



PUR and PIR  
Ecotoxicology and  
Environmental Risk Profile of  
Monomers and Degradation  
Products

Prepared for:

**Saint Gobain  
Location City**

Prepared by:  
**ENVIRON**

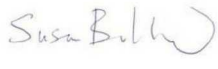
Date:  
**March 2011**

Project or Issue Number:  
**FR12SGB002**

---

**ENVIRON**

---

Contract/Proposal No:	FR12SGB002
Issue:	1
Author :	Henk Verhaar
Project Manager/Director (signature):	Sue Bullock & Fred Hamilton
	
Date:	4 <sup>th</sup> March 2011

*This report has been prepared by ENVIRON with all reasonable skill, care and diligence, and taking account of the Services and the Terms agreed between ENVIRON and the Client. This report is confidential to the client, and ENVIRON accepts no responsibility whatsoever to third parties to whom this report, or any part thereof, is made known, unless formally agreed by ENVIRON beforehand. Any such party relies upon the report at their own risk.*

*ENVIRON disclaims any responsibility to the Client and others in respect of any matters outside the agreed scope of the Services.*

Version Control Record				
Issue	Description of Status	Date	Reviewer Initials	Authors Initials
1	Final	04.03.11	OC	HK

## Table of Contents

1	Introduction	1
1.1	Polyurethanes	1
1.2	Polyisocyanurates	2
1.3	Remit	2
2	High-priority substances	3
2.1	Diisocyanates and degradation products	3
2.2	Polyols	9
2.3	Starting materials	10
2.4	Additives	11
3	Medium-priority substances	14

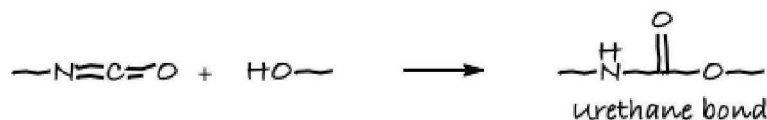
## List of Tables

Table 1. Phys-chem properties for commercial mixture of 2,4 TDI and 2,6-TDI (80/20).	3
Table 2. Empirical Data for Bioaccumulation of TDA	4
Table 3. Empirical Data for TDI and its degradation products	4
Table 4. High Priority Substance Assessment Overview	12
Table 5. Medium Priority Substance Assessment Overview	14

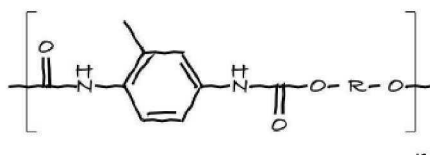
# 1 Introduction

## 1.1 Polyurethanes

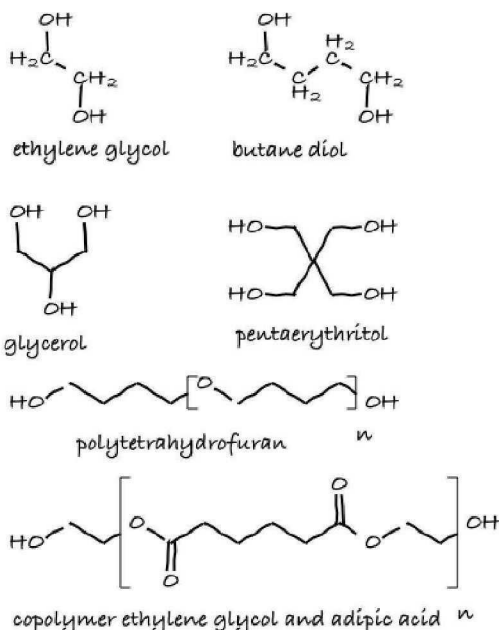
Polyurethanes are polymers containing multiple urethane linkages:



A urethane linkage is made by reacting an isocyanate group with a hydroxyl (alcohol) group. Although homopolymers with urethane linkages are theoretically possible, in practice, PUR's are copolymers from bifunctional isocyanates, like toluene diisocyanate, with multifunctional alcohols, usually diols, diol esters, or diol ethers, for linear polymers, not unlike polyamides (nylon). Tri- and higher functional alcohols are also possible, for three-dimensional, crosslinked resins.



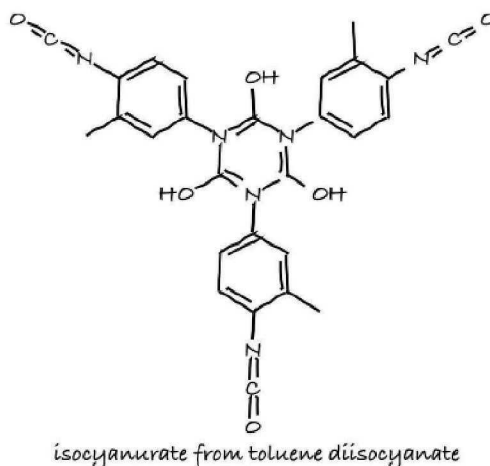
While there is a relatively limited selection of isocyanates that is used for PUR production (toluene diisocyanate, methylene diphenylisocyanate, hexamethylene diisocyanate, and a few others), a multitude of so-called polyols is used, to tailor the properties of the resulting polymer. Polyols can range from simple diols such as ethanediol (ethylene glycol) and butanediol, and other simple multifunctional alcohols such as glycerol or pentaerythritol, to simple polyethers like polyethyleneglycols, polypropylene glycols or polytetrahydrofuran (poly(tetramethyleneether) glycol), to natural polyols like castor oil or oxidized triglyceride or fatty acid derivatives, to (short) polyesters with alcohol terminuses, such as resulting from the reaction between adipic acid and diols, phthalic acid and diols ('PET') or even polylactic acid derivatives.





