Eco-profiles of the European Plastics Industry

Diphenylmethane diisocyanate (MDI)

A report by

I Boustead

for

Plastics*Europe*

Data last calculated

March 2005

IMPORTANT NOTE

Before using the data contained in this report, you are strongly recommended to look at the following documents:

1. Methodology

This provides information about the analysis technique used and gives advice on the meaning of the results.

2. Data sources

This gives information about the number of plants examined, the date when the data were collected and information about up-stream operations.

In addition, you can also download data sets for most of the upstream operations used in this report. All of these documents can be found at: www.plasticseurope.org.

Plastics*Europe* may be contacted at

Ave E van Nieuwenhuyse 4
Box 3
B-1160 Brussels

Telephone: 32-2-672-8259
Fax: 32-2-675-3935

CONTENTS

POLYURETHANE

Polyurethanes (PUR) were first produced in 1937 by Otto Bayer and his co-workers in Germany and represent a family of polymers rather than a single polymer. Urethane polymers can be produced with a wide variety of properties, ranging from soft flexible foams and fibres through to hard solids so that they can be used in a diverse range of applications.

There are five main areas of use for polyurethanes:

(1) the furniture and mattress sector, which uses almost exclusively flexible foams,

(2) the automotive industry which provides a market for flexible foams, filling foams, rigid and flexible integral skin foams as well as elastomers for engineering components,

(3) the consumer sector, which is diversified in a manner similar to the automotive industry,

(4) the building industry, which is by far the largest consumer of rigid foams as insulation materials, and

(5) refrigeration engineering, which represents the second largest area for use of rigid polyurethane foams as insulation materials.

For further details on the applications of polyurethane materials, see, for example, Oertel.[1]

Despite these differing properties, the polymers have one common characteristic in that they all incorporate the urethane group (-NH-CO-O-) into their structure. However, the polymers differ from simple thermoplastic polymers, such as the polyolefins, in that they are not sold as ready-made polymers but as precursors that are mixed at the conversion stage. These precursors are commonly polyols (compounds containing multiple -OH groups) and diisocyanates (compounds containing -NCO groups). The primary reaction during the production of polyurethanes is of the form:

$$\text{-NCO} + \text{HO-} \rightarrow \text{-NH-CO-O-}$$

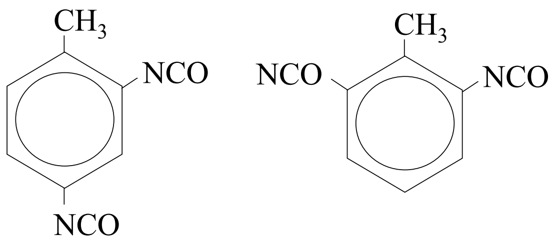
---

[1]Oertel, G. (ed) *Polyurethane Handbook.* ISBN 3-446-17198-3. Hanser Publishers, Munich, Vienna, New York. (1993).

DIISOCYANATES

The principal raw materials for polyurethane precursors are crude oil and natural gas. The diisocyanates having the greatest commercial importance originate from the aromatic content (benzene and toluene), while the polyols come almost exclusively from the aliphatic content. Some renewable materials are also used as raw material sources for polyols.

Diisocyanates are obtained by phosgenation of diamines which are produced, via a number of intermediate steps, from aromatic hydrocarbons. The diisocyanates with the greatest technical importance are tolylene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI). Commercial TDI is marketed as a mixture of the 2,4- and 2,6- isomers, predominantly at a ratio of 80:20 (See Figure 1)



2,4-TDI 2,6-TDI

Figure 1. Isomers of tolylenediisocyanate.

Figure 2 shows the structural formula of diphenylmethane 4,4'-diisocyanate (MDI monomer) and the product derived from it with a functionality greater than 2 (MDI polymer).

