EU Chemicals legislation

A closer look at isothiazolinones, formaldehyde releasers and other biocides for metalworking fluids

WALLENIUS WATER INNOVATION

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Preface

The new stricter chemicals legislation being implemented in the EU right now is profoundly affecting the chemical industry as a whole, the metalworking industry being no exception. As the final registration deadline of REACH has passed, the focus now shifts towards evaluation of substances, identifying substances of potential concern and finding proper regulatory management strategies to address the risks.

Biocides are chemicals specifically developed to control microorganisms and often affect other living organisms, such as our human bodies. Because of these properties, they are regulated strictly within the Biocidal Products Regulation (BPR). The list of biocides available for use to control microorganisms is rapidly decreasing, in some cases because they are not approved and in other cases because their classification makes them virtually unusable.

In this paper, I will go into detail on the cases of two specific groups of biocides commonly used within the metalworking industry, isothiazolinones and formaldehyde releasers. The reading will require some basic knowledge on the chemicals legislation of the EU. Please read our previous paper "Chemicals legislation – How EU's new guidelines affect workshops" for a more basic insight into the EU's chemical legislation.

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Abbreviations

ATP – Adaptation to Technical Progress

BPC – Biocidal Products Committee

BPR – Biocidal Products Regulation

CLP – The Classification, Labelling and Packaging Regulation

ECHA – European Chemicals Agency

GCL – Generic Concentration Limit

RAC – Committee for Risk Assessment

REACH – Regulation of Registration, Evaluation, Authorisation and Restriction of Chemicals

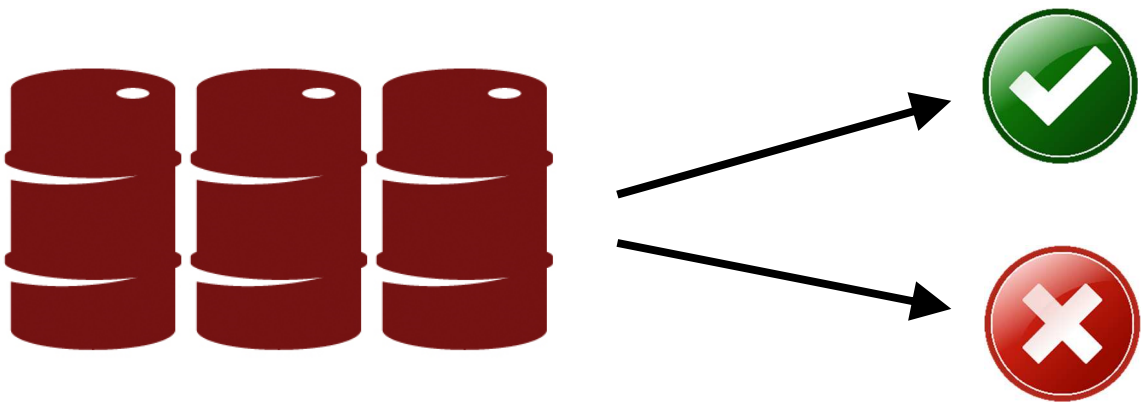
SCL – Specific Concentration Limit

Status of the BPR (January 2019)

Of the 31 biocidal substances originally submitted for evaluation within Product type 13 (the group that MWF biocides belong to) of the Biocidal Products Regulation (BPR):

- Five substances have been withdrawn, the applicant no longer supporting the dossier.
- One substance has been given a non-approval decision due to the unacceptable risks for the groundwater that the metabolites present.
- Six substances have been approved by the EU commission, one of which is a candidate for substitution.
- Two substances have been given a positive opinion by the Biocidal Products Committee (BPC) and are awaiting approval by the EU Commission. Both are candidates for substitution.
- Two substances are in the process of getting an opinion from the BPC

The remaining 15 substances are still in the process of Competent Authority Evaluation.



Formaldehyde releasers

Formaldehyde releasers are a group of biocides with quite diverse chemical structures but with one thing in common; they release formaldehyde when in aqueous solution or when in contact with biological tissues. There are eleven different formaldehyde releasers available for use in the metalworking industry. Three of these are possible to formulate into metalworking fluid concentrates and are consequently the most commonly used. The remaining eight are mainly used as tank side additives.