## 1.2 Polyisocyanurates

Polyisocyanurates are produced from the same basic ingredients as polyurethanes, with one important difference; the ratio between diisocyanate component and polyol component is such (usually around 3-4:1) that most of the diisocyanate trimerizes to isocyanurate before reacting with the polyols.



Since these isocyanurates already contain more than two functionalities, crosslinked polymers will form even with bifunctional polyols, usually a polyester diol.

## 1.3 Remit

Saint Gobain has asked ENVIRON to prepare supporting information package for PUR and PIR insulation material concerning sustainability, safety, product stewardship and other issues. The remit includes the ecotoxicological properties of the starting materials for polymer production (monomers, solvents, additives (including fire retardants), catalysts, blowing agents), residual substances and degradation products that may be emitted from final product in in-use situations, pyrolysis products resulting from unplanned incineration (i.e. building fires), and end-of-life conditions (incineration, landfill, recycling reuse). A list of potential substances and chemical structures relevant for this evaluation was prepared by ENVIRON. The substances on this list were classified as being of high, moderate, or low priority. The current report presents the ecotoxicological information for these substances.

## 2 High-priority substances

### 2.1 Diisocyanates and degradation products

#### 2.1.1 Toluene diisocyanate

Toluene diisocyanate is a High Production Volume substance in the EU, and a HPV dataset was submitted for TDI under the HPV chemicals program. The ecotoxicological information database for TDI is largely complete. Toluene diisocyanate was also subject to the 2010 REACH registration deadline, and one or more registration dossiers have been submitted to ECHA.

TDI is sparingly soluble in water, but rapidly hydrolyses when in contact with water. Large amounts of solid or liquid TDI in water will form masses of TDI with insoluble crusts of hydrolysis products, rendering the remaining TDI unavailable for dissolution (and for biota). It is not biodegradable. It does not bioaccumulate. Observed acute toxicity to fish is generally over 100 mg/L, with one test showing an  $LC_{50}$  of 46 mg/L. Due to rapid hydrolysis, any observed effects are due to hydrolysis products. The widely varying  $LC_{50}$  values observed may reflect differences in hydrolysis under different conditions. Acute toxicity to *Daphnia* varies from ca 12 mg/L to 750 mg/L. TDI is not toxic to algae or bacteria. In a chronic *Daphnia* test with 1h hydrolysates, no effects were observed at the highest concentrations obtainable ( $NOEC \geq 0.5$  mg/L). TDI appears non-toxic to terrestrial organisms.

Environment Canada, the Canadian environmental protection agency, has published an up-to-date comprehensive environmental risk assessment of TDI, and concludes that TDI does not pose an environmental risk. Below are reproduced several tables from their Existing Substances Evaluation Profile for Toluene Diisocyanates.

**Table 1. Phys-chem properties for commercial mixture of 2,4 TDI and 2,6-TDI (80/20).**

Property	Type	Value	Temperature (C°)	Reference
log Kow	Modeled	3.74	25	Kowwin v.1.67
log Kow	Experimental	3.4		Yakabe et al, 2000
Melting point	Experimental	11-14 °C		HSDB (2003)
Boiling point	Experimental	251 °C		HSDB (2003)
log Koc	Modeled	0.35-3.96		PCKOCWIN v.1.66; ASTER
Vapour Pressure	Experimental	0.0015 kPa/	20	Fisk and Langer, 1995
		0.000661 mm Hg		
		0.023 mm Hg	25	HSDB, 2003
Henry's Law Constant	Modeled	1.11 e-5 atm-m <sup>3</sup> /mole	25	EPIWINv3.12
Water solubility	Experimental	insoluble in water		Pemberton, D. and Tury, B (2004)

**Table 2. Empirical Data for Bioaccumulation of TDA**

Test Organism	Substance	Type	Endpoint	Value wet wt (L/Kg) (range if applicable)	Reference
Fish (Carp)	TDA	Experimental	BCF	<5 to <50	MITI 1992

**Table 3. Empirical Data for TDI and its degradation products**

Compound	Test Organism	Type of Test	Endpoint	Value (mg/L)	Reference
TDI (mixed isomers)	Fish (Oncorhynchus mykiss)	Acute (96h)	LC50	133	Tadokoro et al 1997
2,4-TDI	Fish (Pimephales promelas)	Acute (96h)	LC50	164	Curtis et al, 1979
TDI (mixed isomers)	Shrimp (Mysidopsis bahia)	Acute (48h)	EC50	18.3	Tadokoro et al , 1997
TDI (mixed isomers)	Daphnia	Acute (48h)	EC50	12.5	Tadokoro et al , 1997
TDI (mixed isomers)	Algae (Chorella vulgaris)	Acute (96h)	EC50	4300	Tadokoro et al , 1997
2,4-TDI	Grass Shrimp (palaemonetes pugio)	Acute (96h)	EC50	508.3	Curtis et al, 1979
2,4-TDA	Daphnia magna	Acute (48h)	EC50	1.6	Pederson et al ,1998
2,4-TDA	Fish (Orange-red killifish)	Acute 48(h)	LC50	850 mg/L	MITI 1992

