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REACH and Safe Use of Chemicals in Mixtures

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27.03.2007

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Objectives

- “Save Use” under REACH
- Consequences of REACH for Downstream Users
- Applicability of Banding Models
- The critical component approach
- Provide a forum for discussion

REACH and Safe Use of Chemicals

- Aim of REACH**:** to ensure safe use of chemicals

- Important criterion for safe use:

Exposure Level ≤ DNEL

↓ How can this be achieved?

➢ Banding models**:** practical methods for deriving DNELs, Exposure Potentials and Risk Reduction Measures in case no TLVs or measured exposure values are available.

Some REACH Challenges for Downstream Users (I)

- REACH will require exposure, hazard, and risk assessments of ca. 30 000 registered substances nearly always occuring in ***mixtures***
- > 2 million businesses in Germany use “chemicals” – Henkel is an important provider of preparations
- For Small and Medium Enterprises (SME) labels and safety data sheets are the main sources of toxicological information. Many SMEs will have difficulties applying risk assessments to chemicals and thus will depend on their suppliers
- Distributors will have to draw up anticipated workplace risk assessments to accompany their products
- SMEs want *practical* help and methods that are compatible with their current procedures

Some REACH Challenges for Downstream Users (II)

A number of key issues in the context of REACH are unique to preparations and can not be addressed by extrapolation of the approaches developed for pure substances:

- the preparation of Safety Data Sheets,
- the development of Exposure Scenarios,
- the identification of Risk Reduction Measures, and
- the way in which DNELs and PNECs for preparations are derived.

Furthermore,

- only ca. 700 chemicals have TLV- values. For major components in a preparation DNELs will not be available before the last registration under REACH after 11 years.

➢ These issues need urgently to be addressed and pragmatic, proportionate and ***workable*** solutions have to be found.

Proposals for Possible Solutions

1) A critical component approach (i.e., the substance in the mixture with the highest risk potential represents the whole preparation)

2) A tiered approach including a screening level for inhalative and dermal pathway to sort out mixtures/substances requiring a more detailed approach

3) Compatibility with the VCI Use and Exposure Matrix to communicate information up and down the supply chain

➢ The first two points will be addressed in more detail.

1) The Critical Component Approach

Focusing on the substances with the highest risks (critical component approach) is a valuable instrument to overcome the complexity in assessing preparations.

General concept:

- Use of the banding system to identify the critical component based on hazard-, exposure-, and risk- assessment for all substances in a mixture.
- If necessary, additivity of effects has to be taken into account.
- For all relevant exposure pathways focus on the substance(s) in the highest risk band(s).
- Apply adequate risk measures to control the critical components risks. De facto, any lesser risk levels will also be controlled

2) Banding Hazard, Exposure, Risk, & Control

➢ The COSHH Concept (Brooke, 1998), the RIP 3.2-2 P-TGD, the BAUA protection levels (e.g. Packroff et al. 2006), the ILO Chemical Control Toolkit, the TNO Stoffenmanager, and the ECETOC TRA already have so called banding models included:

- Banding concepts work with categories (groups).
- Categorization of Hazards is based upon EU Classification criteria.
- Categorization of Exposure is based upon quantity and availability.
- If hazard & exposure can be banded, it is also possible to associate the risk and risk reduction measures with a control band.
- If available, more reliable TLVs/DNELs/Exposure values replace initial category values.

Brief Outline of the Banding Methodology for Assessment of Vapors (Brooke, 1998)

Hazard band	Amount	Volatility
A - skin / eye irritants B- harmful C- toxic, corrosive, skin sensitiser D- very toxic, harmful to reproduction E- cancer, asthma, genetic damage	Small (g, ml) Medium (kg, l) Large (t, m3)	Low (vapours < 5 hPa) Medium (vapours 5 - 250 hPa) High (vapours > 250 hPa)

Increasing risk

DNEL

Derived Exposure Level (DEL)

