HAZBREF Case Studies and Sector Guidance for the Textile Industry

TALLINN CONFERENCE, 21 - 22.05.2019, Tallinn

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Agenda

1. What we have done so far
2. Preliminary Case Study results
3. Case Studies related BAT Recommendations

What we have done so far

Case studies

- Acquisition and selection of 4 plants in Germany (2), Sweden and Poland
- Analysis of the selected sample plants
  - Development of an analysis grid for investigation and evaluation of techniques and chemicals management
  - Preparation of a list of all chemicals used (including substances in mixtures) – has been submitted to the project partners
  - Identification of hazardous substances used (also in mixtures) based on information from the material safety data sheets (and assessments of the operators)

What we have done so far

Case studies

- Identification of BAT candidates for emission prevention
  - Commented list of processes and practices with regard to techniques for the prevention or control of emissions of hazardous substances
- Analysis of legal requirements
  - Evaluation of information provided by plant operators on the procedure, coordination and content of licensing procedures
  - Discussions with plant operators and staff competent for chemicals management; practical problems with the implementation of REACH and other relevant legislation

What we have done so far – from case studies to BAT

What we have done so far – textile finishing requires manifold chem. products

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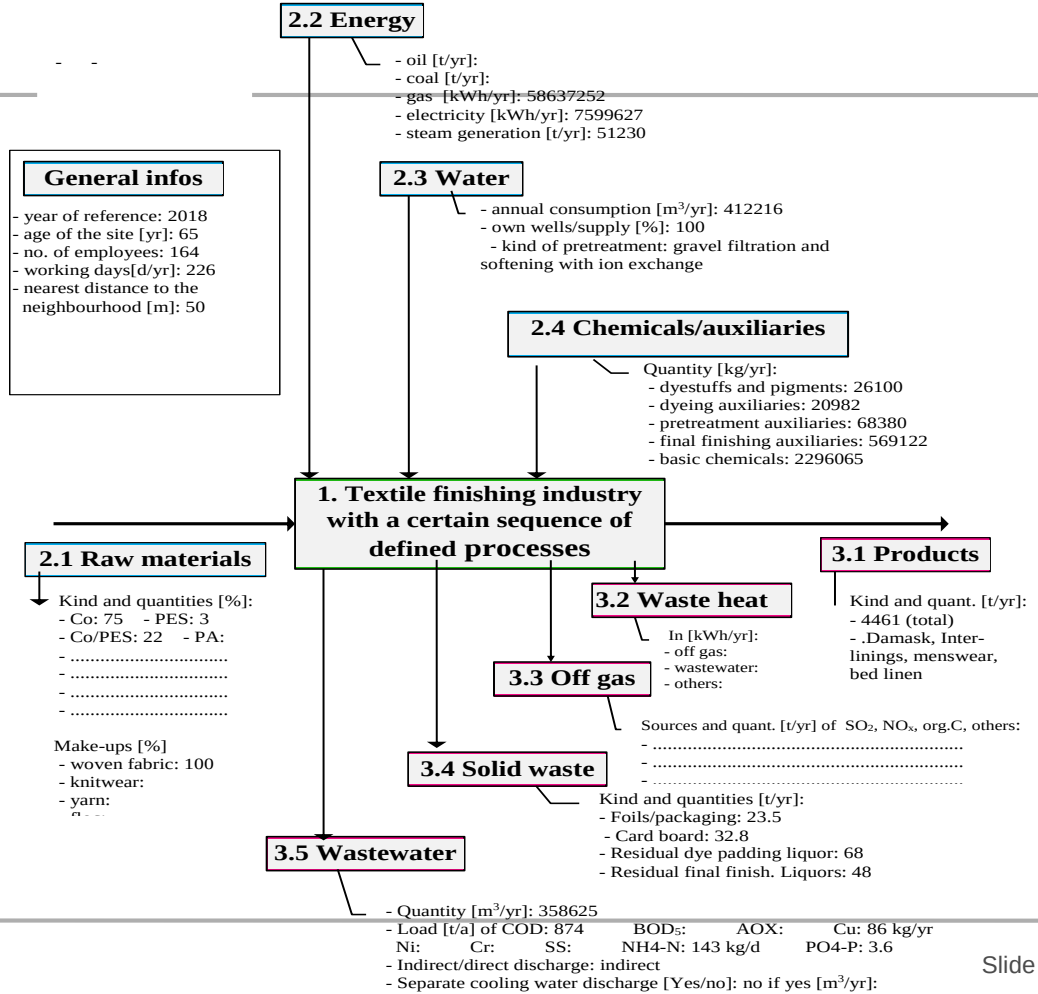
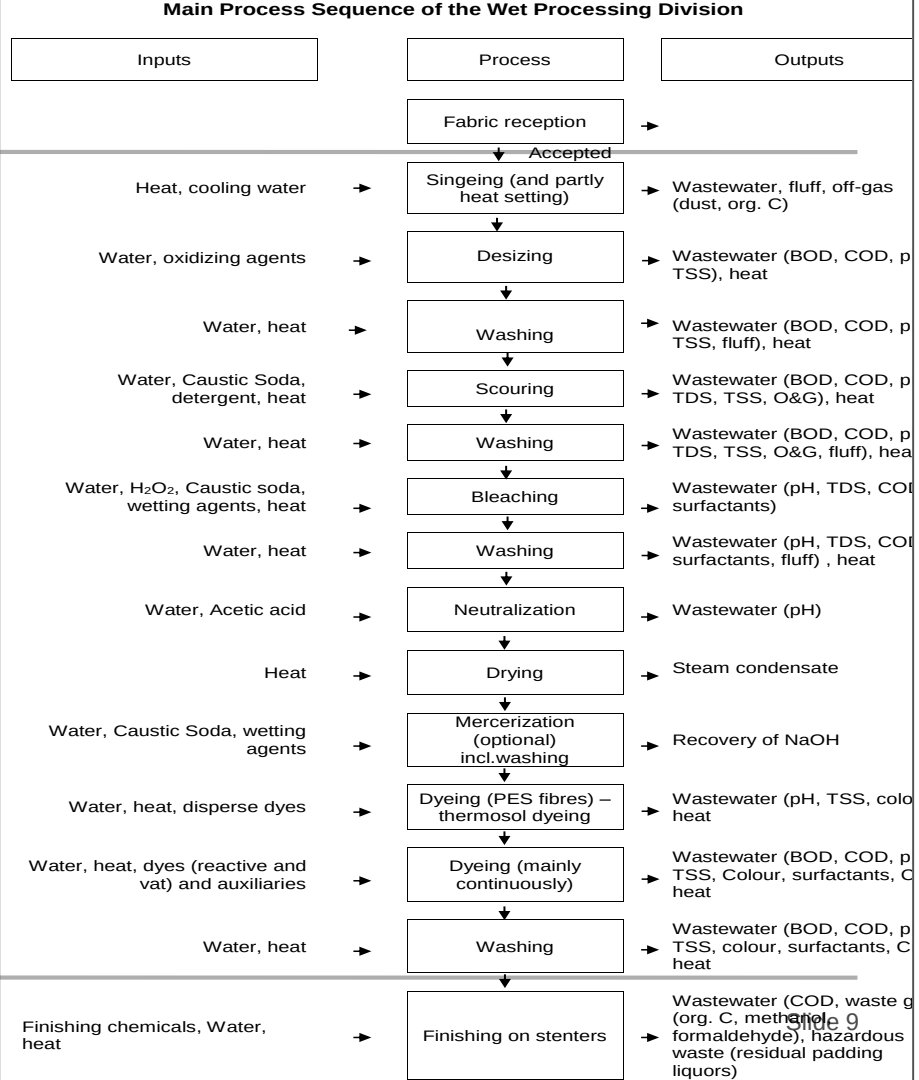
What we have done so far

Annual mass stream overview



What we have done so far –

(main) Process sequence



What we have done so far – Chemical list – available to project partners

Form 3

3. Textile auxiliaries for dyeing and printing

- 3.1 Dyestuff solubilizing and hydrophobic agents
- 3.2 Dispersing agents and protective colloids
- 3.3 Dyeing wetting agents, deaeration agents
- 3.4 Levelling agents
- 3.5 Carriers
- 3.6 Crease-preventing agents
- 3.7 Dyestuff protecting agents, boildown protecting agents
- 3.8 Padding auxiliaries
- 3.9 Fixing accelerators for continuous dyeing and printing
- 3.10 Aftertreatment agents for fastness improvement

