

Formaldehyde and -donors

Risk assessment for users of cooling lubricants

Issue 07/2015

FB HM-029

The implementation of a risk assessment in accordance with the Regulation on Hazardous Substances [1] places great demands on the expertise of the individuals assigned to perform the assessment. The task is particularly complex if

- classification and labelling is not just required for the active ingredient (= formaldehyde donors, FAD) but also for impurities and unreacted base material (= formaldehyde) in preparations/mixtures,
- the composition in use changes due to dilution (intended) and decomposition (not always intended, e.g. due to low pH value),
- formaldehyde is reclassified to C1B - H350 (may cause cancer) by the EU (ECHA) based on the 7th ATP in January 2016 [2],
- products (preparations, mixtures) have to be identified with a formaldehyde content of 0.1% or greater.

All four requirements are relevant for formaldehyde donors.

1 Properties of formaldehyde (CAS no. 50-00-0; EINECS no. 200-001-8)

Besides the current intense discussion on the carcinogenic effect of formaldehyde, the risk assessment and the selection of protective measures must also take into account that

- formaldehyde has a sensitising effect
- formaldehyde deposits may have a sensitising effect (also refer to TRGS 401 [3])
- formaldehyde may cause sensory irritations to eyes and airways depending on the air concentration.

The hazardous properties are currently partially taken into account in the form of standardised classification and labelling in accordance with CLP [4] and in some cases still specified in the old substance directive.

The classification and labelling of treated biocidal products depends heavily on the **concentration of free formaldehyde**. The concentration of the active ingredients in biocidal products and the application description is provided on the label. The different active ingredients may mathematically release between 20 and 47% of the formaldehyde.

Most cooling lubricant (CL) concentrates contain biocidal active ingredients, which deliver the required content of total formaldehyde when the recommended cooling lubricant application concentration is freshly applied. Aqueous cooling lubricants (aq-CL) are normally controlled with total formaldehyde contents between 350 and 800 ppm.

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The active ingredient concentration for the specific activity must also be known when applied in order to derive effective protective measures from the risk assessment. See section 5.

For the sake of completeness, it must be noted that formaldehyde is always present as formaldehyde hydrate in aqueous solutions.

2 Properties of formaldehyde donors

Tables 1 to 3 list the most important formaldehyde donors at this time.

Formaldehyde and -donors - Risk assessment for users of cooling lubricants

Substance name			Classification and labelling			
Abbreviation	Chem. name (active ingredient)	CAS no. EC no.	Concentration limits (%)	Classification	R phrases	WHC active ingredient
EG Form (EDDM)	Reaction product of ethylene glycol with paraformaldehyde 1,6-Dihydroxy-2,5-dioxahexane ((Ethylendioxy)dimethanol)	3586-55-8 222-720-6	≥ 25	X _n	22-38-41-52	1
			≥ 20 to 25	X _i	38-41	
			≥ 10 to 20	X _i	41	
			≥ 5 to 10	X _i	36	
			< 5	-	-	
HHT	1,3,5-Tris-(2-hydroxyethyl)-hexahydro-1,3,5-triazine (2,2',2''-(Hexahydro-1,3,5-triazine-1,3,5-triyl)-triethanol)	4719-04-4 225-208-0	≥ 25	X _n	22-43	1
			≥ 0.1 to 25	X _i	43	
			< 0.1	-	-	
			(additional different manufacturer classifications)			
MBO	3,3'-Methylene-bis-(5-methylloxazolidine)	66204-44-2 266-235-8	≥ 5	C	21/22-34-52	1
			< 5	-	-	
			(manufacturer classification)			
HPT	1,3,5-Tris-(2-hydroxypropyl)-hexahydro-1,3,5-triazine	25254-50-6 246-764-0	> 25	X _n	22-36/38-43-52	1
			≥ 1 to 25	X _i	43	
			< 1	-	-	
			(manufacturer classification)			
TMAD	Tetrahydro-1,3,4,6-tetrakis-(hydroxymethyl)imidazo-[4,5-d]imidazole-2,5(1H,3H)-dione	5395-50-6 226-408-0	≥ 33	N, X _i	43-52	2
			< 33	-	-	
			(manufacturer classification)			
BHF	Benzylalcohol-mono(poly)-hemiformal (Benzyloxy-methanol)	14548-60-8 238-588-8	> 25	X _n	21/22-37/38-41	1
			(manufacturer classification)			
DMDMH	1,3-Bis-(hydroxymethyl)-5,5-dimethyl-imidazolidine-2,4-dione	6440-58-0 229-222-8	(different manufacturer classifications)			