Control Approaches (Protection Levels) from 1 - 4

1. GENERAL VENTILATION A good standard of general ventilation	Least reduction in exposure
2. ENGINEERING CONTROL LEV eg single-point extractor close to source, ventilated partial enclosure.	↓
3. CONTAINMENT Enclose or contain – small breaches may be OK	Most reduction in exposure
4. SPECIAL Expert advice is needed – seek help	Get advice

Risk Assessment Example

(automatically performed for each substance in a formulation)

- Allocate Hazard Band
- Assign Quantity Group
- Assign Availability Group
- Combine Quantity & Availability to derive Exposure Predictor Band
- Compare Hazard and Exposure Predictor Bands
- If Exposure > Hazard: Find the appropriate Risk Reduction Measure

Hazard group allocation

Corresponding EU R-Phrases	Hazard Band	Target airborne concentration range (DNEL)
R10-12,19, R36, R38, R50-53, R59,R65,R66. Substances not allocated to another band	A	>50 to 500 ppm
R20, R21, R22, R21/22, R20/21/22, R67	B	>5 to 50 ppm
R23/24/25, R33, R34, R35, R37, R39/23/24/25, R40/20/21/22, R41, R43, R48/20/21/22	C	>0.5 to 5 ppm
R48/23/24/25, R26/27/28, R39/26/27/28, R40 Carc. Cat. 3, R68 Muta cat 3 (formerly R40 Muta cat 3), R62, R63, R64	D	<0.5 ppm
R42, R45, R46, R49, R60, R61, R68	E	Carcinogens or asthmagens: Seek specialist advice

Exposure Assessment I:
Assign Quantity Used-Groups

Amount used	Solid	Liquid
Small	< 1000 g	< 1000 ml
Medium	1-1000 kg	1-1000 l
Large	> 1t	> 1 m3

800 ml = Small

Exposure Assessment II: Assign Volatility-Groups

Volatility	BP	VP
Low	> 150 °C	< 5 hPa
Medium	50-150 °C	5-250 hPa
High	< 50 °C	> 250 hPa

1hPa = Low

Exposure Assessment III:
Combine Availability and Quantity

Control approach	Exposure predictor band (DEL in ppm)				
	mg & low/med.; solid in liquid	g & low; mg & high	g & med./high; kg/to& low	kg & med./high; to & med.	to & high
General ventilation	≤ 0.5	0.5 – 5	5 – 50	50 – 500	> 500
Local exhaust	≤ 0.05	0.05 – 0.5	0.5 – 5	5 – 50	50 – 500
Containment	≤ 0.005	0.005 – 0.05	0.05 – 0.5	0.5 – 5	0.5 – 5

Control approach selection based on DEL/DNEL

Amount used	Low dustiness or volatility	Medium volatility	Medium dustiness	High dustiness or volatility
Hazard group A				
Small	1	1	1	1
Medium	1	1	1	2
Large	1	1	2	2
Hazard [illegible]				
Small	1	[illegible]	[illegible]	1
Medium	1	[illegible]	[illegible]	2
Large	1	[illegible]	[illegible]	3
Hazard group C				
Small	1	2	1	2
Medium	2	3	3	3
Large	2	4	4	4
Hazard group D				
Small	2	3	2	3
Medium	3	4	4	4
Large	3	4	4	4
Hazard group E				
For all hazard groups, substances, chose control approach 4				

General ventilation

Necessary Information

Core data:

- Concentration of chemicals in product
- Rough estimate of quantity handled
- EU R-Phrases of chemicals in product
- Inhalation: Vapour pressure/dustiness
- Dermal: Log Kow & mol. Weight

Additional (task/process- specific) information:

- Application temperature?
- Creation of aerosols?
- Indoor or outdoor use?
- Substance used for more than 30 minutes a day?
- Large or small working area?