They conclude that:

*Based on the available information, the three TDI substances do not persist in the environment and are not bioaccumulative. Information on concentrations of toluene diisocyanate in the environment has not been identified at this time. The experimental and modeled ecotoxicological data does indicate that while toluene diisocyanate could cause low to moderate harm to aquatic organisms, at relatively low concentration in the water. Information on potential impacts in other environmental compartments has not been identified.*

and that TDI is not a PBT substance.

Yakabe *et al*<sup>1</sup> investigated the fate of TDI (and MDI) in water, and concluded that little or no TDI or hydrolysis products actually end up in the aqueous phase.



## 2.1.2 Methylene diphenyldiisocyanate

Methylene diphenyldiisocyanate is a High Production Volume substance in the EU, and a HPV dataset was submitted for MDI under the HPV chemicals program. The ecotoxicological information database for MDI is largely complete. Methylene diphenyldiisocyanate was also subject to the 2010 REACH registration deadline, and one or more registration dossiers have been submitted to ECHA.

MDI is sparingly soluble in water, but hydrolyses when in contact with water; hydrolysis is slower than for TDI, due to the higher viscosity of MDI. Large amounts of solid MDI in water will form masses of MDI with insoluble crusts of hydrolysis products, rendering the remaining MDI unavailable for dissolution (and for biota). It is not biodegradable. It does not bioaccumulate. MDI is not acutely toxic to fish and Daphnia, with reported LC0 values over 500 mg/L, expressed as parent compound. Due to rapid hydrolysis and low solubility, any observed effects will be due to hydrolysis products. MDI is not toxic to algae or bacteria. In a chronic Daphnia test with 1h hydrolysates, no effects were observed at the highest concentrations obtainable (NOEC  $\geq$  10 mg/L). MDI appears non-toxic to terrestrial organisms.

In 2005, the EU ECB published a comprehensive risk assessment for MDI. We reproduce parts of the environmental effects assessment here:

*All data reported hereafter concern polymeric MDI, monomeric MDI or even mixtures of both. However, it is very likely that the toxicity of generic MDI to species involved in ecotoxicity tests is similar to that of the tested MDI mixtures. In all tests performed, MDI had to be either added to water or to some moistened material. Considering the high reactivity of MDI with water it is most probable that it was the breakdown products that were being tested not MDI. Indeed, when attempts were made to measure MDI concentrations in experimental media, the results were always below the detection limits as in Heimbach's (1993) study where water samples removed from two ponds, dosed with 1g/l and 10g/l polymeric MDI, on days 0, 1, 7, 14, 28, 56 and 112 and were found to contain levels of MDI lower than the detection limit (i.e. 5-10µg l<sup>-1</sup>).*

*The hydrolysis products of MDI and water are dependent on the conditions of the mixing of the MDI with water. Under conditions of low dispersion the immediate products are insoluble, solid and inert polyureas. Under conditions of high dispersion, some MDA (methylenedianiline) as an initial hydrolysis product may be formed, however, given its extreme reactivity with MDI, MDA is rapidly transformed. Thus when measurements were made, concentrations ranged from 5 mg/l to lower than the detection limits. Nevertheless, since MDA is very toxic to organisms (see MDA Risk Assessment Report (EC, 2000) and EC50 values reported in Section 3.2.1 and 3.2.3), the possible hazard to aquatic organisms due to MDA formation when MDI enters the water compartment is not to be overlooked. This aspect is treated theoretically in Section 3.3.*

*[...]*

*No lethal effect has been observed in short-term studies even with nominal concentrations of 3,000 mg/l. Although the authors of the studies did not check the MDI concentrations at the end of the test period it is most likely that MDI disappeared from the media after addition to the water (see Section 1.3.6 water solubility) and so*



*it is probable that the absence of an effect in the tests was due to the instability in water of MDI and the inertness of its hydrolysis products.*

*It should also be noted that even when MDA (methylenedianiline) was formed during the experiments, the levels of this product in the media must have been very low as toxic effects to the animals were not noted. The MDA concentration in the medium of acute toxicity tests was only measured in one study (Rhône-Poulenc, 1977). An initial concentration of 500 mg/l of MDI added to the fish medium by stirring for 18 hours yielded concentrations of, respectively 3.5 mg/l and 4 mg/l of MDA for polymeric MDI or 4,4'-MDI after a 24 hours incubation period. As this MDA level is at least ten times lower than the LC50 of MDA for fish (from 32 to 65 mg/l, Risk Assessment Report MDA (EC, 2000)) no mortality to tests organisms was observed. Caspers and co-workers (1986) reported a markedly increased toxicity to fish when MDI was dispersed into the experimental medium by high speed shearing, although the data obtained were not reported by the authors because they were inconsistent, the increased toxicity might have been caused by an increased MDA yield in the medium. Nevertheless the results are probably specific for this dispersing method and do not reflect situations which might occur in the environment.*