The discussion on formaldehyde releasers started already back in 2014 when the European Commission published the 6th Adaptation to Technical Progress (ATP) to CLP with new updated harmonised classification for formaldehyde. The classification on carcinogenicity was made more strict, from H351 - Suspected of causing cancer, to H350 – May cause cancer. Since substances that are carcinogens in category 1A or 1B should, in principal, not be approved as active substances within the Biocidal Products Regulation (BPR), this urged the legislators to look more closely at the formaldehyde releasing biocides as well. MBM, MBO and HPT which are the three most commonly used formaldehyde releasers were the first to be evaluated. Most of the discussion revolved around whether classification should be based on the amount of "free, unbound" or "technically releaseable" formaldehyde. ECHA's expert group on classification and labelling, the Committee for Risk Assessment (RAC), concluded in its opinions in December 2015 that since the substances release formaldehyde when in contact with biological tissues it is not relevant whether the user is exposed to free or bound formaldehyde and recommended that all three substances be classified as Carc. 1B – May cause cancer. The European Commission agreed with the opinion of the RAC to classify these substances as Carc. 1B , with the addition of a note reading: "The classification as a carcinogen need not apply if it can be shown that the maximum theoretical concentration of releasable formaldehyde, irrespective of the source, in the mixture as placed on the market is less than 0,1 %.".

This means that for example a product or mixture containing MBO, which contains 45 % releasable formaldehyde, only needs to be labelled as Carc. 1B if it contains 0.22 % MBO or more. However, given that formaldehyde releasers are normally formulated in concentrates in levels around 5 % to give sufficient biocidal function, this means that the concentrations that can be used without having to classify the mixture as carcinogenic give a too weak biocidal function. The commission decision was published in May 2017 in the 10th ATP to CLP which began to apply on 1st of December 2018.

A MAJOR SHIFT

This new classification has caused a major shift in how users and formulators chose to preserve their fluids. All large process fluid suppliers have phased out or are in the process of phasing out formaldehyde releasers from their products. Due to the environmental, health and safety requirements that the new classification puts on users of these formaldehyde releasers, most users demand fluids that are free from these biocides.

The remaining eight formaldehyde releasers that have yet to receive harmonised

classification have the same mode of action as those that have now been classified and will in all likelihood get the same harmonised classification in regards to carcinogenicity once they have been evaluated. This is something that the biocide suppliers are well aware of but despite this, most suppliers do not label them as carcinogenic. Consequently, some users continue to use them as tank side additives, aware or unaware, that they likely present the same risks as the other formaldehyde releasers.

However, most users will not accept a much shorter fluid lifetime just because they cannot use formaldehyde releasers and consequently other options of fluid preservation such as isothiazolinones have to be explored.

Isothiazolinones

Isothiazolinones are a group of biocides used in for example make-up, hygiene products, washing-up liquids, water based glues and paints. Some 10-20 years ago, these biocides were also common in process fluids, both as tank side additives and as part of the concentrate. As tank-side additives, they were often sold under the brand name Kathon. However, after reports on an increased frequency of contact allergy towards isothiazolinones, they were removed from process fluids in most countries and replaced with formaldehyde releasers. The recent reclassification of the three most commonly used formaldehyde releasers as carcinogenic has caused a reappearance of isothiazolinones on the process fluid market.

All isothiazolinones available on the market for use in metalworking fluids are classified as more or less allergenic. One problem with the isothiazolinones is that they are out of phase when it comes to their classification. Those that have recently had their classification evaluated have all had harsh judgements with more strict classification as a result. However, some of the isothiazolinones have not yet received a harmonised classification or have a harmonised classification that is derived from an older regulatory system.