Example Screenshot HEAL (Human Exposure Assessment Levels) Tier 1: “Critical Component” and “Save Amount”

Search for products | Reset entries | Report

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SAP:	2020
Product name:	2 Component Epoxy Resin
Product group:	Floor coating
Product type:	Reaction resin
Business unit:	X
Process T (°C):	21
Exp. duration:	8 hrs
Substance owner:	
pH Value	
Labeling	
Spray Appl / Dust.	No

Dermal exposure	Eye Irritation
Pesonal Protection (e.g. cloves)	Under construction
9003-36-5	Bisphenol-F-Harz
Inhalation exposure	
Engineering control necessary (>10 kg)	
2855-13-2	Isophorone diamine

R-Phrase | HEAT to HEAL | MAK/DNEL | Penetration

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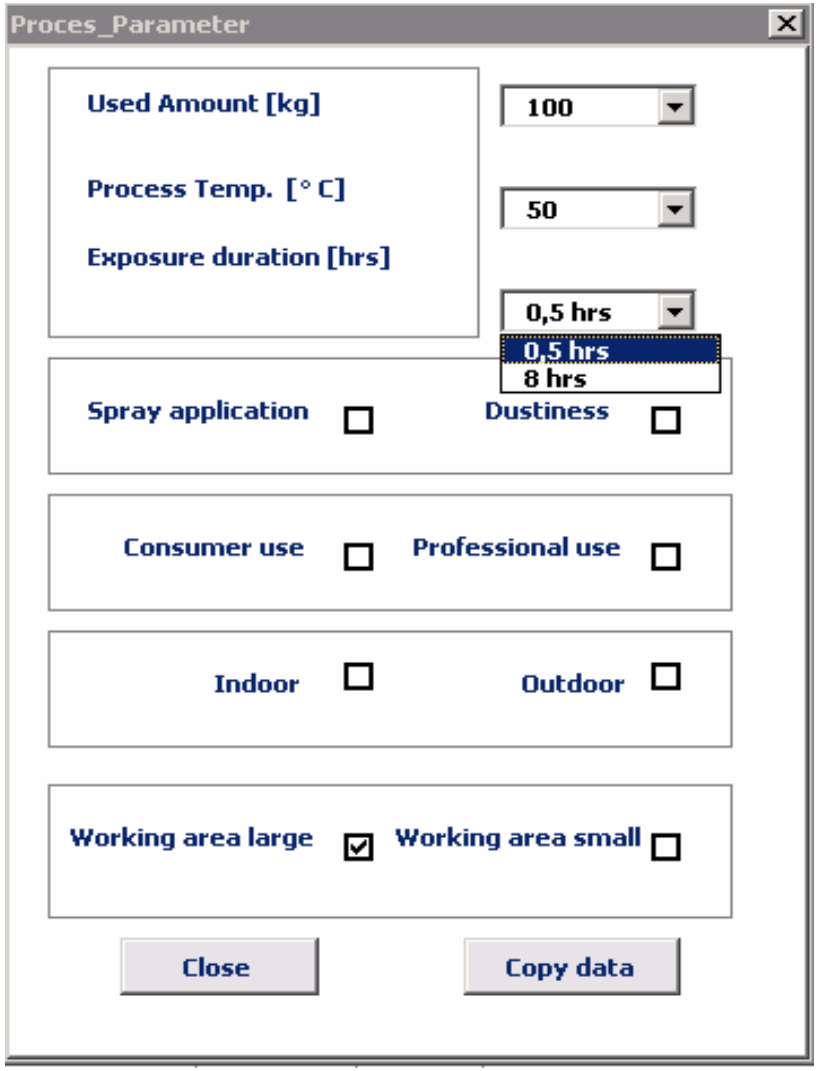
Amount

