The REACh Regulation: The Need of Substitution of Critical Substances in Propellants

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***Abstract**: REACh (Registration, Evaluation, Authorization and Restriction of Chemicals) is a regulation of the European Union, adopted to improve the protection of human health and the environment from the risks that can be posed by chemicals, while enhancing the competitiveness of the EU chemicals industry.*

In this contribution we present results of our study which aim is to evaluate the environmental friendliness of common gun propellant ingredients and to propose environmentally more acceptable substitutes for harmful materials. Therefore, we collected the toxicological and eco-toxicological data for a selected number of ingredients of common used gun propellants in order to carry out an initial assessment under the REACh regulation. Some substances were identified as critical and it was started to find suitable substitutes which were also assessed with regard of the REACh regulation.

***Keywords**: REACh, Propellant, Dibuthylphthalate, DNDA.*

1. Introduction

The REACh (Registration, Evaluation, Authorization and Restriction of Chemicals) regulation entered into force on 1st of June 2007. Since this date all chemicals produced, used or imported in the European Union had to be registered and tested regarding their impact to health and environment.

The ECHA (European Chemicals Agency, Helsinki, Finland) is an agency of the European Union to administer the registration, evaluation, authorisation and restriction of chemicals. In the moment 13052 unique substances are registered at the ECHA (25th of February 2015). ECHA works together with the European Commission and the EU Member States for the safety of human health and the environment by identifying the needs for regulatory risk management at EU-wide level. When necessary the Member States or ECHA

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(on a request from the Commission) initiate the authorisation requirements, restrictions, or the need for harmonised classification and labelling of chemicals of concern.

Substances with certain hazardous properties can be of concern for human health and/or the environment. Such chemicals can be identified and will be put on the SVHC (Substance of Very High Concern) list so that they have to be authorised by the ECHA before producing, importing or using in the EU. Member State, ECHA or European Commission may propose a substance to be identified as a SVHC. In the moment 161 substances are on this list including 2,4-dinitrotoluene, benzyl-butyl-phthalate, bis-(2-ethylhexyl)phthalate, di-butyl-phthalate, di-isobutyl-phthalate or diphenylamine. The list will be amended continuously. A substance which is once on the list will be always on the list.

Substances identified in the SVHC list are eventually included in Annex XIV of the REACH Regulation. Once included in that Annex, they cannot be placed on the market or used after a date unless the company is granted an authorization. In the moment 31 substances are on this authorization list e.g. 2,4-dinitrotoluene, di-butyl-phthalate or lead chromate.

2. Toxicological and eco-toxicological specifications

2.1 Toxicity and CMR behaviour

The toxicity of a substance is differentiated between the acute (effect after non-recurring application), sub-acute, sub-chronic and chronic (application longer than 6 months) toxicity. The acute toxicity of a substance is characterised by the LD 50 value (lethal doses) which represents the doses which kills 50 % of an animal population. In the characterisation of the toxicity the exposure way has to be included. Here a differentiation between an oral, dermal or inhaling incorporation can be made.

REACh attaches importance to substances classified as carcinogenic, mutagenic or toxic for reproduction (CMR). Substances are classified in three categories (1A, 1B and 2).

- Category 1 A (formerly 1): Classification is based on human evidence (epidemiological data),
- Category 1 B (formerly 2): Classification is based on animal evidence,
- Category 2 (formerly 3): substances and preparations of concern for humans because of the possible CMR effects but for which there is not enough information available to classify these substances and preparations in category 1A or 1B.

2.2 Eco-toxicity

Eco-toxicology deals with the decomposition and distribution behaviour of chemical compounds and their effect on functions (material and energy cycles) and structures (populations and their interactions) of ecosystems (air, soil, water).

To handle the wide range of issues in environmental toxicology very different investigation methods have been developed, some of which are used in the laboratory but also

in nature itself. In the laboratory, standardized tests with high reproducibility were carried out; their significance may be small in terms of natural environment with infinitely many interactions. Therefore, if possible, studies carried out in the so-called model ecosystems. Due to this very complex system and the multitude of different data which are presented in literature an assessment of substances is very difficult.

Besides of the acute toxicity in the aquatic system the persistence and biodegradability (PBT) behaviour as well as the mobility and water solubility of the substance is important.

Persistence: This term is derived from the Latin word for "persistere" (= hesitation). It means that a substance is poorly degradable and persists for a long time. Neither organisms such as bacteria, nor other naturally occurring environmental factors such as hydrolysis are able to contribute to a significant decomposition within a certain period.

Biodegradability: A substance in a living organism is consumed through food or through the surrounding medium (such as water, soil and air) and enriched. Frequently, fat-soluble (lipophilic) substances show such behaviour. They then accumulate mainly in fatty organs such as the liver.