*No direct toxic effects have been observed in long-term studies with nominal concentrations of up to 10 g/l. But it must be noted that indirect impact on fish through decrease of their natural food (cladocerans) in an artificial pond to which was added 10 g/l of polymeric MDI was observed by Heimbach et al. (1996).*

*[...]*

*No lethal effects have been observed in short-term studies even with nominal concentrations of 1,000 mg/l with the exception of one study (Caspers et al., 1986) where MDI was dispersed into the medium by high speed shearing instead of usual stirring; this must have led to an increased production of MDA (methylenedianiline) which could be responsible of the lethal effect caused to the daphnids since daphnids are quite sensitive to MDA as indicated by the relatively low EC50 for *Moina macropa* (2.3mg/l; Risk Assessment Report MDA (EC, 2000)). As stated in Section 3.2.1.1., the authors considered these data as irrelevant because the dispersing method does not reflect a situation that might happen in the real environment.*

*Long-term studies show that MDI has only indirect effects on aquatic invertebrates. However, the potential negative impact on benthic organisms of the polyurea crust resulting from the reaction of MDI with water should be considered. In the study reported by Heimbach et al. (1996) there was a physical effect noted on the benthic organisms. On a local scale an accidental spill would have a dramatic effect on those organisms. However, if the crust is removed from the sediment as a restoration measure, a re-colonisation of the covered area by animals from the surroundings will most probably occur within a short time.*

*[...]*

*No significant negative impact of the MDI was observed towards algae except the physical hindrance of macrophyte emergence due to the polyurea solid crust formation. As an indication of the potential indirect hazard due to MDA (methylenedianiline) formation: the EC50 for *Scenedesmus subspicatus* (72 hours) is 21 mg/l as determined in a separate, similar test where MDA toxicity to this alga was tested (see RAR MDA (EC, 2000)).*

[...]

*No toxic effect of MDI was observed on microorganisms but as stated before it is most likely that MDI disappeared from the test media very briefly after addition to the aqueous media (see Section 3.2) and so it is not possible to determine if the absence of the effect in the performed test is due to true innocuousness of the tested substance or rather to its particular instability in water.*

[...]

*No toxic effect of MDI was observed on the terrestrial organisms tested but it must be stated that in the tests performed, MDI was in contact with water (in moist soils) and so it is very likely that the MDI concentrations tested were much lower than the nominal ones mentioned by the authors and one should be very cautious about the conclusions that can be drawn from the data available. As an indication of the potential indirect hazard due to MDA (methylenedianiline) formation the EC50 for *Eisenia fetida*, *Avena sativa* and *Lactuca sativa* are respectively of 444, 353 and 128 mg/kg dw soil as determined in separate, similar tests where MDA toxicity to these organisms was tested (see RAR MDA, (EC, 2000)).*

Yakabe *et al*<sup>1</sup> investigated the fate of MDI (and TDI) in water, and concluded that little or no MDI or hydrolysis products actually end up in the aqueous phase.

It should be clear that MDI does not appear to pose an environmental hazard.

### 2.1.3 Methylene dianiline

Methylene dianiline is a High Production Volume substance in the EU, and a HPV dataset was submitted for MDA under the HPV chemicals program. The ecotoxicological information database for MDA is largely complete. Methylene dianiline was also subject to the 2010 REACH registration deadline, and one or more registration dossiers have been submitted to ECHA.

At ca. 1 g/L, MDA is reasonably soluble in water. It is not biodegradable. It does not bioaccumulate. Observed acute toxicity to fish is generally over 30 mg/L. With an acute EC50 to *Daphnia* of 2.3 mg/L it is toxic to aquatic invertebrates. With EC50 values to algae around 10 mg/L, MDA is harmful to toxic to algae. It is not toxic to bacteria. In a chronic test with fish, a NOEC of 0.15 mg/L was observed. MDA appears relatively non-toxic to terrestrial organisms. It should be noted here that although MDA, as a potential hydrolysis product of MDI, appears to be more toxic than its potential parent compound, hydrolysis studies and toxicity studies with MDI and MDI hydrolysate suggest that little or none MDA enters the aqueous environment due to MDI hydrolysis.

In 2001, the EU ECB published a comprehensive risk assessment for MDA. We reproduce parts of the environmental effects assessment here:

*More than 98% of the MDA are processed to methylenediphenyldiisocyanate (MDI) by reaction with phosgene. Releases to water are expected to be not significant, since any application of cleaning water is scrupulously avoided to prevent deleterious effects on product quality (HMSO, 1995; Gilbert International Isocyanates, 1996).*

*The releases into the atmosphere during production of MDA and processing to MDI are expected to be not significant for the environmental risk assessment.*



MDA can be formed by hydrolysis of MDI under certain conditions. However, this reaction is depending on the ratio of MDI/water mixing: If the pure isocyanate is spilled into water, polyurea is formed as the main product, while with small MDI amounts mixed with a great excess of water MDA will be formed (Hirzy, 1985). These results are confirmed by Gilbert International Isocyanates (1996): In any case the course of reaction of MDI with water depends on the reaction conditions. Generally if the diisocyanate is spilled into water polyurea is formed as the main product with no detectable or only trace amounts of MDA. Only when small amounts of MDI are vigorously mixed with a great excess of water is MDA formed in significant yield, and then of necessity at very low concentrations (Gilbert International Isocyanates, 1996). As polyurea would cause deleterious effects on the equipment, any application of cleaning water is avoided at the technical processes.