Table 1: Classification and labelling of biocidal products (Preparations Directive)

Use and application							Notes	
Active ingredient	Effect			Manufacturer recommendations on the concentration of the active ingredients [%] <i>[calculated total formaldehyde concentration [ppm]]</i>		Method of analysis (steam distillation)	Behaviour in CL	Comments
	Bacteria	Fungi	Algae	Pre-Concentrate	Preventive preservation (aq-CL) Intermittent (emergencies) (aq-CL)			
EC form (EDDM)	+++	+	+	1-3	Preferred in combination products	Photometer, HPLC	Odour-intensive	
HHT	+++	+	-	2-3	0.15 <i>615</i> 0.2 <i>820</i>	Photometer, HPLC	Increases pH value	Sensitisation potential exists for > 0.1%. Do not use in areas in which employees are already sensitised. Main application as bactericide.
MBO	+++	+	-	2-3	0.1 - 0.15 <i>480-720</i> 0.15 - 0.2 <i>720-960</i>	Photometer, GC, HPLC	Increases pH value, odour-intensive	
HPT	+++	-	-	2-3	0.15 <i>420</i> 0.3 <i>840</i>	Photometer, HPLC	Increases pH value. Odour intensive	Sensitisation potential exists for > 1%. Do not use in areas in which employees are already sensitised. Main application as bactericide.
TMAD	+	-	-	2-3	Preferred in combination products	Photometer, HPLC	Odourless and non-foaming	Inert as other n-formals. Only use in combination products. Determination of formaldehyde content affects excessive effectiveness
BHF	+++	+	-	1.5-3	0.1 - 0.2 <i>220-440</i> 0.15 - 0.2 <i>440-660</i>	Photometer, HPLC	Reduces pH value, very odour intensive	
DMDMH	++	-	N/S	1.5 - 3	0.15 - 0.3 <i>480-960</i> N/S	Photometer, HPLC	Reduces pH value.	

Table 2: Use and application of biocidal products (Preparations Directive)

(N/S: not specified)

