

Boric acid- / Boric MWF

Chemicals legislation, risk assessment, protective measures

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The topic of risk assessment places high demands on the skills of instructed persons. In case of boric acid (and some compounds, see table 1), the execution is particularly complex since existing studies for the assessment of the hazard have been discussed controversially for years.

In September 2008, the European Union published the 30th ATP of the EU Dangerous Substances Directive 67/548/EEC [1], which should enter into force on 1st June 2009. In the meantime, the CLP-Regulation [2] has been issued as legal successor, and the 30th ATP for substances (together with the 31st ATP) in conjunction with the CLP-Regulation in the form of the 1st ATP [3] came into effect on 1st December 2010. For MWF concentrates (preparations, according to CLP-Regulation mixtures) the CLP-Regulation will apply as of 01.06.2015. Until then, preparations according to 99/45/EC have to be classified and labelled in conjunction with Annex VI of the CLP-Regulation.

Since the classification and labelling will have a considerable impact on the production and use of boric acid-based MWF, it should be communicated in good time before the classification according to the CLP-Regulation comes into effect (incl. 1st ATP) which classification and labelling is applicable and which protective measures (specific to the task!) will have to be implemented.

Table of contents

- 1 Classification and labelling of boric acid
- 2 Determination of free boric acid by ¹¹B-NMR-spectroscopy
- 3 Air limit values and risk assessment
- 4 Activities with water-miscible metal working fluid (MWF-concentrate)
- 5 Activities with water-mixed MWF (MWF emulsion or solution)
- 6 Hydrolysis of boric acid derivatives (compounds, salts, complexes) after absorption by humans
- 7 Summary and limits of application

Index-No.	Chemical name	EC-No.	CAS-No.	Classification		Labelling		Specific concentration limits
				Hazard - class, - category - coding	Coding of hazard warnings	Pictogram, coding of signal words	Coding of hazard warnings	
005-007-00-2	Boric acid [1, crude natural, containing not more than 85 per cent of H ₃ BO ₃ calculated on the dry weight [2]	233-139-2 [1] 234-343-4 [2]	10043-35-3 [1] 11113-50-1 [2]	Repr. 1B	H360FD	GHS08 Dgr	H360FD	Repr. 1B; H360FD: C ≥ 5,5 %
005-008-00-8	Diboron trioxide;boric oxide	215-125-8	1303-86-2	Repr. 1B	H360FD	GHS08 Dgr	H360FD	Repr. 1B; H360FD: C ≥ 3,1 %
005-011-00-4	Disodium tetraborate, anhydrous Boric acid, disodium salt [1] Tetraboron disodium heptaoxide, hydrate [2] Orthoboric acid, sodium salt [3]	215-540-4 [1] 235-541-3 [2] 237-560-2 [3]	1330-43-4 [1] 12267-73-1 [2] 13840-56-7 [2]	Repr. 1B	H360FD	GHS08 Dgr	H360FD	Repr. 1B; H360FD: C ≥ 4,5 %
005-011-01-1	Disodium tetraborate decyhydrate Borax decahydrate	215-540-4	1303-96-4	Repr. 1B	H360FD	GHS08 Dgr	H360FD	Repr. 1B; H360FD: C ≥ 8,5 %
005-011-02-9	Disodium tetraborate pentahydrate Borax pentahydrate	215-540-4	12179-04-3	Repr. 1B	H360FD	GHS08 Dgr	H360FD	Repr. 1B; H360FD: C ≥ 6,5 %
R1B H360FD Dgr	Substance probably toxic to reproduction. The classification of a substance in category 1B is largely based on data collected by means of animal studies. Such data must give distinct proofs for the impairment of the sexual function, fertility and the development in the absence of other toxic effects. May damage fertility or the unborn child Signal word „Danger“							

Table 1: Excerpt from 1. ATP/CLP Annex II

1 Classification and labelling of boric acid

The classification and labelling of the mixture that has been placed on the market (e. g. of the MWF-concentrate) is dependent on the content of free boric acid according to Annex VI CLP. The differentiation between boron compounds and free boric acid is of importance for the assessment.

Depending on the progress in implementing the EC-CLP-Regulation, the following classifications and labellings have to be applied.

1.1 For boric acid as substance:

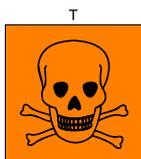


Signal word:
Danger

Classification and labelling:

Toxic to reproduction
Category 1B: Substance probably toxic to reproduction
H 360F: May damage fertility
H 360D: May damage the unborn child

1.1.1 Classification until 31.05.2015 for mixtures containing $\geq 5,5$ % free boric acid: (Labelling threshold [3])



Classification:

Toxic to reproduction
Category 2;
R 60-61

Labelling:

T - Toxic,
R 60-61;
S 53, 45

1.1.2 Classification starting on 01.06.2015 at the latest for mixtures containing $\geq 5,5$ % free boric acid (Replacement of the EC-Preparations Directive 99/45/EG by CLP)



Signal word:
Danger

Classification and labelling:

Toxic to reproduction
Category 1B: Substance probably toxic to reproduction
H 360F: May damage fertility
H 360D: May damage the unborn child

Ask your MWF producer for binding specifications. The concentration can usually be found in the safety data sheet.