Releases of MDA into the atmosphere during the further (non-MDI) uses do not occur in significant amounts.

Diffuse releases can occur from MDA or MDI (after hydrolysis) chemically reacted in polyurethane or epoxy matrices during use and disposal of polymer products. Trace amounts of residual monomers may be released via migration and leaching.

[...]

MDA is not readily biodegradable. The three available tests on ready biodegradation (OECD 301 B and 301 C) indicate 0 to 19% degradation after 28 days. The used substance concentration of 10, 20 and 100 mg/l could not have inhibiting activity on the microbial population, since the EC50 for activated sludge was determined to >100 mg/l (Ciba Geigy, 1985; MITI, 1993; Yakabe, 1993, Bayer AG, 1986).

[...]

In a bioaccumulation test on carp BCFs of 3 - 14 resp. <3.1 - 15 were determined after 6 weeks at concentrations of 200 and 20 µg/l (MITI, 1993). These values indicate a low bioaccumulation in fish.

[...]

[Fish:] Only results from short-term tests are available. The acute effect concentrations (LC50) range from 32 mg/l to 65 mg/l.

[...]

[Crustaceans:] Results from short-term tests

*Moina macrocopa* 24 h-EC50 = 2.3 mg/l

Results from long-term toxicity tests

*Moina macrocopa* 14 d-NOEC = 0.15 mg/l

[...]

[Algae:] *Scenedesmus subspicatus* 72 h-EC50 = 21 mg/l

Note that the reported effect values are generally those included in the HPV dataset. The overall conclusion is that MDA is not dangerous to the environment.

## 2.2 Polyols

In general, it can be stated that the polyether and polyester polyols are water-soluble, may be surface active, will not bioaccumulate, and are considered safe for use in various other applications, as such, or as monomers for polymeric products. The natural polyols, such as castor oil and hydroxylated (oxidized) unsaturated triglycerides and fatty acids, are also to be considered safe. As an example, a few common polyols will be addressed here.

### 2.2.1 1,4-Butanediol

1,4-Butanediol, a common difunctional alcohol, is a High Production Volume substance in the EU, and a HPV dataset was submitted for MDI under the HPV chemicals program. The ecotoxicological information database for MDI is largely complete. 1,4-Butanediol was also subject to the 2010 REACH registration deadline, and one or more registration dossiers have been submitted to ECHA.

1,4-Butanediol is liquid at (current) room temperature, and is miscible with water; it has a log P value of -0.88 and is readily biodegradable. It is not expected to bioaccumulate. It is not acutely toxic to aquatic organisms, fully in line with its classification as a non-polar narcosis, or baseline substance, and in agreement with its octanol/water partition coefficient.

### 2.2.2 Polytetrahydrofuran – poly(tetramethylene ether) glycol

Polytetrahydrofuran (PTH), also called poly(tetramethylene ether) glycol, is a chemical compound with formula  $(C_4H_8O)_n(OH)_2$  or  $HO-(CH_2)_4O)_n-OH$ . It can be viewed as a polymer of tetrahydrofuran, or as the polyether derived from 1,4-butanediol. The product is commercially available as polymers of low average molecular weights, between 250 and 3000 daltons. In this form it is a white waxy solid that melts between 20 and 30 °C.<sup>1</sup>

It is not biodegradable, and is not expected to be toxic to aquatic organisms, due to low aqueous solubility, and the molecule(s) being too large for bioaccumulation.

### 2.2.3 Polyethylene adipate

Polyethylene adipate (PEA) is a (short chain) copolymer with alternating adipic acid (a terminal dibasic carboxylic acid) and ethylene glycol units; the terminal ends are predominantly glycolic – if not, they would not be suitable as PUR components. As a PUR precursor, it is usually available as oligomers with an average molecular weight around 3000 daltons. Relatively little is known about its environmental properties, although, it being a polar polymer, it is unlikely to be toxic to aquatic organisms, or to be very mobile in the environment. Short chain PEA is biodegradable (see e.g. Tokiwa *et al.*<sup>2</sup>), and at least some of it will hydrolyse during the process. Most of the PEA will be mineralized during degradation, but some will (transiently) be present as the original monomers, adipic acid and ethylene glycol, neither of which is labeled for environmental effects. Both are HPV chemicals and have complete environmental data sets.

---

<sup>1</sup> Source: Wikipedia

<sup>2</sup> Tokiwa, Y., Calabia, B.P., Ugwu, C.U., and Aiba, S. (2009). Biodegradability of Plastics. *International Journal of Molecular Sciences* **10**. pp. 3722-3742.