Pos	Substance	Name	CAS	Conc.	R-Phrase	Control approach
10	14	Epoxidharz MG > 700	25067-38-6	20-25	R36/38	1
20	26	Bisphenol-F-Harz	9003-36-5	10-15	R36/38, R43, R51/53	1
30	18	Monoglycidylether auf Basis eines C12-C1	6809-97-2	2-5	R36/38, R43, R52/53	1
40	19	Hexandioldiglycidylether	16096-31-4	1-2	R36/38, R43, R52/53	1
50	20	SiO2 (amorph)	14808-60-7	30-40		1
60	21	Titandioxid	13463-67-7	2-5		1
70	16	Isophorone diamine	2855-13-2	5-10	R21/22, R34, R43, R52/53	2
80	22	Benzylalkohol	100-51-6	2-5	R20/22	1
90	23	Salicylsäure	69-72-7	1-2	R22, R41	1
100	25	M-XYLYLENDIAMIN (MXDA)	1477-55-0	1-2	R20/22, R34, R43, R52/53	1

0,5	1
1	1
2,5	1
5	1
7,5	1
10	1
15	2
30	2
50	2
75	2
100	2
150	2
200	2

Example Screenshot: Entry of specific Process Data



HEAL Tier 2: Exposure Calculation for the Critical Component IPDA in a 2-Component Epoxy Floor Coating

Air concentration other...specify next page

Parameter	Selection	Value	Ref.
room size	-	100 m³	
air exchange	leaky home	2,5 h⁻¹	[4]
weight of product used	-	20000 g	
weight fraction of substance	-	7,7 %	
vapor pressure of substance at 20°C	other...specify next page	0,02 hPa	[5]
air pressure	- St	1013,25 hPa	
exposure duration	-	180 min	
use duration	-	120 min	

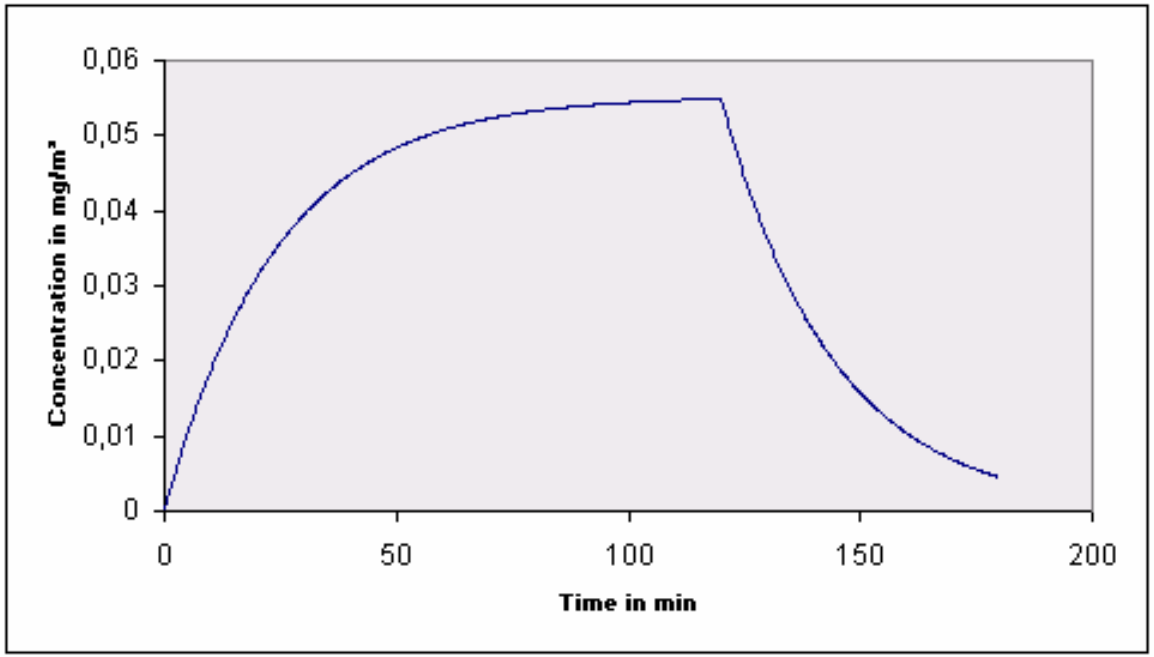
Inhalative Exposure

Parameter	Selection	Value
Body weight	Man 1	70 kg
Inhalation rate	-	0,0105556 m³.min⁻¹
Bioavailability	-	100 %