Depending on the relevant hazard level of activities, the Ordinance on Hazardous Substances [4] requires protective measures. The most comprehensive protective measures have to be implemented if a mixture contains $\geq 5,5\%$ of free boric acid.

1.2 For mixtures containing $\geq 0,1$ % and $< 5,5$ % free boric acid

For these mixtures, the ordinary protective measures for activities with MWF according to BGR/GUV-R 143 [5] are to be adhered to.

1.3 For mixtures containing $< 0,1$ % free boric acid

A special case is represented by boracic MWF-concentrates (or particular additives) which contain free boric acid in a concentration below 0,1 % and are thus free from labelling, classification and the duty of declaration. When using these products, boric acid may be released in the application as a result of hydrolysis (= reaction with water). This has to be taken into account in the risk assessment as well (see clauses 5 and 6). Get the confirmation from your supplier, whether boric acid is released in the application (see clause 3).

In this case too, the common protective measures for activities with MWF according to BGR/GUV-R 143 [5] are to be adhered to.

1.4 Declaration of boric acid: MAC (maximum allowable concentration) for boric acid and its monitoring

Boric acid has a MAC in the TRGS 900 [6]. MWF producers and users are required to give proof of its adherence within the framework of a risk assessment.

Irrespective of whether boric acid is still contained in the water-miscible MWF or can be released in water-mixed MWF, it has to be declared for all boracic MWF in clause 8 of the safety data sheet.

2 Determination of free boric acid by ^{11}B -NMR-spectroscopy

The quantification of free boric acid in the alkaline buffered MWF concentrate is difficult because chemical methods disturb the balance and lead to wrong results. For this reason and based on already available results of two MWF producers, the ^{11}B -NMR-Spectroscopy has been chosen.

This method has been applied for several decades to determine the molecular structure of organic and inorganic compounds. There exists a variety of publications in which the content of free boric acid apart from all sorts of boric acid derivatives (boric esters, salts, complex compounds) has been determined as a function of different framework conditions.

52 samples of MWF concentrates from 5 different producers have been examined. As relevant data, the producers have indicated or determined the following:

1. Quantity of boric acid used, formulation-defined
2. Quantity of alcanolamine used
3. Quantity of mineral oil / ester oil used
4. pH-value of concentrate

On the basis of the spectra, the quantity of free boric acid was determined. It could be identified that only in one of the 52 samples of MWF-concentrates the content of free boric acid reached 5.6 % which was just above 5.5 %. With 18 % boric acid (formulation-defined), this sample is above the typical contents.

For all 52 samples, the "index" (= ratio of free boric acid divided by the applied formulation-defined boric acid) was determined. Considering the product- and manufacturing-specific characteristics, the "index" usually ranges from 0.08 to 0.5. A predicted dependence solely on the pH-value of the concentrate could not be determined.

Result:

In 51 samples of MWF concentrates, the content of free boric acid is below the limit of 5.5 % and thus does not lead to any labelling. The contents of boric acid (formulation-defined) were between approx. 6 and 18 %.

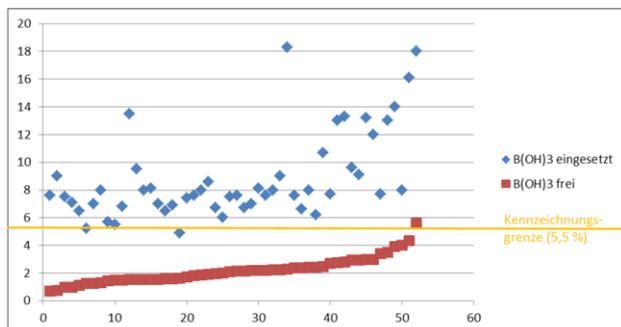


Figure 1: Content of free boric acid (red squares) and formulation-defined boric acid (blue squares)

3 Air limit values and risk assessment

Since March 2007, a health-based MAC (maximum allowable concentration) of 2.6 mg boric acid / m³ (corresponds to 0.5 mg boron/m³ = measuring component) is in force in Germany which is included in the TRGS 900. The remark "Y" in TRGS 900 also indicates that no risk of foetal damage has to be expected if the MAC is adhered to.

The definition of a MAC means that, if adhered to, acute or chronic harmful health effects are usually not to be expected.