## 2.3 Starting materials

### 2.3.1 4-Methyl-m-phenylenediamine

4-Methyl-m-phenylenediamine is a High Production Volume substance in the EU, and a HPV dataset was submitted for it under the HPV chemicals program. The ecotoxicological information database is largely complete. 4-Methyl-m-phenylenediamine was also subject to the 2010 REACH registration deadline, and one or more registration dossiers have been submitted to ECHA.

4-Methyl-m-phenylenediamine is soluble in water. Results from ready biodegradability studies vary greatly, but it appears that it is at least inherently biodegradable. It does not bioaccumulate. It is not acutely toxic to fish with a lowest reported  $LC_{50}$  of 219 mg/L; it is toxic to invertebrates, but not to algae or microorganisms. In chronic *Daphnia* tests, NOECs were between 0.1 and 1 mg/L. TDI appears non-toxic to terrestrial organisms (earthworms and plants).

The EU risk assessment considers that no emission of 4-methyl-m-phenylenediamine from production of TDI is expected. It is classified as R51/53.

### 2.3.2 Phosgene

Phosgene is a High Production Volume substance in the EU, and a HPV dataset was submitted for it under the HPV chemicals program. The ecotoxicological information database is empty. Phosgene was also subject to the 2010 REACH registration deadline, and one or more registration dossiers have been submitted to ECHA.

Phosgene is soluble in water but rapidly hydrolyses. No EU risk assessment is available, but based on the 4-methyl-m-phenylenediamine risk assessment (see above) it can be concluded that no emission of phosgene from production of TDI is expected.

### 2.3.3 Tetrahydrofuran

Tetrahydrofuran (THF) is a High Production Volume substance in the EU, and a HPV dataset was submitted for it under the HPV chemicals program. The ecotoxicological information database is complete. THF was also subject to the 2010 REACH registration deadline, and one or more registration dossiers have been submitted to ECHA.

THF is a very common solvent. It is readily biodegradable, it is not expected to bioconcentrate, and in fact will not remain in water, due to low aqueous solubility and high volatility. It is not toxic to aquatic or terrestrial organisms.

### 2.3.4 Adipic acid

Adipic acid is a High Production Volume substance in the EU, and a HPV dataset was submitted for it under the HPV chemicals program. The ecotoxicological information database is relatively complete. Adipic acid was also subject to the 2010 REACH registration deadline, and one or more registration dossiers have been submitted to ECHA.

Adipic acid is readily biodegradable, soluble in water, and is not expected to bioconcentrate, based on its octanol/water partition coefficient. It is not toxic to aquatic or terrestrial organisms.

## 2.4 Additives

### 2.4.1 Pentane

Pentane is used as a blowing agent. It is almost insoluble in water under normal conditions, and can be regarded as a model baseline toxicity compound. Pentane was also subject to the 2010 REACH registration deadline, and one or more registration dossiers have been submitted to ECHA. Pentane is a HPV chemical with a limited environmental data set. It is labeled for environmental effects as R51/53, although it is not expected to be either persistent (it is readily biodegradable) or bioaccumulating. Due to its high volatility (boiling point 32°C) it is not expected to enter or remain in the aqueous phase. Photochemical degradation is rapid, and it is acknowledged as not being a greenhouse gas; it is considered as a substance that can lead to the formation of photochemical smog. In 2003, the EU ECB published a comprehensive risk assessment for pentane. Risks for the aquatic compartment were considered low; for the atmosphere, there is a non-negligible risk due to the formation of photochemical smog. Acute aquatic effects (LC<sub>50</sub>) were observed in the 1-10 mg/L range (leading to the R51 classification), although rapid biodegradation and high volatility mean that these findings are by and large irrelevant.

### 2.4.2 Triethyl phosphate

Triethyl phosphate is a phosphate flame retardant. It was subject to the 2010 REACH registration deadline, and one or more registration dossiers have been submitted to ECHA. It is a HPV chemical, with a relatively complete environmental data set. It is not labeled for environmental effects. It is miscible with water, does not biodegrade and is not susceptible to hydrolysis.

Additionally a SIDS Initial Assessment Profile has been drawn up for triethyl phosphate. Conclusions generally coincide with those from the HPV program. Emission of flame retardant triethyl phosphate to the environment is thought to be possible from production and inclusion into polymeric matrices, but to be negligible from in-use situations.

### 2.4.3 Tris(1-chloroisopropyl)phosphate

Tris(1-chloroisopropyl)phosphate (TCPP) is a phosphate flame retardant. It was subject to the 2010 REACH registration deadline, and one or more registration dossiers have been submitted to ECHA. It is a HPV chemical, with a limited environmental data set. It is not labeled for environmental effects. It is soluble in water, is not readily biodegrade and is not susceptible to hydrolysis. It does not bioaccumulate. It is harmful to fish and aquatic invertebrates, with LC<sub>50</sub> values > 30 (50) mg/L, and harmful to algae, with LC<sub>50</sub> values generally > 50 mg/L. It is not harmful to microorganisms. No chronic toxicity data were available.