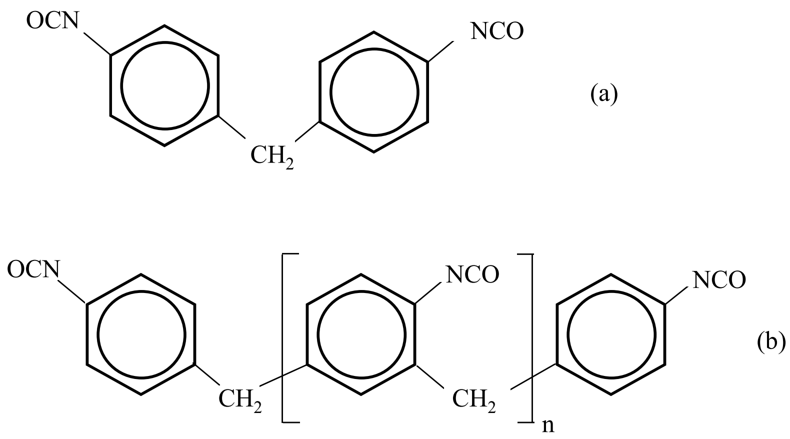


Figure 2. Structures of (a) MDI monomer and (b) MDI polymer.

POLYOLS

The polyols used in polyurethane production are predominantly hydroxy-polyethers, rather than hydroxy-polyesters. They are produced by alkoxylation. Depending on the degree of cross-linking required, the starting alcohols used for hydroxy-polyethers may be divalent glycols (ethylene, propylene and other glycols) or multivalent alcohols (e.g. glycerol, sucrose). The epoxides used are generally propylene oxide and ethylene oxide. The typical reaction for the production of polyether-polyols is shown in Figure 3.

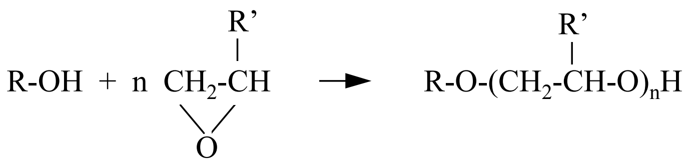


Figure 3. Formation of polyether polyols.

Process routes

The process routes for the production of polyurethane precursors are considerably more complex than for the tonnage thermoplastics described in earlier reports. The principal steps in the production of MDI and TDI are shown in Figures 4 and 5 respectively. In the diagrams, the operations TDI production and MDI production include all distillation steps carried out to produce saleable products. The MDI data given in this report are applicable to both MDI monomer and polymer; differences between the two have been found to be insignificant. A variety of different polyols are used in the production of different specifications of polyurethane and the principal operations are shown schematically in Figure 6.

In these figures, ancillary operations have been omitted as have some of the minor additions to the process chemistry. Note however, that in Figure 6, propylene oxide may be produced by three different routes. These are:

Route 1

From ethylbenzene and propylene according to the reaction

$$\underset{\text{ethylbenzene}}{C_6H_5.C_2H_5} + O_2 + \underset{\text{propylene}}{C_3H_6} \rightarrow \underset{\text{propylene oxide}}{C_3H_6O} + \underset{\text{phenyl ethanol}}{C_6C_5.CH(OH).CH_3}$$

In practice, this reaction is taken further so that phenyl ethanol is converted to styrene and polystyrene.

Route 2

From iso-butane and propylene according to the reaction

$$\underset{\text{iso-butane}}{C_4H_{10}} + O_2 + \underset{\text{propylene}}{C_3H_6} \rightarrow \underset{\text{propylene oxide}}{C_3H_6O} + \underset{\text{t-butyl alcohol}}{(CH_3)_3.C.OH}$$

In some instances this reaction is taken further so that the t-butyl alcohol is converted to iso-butene or methyl tert-butyl ether (MTBE)

Route 3

Via the chlorohydrin process when the overall reaction is of the form

$$\underset{\text{propylene}}{C_3H_6} + Cl_2 + CaO \rightarrow \underset{\text{propylene oxide}}{C_3H_6O} + CaCl_2$$

In practice, sodium hydroxide is frequently used instead of calcium oxide.

In the calculations, all process streams have been traced back to the extraction of raw materials from the earth. Transport of intermediates between sites has been included but on-site transport is assumed to be included in the data provided by the site operator. Services such as cooling water, steam, compressed air and nitrogen and oxygen gases have been included. Catalysts have been excluded from the system.

