

Antimicrobials & Biocides

Background:

Antimicrobials and biocides are a group of chemicals that may be intentionally applied/used in textile, leather and footwear industries to preserve or increase the shelf life of formulations and to preserve semi-finished or finished articles when intentionally applied, providing effects such as odour control, and/or insect/fungus/microbes repellency.

Biocides, in general, have the purpose of destroying, deterring, rendering harmless, preventing or controlling activity of harmful organisms,. Whereas hazardous properties are in general unwanted within textile and leather chemicals, these properties are a precondition for the purpose of biocides to control harmful living things.

Biocides used as in-can-preservatives can be found as residues on fabrics and leather articles. But the concentrations of active biocides found on finished articles are in general below the minimum inhibitory concentration, therefore their use does not pose a risk to humans or the environment.

Leather intermediates (wet blue, wet white, etc) can travel a long distance before being processed. Transport and storage are therefore unavoidable, and the material must be protected from deterioration.

Uses in textile & footwear supply chains:

Biocides are applied:

- For antimicrobial treatment of textiles
Note: Usually antimicrobial treatment of finished leather is not necessary.
- For preservation of raw hides, leather intermediates (intermediate tanned leather, wet blue, wet white) and furs in order to protect them from microbial infestation and decay.
- As in-can preservatives for aqueous textile and leather processing chemical formulations.¹

Biocides can also be used in cleaning agents directly or indirectly. E.g. as intentional active agents in the soaps, detergents, disinfectants, etc, used to clean final fabric and/or floor cleaners, etc., which means there is a chance of contamination in the final articles/wastewater.

Harmful effects of biocides and antimicrobials

Most of the biocides listed in the ZDHC MRSL found in the textile and footwear industries show varied harmful effects; being toxic, contact irritant, very toxic to aquatic life, and persistent in the environment, etc. Therefore, excessive use can be detrimental to the environment.

All these effects are not caused by each individual antimicrobial or biocide, but certain health and environmental hazards are common to these substances.

On the other hand, these hazardous properties are necessary to protect against microbes, fungi and insects to maintain the usability and stability of aqueous products and leather intermediates for as long as possible.

1) Chemistry and terminologies:

Currently there are four substances restricted in the ZDHC MRSL and banned from intentional use in the textile, leather and footwear industries.

- DMFu (Dimethyl fumarate)
- Permethrin
- Triclosan
- Orthophenylphenol (OPP)

1.1. Dimethyl fumarate(DMFu) CAS No. 624-49-7

Dimethyl fumarate is an ester of fumaric acid. It is a trans-isomer of butane-1,4-dicarboxylic acid. DMF (dimethyl fumarate) can sometimes be easily confused with DMF (dimethylformamide) and may be abbreviated in the same way. Therefore, dimethyl fumarate is sometimes abbreviated as DMFu in some literatures.

DMFu has no harmonised classification according to EU Reach Annex VI. But at a very low concentration, DMFu is known to cause contact allergic dermatitis (CAD).²

Use of DMFu is restricted in the EU since 2009 ([DMFu-EU-REACH-restriction-entry41](#))
There is no approval from authorities for use of DMFu as a biocide.

1.2 Permethrin CAS No. 52645-53-1

Permethrin can be found in different isomer forms due to its chiral nature and across the double bonds. The CAS number, however, will remain the same as it is for the racemic mixtures. Permethrin can be detected/tested by using LC-MS or GC-MS analysis.

There is a harmonised classification in EU CLP Annex VI: Permethrin
The U.S. EPA has classified permethrin as "likely to be carcinogenic to humans".³

In many situations, deliberate use of permethrin in the textile, leather and footwear industries is not permitted. However, it should be noted that permethrin is approved for use on wool curtains, carpets, rugs and floor coverings under BPR PT 18.⁴ Permethrin is permitted for use in personal protective equipment (PPE) (EU 2016/425, EPA registered product, APVMA registered product, PMRA registered product, etc.).⁵ Additionally, it is sometimes only allowed for specific purposes, such as military ones. All efforts should be made to maximise the chemical finish durability and to minimise losses to the environment.

Link to EU Biocidal Product Regulation (BPR) : [Permethrin-BPR-approval](#)

1.3 Triclosan CAS No. 3380-34-5

Triclosan is a chlorinated phenolic compound (a class of compound that is generally used as antimicrobial products). There are several testing methods available these days for detecting triclosan at ppb (ug/kg) to ppt (ng/kg) levels. However, a well-accepted industrial and regulatory technique is LC-MS/MS (triple quad) method due to its sensitivity and selectivity.

There is a harmonised classification in EU CLP Annex VI: Triclosan

Due to its toxicity and its persistency in the environment, triclosan is hazardous. Thus, accumulation in the environment is possible.

Triclosan is not approved in the EU according to BPR PT9 (Fibre, leather, rubber and polymerised materials preservatives): Link BPR: [Triclosan-BPR-approval](#)

1.4 Orthophenylphenol (OPP) and their salts CAS No. - 90-43-7)

Orthophenylphenol (OPP) is a substance from a class of compounds called phenols. Orthophenylphenol can be used by itself or with sodium or potassium salts. It can be detected in ppm levels conveniently by using advanced instrumentation such as HPLC or LCMS. Lower concentrations can be detected using the LC-MS/MS method.