Systemic exposure

new

0,984 µg/kg BW/use



	Conc. in mg/m3
Max. value	0,05489531
Average value	0,0362950
Factor	1,5

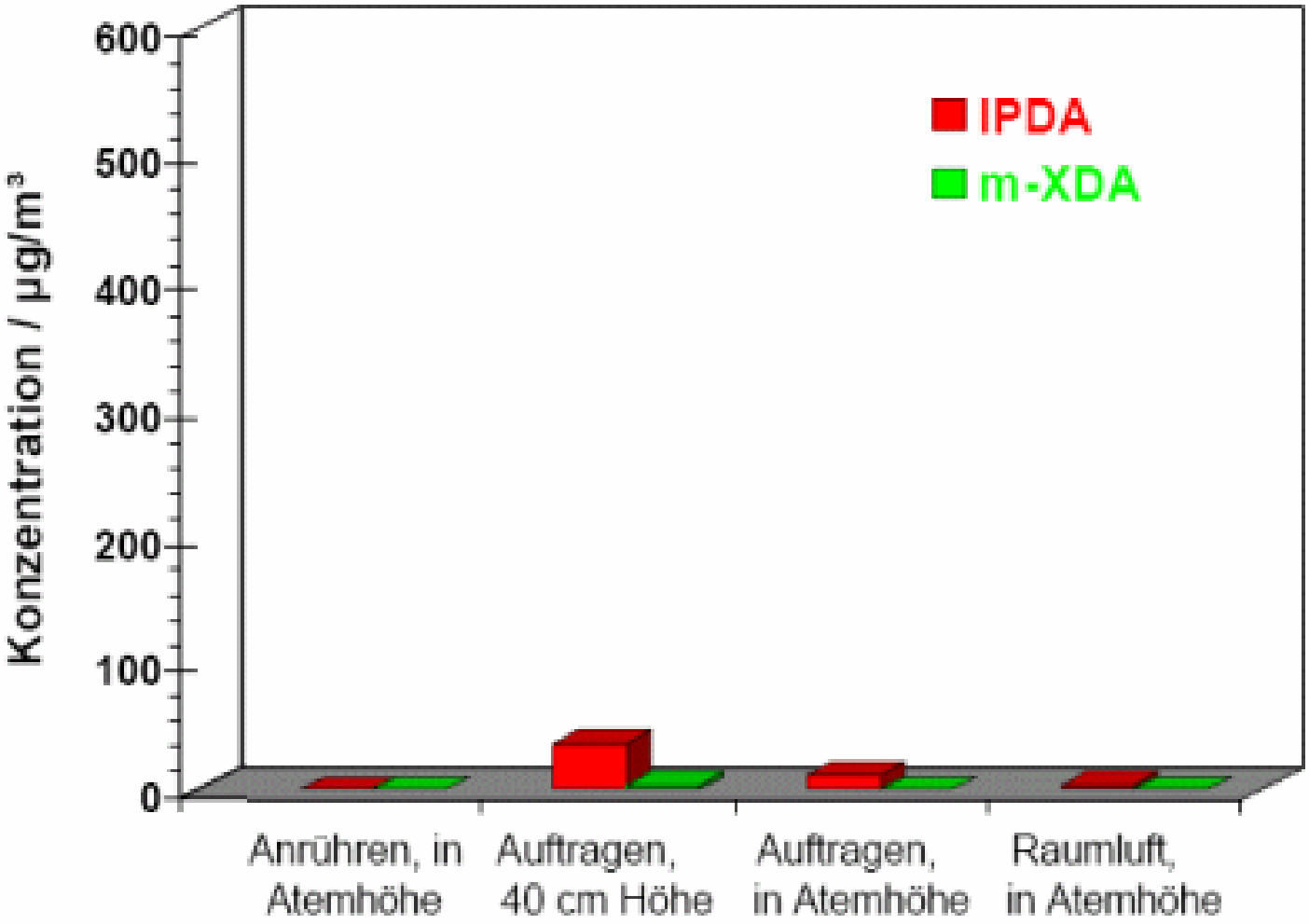
Start

Comparison with measured Data (BG Bauwirtschaft, 2005)