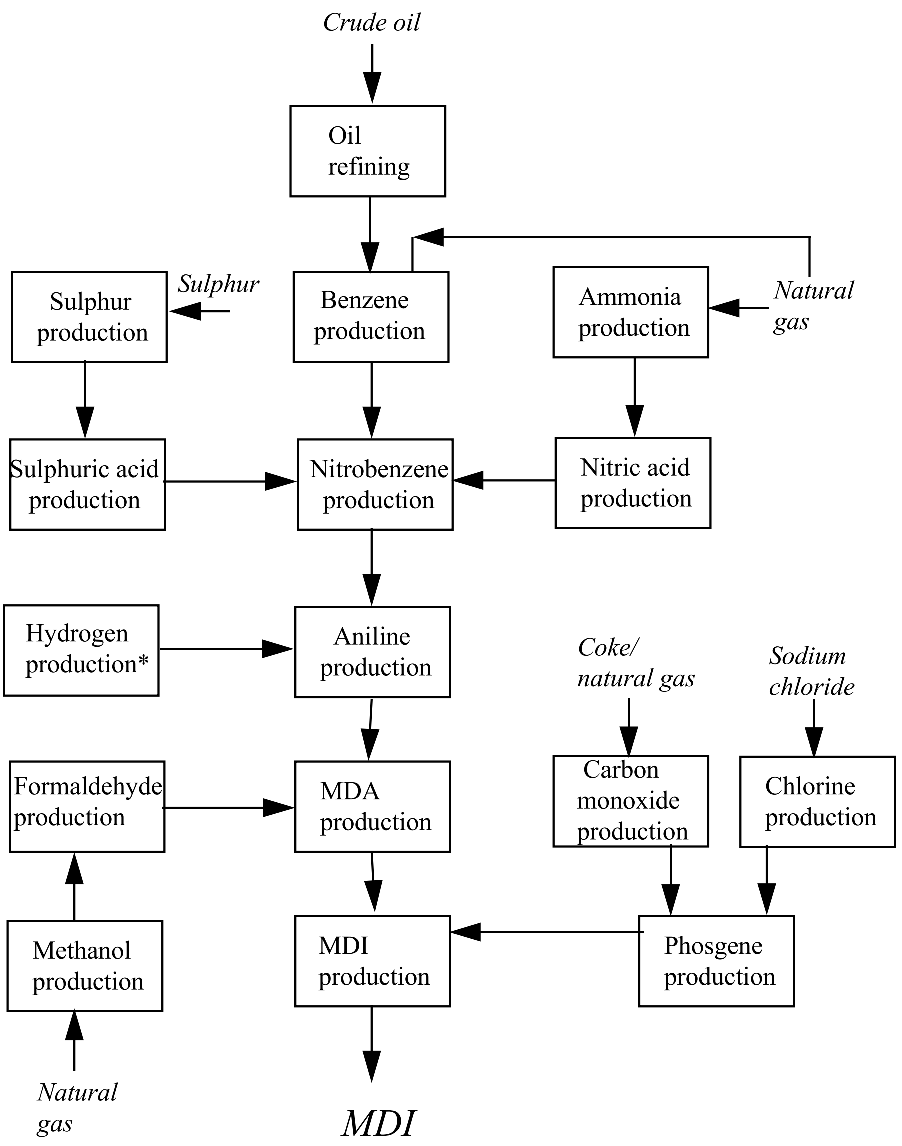


Figure 4
Schematic diagram showing the principal operations leading to the production of MDI.
* Note that hydrogen can be produced by a variety of different methods; e.g. from the electrolysis of sodium chloride, as a by-product in hydrocarbon cracking, etc.