Formaldehyde and -donors - Risk assessment for users of cooling lubricants

Substance name			Classification		Labelling			Specific concentration limits M factors	
Abbreviations	Chem. name (active ingredient)	CAS no. EC no.	Hazard class, hazard category and hazard coding	Hazard information coding	Pictogram, signal word code	Hazard information coding	Additional hazard feature coding		
EG Form, (EDDM)	Reaction products of ethylene-glycol with paraformaldehyde ((Ethylendioxy)dimethanol, 1,6-Dihydroxy-2,5-dioxahexane)	3586-55-8 222-720-6	Acute Tox. 4 Skin Irrit. 2 Eye Dam. 1	H302 H315 H318	GHS07 GHS05 Dgr	H302 H315 H318			
HHT	1,3,5-Tris-(2-hydroxyethyl)-hexahydro-1,3,5-triazine (2,2',2''-(Hexahydro-1,3,5-triazine-1,3,5-triyl)-triethanol)	4719-04-4 225-208-0	Acute Tox. 4 (*) Skin Sens. 1	H302 H317	GHS07 Wng	H302 H317		Skin Sens. 1; H 317: C ≥ 0.1 %	
MBO	3,3'-Methylene-bis-(5-methyloxazolidine)	66204-44-2 266-235-8	Acute Tox. 4 Acute Tox. 4 Skin Corr. 1C	H 302 H 332 H 314	GHS 07 GHS05 Dgr	H 302 H 332 H 314			
HPT	1,3,5-Tris-(2-hydroxypropyl)-hexahydro-1,3,5-triazine	25254-50-6 246-764-0	Acute Tox. 4 Skin Irrit. 2 Skin Sens. 1 Eye Irrit. 2	H302 H315 H317 H319	GHS07 Wng	H302 H315 H317 H319			
TMAD	Tetrahydro-1,3,4,6-tetrakis-(hydroxymethyl) imidazo-[4,5-d]imidazol-2,5(1H,3H)-dione	5395-50-6 226-408-0	Skin Sens.1 Aquatic Chronic. 2	H317 H411	GHS07 GHS09 Wng	H317 H411			
BHF	Benzylalcohol-mono(poly)-hemiformal (Benzyloxy-methanol)	14548-60-8 238-588-8	Acute Tox. 4 Acute Tox. 4 Eye Irrit. 1 STOT SE 3 Skin Irrit. 2	H312 H302 H318 H335 H315	GHS 05 GHS 07	H 312 H 302 H 318 H 335 H 315			
DMDMH	1,3-Bis-(hydroxymethyl)-5,5-dimethyl-imid-azolidine-2,4-dione	6440-58-0 229-222-8	No standardised information in CLP Refer to SDB						

Table 3: Classification and labelling of biocidal products (CLP)

3 Air limit values, exposure situation

TRGS 900 [5] contains a legally binding threshold limit value (TLV) for formaldehyde of the same amount as that proposed by the MAK commission: 0.37 mg/m³ [6]. The SCOEL (Scientific Committee for Occupational Exposure Limits) has recommended a value of 0.25 mg/m³ [7] since 2008.

Concentration (mg/m ³)	Cumulative frequency in % (percentile)
0.020	50
0.049	75
0.100	90
0.150	95
0.392	99
0.670	100
Number of measured values: 335	
Number of operations: 135	
Number of different types of operations: 25	

Table 4: Data from the IFA MEGA exposure database

An evaluation of formaldehyde measurements in the air in mechanical production work areas (i.e. simultaneous exposure to cooling lubricants) results in the above data for the period between 1999 and 2009. Experience has shown that the statistically evaluated data provides a higher exposure than would be displayed by a "non-incident-related" average. (more recent data is expected to be available at the end of 2014)

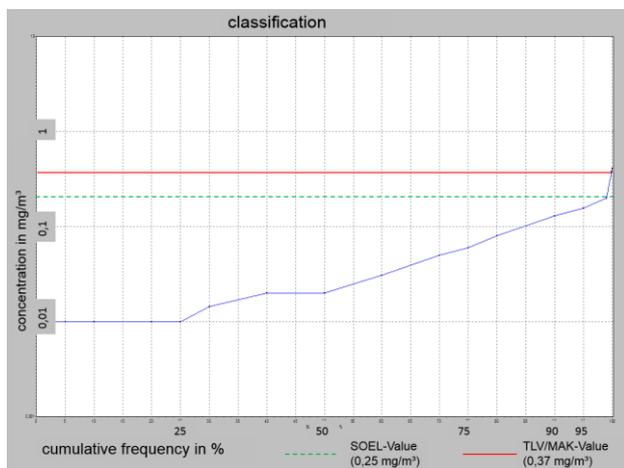


Figure 1: Exposure distribution

3.1 Assessment:

The 95th percentile (= 95% of all measurements) lies well below the limit value recommended by the MAK commission, while the discussed SCOEL limit value of 0.2 ppm = 0.25 mg/m³ is complied with in over 95% of all measurements performed.

If the protective measures described in Section 5 are complied with, the risk assessment can be concluded with a finding that the "protective measures are adequate". The continued applicability of this DGUV information must be reviewed if processes change and at regular intervals, and the results must be documented.

