MATERIAL SAFETY DATA SHEET

Product Range: **Polyurethane hardener**

1. IDENTIFICATION OF PREPARATION AND COMPANY

Product Name : **PURCELL SP 500-3800 -A**
Product Code : 2912
Chemical name: **4,4'-Methylenediphenyl diisocyanate, oligomers**
CAS number : 25686-28-6.

Application of the substance/the preparation :
Purcell SP 500-3800-B is a hardener componemt for water proofing material.

Company Identification: BYTECH BOYA VE YAPI KIMYASALLARI SAN. VE TIC. LTD.
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2. HAZARDS IDENTIFICATION

2.1 **Classification of the substance**
2.1.1. **Classification according to Regulation (EC) No 1272/2008 (CLP)**

Hazard classes / categories	Hazard statement	Remarks
Acute Tox. 4	**H332** Harmful if inhaled.	
Skin Irrit. 2	**H315** Causes skin irritation.	Concentration range (%): >= 5
Eye Irrit. 2	**H319** Causes serious eye irritation.	Concentration range (%): >= 5
Resp. Sens.1	**H334** May cause allergy or asthma symptoms or breathing difficulties if inhaled.	
Skin Sens. 1	**H317** May cause an allergic skin reaction.	
Carc. 2	**H351** Suspected of causing cancer <state route of exposure if it is conclusively proven that no other routs of exposure cause the hazard>.	
STOT SE 3	**H335** May cause respiratory irritation.	Concentration range (%): >= 5
STOT RE 2	**H373** May cause damage to organs <or state all organs affected, if known> through prolonged or repeated exposure <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard> respiratory system, inhalation.	

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2.1.2. **Classification according to 67/548/EEC**

Classification	R-phrases
Xn - Harmful.	**R20** Harmful by inhalation.
Xn - Harmful.	**R48/20** Harmful: danger of serious damage to health by prolonged exposure through inhalation.
XI – Irritant.	**R36/37/38** Irritating to eyes, respiratory system and skin.
	R42/43 May cause sensitisation by inhalation and skin contact.
Carc. Cat. 3	**R40** Limited evidence of a carcinogenetic effect.

S-phrases:

S38	In case of insufficient ventilation, wear suitable respiratory equipment.
S1/2	Keep locked up and out of reach of children.
S23	Do not breathe vapour.
S36/37	Wear suitable protective clothing and gloves.
S45	In case of accident or if you feel unwell, seek medical advice immediately (show the label whe possible).

Notes:

Note C
Note 2

2.2. **Label elements**

2.2.1. **Labelling according to Regulation (EC) No 1272/2008 (CLP)**

Product identifier: **ONGRONAT 3800**
Substance: **4,4'-Methylenediphenyl diisocyanate, oligomers**
EC number: **500-040-3**

Hazard pictograms:

GHS07

GHS08

Signal word: Danger.

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Hazard statements:

H351	Suspected of causing cancer <state route of exposure if it is conclusively proven that no other routs of exposure cause the hazard>.
H332	Harmful if inhaled.
H319	Causes serious eye irritation.
H335	May cause respiratory irritation.
H315	Causes skin irritation.
H334	May cause allergy or asthma symptoms or breathing difficulties if inhaled.
H317	May cause an allergic skin reaction.
H373	May cause damage to organs <or state all organs affected, if known> through prolonged or repeated exposure <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard> respiratory system, inhalation.

Precautionary statements:

P260	Do not breathe dust/fume/gas/mist/vapours/spray.
P280	Wear protective gloves/protective clothing/eye protection.
P285	In case of inadequate ventilation wear respiratory protection.
P302+P352	IF ON SKIN: Wash with plenty of soap and water.
P304+P340	IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing.
P305+P351+P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P309+P311	IF exposed or if you feel unwell: Call a POISON CENTER or doctor/physician.

Supplemental Hazard Information (EU):
EUH204 Contain isocyanates. May produce an allergic reaction.