1) Mixing of 2-Component Epoxy Floor Coating

2) Application of Epoxy Floor Coating in a Garage

Measured IPDA & m-XDA Concentrations during Mixing and Processing match the calculated Values



Example Screenshot for a possible SDS Annex

29.08.2006 **Chemical Safety Assessment (DRAFT)**

HEAL V1.0

Muster XYZ white

SAP:	**42664**
Chemical or product name:	**Muster XYZ white**
Product group:	**Joint sealants**
Product type:	**Joint sealant, acrylate**
Business unit:	**UA**
Person responsible	**Mustermann, Helmut, AAT, Additives/Fillers; Düsseldorf; ++49 211 797-7894**
Application temperature (°C):	**21**
Exposure duration:	**8 hrs**
pH:	**7,5 - 8,5**
Labeling:	**N.n**

A risk assessment has been carried out using a COSHH Essentials approach adapted to the conditions under the REACH legislation (see safety report). COSHH Essentials has been developed by the UK Health and Safety Executive in collaboration with industry to provide risk management information based on a hazard, exposure, and risk- assessments.

Core Data for critical Substance

Route of Exposure: inhalation

Critical substance:	**Triethylene glykol**	CAS-Number:	**143-22-6**
Hazard Data :	**R41**	Hazard Band:*	**C**
Vapour Pressure (hPa):	**Low**	Dustiness:*	
Inhalat. Availability:		Conc.range in product (%):	**0 - 5**

General advice for inhalational and dermal contact

1) General ventilation conditions:

A good standard of general ventilation is sufficient protective if the product quantity processed during a workig day is **300 kg** Higher amounts > **300 kg** are possible if the exposure duration < 0,5 hours/day.