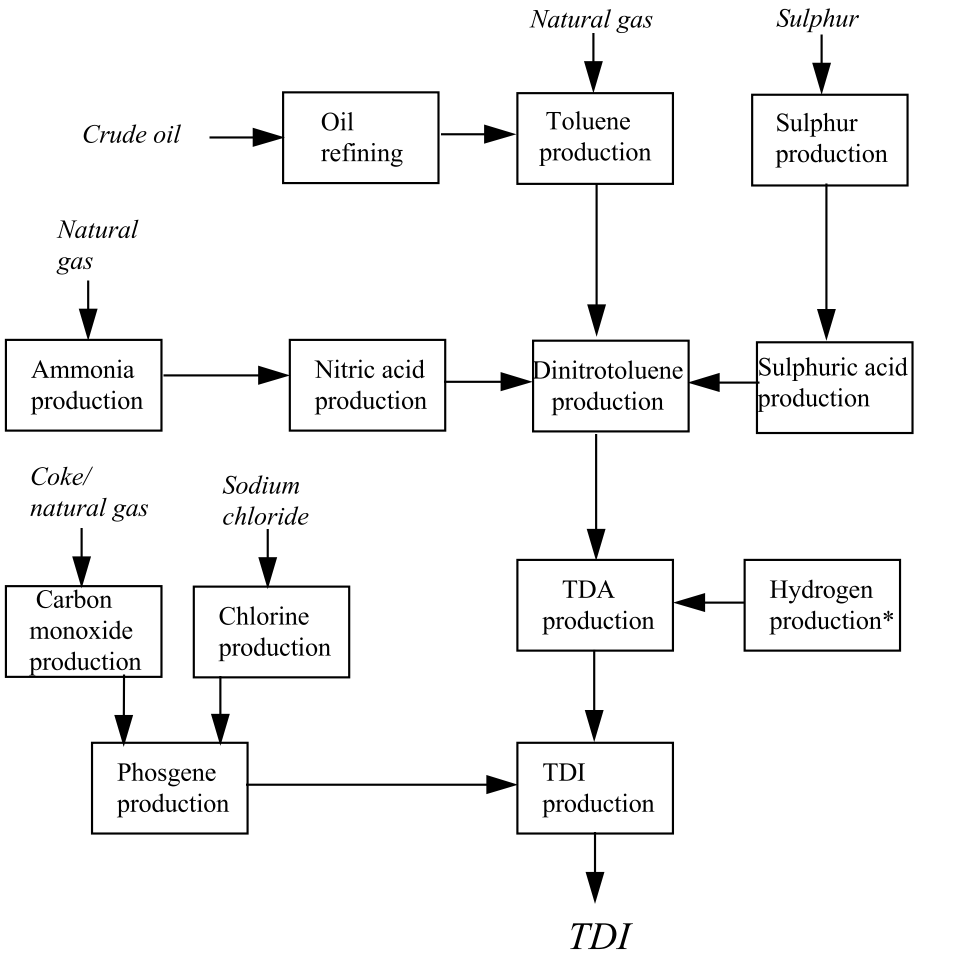


Figure 5
Schematic diagram showing the principal operations leading to the production of TDI.
* Note that hydrogen can be produced by a variety of processes; e.g. during the electrolysis of sodium hydroxide, as a by-product in hydrocarbon cracking, etc.

ECO-PROFILE OF MDI

Table 1 shows the gross or cumulative energy to produce 1 kg of MDI and Table 2 gives this same data expressed in terms of primary fuels. Table 3 shows the energy data expressed as masses of fuels. Table 4 shows the raw materials requirements and Table 5 shows the demand for water. Table 6 shows the gross air emissions and Table 7 shows the corresponding carbon dioxide equivalents of these air emissions. Table 8 shows the emissions to water. Table 9 shows the solid waste generated and Table 10 gives the solid waste in EU format.

Table 1
Gross energy required to produce 1 kg of MDI. (Totals may not agree because of rounding)

Fuel type	Fuel prod'n & delivery energy (MJ)	Energy content of delivered fuel (MJ)	Energy use in transport (MJ)	Feedstock energy (MJ)	Total energy (MJ)
Electricity	10.43	4.59	0.37	-	15.39
Oil fuels	0.51	10.70	0.20	16.17	27.59
Other fuels	1.77	28.32	0.12	17.77	47.98
Totals	12.72	43.61	0.69	33.94	90.96

Table 2
Gross primary fuels required to produce 1 kg of MDI. (Totals may not agree because of rounding)

