Current requirements for the registration of products under the REACH system using an example of ecological solvents

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Introduction

The REACH system is among the biggest projects which have been recently adopted by the European Union. Its priority is to provide the proper level of protection of human health and the environment, and simultaneously it aims to preserve the competitiveness of the European enterprises present on the international market.

The REACH regulation applies to the enterprises, mainly manufacturers and importers of chemical substances, mixtures and some articles. This regulation introduces quite a complex and expensive process which, however distributed in time, begins with the obligation of the pre-registration of a substance involving the study and the assessment until sharing with users the information on the methods of safe use of the registered substances [1].

The REACH regulation adopts the rule according to which the larger the quantities of produced or imported substance are, the higher requirements on the scope of the information, data, tests and control studies have to be included into the documents attached to the registration application (Tab. 1).

Table 1

Requirements set out in the annexes depending on the tonnage range

Tonnage range	Annex VI	Annex VII	Annex VIII	Annex IX	Annex X	Annex XI
1 - 10 (tpa)	+	+ (+ Annex III)	-	-	-	+
10 – 100 tpa	+	+	+	-	-	+
100 – 1000 tpa	+	+	+	+	-	+
≥ 1000 tpa	+	+	+	+	+	+

The annexes VII ÷ X set out the standard information requirements for four tonnage ranges from 1 tonne per annum to ≥ 1000 tonnes per annum. The standard requirements for the lowest tonnage are presented in the Annex VII. If the next tonnage threshold is exceeded, the requirements set out in the adequate annexes should refer to it. The other 3 annexes: III, VI, IX specify the general criteria applied to the requirements set out in the annexes VII ÷ X.

The first (free of charge) duty of an enterprise was to pre-register so called phase-in substances (registered in the EU until 1981) - within the deadline from 1st June to 1st December 2008. This determines the ability to benefit from the transitional period for the registration (Fig. 1):

- until 1st December 2010 - carcinogenic, mutagenic or toxic for reproduction (CMR, categories 1 and 2) substances above 1 tonne per annum, substances which are very toxic to aquatic organisms (R 50/53) at least 100 tonnes per annum and other substances being manufactured or imported in quantities above 1000 tonnes per annum
- until 1st June 2013 - manufactured or imported substances in quantities from 100 to 1000 tonnes per annum
- until 1st June 2018 - manufactured or imported substances in quantities from 1 to 100 tonnes per annum.

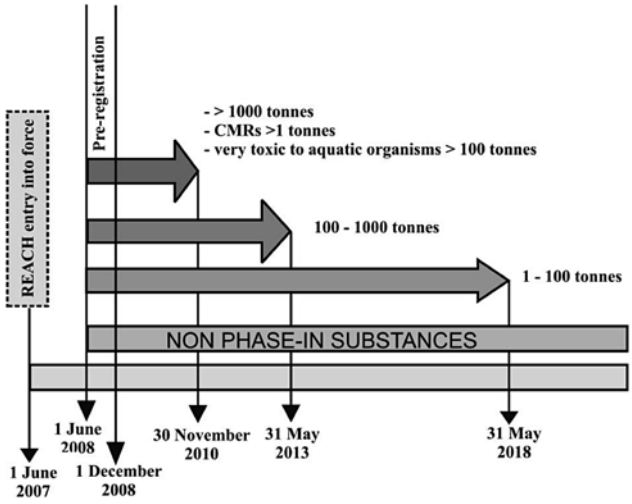

Fig. 1. Deadlines for registration

Recent amendments to the REACH regulation

The up-to-date amendments which have been recently introduced into the REACH regulation are presented below.

Commission Regulation (EU) No. 143/2011 [2] entered into force on 17 February 2011, amending Annex XIV to the Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the registration, evaluation, authorisation and restriction of chemicals (REACH). The above mentioned regulation [2] introduces six substances from a candidate list into a so far empty Annex XIV referring to the list of substances subject to authorisation (Tab. 2).