An analysis of the Institut für Arbeitsschutz (IFA) [7] for developing an exposition scenario for boron and its compounds (in case of water-mixed MWF: boron is indicated) shows for the 95th %-percentile (i.e. statistically for 95 % of all measurements made) in the mechanical production an exposition level of 0,024 mg/m³, which corresponds to 4,8 % of the MAC (corresponds to an assessment index of 0,048 according to TRGS 402).

Bor and its compounds, Duration of sampling ≥ 1 h and exposition duration ≥ 6 h					
Field of work	Number of measured data	Number of companies	Concentrationen in mg/m ³		
			50%-Value	90%-Value	95%-Value
Turning, Grinding, Milling	36	22	0,002	0,007	0,024

Table 2: Excerpt from IFA-analysis

For performing a risk assessment, the user has to know whether boric acid is released in the application.

This has to be asked e.g. for products according to clause 1.3.

4 Activities with water-miscible metal working fluid (MWF) (MWF-concentrate)

If the applied MWF-concentrate contains **more** than 5,5 % free boric acid, the particular protective measures for activities with CMR-substances according to the GefStoffV (Ordinance on Hazardous Substances) have to be applied. If

no aerosol creation takes place, compliance with the MAC can reliably be assumed.

In all other cases, the general protective measures have to be applied. Depending on the activity, they can be taken from BGR/GUV-R 143.

4.1 Boron-free products

The regulations regarding boric acid do not apply to these products.

4.2 Boric acid content < 0,1 % (according to individual manufacturer's proof)

These products are not subject to the duty of declaration in terms of SVHC-/list of candidates. Even though this is still intensively discussed, according to the findings so far, this can be achieved by the use of specific boric acid derivatives (e. g. polyborates, boric-acid esters).

4.3 Boric acid content < 5,5 % (formulation-defined, mass percentage)

These products are concerned; however, under no conditions there exists an obligation for labelling. No further examinations as described in clause 3 will be necessary.

4.4 Boric acid content ≥ 5,5 % (formulation-defined, mass percentage)

See clause 1.1.1 and 1.1.2.

For particular cases in which the limit of **5,5 % of free boric acid** is exceeded, the obligation to label is applicable as above.

After discussion, the MWF users share the unanimous opinion that for this case such products should be substituted.

5 Activities with water-mixed MWF (MWF emulsion or solution)

Due to the dilution with water, it can be excluded that the value of 5,5 % boric acid will be exceeded for the water-mixed MWF (even in case of 30 % emulsions or solutions).

The required preventive measures according to the Ordinance on Hazardous Substances are described in BGR/GUV-R 143 depending on the respective activity. The effectiveness can be proven for example by adhering to the MAC (see no. 3).

6 Hydrolysis of boric acid derivatives (compounds, salts, complexes) after absorption by humans

Beyond the subject „classification and labelling“, it is increasingly discussed that not only free boric acid but all compounds containing boric acid have the same effects on humans. This assumption is explained by the fact that all boric acid compounds are exposed to an acid pH-value and thus hydrolyze when being absorbed in the human body.

If the absorption by "breathing in" is regarded, it is pointed out to the above mentioned clauses 3 and 5, in particular to the definition of the MAC.

If the absorption by „swallowing“ is considered, the risk assessment has to take into account in particular that swallowing is prevented by suitable measures.

According to all available current information, skin contact is not relevant since there is no absorption (no skin absorption in case of non-damaged skin).

7 Summary and limits of application

This DGUV Information (formerly Expert Committee information sheet) is based on experience gathered by the Expert Committee Woodworking and Metalworking, Subcommittee Effects upon Health and Media of the DGUV and has been prepared in cooperation with MWF producers and users and the IG Metall.

It should particularly help to implement the requirements of the European chemicals legislation and the Ordinance on Hazardous Substances.

According to the CLP-Regulation, boric acid and certain sodium borates have been considered since 01.12.2010 to be substances of category 2 which are toxic to reproduction (R 60, R 61). The corresponding concentration limit for boric acid in preparations (from 01.06.2015 „mixtures“) amounts to 5,5 %.

If the MAC of 2,6 mg boric acid/m³ is adhered to, activities with boric acid or boric preparations / mixtures are possible without an increased health risk.

When applying the results of the IFA-exposition scenario for the field of work „Mechanical production“ (e.g. turning, grinding, milling) the result “Sufficient protective measures according to the Ordinance on Hazardous Substances” can be established.

The analyses described in clause 2 were carried out in the „Institut für anorganische Chemie of the Universität Stuttgart“ in February 2009.

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

This DGUV-Information replaces the same-titled version, which was published as draft version 10/2013. Further DGUV-Information and information sheets of the Expert Committee Woodworking and Metalworking can be downloaded from the Internet [8].

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.

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