Fuel type	Fuel prod'n & delivery energy (MJ)	Energy content of delivered fuel (MJ)	Fuel use in transport (MJ)	Feedstock energy (MJ)	Total energy (MJ)
Coal	3.10	5.49	0.11	0.46	9.16
Oil	1.09	11.00	0.41	17.61	30.11
Gas	3.52	28.81	0.09	15.83	48.24
Hydro	0.32	0.18	0.01	-	0.51
Nuclear	4.05	1.83	0.07	-	5.95
Lignite	0.40	0.25	<0.01	-	0.66
Wood	<0.01	<0.01	<0.01	0.01	0.01
Sulphur	<0.01	<0.01	<0.01	0.03	0.03
Biomass (solid)	0.03	0.02	<0.01	<0.01	0.05
Hydrogen	<0.01	0.60	<0.01	-	0.60
Recovered energy	<0.01	-4.65	<0.01	-	-4.65
Unspecified	<0.01	<0.01	<0.01	-	<0.01
Peat	<0.01	<0.01	<0.01	-	<0.01
Geothermal	0.03	0.02	<0.01	-	0.05
Solar	<0.01	<0.01	<0.01	-	<0.01
Wave/tidal	<0.01	<0.01	<0.01	-	<0.01
Biomass (liquid/gas)	0.05	0.02	<0.01	-	0.07
Industrial waste	0.03	0.01	<0.01	-	0.04
Municipal Waste	0.06	0.03	<0.01	-	0.09
Wind	0.02	0.01	<0.01	-	0.03
Totals	12.72	43.61	0.70	33.94	90.96

Table 3
Gross primary fuels used to produce 1 kg of MDI expressed as mass.

Fuel type	Input in mg
Crude oil	640000
Gas/condensate	930000
Coal	320000
Metallurgical coal	18000
Lignite	43000
Peat	320
Wood	1200

Table 4
Gross raw materials required to produce 1 kg of MDI.

Raw material	Input in mg
Air	780000
Animal matter	<1
Barytes	350
Bauxite	11
Bentonite	53
Biomass (including water)	14000
Calcium sulphate (CaSO4)	5
Chalk (CaCO3)	<1
Clay	4
Cr	<1
Cu	1
Dolomite	43
Fe	480
Feldspar	<1
Ferromanganese	<1
Fluorspar	3
Granite	<1
Gravel	2
Hg	2
Limestone (CaCO3)	7900
Mg	<1
N2	220000
Ni	<1
O2	150000
Olivine	5
Pb	2
Phosphate as P2O5	7
Potassium chloride (KCl)	2400
Quartz (SiO2)	<1
Rutile	<1
S (bonded)	<1
S (elemental)	3600
Sand (SiO2)	710
Shale	15
Sodium chloride (NaCl)	520000
Sodium nitrate (NaNO3)	<1
Talc	<1
Unspecified	<1
Zn	<1

Table 5
Gross water consumption required for the production of 1 kg of MDI. (Totals may not agree because of rounding)

Source	Use for processing (mg)	Use for cooling (mg)	Totals (mg)
Public supply	77000000	-	77000000
River canal	4200000	110000000	114000000
Sea	290000	46000000	46000000
Well	47000	38000	85000
Unspecified	3400000	86000000	90000000
Totals	85000000	242000000	327000000

Table 6
Gross air emissions associated with the production of 1 kg of MDI. (Totals may not agree because of rounding)