No.	Commercial name	Producer	Chemical characterisation General and individual substances if available (see CAS no.)	Known CAS no.
3.8.1	Ruco Print PMI	Rudolf GmbH	Polyacrylat	55965-84-9
3.11	Peripret PW	Textilchemie Dr. Petry Gm	Polyacrylat Copolymere, wässrige Dispersion	
3.2	Dekol SN New liq	Archroma Distribution and	Polycarboxylat, Copolymerisat, Natriumsalz, in water	
3.8	Primasol NF liq	Archroma Distribution and	Alkylphosphat, Ammoniumsalz, in water	298-07-7 4971-47-5 78-42-2
3.2	Setamol Disperse WS	Archroma Distribution and	naphthalenesulfonic acid-formaldehyde-polycondensate as sodium salt	
3.17	Redulit EX	CHT	Reduktionsmittel	310-73-2 16940-66-2

What we have done so far – Case study – spec. consumption figures

- Spec. consumption of natural gas for boiler house: 9.2 kWh/kg
- Spec. consumption of natural gas for stenters: 2.3 kWh/kg
- Spec. electricity consumption: 1.0 kWh/kg
- Spec. water consumption: 85 l/kg
- Spec. consumption of sizing agents (add-on): 35 g/kg
- Spec. consumption of pretreatment auxiliaries: 35.9 g/kg
- Spec. dyestuff/pigments consumption: 23.6 g/kg
- Spec. consumption of dyeing auxiliaries: 24.8 g/kg
- Spec. consumption of final finishing auxiliaries: 33.9 g/kg
- Spec. basic chemicals: 313.2 g/kg

Note: figures include water content of formulations

What we have done so far – Case study – spec. emission figures

- Spec. wastewater flow: 77.0 l/kg
- Spec. COD emission: 140 g/kg
- Spec. total nitrogen emission: 1.8 g/kg
- Spec. phosphate emission: 0.5 g/kg
- Spec. copper emission: 9 mg/kg
- Spec. sulphate emission: 44.9 g/kg

What we have done so far – Chemical lists

Fundamental issue → often limited and insufficient data

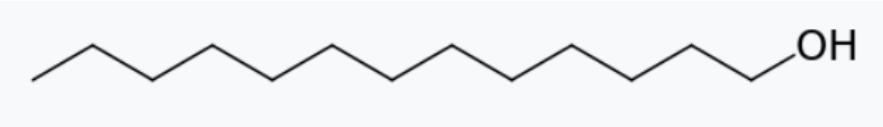
- normally, material safety data sheets (MSDS) are the only source of information for textile finishing industries
- The quality (content of information) of MSDS varies strongly
- Only few chemical suppliers submit MSDS with detailed information (see very good and bad example)
- Consequently, chemicals suppliers should be forced to provide MSDS with sufficient information

What we have done so far – Chemical list – very good MSDS

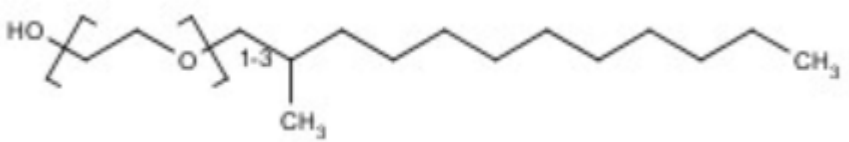
Example of a washing agent

Chemical·component¤	Concentration·in·the·commercial·chemical·product·(weight-%)¤	Mentioned· CAS· number· for·contained·chemical·compounds¤
Isotridecanolethoxylate¤	25·-·30¤	69011-36-5,·polymer¤
Ethoxylated· and· propoxylated· fatty·alcohols·with·a·chain·lengths·of·C·12·and· C15· which· is· linear· and·branched¤	10·-·20¤	120313-48-6;·polymer¤
2-[2-(2-Butoxyethoxy)ethoxy]-ethanol¤	3·-10¤	143-22-6,·205-592-6;¶ 01-2119531322-53¤
Polyacrylic·acid,·copolymer¤	1·-·5¤	polymer¤
Tetraoxahexadecane-1-ol¤	1·-·3¤	1559-34-8;·216-322-1¤
3,6,9,12-Tetraoxahexadecane-1-ol¤	1·-·3¤	112-34-5;·203-961-6;·¶ 01-2119475104-44¤

