tetrachloroethylene remain on the finished product.

As a best practice, a facility doing closed-loop scouring with tetrachlorethylene should monitor its air emissions, water discharge, fabric and work environment and waste disposal. Similarly, health monitoring of workers should be carried out annually (by a blood test) and once in every two years (by a specific clinical test).

Table 12 lists the recommended maintenance activities for the facilities using close-loop solvent scouring.

Table 12: Maintenance activities recommended for closed loop solvent scouring

Sr. No.	Activities	Periodicity
1	Cleaning of air filters washing and dryer Gasket control – eyelid check	Weekly
2	Cleaning solvent filters washing and pre-washing Gasket control	Weekly
3	Cleaning of the drying drum and deodorising Gasket control	Weekly
4	Labyrinth cleaning and water drain filter	Weekly
5	Panel filters	Weekly
6	Belt and chain control	Monthly
7	Control of DC motor brushes	Quarterly
8	Cleaning of basket filters for tetrachloroethylene sludge pumps	Four monthly
9	Complete internal verification of the machine with registration of the interior. (external company)	Annual
10	Replacement of spent coals air filter	At least every 15,000 hours of work (about 36 months)
11	Visual inspection of labyrinth blowers (department operator)	Daily
12	Replacement of spent coals water filters	Max 600 hrs of work

Personal Protective Equipment (PPE)

Based on the risk assessment carried out for tetrachloroethylene usage in a highly-controlled closed-loop system, there is no requirement of use of specialised PPE (excluding safety shoes).

Supplier "To Do" Checklist

If the supplier must use the solvents listed in ZDHC MRSL V3.1 which are marked EC (Emission and Exposure control) or solvent-based formulations containing these solvents, due to quality or performance needs or as a part of time-bound phase-out strategies, then they can follow the below 'TO DO' checklist.

Based on use of solvents or solvent-based formulations, a supplier can implement actions from this document as described below in Table 13 and Table 14, with cross-references to the chapters/sections in the above for a more detailed understanding on the actions required.

Table 13: Checklist for use of ZDHC MRSL listed solvents in situ/on-site

Sr. No.	"To Do" Checklist	Reference Chapter and Section	Page no.
1	Identify if any of the ZDHC MRSL listed solvents are being used on-site.	Introduction, Table 1	15
2	Study the hazard profile of the solvent to understand the hazard and the P-Statements.	Chapter 1, Section 1.2	23
3	Plan actions to substitute the solvents with safer alternatives. Use the information in Chapter 3 to discuss with your chemical vendors and make decisions on the safer alternative.	Chapter 3, Sections 3.1.1, 3.1.2, 3.1.4 and 3.1.5	41, 42, 44, 45
4	If the supplier is a footwear manufacturer, explore the use of solvents and Hot Melt Adhesives given in Chapter 3.	Chapter 3, Section 3.2.1 and 3.2.2	47, 48
5	Study the ZDHC CMS-TIG document and Chapter 4 to implement chemical management practices for storage, handling, PPE and engineering controls.	Chapter 4, Section 4.1 (Storage), 4.2.1 (PPE), 4.2.2 (Engineering controls)	52, 57, 62
6	Monitor VOC emission at the workplace using appropriate devices	Chapter 4, Section 4.2.3.2	66
7	Take appropriate corrective action to reduce VOC emissions.	Chapter 4, Section 4.2.4	69
8	Recover and recycle solvent waste through appropriate techniques.	Chapter 4, Section 4.3	70

Table 13: Checklist for use of ZDHC MRSL listed solvents in situ/on-site

Sr. No.	"To Do" Checklist	Reference Chapter and Section	Page no.
9	Prepare and execute the training plan to train all employees and workers on safe management of solvents.	Chapter 5, Section 5.1 and 5.2	73, 74
10	In case DMFa is used at the facility, implement a phase-out plan through safer substitution for DMFa	Chapter 6, Section 6.1.3	78
11	In case TCE is used at the facility, implement a closed-loop system to reduce exposure to workers and the environment. Where possible, eliminate use of TCE through safer substitution.	Chapter 6, Section 6.2 (for closed-loop system) and Chapter 3 (for substitution)	79, 40

Table 14: Check-list for use of ZDHC MRSL listed solvents as an ingredient in chemical formulations

Sr. No.	"To Do" Checklist	Reference Chapter and Section	Page no.
1	Check the input chemical inventory (CIL) for conformance to the ZDHC MRSL through the ZDHC Gateway database.	Refer to 'ZDHC Knowledge Base' articles on www.roadmaptozero.com → Resources → Support → Gateway	
2	Identify if any of the ZDHC MRSL listed solvents are being used as an ingredient in chemical formulation in the CIL through Section 3 of the SDS of the formulation. In case of any listed solvent used, the supplier should discuss with the chemical vendor for ZDHC MRSL conformant formulation or search for ZDHC MRSL conformant formulation for similar use from the ZDHC Gateway.	Introduction, Table 1 (MRSL listed solvents) Chapter 1, Section 1.3 (SDS-Section 3), Chapter 3, Section 3.1.3 (search from ZDHC Gateway)	15 35 42
3	Study the hazard classification of the formulation to understand the hazard(s) and the P-Statements from Section 2 of the SDS	Chapter 1, Section 1.3 (SDS Section 2)	35
4	Study the ZDHC CMS-TIG document for implementing a CMS. Also, implement chemical management best practices for solvent-based formulations and refer to SDS Sections 4, 7 and 8 to implement precautions for storage, handling, PPE and engineering controls.	Chapter 1, Section 1.3 (SDS Sections 4, 7 and 8), Chapter 4, Section 4.1 (Storage), 4.2.2 (Engineering controls)	35, 36, 52, 62

Table 14: Check-list for use of ZDHC MRSL listed solvents as an ingredient in chemical formulations

Sr. No.	"To Do" Checklist	Reference Chapter and Section	Page no.
5	Calculate the Potential to Emit for VOC emissions from chemical formulations and monitor VOC emissions at the workplace using appropriate devices.	Chapter 4, Section 4.2.3.1(VOCs from formulations) and 4.2.3.2 (VOC monitoring at workplace)	64, 66
6	Take appropriate corrective actions to reduce VOC emissions from chemical inventory.	Chapter 4, Section 4.2.4	69
7	Prepare and execute a training plan to train all employees and workers on safe management of solvents.	Chapter 5, Section 5.1 and 5.2	73, 74
8	Dispose the solvent based formulations in appropriate manner as described in Section 13 of the SDS.	Chapter 1, Section 1.3 (SDS Section 13)	36

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