Emission	From fuel prod'n (mg)	From fuel use (mg)	From transport (mg)	From process (mg)	From biomass (mg)	From fugitive (mg)	Totals (mg)
dust (PM10)	1600	300	15	190	-	-	2100
CO	2400	900	170	860	-	-	4300
CO2	830000	1900000	25000	400000	-1100	-	3200000
SOX as SO2	5300	5100	210	300	-	-	11000
H2S	<1	-	<1	<1	-	-	<1
mercaptan	<1	<1	<1	<1	-	-	<1
NOX as NO2	2500	4200	240	730	-	-	7700
NH3	<1	-	<1	51	-	-	51
Cl2	<1	<1	<1	280	-	-	280
HCl	83	26	<1	3	-	-	110
F2	<1	<1	<1	<1	-	-	<1
HF	3	1	<1	<1	-	-	4
hydrocarbons not specified	1400	340	66	1000	-	1	2800
aldehyde (-CHO)	<1	-	<1	2	-	-	2
organics	<1	<1	<1	180	-	-	180
Pb+compounds as Pb	<1	<1	<1	<1	-	-	<1
Hg+compounds as Hg	<1	-	<1	<1	-	-	<1
metals not specified elsewhere	1	2	<1	<1	-	-	3
H2SO4	<1	-	<1	24	-	-	24
N2O	<1	<1	<1	<1	-	-	<1
H2	230	<1	<1	2400	-	-	2700
dichloroethane (DCE) C2H4Cl2	<1	-	<1	<1	-	<1	<1
vinyl chloride monomer (VCM)	<1	-	<1	<1	-	<1	<1
CFC/HCFC/HFC not specified	<1	-	<1	4	-	-	4
organo-chlorine not specified	<1	-	<1	14	-	-	14
HCN	<1	-	<1	<1	-	-	<1
CH4	30000	950	<1	2500	-	<1	34000
aromatic HC not specified elsewhere	<1	-	<1	70	-	1	71
polycyclic hydrocarbons (PAH)	<1	2	<1	<1	-	-	2
NMVOC	<1	-	<1	14	-	-	14
CS2	<1	-	<1	<1	-	-	<1
methylene chloride CH2Cl2	<1	-	<1	<1	-	-	<1
Cu+compounds as Cu	<1	<1	<1	<1	-	-	<1
As+compounds as As	-	-	-	<1	-	-	<1
Cd+compounds as Cd	<1	-	<1	<1	-	-	<1
Ag+compounds as Ag	-	-	-	<1	-	-	<1
Zn+compounds as Zn	<1	-	<1	<1	-	-	<1
Cr+compounds as Cr	<1	1	<1	<1	-	-	1
Se+compounds as Se	-	-	-	<1	-	-	<1
Ni+compounds as Ni	<1	2	<1	<1	-	-	2
Sb+compounds as Sb	-	-	<1	<1	-	-	<1
ethylene C2H4	-	-	<1	3	-	-	3
oxygen	-	-	-	<1	-	-	<1
asbestos	-	-	-	<1	-	-	<1
dioxin/furan as Teq	-	-	-	<1	-	-	<1
benzene C6H6	-	-	-	1	-	6	6
toluene C7H8	-	-	-	<1	-	1	1
xylenes C8H10	-	-	-	<1	-	<1	<1
ethylbenzene C8H10	-	-	-	<1	-	<1	<1
styrene	-	-	-	<1	-	<1	<1
propylene	-	-	-	2	-	-	2

Table 7
Carbon dioxide equivalents corresponding to the gross air emissions for the production of 1 kg of MDI. (Totals may not agree because of rounding)

Type	From fuel prod'n (mg)	From fuel use (mg)	From transport (mg)	From process (mg)	From biomass (mg)	From fugitive (mg)	Totals (mg)
20 year equiv	2700000	2000000	26000	560000	-1100	16	5300000
100 year equiv	1500000	1900000	26000	460000	-1100	7	3900000
500 year equiv	1100000	1900000	26000	420000	-1100	4	3400000

Table 8
Gross emissions to water arising from the production of 1 kg of MDI. (Totals may not agree because of rounding).