Table 2

List of substances added to Annex XIV

Substance	Intrinsic properties	Transitional procedures	
		Deadline for submitting applications	Sunset date
Musk xylene (5-tert-butylo-2,4,6-trinitro-m-xylene) CAS No.: 81-15-2	vPvB [1]	21.01.2013	21.07.2014
MDA (4,4'-diaminodiphenylmethane) CAS No.: 101-77-9	carcinogenic (category 1 B)	21.01.2013	21.07.2014
HBCDD (hexabromocyclododecane) CAS No.: 3194-55-6	PBT [2]	21.01.2014	21.07.2015
DEHP (bis(2-ehtylhexyl) phthalate) CAS No.: 117-81-7	toxic to reproduction (category 1B)	21.07.2013	21.01.2015
BBP (benzyl butyl phthalate) CAS No.: 85-68-7	toxic to reproduction (category 1B)	21.07.2013	21.01.2015
DBP (dibutyl phthalate) CAS No.: 84-74-2	toxic to reproduction	21.07.2013	21.01.2015

[1] – very persistent and very bioaccumulative substance [3]

[2] – persistent, bioaccumulative and toxic substance [3]

Among phase-in substances, there is hexabromocyclododecane (HBCDD) – a substance of significant importance to the Polish economy. This substance belongs to a group of brominated flame retardants and it is one of the most commonly used antypirenes. HBCDD is mainly used in the production of foamed polystyrene intended for the thermo-insulation of buildings, and in smaller extent it is used in the furniture upholstery and electronic equipment.

The European Chemical Agency has recently started the public consultation on including thirteen substances of very high concern (SVHC) into Annex XIV from the candidate list. This group includes: chromium(VI) oxide; chromic acid; sodium dichromate(VI), potassium dichromate(VI) and ammonium dichromate(VI); potassium chromate(VI) and sodium chromate(VI); trichloroethane; cobalt(II) sulphate and cobalt(II) chloride; cobalt(II) dinitrate; cobalt(II) carbonate; cobalt(II) diacetate.

Another new issue introduced into the REACH regulation refers to amendments to Annex XVII. Pursuant to the Commission Regulation (EU) No 366/2011 of 14 April 2011, Annex XVII regarding the restriction of production, placing on the market and the use of some dangerous substances, mixtures and articles has been amended by adding acrylamide (CAS No. 79-06-1) [4]. On the basis of the European Risk Assessment, it has been identified that the risk for the aquatic environment associated with the use of acrylamide based grouts in construction applications and the risk to other organisms from indirect exposure through contaminated water from the same application should be reduced. Furthermore, concerns for workers and persons exposed via the environment were raised in view of the carcinogenic and mutagenic nature of acrylamide and for its neurotoxicity and reproductive toxicity as a consequence of exposure arising from small and large-scale use of acrylamide based grouts. On the basis of the results of the properties presented above, it has been decided that acrylamide cannot be placed on the market or used as a substance on its own or in a mixture in a concentration equal to or greater than 0.1% by weight for grouting applications after 05.11.2012.

Hydroxyester HE1 – an ecological solvent

European Directive 2004/42/EC, known also as Decopaint Directive, which entered into force on 1 January 2007, is a very important European legislation concerning ecological solvents [5]. This directive refers to the limitation of solvents from decorative paints and vehicle varnishes which were not previously covered by the scope of Directive 1999/13/EC on the limitation of emissions of solvents [6].

In accordance with Directive 2004/42/EC, volatile organic compound (VOC) means any substance having an initial boiling point less than or equal to 250°C measured at a standard pressure of 101.3 kPa.