CMIT/MIT AND MIT

The isothiazolinone mixture CMIT/MIT was first to receive a low specific concentration limit (SCL) for skin sensitisation at 15 ppm (0.0015 %) already in 2010. When CMIT/MIT received this classification, it was phased out of most products, not only process fluids. In consumer products it was usually replaced by the isothiazolinone MIT. The sudden increase in use of MIT was accompanied by a dramatic increase in the number of people diagnosed with MIT allergy. In most cases the source of the allergy was consumer products where the concentration of MIT was below 100 ppm. The case for setting a low SCL for MIT was strong and in October 2018 the European Commission published their decision that MIT will also get an SCL of 15 ppm for skin sensitisation. This decision will apply from 1st of May 2020 and it will greatly affect the usability of MIT in process fluids. Before this decision, MIT did not have harmonised classification, meaning that the suppliers themselves were responsible for classifying the substance. The most commonly used classification for MIT is Skin Sens. 1 which has a general concentration limit (GCL) of 10 000 ppm (1%). This means that until May 2020, MIT can be used as a component in

process fluids in concentrations up to 1000 ppm without even being mentioned on the safety data sheet, a level well above that which can cause skin allergies.

OIT

In late November 2018, the Committee for Risk Assessment (RAC), gave their opinion on another of the isothiazolinones, OIT. This substance already has an old harmonised classification with a SCL for skin sensitisation at 500 ppm. The Finnish Institute of Occupational Health was one of the parties who gave their recommendations to RAC, mentioning several studies that showed evidence of cross-reactivity between the isothiazolinones MIT, OIT and BIT. In their opinion, RAC likely payed particular attention to this as they recommended that OIT also should have a SCL of 15 ppm. If the European commission agrees with the opinion of the RAC, the new classification for OIT will apply approximately from 2022-2023. At the same meeting, RAC gave their opinion on another isothiazolinone, DCOIT. This isothiazolinone is not used in metalworking fluids, however, it is still interesting to follow the legislative development as it is based on the same chemistry. The RAC recommended that this substance should also have a SCL of 15 ppm.

OTHER ISOTHIAZOLINONES

The isothiazolinones used in metalworking fluids that have not yet had their classification reviewed are BIT and BBIT. Both have older harmonised classification, BBIT has Skin Sens. 1 with a GCL of 10 000 ppm, BIT has Skin Sens. 1 with a SCL of 500 ppm. No intention to update their classification have been submitted yet, but is likely to be submitted within this year or the next since harmonised classification is a requirement for active substance approval within the Biocidal Products Regulation.

Boric acid

There have been many twists and turns when it comes to boric acid, and it seems it is not over yet. This time it is the specific concentration limit for reproductive toxicity that is the topic of discussion. Boric acid gained attention already in 2010 when ECHA identified it as a SVHC (Substance of Very High Concern), an action indicating that the use of boric acid would soon require an Authorisation. This had significant effects in industry and companies quickly put boric acid on their phase-out lists of substances that they do not want in their production.

In 2013, Poland submitted a proposal to change the harmonised classification of boric acid from Repr. 1B (H360FD - May damage fertility. May damage the unborn child) to Repr. 2 (H361d - Suspected of damaging the unborn child). The proposal was voted down in the Committee for Risk Assessment (RAC) in 2014 and boric acid sustained its harmonised classification. In the opinion from RAC they had noted that there was justification to review the specific concentration limit for reproductive toxicity for boric acid since the existing specific concentration limit (SCL) had been derived from an older method. But since reviewing the SCL was not part of the proposal no update of the SCL was included in the opinion, only a recommendation that a new proposal should be brought forth to deal with this matter.

NEW CLASSIFICATION PROPOSAL

Sweden submitted a proposal in the beginning of 2018 to remove the existing SCL for boric acid and six other borates and replace them with generic concentration limits at 0,3% which is in line with the new criteria of CLP. A public consultation is ongoing until the end of February 2019 and approximately six months after that the RAC will give its opinion on the proposal. If the proposal has a positive vote in both the RAC and the European Commission, the new classification would start to apply around year 2024.

Future outlook

Replacing formaldehyde releasers in metalworking fluids is a major shift in how the industry handles biodeterioration. It will present changes in how the fluids are handled and it is also likely that new work environmental problems will occur. Historically, whenever isothiazolinones increase in use it has been followed by an increased contact allergy rate and this will likely be the case in the metalworking industry as well.