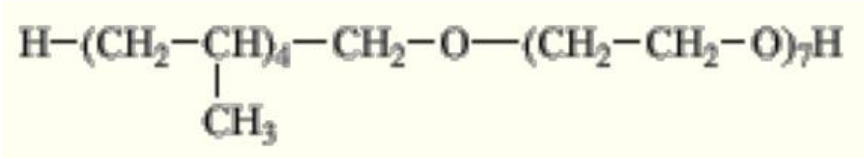
What we have done so far – Chemical list – compounds of a washing agent



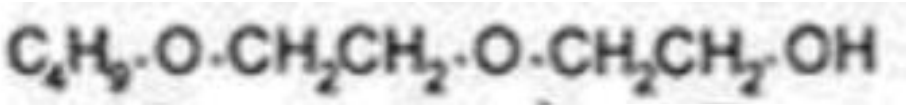
1-Tridecanol



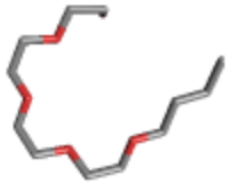
Isotridecanol ethoxylated



Iso-C13 branched primary AE, EO7



2-(2-Butoxyethoxy)ethanol

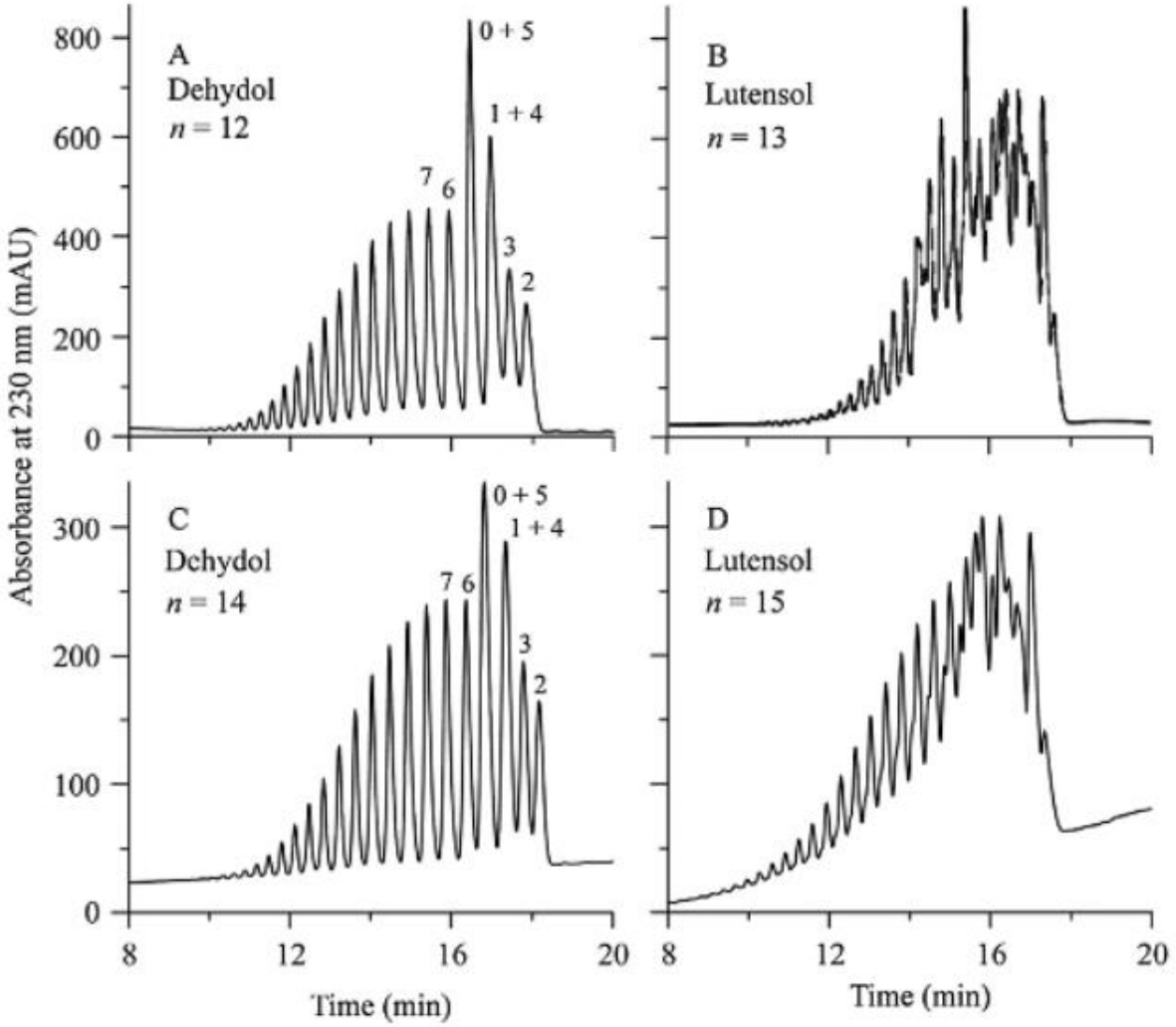


3,6,9,12-Tetraoxahexadecane-1-ol

What we have done so far

Fatty alcohol ethoxylates

Chromatogram of fatty alcohol ethoxylates – technical products indicates that they consist of plenty of homologues, isomers, by-products and impurities



What we have done so far – Chemical list – bad MSDS

Sizing agent

- The MSDS is very short and incomplete
- Composition: “Polymer based on starch, modified” - however, the products consist of pure polyvinyl alcohol (PVA) and does not contain any starch