Emission	From fuel prod'n (mg)	From fuel use (mg)	From transport (mg)	From process (mg)	Totals (mg)
COD	7	-	<1	5400	5400
BOD	1	-	<1	900	900
Pb+compounds as Pb	<1	-	<1	<1	<1
Fe+compounds as Fe	<1	-	<1	3	3
Na+compounds as Na	<1	-	<1	88000	88000
acid as H+	8	-	<1	13	21
NO3-	<1	-	<1	210	210
Hg+compounds as Hg	<1	-	<1	<1	<1
metals not specified elsewhere	2	-	<1	58	60
ammonium compounds as NH4+	7	-	<1	170	180
Cl-	1	-	<1	140000	140000
CN-	<1	-	<1	<1	<1
F-	<1	-	<1	<1	<1
S+sulphides as S	<1	-	<1	<1	<1
dissolved organics (non-	1	-	<1	470	470
suspended solids	95	-	12	2100	2200
detergent/oil	<1	-	<1	15	15
hydrocarbons not specified	7	<1	<1	5	12
organo-chlorine not specified	<1	-	<1	5	5
dissolved chlorine	<1	-	<1	1	1
phenols	<1	-	<1	1	1
dissolved solids not specified	<1	-	<1	8300	8300
P+compounds as P	<1	-	<1	10	10
other nitrogen as N	2	-	<1	62	64
other organics not specified	<1	-	<1	2	2
SO4--	<1	-	<1	7500	7500
dichloroethane (DCE)	<1	-	<1	<1	<1
vinyl chloride monomer (VCM)	<1	-	<1	<1	<1
K+compounds as K	<1	-	<1	74	74
Ca+compounds as Ca	<1	-	<1	160	160
Mg+compounds as Mg	<1	-	<1	15	15
Cr+compounds as Cr	<1	-	<1	<1	<1
ClO3--	<1	-	<1	130	130
BrO3--	<1	-	<1	<1	<1
TOC	<1	-	<1	950	950
AOX	<1	-	<1	<1	<1
Al+compounds as Al	<1	-	<1	1	1
Zn+compounds as Zn	<1	-	<1	75	75
Cu+compounds as Cu	<1	-	<1	<1	<1
Ni+compounds as Ni	<1	-	<1	8	8
CO3--	-	-	<1	140	140
As+compounds as As	-	-	<1	<1	<1
Cd+compounds as Cd	-	-	<1	<1	<1
Mn+compounds as Mn	-	-	<1	<1	<1
organo-tin as Sn	-	-	<1	<1	<1
Sr+compounds as Sr	-	-	<1	<1	<1
organo-silicon	-	-	-	<1	<1
benzene	-	-	-	<1	<1
dioxin/furan as Teq	-	-	<1	<1	<1

Table 9
Gross solid waste associated with the production of 1 kg of MDI. (Totals may not agree because of rounding)

Emission	From fuel prod'n (mg)	From fuel use (mg)	From transport (mg)	From process (mg)	Totals (mg)
Plastic containers	<1	-	<1	<1	<1
Paper	<1	-	<1	5	5
Plastics	<1	-	<1	250	250
Metals	<1	-	<1	1	1
Putrescibles	<1	-	<1	<1	<1
Unspecified refuse	1500	-	<1	<1	1500
Mineral waste	24000	-	120	3700	28000
Slags & ash	16000	5500	48	2700	24000
Mixed industrial	-640	-	5	3900	3300
Regulated chemicals	1900	-	<1	3600	5500
Unregulated chemicals	1400	-	<1	2100	3500
Construction waste	<1	-	<1	79	79
Waste to incinerator	<1	-	<1	2000	2000
Inert chemical	<1	-	<1	6600	6600
Wood waste	<1	-	<1	23	23
Wooden pallets	<1	-	<1	<1	<1
Waste to recycling	<1	-	<1	370	370
Waste returned to mine	45000	-	5	120	45000
Tailings	1	-	4	59	64
Municipal solid waste	-8900	-	-	<1	-8900
Note: Negative values correspond to consumption of waste e.g. recycling or use in electricity generation.					

Table 10
Gross solid waste in EU format associated with the production of 1 kg of MDI. Entries marked with an asterisk (*) are considered hazardous as defined by EU Directive 91/689/EEC