Use of OPP is permitted as chemical preservation for transporting and/or storing raw hides, or tanned semi-finished products (wet-white, wet-blue). Chemical preservation of coated or uncoated finished leather is not permitted.

It is also permitted as an 'in-can preservative' in leather chemical formulations under the BPR PT6 up to the formulation limit of 5000 mg/kg.⁴

There is a harmonised classification in EU CLP Annex VI: OPP

OPP is already approved according to the EU Biocidal Product regulation for various applications: OPP-BPR approval.⁴

The BPR approval covers use as in-can-preservative (Product type 6). For product type 9 (Fibre, leather, rubber and polymerised materials preservatives), OPP is registered for legal authorisation and is under review of the authorities ("Initial application for approval in progress").⁴

2) Safer alternatives to antimicrobials and biocides:

The antimicrobials and biocides used in the textile and leather industries are highly potent chemicals and highly effective. Hence, it is still a challenge to find an exact match to replace them. However, if alternatives have been found to be also effective in the textile or leather application, it is recommended that a case-to-case study and a phase-out process is carried out to replace the current usage of these ZDHC MRSL restricted substances.

Any alternative selected must be carefully vetted to ensure a regrettable substitution is not made. Also, the chosen alternative must be conformant to the latest version of the ZDHC MRSL.

Nevertheless, a formal authorisation by a Competent Authority⁸ is required for biocides used in the ZDHC textile, leather and footwear supply chain, and the authorisation must cover these uses. (More details in the section: Biocides in the ZDHC MRSL).

The current prevalent biocides used in the textile, leather and footwear supply chain are:⁵

- As fungicides: TCMTB, CMK, OIT, IPBC, etc.
- As bactericides CMIT/MIT, BIT, etc.

This list might be helpful for stakeholders looking for guidance on potential alternatives that could be used due to existing registration/authorizations and existing experience on performance.

2) Important regulations:

Because of their hazardous properties, biocides are highly regulated chemicals covered by comprehensive legislation:

- The hazardous properties are documented by H-phrases according to CLP/GHS.⁷
- Specific, additional labelling rules according to biocide regulations must be applied to cover all intended uses.
- Regulations in some countries (e.g. EU, USA etc) cover the marketing and use of biocides through an authorisation by government agencies.
- Prior to authorisation, biocides are extensively evaluated by Competent Authorities. Suppliers need to comply with extensive information requirements covering all aspects of physical-chemical and eco-tox properties of the substance including a full review of potential human health and environmental risks.

3) Biocides in the ZDHC MRSL

In general, for all biocides used in textile, leather, footwear or other chemicals that conform to the ZDHC MRSL, a formal authorisation of the biocide by a Competent Authority is required or at least the biocide must be registered for legal authorisation and is under review for uses in the textile, leather or footwear supply chain (e.g. listed in the EU BPR Annex I as "initial application for approval in progress").⁴

ZDHC MRSL limits the use of authorised biocides to only authorised areas. In addition, they may only be used below the authorised concentration limit and all efforts should be made to avoid them.

Additionally, the ZDHC MRSL lists some specific biocides, which have been known to be used in textile and leather processing. These specific substances are restricted in the ZDHC MRSL for intentional biocidal use with the exception of some specific applications mentioned in the ZDHC MRSL. There must be an approval for these in the authorisation documents.

References:

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<https://www.blauer-engel.de/en/productworld/leather?mfilter%5B0%5D%5Btype%5D=privatecommercial&mfilter%5B0%5D%5Bvalue%5D=commercial&url=https%3A%2F%2Fwww.blauer-engel.de%2Fen%2Fproductworld%2Fleather>
2. Information on Dimethyl Fumarate <https://www.anses.fr/en/content/dimethyl-fumarate-anses-update-available-knowledge>
3. Permethrin as a likely to be a carcinogen
<https://www.federalregister.gov/documents/2020/07/28/2020-14419/permethrin-pesticide-tolerances>
4. Webpage of the European Chemical Agency: BPR Legislation - ECHA (europa.eu)
<https://echa.europa.eu/regulations/biocidal-products-regulation/legislation>
5. Website of US Environmental Protection Agency.
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6. German Federal Institute for Occupational Safety and Health: BAuA - Biocides - The Biocidal Products Regulation - Federal Institute for Occupational Safety and Health
<https://www.baua.de/EN/Topics/Safe-use-of-chemicals-and-products/Chemicals-law/Biocides/Biocides.html>
7. EU Regulation No. 1272/2008 (CLP Regulation; annex VI on Harmonized Classification <https://osha.europa.eu/en/legislation/directives/regulation-ec-no-1272-2008-classification-labelling-and-packaging-of-substances-and-mixtures>
8. Globally Harmonized System of Classification and Labelling of Chemicals (GHS) 9th Revised Edition, United Nations New York, Geneva, 2021;
https://unece.org/sites/default/files/2021-09/GHS_Rev9E_0.pdf

Abbreviations

TCMTB	(Benzothiazol-2-ylthio)methyl thiocyanate
CMK	(p-chloro-m-cresol)
OIT	2-Octyl-2H-Isothiazol-3-One
IPBC	Iodopropynyl butylcarbamate
CMIT/MIT	Chloromethyl-methylisothiazolone
BIT	Benzisothiazolinone
CLP	Classification Labelling and Packaging (ECHA)
GHS	Global Harmonised System of classification and labelling of chemicals