4 Analysis of formaldehyde in cooling lubricants (free and total)

The total formaldehyde content is generally determined when detecting formaldehyde. The formaldehyde deposit is decomposed and the formaldehyde is released by:

- acidic pH value (drop in pH value)
- high temperature
- microbiology
- UV light

Detection of free formaldehyde without decomposing the formaldehyde deposit is difficult as the equilibrium between the formaldehyde deposit and the free formaldehyde is disrupted using the standard methods under 4.1 and 4.2.

4.1 Test strips (semi-quantitative)

Result of the **total formaldehyde** detected by rapid testing (colorimetric, reading range: 0 - 20 - 40 - 60 - 100 mg/l). The test is highly susceptible to interference if it is not performed with adequate precision. Internal experience shows that this does not provide sufficiently accurate results. As a result, this method is not recommended for users.

The measurement is more accurate if the strip colour is evaluated using reflectometric measurement with a calibrated measuring instrument, as is already possible for nitrite and pH measurements in aqueous cooling lubricants.

Sample preparation and calibration methods are currently undergoing testing and validation. This does not require any costly laboratory equipment.

4.2 Photometric method after steam distillation ("Antona")

An appropriate laboratory method to determine the total formaldehyde is acidic steam distillation with subsequent colour reaction and photometry. Brief description of the method:

The chemically bonded formaldehyde in the FAD is released by sulphuric acid and distilled off from the mixture using steam distillation. The free formaldehyde, which is then present in the distilled water, is then left to react with acetyl acetone at 37 °C (dissolved in an alkaline ammonium acetate buffer) and turns a yellow colour. The intensity of the yellow colour is then measured using a UV-VIS photometer and converted to the total formaldehyde content via a calibration curve (prepared from samples of known FAD concentrations).

Other reactions (e.g. with phenylhydrazine) and other methods of analysis (e.g. HPLC) may be used as an alternative to acetyl acetone.

Experience shows that the accuracy of the method is approximately equal to 10% of the measured value. The method applies for aqueous cooling lubricants as well as for cooling lubricant concentrates and biocides containing FADs after corresponding dilution.

Antona distillation represents the standard laboratory method from the manufacture of FADs through to concentration monitoring.

Sample no.	Boron	Mineral oil/ Ester	Prim. amines [%]	Tert. amines [%]	Water [%]	Type n-formal [%]	Type o-formal [%]	¹³ C-NMR - Formaldehyde hydrate
1	-	x	8 - 10	10 - 12	20 - 25	MBO/Triazine approx. 2	-	< LOD
2	x	x	13 - 15	-	20 - 25	MBO/Triazine approx. 2	EG Form approx. 1	< LOD
3	-	x	-	1 - 2	Traces	MBO approx. 1	EG Form approx. 2	< 0.1 %
4	x	x	9 - 11	7 - 10	15 - 20	N-formal approx. 3	-	< LOD
5	-	x	-	-	10 - 15	DMDMH 1.5	-	< 0.1 %
6	-	x	5 - 10	5 - 10	15 - 20	-	EG Form 2.8	< LOD
7	-	-	-	-	40 - 45	MBO 2.5	-	< LOD
8	x	-	6 - 10	15 - 20	25 - 30	N-formal approx. 2	-	< LOD
9	-	-	5 - 7	23 - 26	40 - 45	MBO 3	-	< LOD
10	x	x	3 - 5	5 - 8	20 - 25	-	EG Form 2.5	< LOD

Table 5: Results of the analysis of formaldehyde hydrate in cooling lubricant concentrates (LOD: analytical limit of determination = 0.01%)

4.3 ¹³C-NMR determination of free formaldehyde in cooling lubricant concentrates

This method is extremely time-consuming and expensive, requires special equipment and has previously only been applied by biocide manufacturers, e.g. for the preparation of registration dossiers, which can be viewed as a guarantee that the product "contains formaldehyde below the labelling threshold".

Ten different products from four different cooling lubricant manufacturers were investigated as part of the examination of cooling lubricant concentrates. The products reflect the entire market segment with very different compositions.