Emission	Totals (mg)
010101 metallic min'l excav'n waste	680
010102 non-metal min'l excav'n waste	46000
010306 non 010304/010305 tailings	6
010308 non-010307 powdery wastes	5
010399 unspecified met. min'l wastes	24000
010408 non-010407 gravel/crushed rock	11
010410 non-010407 powdery wastes	6
010411 non-010407 potash/rock salt	2000
010499 unsp'd non-met. waste	2
010505*oil-bearing drilling mud/waste	1800
010508 non-010504/010505 chloride mud	1400
010599 unspecified drilling mud/waste	1500
020107 wastes from forestry	23
050106*oil ind. oily maint'e sludges	<1
050107*oil industry acid tars	130
050199 unspecified oil industry waste	140
050699 coal pyrolysis unsp'd waste	170
060101*H2SO4/H2SO3 MFSU waste	3
060102*HCl MFSU waste	8
060106*other acidic MFSU waste	<1
060199 unsp'd acid MFSU waste	<1
060204*NaOH/KOH MFSU waste	<1
060299 unsp'd base MFSU waste	110
060313*h. metal salt/sol'n MFSU waste	2500
060314 other salt/sol'n MFSU waste	310
060399 unsp'd salt/sol'n MFSU waste	330
060404*Hg MSFU waste	120
060405*other h. metal MFSU waste	360
060499 unsp'd metallic MFSU waste	990
060602*dangerous sulphide MFSU waste	<1
060603 non-060602 sulphide MFSU waste	7
060701*halogen electrol. asbestos waste	97
060702*Cl pr. activated C waste	<1
060703*BaSO4 sludge with Hg	13
060704*halogen pr. acids and sol'ns	220
060799 unsp'd halogen pr. waste	1000
061002*N ind. dangerous sub. waste	<1
061099 unsp'd N industry waste	<1
070101*organic chem. aqueous washes	<1
070103*org. halogenated solv'ts/washes	<1
070107*hal'd still bottoms/residues	2500
070108*other still bottoms/residues	2100
070111*org. chem. dan. eff. sludge	<1
070112 non-070111 effluent sludge	6

continued over …..

Table 10 - continued
Gross solid waste in EU format associated with the production of 1 kg of MDI. Entries marked with an asterisk (*) are considered hazardous as defined by EU Directive 91/689/EEC

070199 unsp'd organic chem. waste	520
070204*polymer ind. other washes	<1
070207*polymer ind. hal'd still waste	<1
070208*polymer ind. other still waste	90
070209*polymer ind. hal'd fil. cakes	<1
070213 polymer ind. waste plastic	1
070214*polymer ind. dan. additives	120
070216 polymer ind. silicone wastes	<1
070299 unsp'd polymer ind. waste	180
080199 unspecified paint/varnish waste	<1
100101 non-100104 ash, slag & dust	15000
100102 coal fly ash	3400
100104*oil fly ash and boiler dust	37
100105 FGD Ca-based reac. solid waste	<1
100113*emulsified hyrdocarbon fly ash	2
100114*dangerous co-incin'n ash/slag	15
100115 non-100115 co-incin'n ash/slag	110
100116*dangerous co-incin'n fly ash	<1
100199 unsp'd themal process waste	3100
100202 unprocessed iron/steel slag	130
100210 iron/steel mill scales	8
100399 unspecified aluminium waste	<1
100501 primary/secondary zinc slags	1
100504 zinc pr. other dust	<1
100511 non-100511 Zn pr. skimmings	<1
101304 lime calcin'n/hydration waste	7
130208*other engine/gear/lub. oil	<1
150101 paper and cardboard packaging	5
150102 plastic packaging	2
150103 wooden packaging	<1
150106 mixed packaging	2500
170107 non-170106 con'e/brick/tile mix	<1
170904 non-170901/2/3 con./dem'n waste	91
190199 unspecified incin'n/pyro waste	<1
190905 sat./spent ion exchange resins	6600
200101 paper and cardboard	<1
200108 biodeg. kitchen/canteen waste	<1
200138 non-200137 wood	<1
200139 plastics	250
200140 metals	<1
200199 other separately coll. frac'ns	-2200
200301 mixed municipal waste	2
200399 unspecified municipal wastes	-7300

Note: Negative values correspond to consumption of waste e.g. recycling or use in electricity generation.

European Diisocyanate and Polyol Producers Association
Avenue E. van Nieuwenhuyse Laan 4,
1160 Brussels
Belgium
Tel: ++32 2 676 7475
Fax: ++32 2 676 7479
Email: main@isopa.org
Website: www.isopa.org

ISOPA is an affiliated organisation within the European Chemical Industry Council (Cefic)

Association of Plastics Manufacturers in Europe
Avenue E. van Nieuwenhuyse Laan 4,
1160 Brussels
Belgium
Tel: ++32 2 675 32 97
Fax: ++32 2 675 39 35
Website: www.plasticseurope.org