A parameter for the assessment of bioaccumulation is the bioconcentration factor BCF. This dimensionless parameter is the ratio between the concentration of a substance in an aquatic organism (such as in a small crustacean or fish) and the surrounding water.

Evidence of a potential to bioaccumulate can also provide the n-octanol-water partition coefficient K_{OW}. It is a dimensionless distribution coefficient that indicates the ratio of the concentrations of a substance in a two-phase system consisting of n-octanol and water. More fat-soluble substances accumulate in the n-octanol phase, more water-soluble in the water phase.

The mobility of a substance can be characterized by the distribution coefficient K_{OC} which described the partition of the organic carbon between the soil and water phase.

2.3 Assessment and legal limit values

Substances of Very High Concern (SVHC) are defined and include substances which are

- Carcinogenic, mutagenic or toxic to reproduction (CMR) or
- Persistent, bioaccumulative and toxic (PBT) or
- Very persistent and very bioaccumulative (vPvB).

So, a high toxicity of a substance is not a kill criterion as long as the substance is not persistent and bioaccumulative. The legal values for the three mentioned criteria are summarized in the next three tables.

Table 1.
Legal limit values for the CMR criterion

	low	medium	high
CMR	No classification	**Category 2**	**Category 1A, 1B**
Toxicity	LD 50 (mg/kg) oral, Rat: > 2000	300 – 2000	< 300
Eco-toxicity	LC 50, acute: > 1 mg/L LC 50, chronic: > 0.1 mg/L	1 – 0.1 mg/L 0,1 – 0.01 mg/L	< 0.1 mg/L < 0.01 mg/L
Persistence	Half-life time: < 28 d	40 – 60 d (water) > 120 d (soil)	> 60 d (water) > 180 d (soil)
Bioaccumulation	BCF: < 2000 log K_{OW}: < 3.0	2000 – 5000 3.0 – 4.5	> 5000 > 4.5
Mobility	Water solubility: < 10 mg/L log K_{OC}: > 2.0	10 – 1000 mg/L 1.0 – 2.0	> 1000 mg/L < 1.0

Table 2.
Legal limit values for the PBT criterion

	low	medium	high
CMR	No classification	**Category 2**	**Category 1A, 1B**
Toxicity	LD 50 (mg/kg) oral, Rat: > 2000	300 – 2000	< 300
Eco-toxicity	LC 50, acute: > 1 mg/L LC 50, chronic: > 0.1 mg/L	1 – 0.1 mg/L 0,1 – 0.01 mg/L	< 0.1 mg/L < 0.01 mg/L
Persistence	Half-life time: < 28 d	40 – 60 d (water) > 120 d (soil)	> 60 d (water) > 180 d (soil)
Bioaccumulation	BCF: < 2000 log K_{OW}: < 3.0	2000 – 5000 3.0 – 4.5	> 5000 > 4.5
Mobility	Water solubility: < 10 mg/L log K_{OC}: > 2.0	10 – 1000 mg/L 1.0 – 2.0	> 1000 mg/L < 1.0

Table 3.
Legal limit values for the vPvB criterion

	low	medium	high
CMR	No classification	**Category 2**	**Category 1A, 1B**
Toxicity	LD 50 (mg/kg) oral, Rat: > 2000	300 – 2000	< 300
Eco-toxicity	LC 50, acute: > 1 mg/L LC 50, chronic: > 0.1 mg/L	1 – 0.1 mg/L 0,1 – 0.01 mg/L	< 0.1 mg/L < 0.01 mg/L
Persistence	Half-life time: < 28 d	40 – 60 d (water) > 120 d (soil)	> 60 d (water) > 180 d (soil)
Bioaccumulation	BCF: < 2000 log K_{OW}: < 3.0	2000 – 5000 3.0 – 4.5	> 5000 > 4.5
Mobility	Water solubility: < 10 mg/L log K_{OC}: > 2.0	10 – 1000 mg/L 1.0 – 2.0	> 1000 mg/L < 1.0

Using these schemes we assessed the main ingredients used in common propellants and a lot of potential substitutes for critical components. Unfortunately, not all the values for all substances are available. In particular, information on persistence and bioaccumulation were scarce so that a final assessment was not possible in all cases.

3. Toxicological and eco-toxicological assessment by REACh

The relevant data for a toxicological and eco-toxicological assessment of the main ingredients of common gun propellants are summarized in the following tables. The valuation was based on the simplified scheme of Ruppert et al. [1].