- Specific COD value: 1470 mg O_2/g, no specific BOD_5 value
- Biodegradability: “>90 % biologically eliminable in the OECD 302 B Test”. Additional information is needed: biodegradable but only under certain conditions: F/M < 0.15 kg BOD_5/kg MLSS x d, temperature of 15 - 37 °C, adaptation required

What we have done so far – Chemical list – high aquatix toxicity of ….

Fatty alcohol ethoxylates – biodegradable but very toxic to aquatic organisms (all trophic levels except bacteria)

- Bacteria (activated sludge) (EC 50) > 100 mg/L
- Algae (EC 50): > 0.1 – 1 mg/L
- Daphnia magna (EC 50): > 1 – 10 mg/L
- Fish (Leuciscus idus) (LC 50): > 0.1 – 1 mg/L

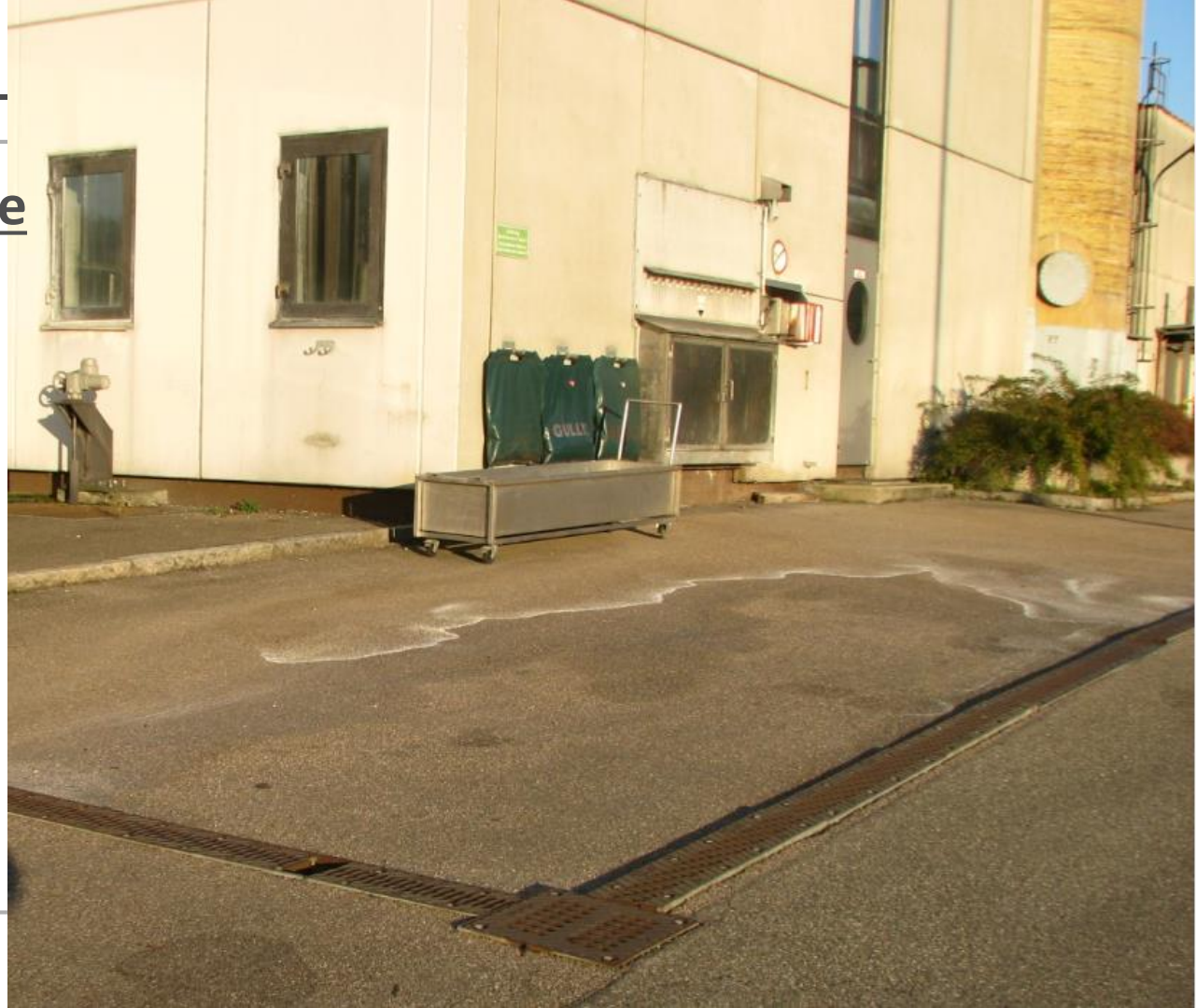
➔ Important to avoid any accidental release