The VOCs risk for the environment results from the fact that they react with the stratospheric ozone in the stratosphere and cause the depletion of the ozone layer acting as a natural UV radiation filter. Whereas in the troposphere under conditions of raised temperature and solar radiation, VOCs react with nitrogen oxides (NOx) generating the tropospheric ozone being one of the elements of smog. The reaction rate, wind effect and the possibility of retarded reaction due to insufficient quantity of sunlight mean that the formation of ozone and the resulting smog can be retarded for a few days and take place hundreds of kilometres away from the source of VOCs emission.

Hydroxyester HE1 is an example of an ecological solvent which is not classified into the group of Volatile Organic Compounds. It is obtained from isobutanal in a sequence of chemical reactions with isobutyraldehade (isobutanal) being the fundamental raw material in the process of aldol condensation with the consecutive Cannizaro-Tiszczenko reaction as presented in Figure 2 [7].

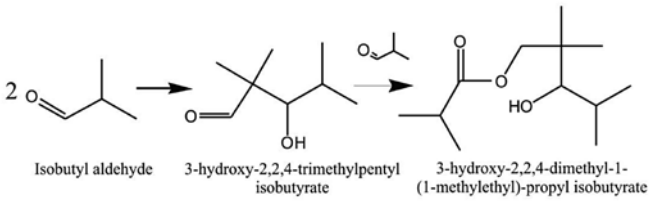

Fig. 2. General scheme of isobutanal condensation aimed to obtain Hydroxyester HE1

Hydroxyester HE1 is a hydrophobic organic solvent mainly used as the coalescent agent in technological processes of water based architecture paints.

Because Hydroxyester HE1 is not classified into the group of Volatile Organic Compounds (boiling temp. 254°C), it is an alternative to toxic solvents and coalescent agents applied in the production process of paints and varnishes whose emissions have been limited along with the entry into force of European Directive 2004/42/EC, known as Decopaint Directive (Fig. 3).

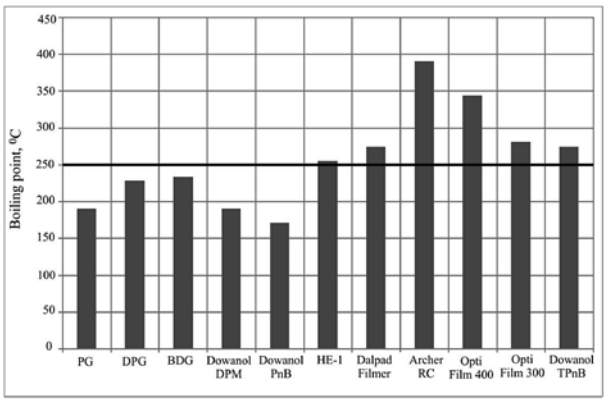

Fig. 3. The list of most important organic solvents used as coalescent agents in the technological processes for paints and varnishes

where:

PG – propylene glycol, DPG – dipropylene glycol, BDG – butyl diglycol, Dowanol DPM – dipropylene glycol methyl ether acetate, Dowanol PnB – monopropylene glycol butyl ether acetate, HE1 – 2,2,4-trimethylpentandiol-1,3 monoisobutyl, Dapad Filmer – mixture of butanol oxypropylates (DOW), Opti Film 300 – hydroxyester HE-1 isobutyric ester, Dowanol TPnB - tripropylene glycol butyl ether acetate

Table 3

Physicochemical tests performed in accordance with chemical safety assessment

No.	Physicochemical studies	Guideline
1	Melting/Freezing point	OECD 102
2	Boiling point	OECD 103
3	Relative density	OECD 109
4	Water solubility	OECD 105
5	Partition coefficient n-octanol/water	OECD 117
6	Flash-point	EC Regulation No 440/2008
7	Self-ignition temperature	EC Regulation No 440/2008
8	Viscosity	OECD 114

Hydroxyester HE-1 is the most common coalescent agent of a new type meeting the standard requirements for VOCs and having the most precise description of its properties. The new proposals concerning coalescent agents with raised boiling temperature such as Dalpad Filmer, Opti Film 400 or Opti Film 300 are more expensive alternatives which have been applied for quite a short period of time. This may also result in the deterioration of paint quality.