Table 4.
Assessment of the most important fillers in common used gun propellants by REACh

Property	RDX	Nigu	K_2SO_4	Na-Oxalate	Cryolite	Akardit II	Centralit I
CMR	Cat. 2	n.d.	-	-	-	-	n.d.
Toxicity	T	-	-	(T)	-	-	-
Aquatic Toxicity	-	-	-	-	-	n.d.	-
Persistence	vP	n.d.	n.d.	n.d.	n.d.	n.d.	
Bioaccumulation	-	-	n.d.	n.d.	n.d.	-	B
Assessment	critical	OK	OK	OK	OK	OK	OK

Table 5.
Assessment of the most important softeners in common used gun propellants by REACh

Property	DIBU	Triacetin	campher	NGL	DEGN	DNT	TEGDN
CMR	Cat. 1B	-	n.d.	Cat. 2	-	Cat. 1B	n.d.
Toxicity	T	-	-	T	T	T	(T)
Aquatic Toxicity	-	-	-	-	-	-	n.d.
Persistence	-	P	-	-	n.d.	P	n.d.
Bioaccumulation	-	-	-	-	-	-	n.d.
Assessment	Annex XIV	OK	OK	critical	OK	Annex XIV	OK

Table 6.
Assessment of the most important binders in common used gun propellants by REACh

Property	Nitrocellulose	CAB
CMR	-	-
Toxicity	-	-
Aquatic Toxicity	-	n.d.
Persistence	vP	n.d.
Bioaccumulation	n.d.	n.d.
Assessment	OK	OK

We identified four substances to be regarded as critical by REACh. These are RDX (carcinogenic), 2,4-Dinitrotoluene (toxic, carcinogenic), Dibuthylphthalate (toxic, carcinogenic, high bioaccumulative) and Nitroglycerine (toxic, Ames test positive, mutagenic). Two of these substances (DNT and Dibuthylphthalate) are listed in the Annex XIV of the REACh regulation so they are forbidden in the EU from February 2015 (Dibuthylphthalate) and August 2015 (DNT), respectively. Additional four substances should

be on a watch. These are diethylene glycole dinitrate (very toxic), Centralit I (high bioaccumulative), Cryolith (toxic, water hazardous) and TEGDN (very water hazardous).

Due to the fact that dibuthylphthalate and dinitrotoluene are not allowed to be used without authorization in the EU from next year it is very urgent to find alternatives for these critical substances. Therefore we started to evaluate potential substitutes regarding their toxicity and eco-toxicity. Octogen (HMX), Fox 7 and Fox 12 were selected as a possible substitute for RDX, DNDA-57, Me-/Et-/Bu-NENA for dinitrotoluene and nitroglycerine, respectively. To substitute dibuthylphthalate a large amount of different softeners can be found in literature. We had a closer look at diisononylphthalate, cyclohexane dicarbone acidester, sebacate, adipate, trimellitate and derivates of ethylene glycol.

Table 7.
Simplified assessment of DNDA-57 and Me-/Et-/Bu-ENA by REACh

	DNDA-57	Me-NENA	Et-NENA	Bu-NENA
Labelling	X_n	no	no	X_n
LD 50 oral rat mg/kg	300 – 2000			
EC daphnia mg/l	> 100			
Bioaccumulation	degradable		possible bioaccumulative	
Log K_{OW}	1.2			
Water solubility g/l	4		insoluble	

From Table 7 the main problem assessing substitutes concerning the REACh conformity becomes clear: in most cases a lot of data are still missing. Especially data about the CMR potential and the persistence and bioaccumulation are not available so that a final assessment is not possible.

4. Summary and outlook

It was shown that the REACh regulation has a large influence on the formulation of propellants. We assessed the main ingredients of common used propellants concerning their toxicological and eco-toxicological properties. We identified four substances with a high risk that they will be under concern of REACh. Dibuthylphthalate and dinitrotoluene are already listed in the Annex XIV of the REACh regulation so it will not be allowed to use them from February and August 2015, respectively in the EU without an authorization by the ECHA.

We started to identify alternatives for these high risk substances and to assess them with regard to the REACh criteria. It becomes clear that there is a lack of data especially concerning the CMR potential and the persistence and bioaccumulation which are the main points of the REACh criteria. Here, a lot of work has to be done in the next years to develop a greener alternative formulation of new propellants. Moreover, we tested some new softeners in first formulations to see how they can be combined with other ingredients. Especially, glass transition point, compatibility, viscosity and theoretical performance were investigated. First formulations with HMX as substitute for RDX and DNDA-57 or NENA`s as substitute for Nitroglycerine were manufactured. These formulations were characterized by preliminary

ballistic tests and show a large potential. Nevertheless, much more tests have to be performed in the future.

5. References

[1] W.H. RUPPERT et al. – *A History of Environmentally Sustainable Energetics*, Insensitive Munitions & Energetic Technology Symposium, Munich, Germany, 2010