Fish kill in a small German river because of an accidential spillage of fatty alcohol ethoxylates – April 2019

What we have done so far -

Proposed BAT for storage

Dedicated unloading area with precautionary measures in case of spillages for liquid bulk chemicals; here: acetic acid, NaOH, KOH, H_2O_2, urea, two main surfactants



What we have done so far –

Proposed BAT for storage

Double walled tanks with overfilling prevention and leakage detection for bulk chemicals (NaOH, KOH, H_2O_2, detergents, urea); for H_2O_2 , explosion prevention is required

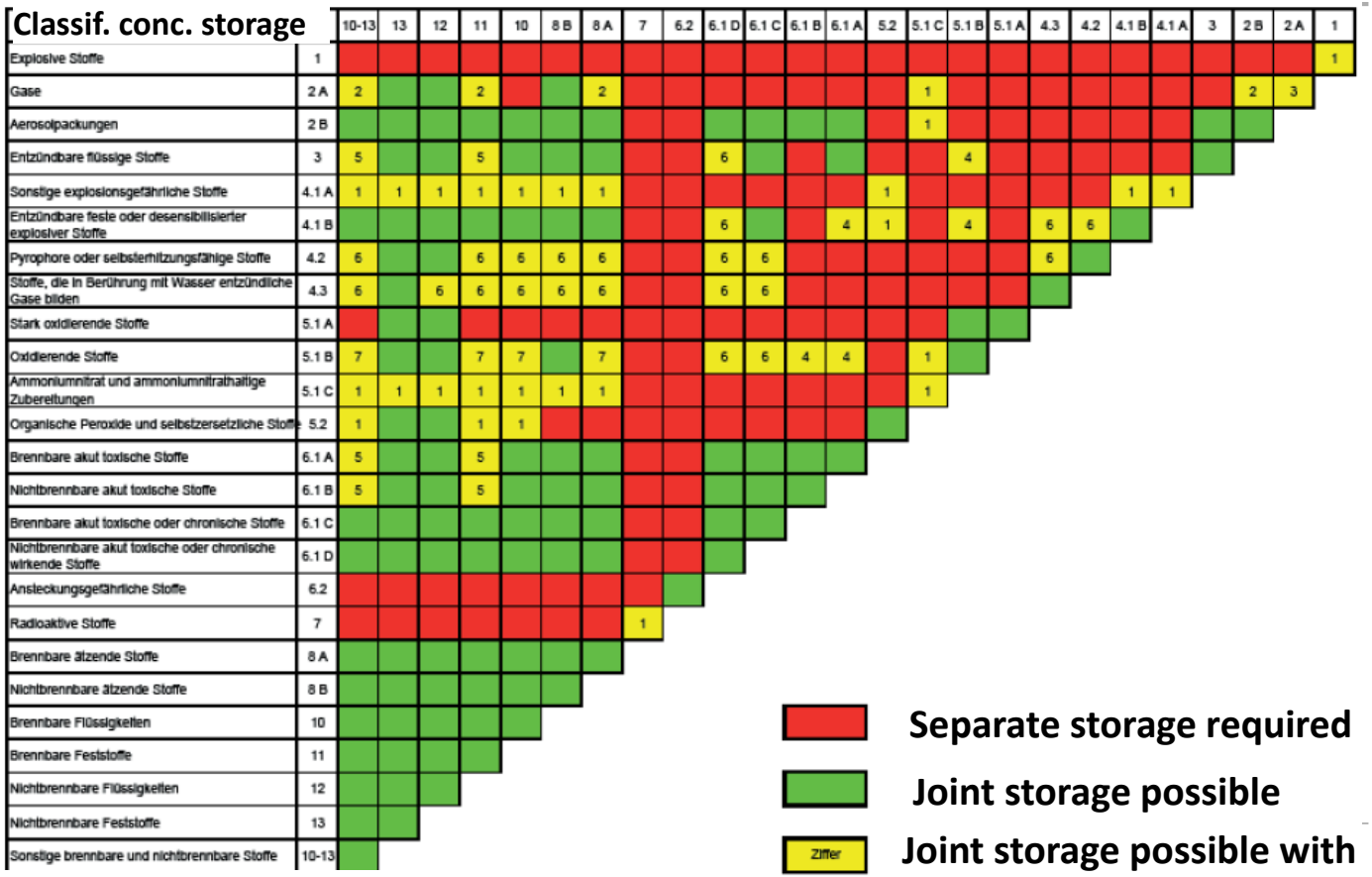
Proposed BAT for storage

All IBCs, small tanks and drums on catchment facility (volume: at least the volume of the biggest tank or IBC)

What we have done so far – proper storage of chemical products

Proposed BAT for storage

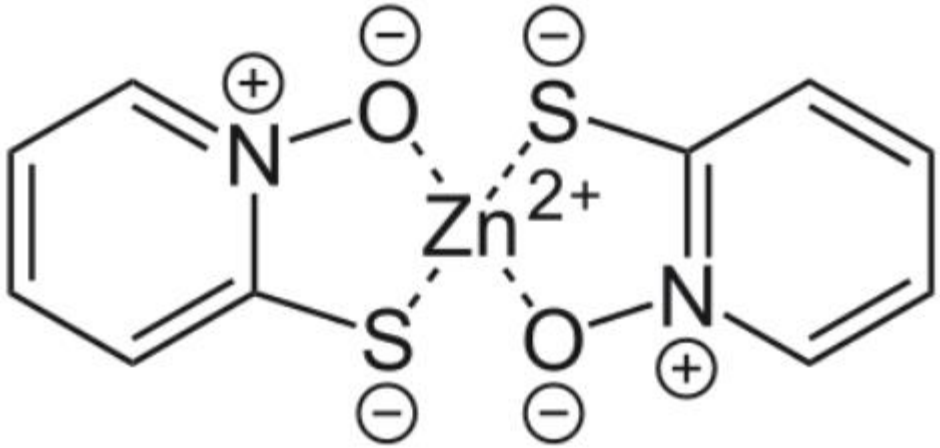
Joint storage – yes/no;
e.g sodium dithionite shall be stored in a separate room (dry and cool)



Source: Technical Rules for Hazardous Substances (TRGS 510)