Pursuant to the guidelines of the REACH regulation, the physicochemical (Tab. 3), toxicological and ecotoxicological (Tab. 4) tests were performed in order to prepare the chemical safety assessment of the substance, i.e. Hydroxyester HE1. The tests were carried out in cooperation with the Institute of Industrial Organic Chemistry *[Instytut Przemysłu Organicznego]* in Warsaw, Branch in Pszczyna in accordance with OECD guidelines and Good Laboratory Practice.

Table 4

Toxicological and ecotoxicological tests performed in accordance with chemical safety assessment

	Toxicological and ecotoxicological tests	OECD guideline
TOXICOLOGICAL TESTS	Skin irritation or skin corrosion	404
	Eye irritation	405
	Skin sensitisation	406
	Mutagenicity: *In vitro* gene mutation study in bacteria	471
	Acute toxicity: by oral route	420
	In vitro gene mutation study in mammalian cells	476
ECOTOXICOLOGICAL TESTS	Short-term toxicity testing on invertebrates (preferred species *Daphnia*)	202
	Growth inhibition study on aquatic plants (algae preferred)	201
	Ready biodegradability	301
	Fish, short-term toxicity testing	203
	Activated sludge respiration inhibition testing	209
	Earthworms, short-term toxicity testing	207
	Effects on soil microorganisms: impact on nitrogen conversion	216
	Effects on soil microorganisms: impact on carbon conversion	217

Discussion on research results

The exemplary results of ecotoxicological studies specifying the risk assessment to human health and the environment are presented below. Hydroxyester HE1 is the exemplary substance.

Soil microorganisms: impact on nitrogen conversion according to OECD guideline No. 216

The agricultural soil was sieved to obtain particles with the size of 2 mm. Organic substrate in the form of dried lucerne was added to the prepared soil. The suitable weighed amounts of tested material at five concentrations listed below were introduced into the soil: 1.6; 8; 40; 200 and 1000 mg/kg of soil.

The control soil and the soil treated with the tested material were re-incubated three times [8].

The experiment lasted for 28 days. After 0 and 28th day of the experiment, the soil samples were collected and the quantity of nitrates generated in the soil were analysed. The determination was based on the spectrophotometric measurement of nitrate ions concentration in the soil extract of 1% solution of potassium sulphate (VI). The measurements of yellow tint intensity formed during the reaction with phenoldisulphonic acid were performed with a spectrophotometer. During testing nitrogen conversion in samples treated with the tested material, average quantities of nitrates were compared with the control quantity and percent deviation for the control value was calculated.

The obtained percent deviations in the tested concentrations for the control values are presented in Table 5. Table 6 presents EC_{50}, EC_{25} and EC_{10} values for the tested material.

Table 5

Percent deviations for control materials

Day	1.6 mg/kg of soil	8 mg/kg of soil	40 mg/kg of soil	200 mg/kg of soil	1000 mg/kg of soil
0	1.1	1.3	-0.3	-0.4	17.4
28	17.5	17.0	10.1	-12.5	-87.9

Table 6

Nitrogen conversion, EC_x values, mg/kg of soil

EC_{50}	EC_{25}	EC_{10}
444.2 (441.3 – 447.1)	278.7 (276.7 – 280.8)	182.8 (181 – 184.5)

The obtained results allowed to draw the following conclusions:

- **EC_{50}**- after 28 days, the concentration of tested material in the soil causing 50% inhibition of nitrogen conversion into nitrates amounts to 444.2 mg/kg of soil
- **EC_{25}**- after 28 days, the concentration of tested material in the soil causing 25% inhibition of nitrogen conversion into nitrates amounts to 278.7 mg/kg of soil
- **EC_{10}**- after 28 days, the concentration of tested material in the soil causing 10% inhibition of nitrogen conversion into nitrates amounts to 182.8 mg/kg of soil.