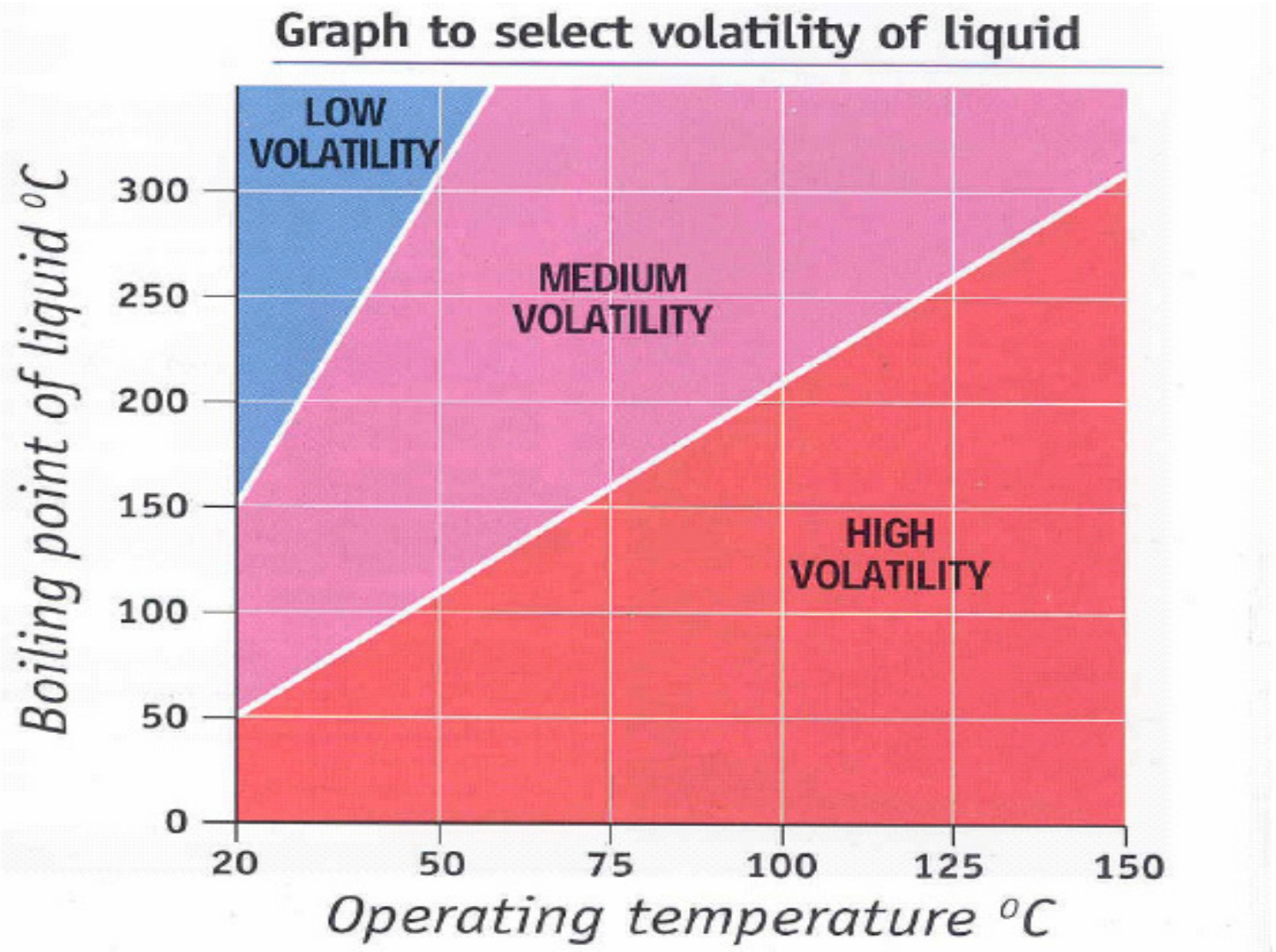
1. Provide a good standard of general ventilation. This can be natural ventilation from doors, windows etc, or controlled, where air is supplied or removed e.g. by a powered fan. If you work in a shop or office, natural ventilation will normally be enough to control dusts and vapours from cleaning materials etc. However, Ensure that enough fresh air is supplied to dilute and remove the dust or vapour produced, e.g. by keeping windows and/or doors open. Between 5 and 15 air changes per hour are recommended.

Conclusions

Banding models may assist industry

- in developing Chemical Safety Assessments and Risk Reduction Measures for preparations under the scope of REACH,
- to screen preparations for substances of concern demanding a higher tiered approach,
- to ease communication in the supply chain,
- and to draw up anticipated workplace risk assessments to accompany products
- Main elements of existing banding models (Inhalation: COSHH; Skin: German AGS) have been adapted to REACH requirements and tested as Level 1 in the IT tool “HEAL” within the RIP 3.2 FEICA – Case Study

Backups: 1) Volatility & operating temperature



Backups 2.1) Proposal for Skin Hazard Bands

- A differentiation is made between local (see table) and systemic effects.
- R-phrases are compared against the concentrations as indicated by the Preparations Directive to estimate a Derived no Effect Concentration in the mixture.
- Similar bands have been derived and laid down in a technical rule by the German AGS.

R-Phrases and combinations for topical skin effects	Hazard Band	DNEC Band
R66 & R- Phrases not assigned	SA	10-100%
R38, R36/38, R37/38, R36/37/38	SB	1-<10%
R34	SC	0,1-<1%
R43, R42/43	SD	<0,1%
R35?	SE	Specialist advice

Backups 2.2) Proposal for Skin availability bands

Rules are developed for the availability of substances for dermal uptake. This is based on molecular weight and log Kow. This approach leads to correction of DNECS by taking into account either 1, 10 or 100% dermal uptake