In 2008, the EU ECB published a comprehensive risk assessment for TCPP, focusing on its use in PUR and PIR insulation. It concluded that TCPP posed little risk to the environment. The document contains a comprehensive emission and environmental exposure review, which is well worth considering. It estimates (worst case) that for indoor in-use situations, the loss of TCPP is ca. 0.5% over the service life of the insulation. It also states that releases from insulation effectively sealed within building walls will be negligible. Leaching emissions from landfills (end-of-life) may be relevant for ground- and surface water. Predicted Environmental Concentrations are low, and are in agreement with monitoring data. No environmental risks were identified and TCPP is not a PBT.



Additionally a SIDS Initial Assessment Profile has been drawn up for TCPP. Conclusions generally coincide with those from the HPV program and the EU RAR. TCPP is harmful to aquatic organisms, but emission of flame retardant TCPP to the environment is thought to be minimal during all relevant life cycle stages.

**Table 4. High Priority Substance Assessment Overview**

Substance	CAS	Function	CLP / Effects (Environmental)	Remarks
Toluene diisocyanate	584-84-9; 91-08-7; 26471-62-5	PUR/PIR monomer	R52/53	Due to behaviour in contact with water, no risk is foreseen under any emission scenario
Diphenylmethane diisocyanate	2536-05-2; 5873-54-1; 101-68-8; 26447-40-5	PUR/PIR monomer	–	Due to behaviour in contact with water, no risk is foreseen under any emission scenario
Methylenedianiline	101-77-9	Hydrolysis product of MDI	R51/53	Emission scenarios do not favour formation of and especially exposure to MDA
1,4-Butanediol	110-63-4	PUR/PIR monomer / Polyol starting material	–	Not likely to be present during any phase of PUR and PIR lifecycle other than polyol production.
Polyethylene adipate	24938-37-2	PUR/PIR monomer	–	Polymer; monomers are not harmful to aquatic life
Poly(tetramethylene ether) glycol	25190-06-1	PUR/PIR monomer	–	Polymer; monomer is not harmful to aquatic life
2,4-toluenediamine	95-80-7	TDI starting material	R51/53	No emission expected
Phosgene	75-44-5	TDI/MDI starting material	–	No emission expected
Tetrahydrofuran	109-99-9	Polyol starting material	–	No emission expected
Adipic acid	124-04-9	Polyol starting material	–	No emission expected
Pentane	109-66-0	Blowing agent	R51	Will not persist in the environment; does not pose a risk to aquatic life
Triethylphosphate	78-40-0	Flame retardant	–	Emission considered negligible

Trichloro methylethyl phosphate	13674-84-5	Flame retardant	—	Emission considered negligible
---------------------------------------	------------	--------------------	---	-----------------------------------



### 3 Medium-priority substances

**Table 5. Medium Priority Substance Assessment Overview**

Substance	CAS	Function	CLP / Effects (Environmental)	Remarks
Ethylene glycol	107-21-1	Monomer for polyester polyol production	–	Not likely to be present during any phase of PUR and PIR lifecycle other than polyol production.
1,4-butanediol	110-63-4	Monomer for polyester polyol production / polyol	–	Not likely to be present during any phase of PUR and PIR lifecycle other than polyol production.
1,6-hexanediol	629-11-8	Monomer for polyester polyol production / polyol	–	Not likely to be present during any phase of PUR and PIR lifecycle other than polyol production.
Hydroquinone bis(2-hydroxy ethyl ether)	104-38-1	Monomer for polyester polyol production	– Not harmful to aquatic organisms	Not likely to be present during any phase of PUR and PIR lifecycle other than polyol production.
Pentamethyl diethylene triamine	3030-47-5	Catalyst	– Not harmful to aquatic organisms	Limited amounts present, low exposure
Potassium acetate	127-08-2	Catalyst	– Not harmful to aquatic organisms	Limited amounts present, low exposure; note: about as harmful as vinegar
Potassium octoate	764-71-6	Catalyst	– Not harmful to aquatic organisms	Limited amounts present, low exposure; note: this is a true soap, and is present in soaps produced from coconut oil/coco fatty acids
Perfluorocarbons		Blowing agent		(To be) phased out
Silicon-based antifoamers		Antifoamers		These are usually short-chain silicone polymers, and are used in many household products, including cosmetics and foods. Chemically and toxicologically generally inert
Hydroxybenzotriazoles	2592-95-2	Catalyst	– Not harmful to aquatic	Limited amounts present, low exposure; note: explosive