As fewer and fewer biocides become available the importance of system design and maintenance becomes more clear and there is a growing understanding in the industry that not everything can be solved by adding biocides. It is possible to solve work environment problems with new technology. Several major industrial companies use solutions based on UV light instead of biocides to reduce bacteria in process fluids as it is a safe, environmentally friendly and economical alternative.

We see an increased awareness and interest for work environmental issues in the industry. The demand for a safer work environment is growing and in today's competitive industry it is important for employers to stay attractive and avoid losing competent employees. We must take the steps towards a non-toxic work environment and to stop using biocides is one of the biggest challenges that the industry is facing today.

List of biocides

	OTHER IDENTIFIER	ACTIVE SUBSTANCE	EC NO.	CAS NO.
FORMALDEHYDE RELEASERS (MAY CASUE CANCER)	Benzylhemiformal/BHF	(benzyloxy)methanol	238-588-8	14548-60-8
	EGBHF/EDDM	(ethylenedioxy)dimethanol (Reaction products of ethylene glycol with paraformaldehyde (EGForm))	222-720-6	3586-55-8
	DMDMH	1,3-bis(hydroxymethyl)-5,5-dimethylimidazolidine-2,4-dione	229-222-8	6440-58-0
	HHT	2,2',2"-(hexahydro-1,3,5-triazine-1,3,5-triyl) triethanol (1,3,5-tris(2-hydroxyethyl) hexahydro-1,3,5-triazine)	225-208-0	4719-04-4
	EDHO	7a-ethyldihydro-1H,3H,5H-oxazolo[3,4-c]oxazole	231-810-4	7747-35-5
	cis-CTAC	cis-1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride	426-020-3	51229-78-8
	CTAC	Methenamine 3-chloroallylochloride	223-805-0	4080-31-3
	MBM	N, N'-methylenebismorpholine	227-062-3	5625-90-1
	Oxazolidin/MBO 3,3'-methylenebis[5-methyloxazolidine]	Reaction product of paraformaldehyde and 2-hydroxypropylamine (ratio 3:2)	N/A (266-235-8)	N/A (66204-44-2)
	HPT α,α',α''-trimethyl-1,3,5-triazine-1,3,5(2H,4H,6H)-triethanol	Reaction products of paraformaldehyde with 2-hydroxypropylamine (ratio 1:1)	- (246-764-0)	- (25254-50-6)
	TMAD	Tetrahydro-1,3,4,6-tetrakis(hydroxymethyl)imidazo[4,5-d]imidazole-2,5(1H,3H)-dione	226-408-0	5395-50-6
ISOTHIAZOLINONES (MAY CAUSE ALLERGIES)	BIT	1,2-Benzisothiazol-3(2H)-one	220-120-9	2634-33-5
	MIT	2-methyl-2H-isothiazol-3-one	220-239-6	2682-20-4
	BBIT	2-n-butyl-benzo[d]isothiazol-3-one	420-590-7	4299-07-4
	OIT	2-octyl-2H-isothiazol-3-one	247-761-7	26530-20-1
	C(M)IT/MIT	Mixture of 5-chloro-2-methyl-2H-isothiazol-3-one (EINECS 247-500-7) and 2-methyl-2H-isothiazol-3-one (EINECS 220-239-6)	Mixture	55965-84-9
OTHERS	Diamine	N-(3-aminopropyl)-N-dodecylpropane-1,3-diamine	219-145-8	2372-82-9
	IPBC	3-iodo-2-propynyl butylcarbamate	259-627-5	55406-53-6
	DBNPA	2,2-dibromo-2-cyanoacetamide	233-539-7	10222-01-2
	Free radicals	Free radicals generated in situ	-	-
	Phenoxyethanol	2-phenoxyethanol	204-589-7	122-99-6
	Chlorocresol/CMK	4-chloro-3-methylphenol	200-431-6	59-50-7
	OPP	Biphenyl-2-ol	201-993-5	90-43-7
	NaPy, Na-Pyrithione	Pyridine-2-thiol 1-oxide, sodium salt	223-296-5	3811-73-2

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