The analyses were performed using the cooling lubricant concentrate without further dilution.

The results of the analysis (see Table 5) show that the labelling threshold for formaldehyde of 0.1% was not reached by all ten products.

5 Risk assessment for selected activities, protective measures

A comprehensive overview of the risk assessment and the protective measures to be implemented for activities using cooling lubricants or biocidal products is provided by BGR/GUV-R 143 [8]. In principle, the following must be observed for activities with biocides:

- The manufacturer recommendations for active ingredient concentrations must be complied with,
- No storage above temperatures of 40°C,
- Always keep containers tightly closed,
- Never mix biocidal products together.

5.1 Activities with FAD biocidal products

A preservation plan with the following details is recommended if a biocide needs to be added to aqueous cooling lubricant:

1. Type of biocide,
2. Biocide concentration during the period of use in consideration of the required refills due to cooling lubricant losses,
3. The maximum permitted biocide concentration specified by the biocide supplier, which must not be exceeded.

Before adding the biocide, check whether the pH value of the aqueous cooling lubricant is within the normal range (pursuant to the manufacturer information), as the FAD decomposes in the acidic range and releases large quantities of formaldehyde.

The addition of biocide at a low pH value is "not in line with the intended use" and is extremely dangerous due to the release of formaldehyde.

If deviations occur, use appropriate additives to raise the pH value to the normal range.

Once the biocide is added (intermittent preservation) the system should continue pumping for a further 1 to 2 hours.

Typical activities with exposure to formaldehyde may include the opening of containers/drums, filling/decanting, adding to aqueous cooling lubricants.

This may result in skin contact, inhalation of vapour or the spraying of the biocidal product. The active ingredient may be present in concentrations of up to 100%.

Appropriate protective measures include:

Technical: dosing units, filling/decanting equipment, (potentially) extraction/ventilation

Organisational: checking the pH value, adjusting it to the target value if required, operating instructions and training

Personal: safety goggles, gloves, apron if there is a risk of spray

5.2 Activities with cooling lubricant concentrate that contains FAD

When dosing, typical activities with exposure to formaldehyde include opening containers/drums, filling/decanting, diluting (if necessary), addition to the circulation system.

This may result in skin contact, inhalation of vapour or the spraying of cooling lubricant concentrate. The active ingredient in FAD is normally present at a concentration of 3%.

Appropriate protective measures include:

Technical: mixing units

Organisational: adjusting the target value, operating instructions and training

Personal: safety goggles, gloves, apron if there is a risk of spray

5.3 Activities with aqueous cooling lubricants containing FADs (emulsion, solution)

Typical activities with exposure to formaldehyde include machine operation, tool handling, maintenance and service measures, monitoring target values, etc.

This may result in skin contact, inhalation of vapour and aerosols or the spraying of aqueous cooling lubricant. The active ingredient may be present in concentrations of up to 0.3 % in FAD. According to manufacturer recommendations, the concentration of formaldehyde (total formaldehyde, **red numbers** in Table 2) may not exceed 1,000 ppm.

Appropriate protective measures include:

Technical: encapsulation, extraction, ventilation measures

Organisational: check and adjust the target values for cooling lubricants, maintenance and servicing, operating instructions and training

Personal: safety goggles (if there is a risk that cooling lubricant may be sprayed into the eyes), skin protection, gloves (if applicable and if there is no risk of them being pulled into a machine)

5.4 System cleaning with products containing FADs

When adding system cleaners, typical activities with exposure to formaldehyde include opening containers/drums, filling/decanting, diluting (if necessary), addition to the circulation system.

The addition of system cleaners must take place at least 8 hours before the planned replacement of the cooling lubricant circuit.

This may result in skin contact, inhalation of vapour and aerosols or the spraying of aqueous cooling lubricant. The active ingredient may be present in concentrations of up to 0.3 % in FAD. According to manufacturer recommendations, the concentration of formaldehyde (total formaldehyde, **red numbers** in Table 2) may not exceed 0.1% (1,000 ppm).