What we have done so far – example for identified hazardous substances

Zinc pyrithione – a fungicide CAS no: 13463-41-7



What we have done so far – example for identified hazardous substances

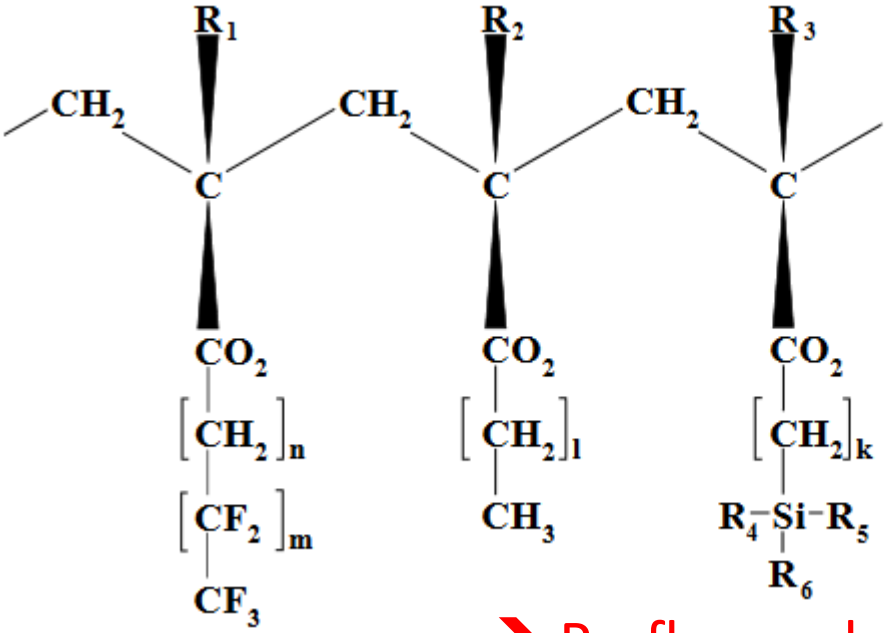
Zinc pyrithione – biodegradable but extremely toxic to aquatic life (all trophic levels):

- Bacteria (activated sludge) (EC 50) > 2.2 mg/L
- Algae (Selenastrum capricornutum (EC 50): > 0.028 mg/L
- Daphnia magna (EC 50): > 0.0082 mg/L
- Fish (Pimephales promelas) (LC 50): > 0.0026 mg/L

➔ "biodegradable in biol. WWTP" – BUT: only at very low concentrations (below inhibiting/toxic level)

➔ **proposed BAT: Zero emission of any concentrated liquor – better to avoid the application at all**

Fluoroalkylacrylate copolymer



$R_{1\text{-}3}$: H, CH_3

k : 2-5
l : 7-21
n : 1-4
m : 6-12

➔ Perfluoro chain can be cleaved

What we have done so far – example for identified hazardous substances

MSDS does not contain sufficient information on biodegradability/bioeliminability and ecotoxicity

Biodegradability/bioeliminability: > 70 % (OECD 302 B) – will release perfluorinated chains

Bacteria toxicity (activated sludge): > 1000 mg/L

Fish toxicity (LC 50): > 10 – 100 mg/L

➔ proposed BAT: Zero emission of any concentrated liquor – better to avoid the application at all

SVHC list, WFD prioritysubstances, ZDHC MRSL and Research List etc.

➔ Taking into account the hazard-based lists of chemicals such as the textile relevant substances of the SVHC List, the priority substances of the Water Framework Directive, the ZDHC MRSL and ZDHC Research List and others – not many textile chemicals can be found

Permit conditions – integrated permits

1. Chemicals compounds – restrictions and conditions to minimise/prevent the use of certain hazardous substances and concerning the storage/handling of chemical products
2. Permit of intake water if abstracting from natural sources with conditions concerning the minimisation of water consumption
3. Wastewater: ELVs and conditions/stipulations for individual streams or liquid residues (e.g. residual padding liquors), conditions/stipulations on third-party monitoring (frequency and parameter list)

Permit conditions – integrated permits

4. Self-monitoring for wastewater emissions from 24-h-flow proportionally taken composite samples (COD, colour, conductivity, pH, total nitrogen, ammonium/ammonia, phosphate, total P etc., ecotoxicity in case of direct discharge)
5. Emissions to air: process-specific ELVs and conditions/ stipulations includin the prescription of third-party monitoring of emissions to air from certain processes
6. Solid and liquid waste: conditions/stipulations concerning recycling/recovery and disposal of solid and liquid wastes (e.g. residual padding liquors)

Permit conditions – integrated permits

7. Conditions concerning energy efficiency (e.g. waste heat recovery from wastewater and waste gas)
8. Occupational health and safety aspects

➔ **Integrated permits represent the ideal situation (still rarely the case in practice)**
– model permits can be developed

BAT

- Proposal – to have BAT
  - On textile-specific storage and handling issues
  - on the prevention/ minimisation of certain hazardous substances
  - Zero emission of certain process liquors such as residual padding liquors and residual printing pastes/inks containing substances of concern

What to do next?

Development of a textile sector guideline

- Consolidation of results from HAZBREF countries
- Discussion of the (very) first draft of the sector guideline specifying content, layout, and sections
- To continue the technical discussion with the project partners of the HAZBREF
- Panel discussion this afternoon

Thank you very much