			organisms	
Zinc dibutyl thiocarbamate	137-30-4	Catalyst / preservative	R50/53 Very toxic to aquatic organisms	Limited amounts present, low exposure, rapidly hydrolyses in water; note: this is the fungicide ziram
2,6-ditertiary butylcatechol	I'm assuming here 1020-31-1, 3,5-di-tert-butylcatechol	Stabilizer	–	
4-Hydroxy benzophenone	1137-42-4	UV stabilizer	–	
Hindered amine light stabilizers	derivatives of 2,2,6,6-tetramethyl piperidine	UV stabilizers	Example: 70624-18-9 Very toxic to fish	
Phosphites	?			
Lead				Heavy metals are present in trace amounts, will not likely enter the environment except in case of fire or in the waste stage.
Barium				
Cadmium				
Tin				
Zinc	7440-66-6			
Hydrogen cyanide	74-90-8	Pyrolysis product in case of fire or incineration	R50/53 (not sure why the R53; cyanide should in fact not be classified as persistent)	Will be released in case of fire. Waste incineration processes should minimize formation or emission of hydrogen cyanide
Acetonitrile	75-05-8	Pyrolysis product in case of fire or incineration	–	Will be released in case of fire. May further decompose to HCN
Acrylonitrile	107-13-1	Pyrolysis product in case of fire or incineration	R51/53 (not sure why the R53; acrylonitrile should in fact not be classified as persistent)	Will be released in case of fire. Waste incineration processes should minimize formation or emission of acrylonitrile. May further decompose to HCN
Glutaraldehyde	111-30-8	Pyrolysis product in case of fire or	R50	All organic pyrolysis processes will emit glutaraldehyde, unless the temperature is high to ensure

		incineration		complete combustion
Benzaldehyde	100-52-7	Pyrolysis product in case of fire or incineration	–	All organic pyrolysis processes will emit benzaldehyde, unless the temperature is high to ensure complete combustion
Pyridine	110-86-1	Pyrolysis product in case of fire or incineration	–	All pyrolysis processes of nitrogen-containing organic substances will emit pyridine, unless the temperature is high to ensure complete combustion
Benzonitrile	100-47-0	Pyrolysis product in case of fire or incineration	–	All pyrolysis processes of nitrogen-containing organic substances will emit benzonitrile, unless the temperature is high to ensure complete combustion
Diamino toluene	2687-25-4	Pyrolysis product in case of fire or incineration	–	
Sulfur dioxide	7446-09-5	Pyrolysis product in case of fire or incineration	– SO <sub>2</sub> will rapidly convert into sulfates/sulfites on contact with water	Pyrolysis processes of sulfur-containing matter may emit SO <sub>2</sub> , unless the temperature is high to ensure complete combustion
Carbon Monoxide	630-08-0	Pyrolysis product in case of fire or incineration	– CO is not stable in water	All pyrolysis processes of organic matter will emit CO; the amount depending on temperature and fuel/oxygen ratio
Carbon dioxide	124-38-9	Pyrolysis product in case of fire or incineration	–	All pyrolysis processes of organic matter will by necessity emit CO <sub>2</sub> ; the amount depending on temperature and fuel/oxygen ratio; we wish to emphasize that we do not consider CO <sub>2</sub> a harmful substance
Hydrogen chloride	7647-01-0	Pyrolysis product in case of fire or incineration	–	All chlorine-containing polymers will emit HCl under certain pyrolytic conditions
Polynuclear aromatic hydrocarbons		Pyrolysis product in case of fire or		All organic pyrolysis processes will emit PAH, unless the temperature is high enough that no yellow flames

		incineration		are apparent
Diethylene glycol	111-46-6	Pyrolysis product in case of fire or incineration	–	Formation of these compounds is not likely in full fire conditions – they may form during initial smouldering
Trimethylolpropane	77-99-6	Pyrolysis product in case of fire or incineration	–	Formation of these compounds is not likely in full fire conditions – they may form during initial smouldering
Adipic acid	124-04-9	Pyrolysis product in case of fire or incineration	–	Formation of these compounds is not likely in full fire conditions – they may form during initial smouldering
Acrolein	107-02-8	Pyrolysis product in case of fire or incineration	R50	All organic pyrolysis processes will emit acrolein, unless the temperature is high to ensure complete combustion
Ammonia	7664-41-7	Pyrolysis product in case of fire or incineration		All nitrogen-containing polymers will emit (some) ammonia under conditions of pyrolysis
Formaldehyde	50-00-0	Pyrolysis product in case of fire or incineration	– Hydrolysis in water is rapid; no harmful effects on aquatic organisms are expected	Many synthetic polymers and some natural ones (including wood) will emit formaldehyde under conditions of pyrolysis
Chlorinated Dibenzo-p-dioxins		Pyrolysis product in case of fire or incineration		All fires in which organic material and chlorine are present at the 'reaction site' will produce chlorinated dibenzodioxins, unless the temperatures are high enough to combust these substances/prevent them from being formed
Chlorinated Dibenzofurans		Pyrolysis product in case of fire or incineration		All fires in which organic material and chlorine are present at the 'reaction site' will produce chlorinated dibenzofurans, unless the temperatures are high enough to combust these substances/prevent them from being formed



Fire smoke		Pyrolysis product in case of fire or incineration		All fires emit smoke; the specific smoke components for PUR and PIR have been listed above; smoke is not a primary ecotoxicological (aquatic) concern
Particulate matter		Pyrolysis product in case of fire or incineration		All fires emit particulate matter; particulate matter is not a primary ecotoxicological (aquatic) concern
Diethylene glycol		Microbial degradation	–	If formed under conditions of microbial degradation, further biological decomposition is fully expected
Trimethylol propane		Microbial degradation	–	If formed under conditions of microbial degradation, further biological decomposition is fully expected
Adipic acid		Microbial degradation	–	If formed under conditions of microbial degradation, further biological decomposition is fully expected