Appropriate protective measures include:

Technical: encapsulation, extraction, ventilation measures

Organisational: check and adjust the target values for cooling lubricants, maintenance and servicing, operating instructions and training

Personal, when adding system cleaner: safety goggles, gloves, apron if there is a risk of spray

Personal, for machine operators: safety goggles (if there is a risk that cooling lubricant may be sprayed into the eyes), skin protection, gloves (if applicable and if there is no risk of them being pulled into a machine)

5.5 System cleaning, residual contents of aqueous cooling lubricants containing FADs

This may result in skin contact, inhalation of vapour and aerosols or the spraying of aqueous cooling lubricant.

Appropriate protective measures include:

Organisational: operating instructions and training

Personal: safety goggles, skin protection, gloves, cooling lubricant-resistant safety boots, respiratory protection when cleaning with high pressure cleaners (particle filtering half masks FFP2 or half masks with particle filter P2; pursuant to BGR/GUV-R 143).

6 Summary and limits of application

The risk due to formaldehyde cannot simply be transferred to formaldehyde donors on a one-to-one basis.

Formaldehyde donors may continue to be used if attention is paid to a few problem areas (BPR product authorisation, labelling of free formaldehyde contained in the product).

The risk assessment within the meaning of this DGUV information sheet to determine whether the protective measures specified in Section 5 are performed when activities are carried out.

If this is the case, the user of formaldehyde donors can assume that the requirements of the Regulation on Hazardous Substances have been met. This also means that there is no obligation to perform measurements for formaldehyde in the air in the room. (also refer to the finding under Section 3.1)

The analyses under Point 4.3 were performed by Spectral Service AG in the fourth quarter of 2013.

The Expert Committee Woodworking and Metalworking is composed of representatives of the German Social Accident Insurance Institutions, federal authorities, social partners, manufacturers and users.

Apart from updated references to regulations and rules, this DGUV information is identical with the same-titled version which has been issued as version 08/2014.

Further DGUV-Information and information sheets of the expert committee woodworking and metalworking (Fachbereich Holz und Metall) can be downloaded from the internet [9]. The present document is the English translation of the German DGUV-Information FB HM-029, Issue 07/2015.

As to the aims of the DGUV-Information, refer to DGUV-Information FB HM-001, "Aims of the DGUV-Information published by the expert committee woodworking and metalworking".

Bibliography:

- [1] Regulation on protection against hazardous substances (Gefahrstoffverordnung – GefStoffV) of 26 November 2010 (Federal Law Gazette I p. 1643), last amended by Article 2 of the Regulation of 3 February 2015 (Federal Law Gazette I p 49)
- [2] EU Regulation no. 2015/491 of 23 March 2015 (OJEU L 78/12)
- [3] TRGS 401 "Gefährdung bei Hautkontakt - Ermittlung, Beurteilung, Maßnahmen" (Risk due to skin contact - determination, evaluation and measures); Joint Ministerial Gazette 2011 p. 175 of 30/03/2011
- [4] EU Regulation no. 1272/2008 of 16 December 2008 OJEU L 351/1, last amended by EU Regulation no. 487/2013 (4th ATP)
- [5] TRGS 900 "Arbeitsplatzgrenzwerte" (threshold limit values), last amended and supplemented: Joint Ministerial Gazette 2015 p. 139-140 of 2 March 2015
- [6] MAK and BAT values list 2013, Senate Commission to investigate hazardous working substances, Announcement 49
- [7] See <http://ec.europa.eu/social/main.jsp?catId=148&langId=de&intPagelId=684>
- [8] DGUV-Rule 109-003 (up to now BGR/GUV-R 143): Tätigkeiten mit Kühlschmierstoffen (Activities with cooling lubricants), dated: 03/2011
- [9] Internet: www.dguv.de/fb-holzundmetall Publications or www.bghm.de webcode: <626>

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