	MG ≥ 1000	**MG ≥ 600 < 1000**	**MG < 600**
Log Pow ≥ -0,5 & ≤ 4	Low	Medium	High
Log Pow ≥ -1,5 < -0,5 OR > 4 ≤ 6	Low	Medium	Medium
Log Pow > 6 OR < -1,5*	Low	Low	Medium

Backups: 3) R-phrases & hazard under prediction

- In principle, the R-phrase is assigned by the supplier or manufacturer and is essential for establishing one of five exposure control bands. How protective is the target exposure control band?
- For well investigated substances occupational exposure limits tend to fall within an appropriate band, but in a few cases (ca. 2%) may be less than the lower end of the band (Fairhurst 2004).
- However, R-Phrases do not assure that some effects will not occur, especially if basic tests are missing.

⇒To minimize a false sense of security it is necessary to deal with uncertainty

R-Phrases and MAK/TLV values

Buch-stabe	R-Sätze (einzeln oder kombiniert)	Mittelw. ± Stdab. (Zahl) der MAK/TLV-Werte *	COSHH bands (ppm)
(F[+],O, N,E)	R 10, 11,12,19,50-53, 59, 65-67 :	1627,7 ± 635,3 (25) mg/m³	50-500
Xi,	R 36,37,38:	182,3 ± 132,1 (19) mg/m³	50-500
Xn	R 20,21,22:	125,8 ± 94,8 (27) mg/m³	5-50
T	R 23,24,25:	27,8 ± 24,9 (9) mg/m³	0,5 - 5
C(Xi)	R 34, R41:	25,4 ± 18,6 (13) mg/m³	0,5 - 5
C	R 35 :	8,4 ± 7,1 (15) mg/m³	0,5 - 5
Xi	R 43:	4,8 ± 2,6 (9) mg/m³	0,5 - 5
Xn	R 40 (Carc. Cat. 3):	7,0 ± 6,7 (16) mg/m³	< 0,5
T+	R 26,27,28:	3,9 ± 3,1 (16) mg/m³	< 0,5
T(+)	R 45:	0,78 ± 1,36 (36) mg/m³	Specialist adv.
Xn	R 42:	0,5 ± 0,3 (6) mg/m³	Specialist adv.
T(+)	R 49:	0,071 ± 0,066 (4) mg/m³	Specialist adv.

Backups: 4) limited modification of predicted exposure based on time-weighting

- A threshold of 30 minutes' use per day (1 hr if the material is not used every working day) was built in, below which the Control Approach drops from 3 (containment) to 2 (engineering control), or from 2 to 1 (general ventilation).
- Reasoning: The COSHH model is precautionary and provides exposure estimates that equate to the shift average exposure (8 hrs/d / 5 d/w / 40 y). The level of control needed for (undefined) short-term activity did not hold the same degree of 'reasonable practicability' as the level of control for prolonged use.
- An increase in control approach (e.g. 1 to 2) affords at least a 10-fold increase in protection from dusts and vapours. Exceeding an 8-hour limit value ten-fold over 30 minutes, with no further exposure equates to the limit value over 5 hours (30 x 10), i.e. less than 8 hours.

Potential issues: 5) Modification of predicted exposure based on formation of aerosols or indoor/outdoor use

Even if evaporation at 20°C is negligible a high concentration of airborne particles can be reached quickly when dispersed, e.g:

- spraying of the substance or preparation using a spray gun, aerosol can or airless spraying at over 1000 psi, use as a metalworking fluid/lubricant in open applications, degreasing in solvent vapour, roller application or brushing of highly volatile material.

On the other hand, if a substance is applied outside closed rooms, the dilution effect will lead to much lower concentrations.

Consequences:

- On spraying use the highest availability band for *all* ingredients
- Use outside closed rooms should trigger the next lowest exposure band

Backups. The HSE COSHH Essentials 2002 (Control of Substances Hazardous to Health)

Results of a telephone survey of 500 COSHH Essentials purchasers in UK:

- 80% had used it
- Only 5% found it difficult to use
- 75% had taken action
- 95% would recommend to other businesses
- ⇒ Users seem to like it…