Soi_l microorganisms: impact on nitrogen conversion according to OECD guideline No. 217

In this case, the agricultural soil sieved to obtain particles with the size of 2 mm was used. The tested material was used at five concentrations: 1.6; 8; 40; 200 and 1000 mg/kg of soil. The control soil and the soil treated with the tested material were re-incubated three times [9].

The experiment lasted for 28 days. After 0 and 28th day of the experiment, the soil samples were collected and the substrate-induced level in the soil was analysed. The method based on Substrate-Induced Respiration measurement (SIR method) was used to determine the intensity of soil respiration. The determination was based on measuring the pressure difference in the closed system. CO_2 released during the respiration processes was bound to an absorbent (45% KOH soln.). This caused the pressure drop proportional to the soil respiration. During testing carbon conversion

in samples treated with the tested material, average quantities of oxygen consumption were compared with the control quantity and percent deviation for the control value was calculated.

The quantity of consumed oxygen was calculated from the following dependence:

$$SR = M_R(O_2) \cdot V_{fr} \cdot \Delta p / R \cdot T \cdot m_{ds.}[mg/kg of soil\ d.m.] \quad (1)$$

where:
SR – soil respiration
M_R –molecular mass of oxygen, mg/mole
p – pressure drop in the measurement system, hPa
R – gas constant, $1 \times mbar \times mole^{-1}K^{-1}$
T – incubation temperature, ^0K
m_{ds} – dry mass of soil sample in the measurement system, kg
V_{fr} – free gas volume [10]

$$V_{fr} = V_{tot} - V_{av} - V_{aa} - V_{hs}, \quad (2)$$

where:
V_{tot} – total volume of gaseous space in the measurement vessel [10]
V_{av} – internal volume of absorbent vessel [10]
V_{aa} – absorbent volume [10]
V_{hs} – volume of soil with required humidity [10]

The obtained percent deviations in the tested concentrations for the control values are presented in Table 7. Table 8 presents EC_{50}, EC_{25} and EC_{10} values for the tested material.

Table 7

Percent deviations for control materials

Day	1.6 mg/kg of soil	8 mg/kg of soil	40 mg/kg of soil	200 mg/kg of soil	1000 mg/kg of soil
0	1.4	-1.5	0.0	-2.9	-17.2
28	-0.1	2.3	-0.1	-2.6	53.5

Table 8

EC_x values, mg/kg of soil

EC_{50}	EC_{25}	EC_{10}
> 1000	> 1000	> 1000

The obtained results allowed to draw the following conclusions:

- **EC_{50}**- after 28 days, the concentration of tested material in the soil causing 50% inhibition of carbon conversion into carbon dioxide exceeds 1000 mg/kg of soil
- **EC_{25}**- after 28 days, the concentration of tested material in the soil causing 25% inhibition of carbon conversion into carbon dioxide exceeds 1000 mg/kg of soil
- **EC_{10}**- after 28 days, the concentration of tested material in the soil causing 10% inhibition of carbon conversion into carbon dioxide exceeds 1000 mg/kg of soil.

The presented results of physicochemical, toxicological and ecotoxicological tests show that Hydroxyester HE1 is safe in use and it does not present any risk to human health and the environment.

Conclusions

Pursuant to the Regulation of the Minister of Health of 4 September 2007 amending the regulation concerning criteria and classification methods of chemical substances and mixtures [6] and on the basis of the results from physicochemical, toxicological and ecotoxicological tests, it has been concluded that the tested substance – Hydroxyester HE1, is safe and does not present any risk to human health and the environment.

Because Hydroxyester HE1 has very good properties and meets the requirements set out by the European Union, it can replace alkyl ethers classified as Volatile Organic Compounds and can be commonly used in the technological processes of water based paints and varnishes.

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