Notes:
Note C
Note 2

2.3. **Other hazards**: All MDI analogues included in the category are not persistent (P) and not bioaccumulation (B) criteria, but they meet the criteria for toxicity (T) in accordance with Annex XIII of 1907/2006/EC.

3. COMPOSITION/INFORMATION ON INGREDIENTS

3.1. **Substance**

Chemical name	EC number	CAS number	Typical concentration % (w/w)
4,4'-Methylenediphenyl diisocyanate, oligomers	500-040-3	25686-28-6	>99

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4. FIRST AID MEASURES

4.1. **Description of first aid measures**
General advice: Soiled, fairly soaked clothing and shoes must be immediately removed and disposed of.

4.1.1. **In case of inhalation:** If inhaled, remove to fresh air. If not breathing, give artificial respiration. Get medical attention immediately.

4.1.2. **In case of skin contact:** In the event of contact with the skin, preferably wash with a cleanser based on polyethylene glycol or with plenty of warm water and soap. Consult a doctor in the event of a skin reaction. Wash the less clothing before reuse. Clean shoes thoroughly before reuse.

4.1.3. **In case of eye contact:** Hold the eyes open and rinse with water for a sufficiently long period of time (at least 10 minutes). Get medical attention immediately.

4.1.4. **In case of ingestion:** DO NOT induce the patient to vomit, medical advice is required. Never give anything by mouth to an unconscious person. Provided the patient is conscious, wash out mouth with water.

4.1.5. **Information to physician:** The product irritates the respiratory tract and may trigger sensitisation of the skin and respiratory tract. Treatment of acute irritation or bronchial constriction is primarily symptomatic. Following severe exposure the patient should be kept under medical review for at least 48 hours.

4.2. **Most important symptoms and effects, both acute and delayed:** Headache, nausea, shortness of breath, sore throat, redness on the skin. Repeated or prolonged contact may cause skin sensitization. Repeated or prolonged inhalation exposure may cause asthma.

4.3. **Indication of any immediate medical attention and special treatment needed:** Depending on the degree of exposure, periodic medical examination is suggested.

5. FIRE FIGHTING MEASURES

5.1. **Extinguishing media**
Suitable extinguishing media: Foam, CO_2 or dry powder. Water spray may be used if no other available and then in copious quantities.
Unsuitable extinguishing media: High volume water jet.

5.2. **Special hazards arising from the substance:** Carbon oxides (CO, CO_2) nitrogen oxides (NO, NO_2 etc.) hydrocarbons, isocyanate vapors and hydrogen cyanide can be released in case of fire.

5.3. **Advice for firefighters**
Reaction between water and hot isocyanate may be vigorous. Prevent washings from entering water courses, keep fire exposed containers cool by spraying with water.
Special protective equipment: Fire-fighters should wear appropriate protective equipment and self-contained breathing apparatus (SCBA) with a full face-piece operated in positive pressure mode. PVC boots, gloves, safety helmet and protective clothing should be worn.

5.4. **Further information:** In the event of fire and/or explosion do not breathe fumes. Fire in vicinity poses risk of pressure build-up and rupture. Containers at risk from fire should be cooled with water and, if possible, removed from the danger area. Due to reaction with water producing CO_2 gas, a hazardous build-up of pressure could result if contaminated containers are re-sealed. Containers may burst if overheated.
Fire risk class in Hungary: “D” (Moderately flammable).

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6. ACCIDENTAL RELEASE MEASURES

6.1. **Personal precautions, protective equipment and emergency procedures:** Immediately contact emergency personnel. Evacuate the area. Keep upwind to avoid inhalation of vapours. Clean-up should only be performed by trained personnel. Keep unauthorized persons away.
6.1.1. **For non-emergency personnel:** Remove not affected people. Inform the relevant authorities.
6.1.2. **For emergency responders:** People dealing with major spillages should wear full protective clothing including respiratory protection. Use suitable protective equipment (section 8).

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6.2. **Environmental precautions:** Do not allow contaminated extinguishing water to enter the soil, ground-water or surface waters. Avoid dispersal of spilt material and runoff and contact with drains and sewers.
6.3. **Methods and material for containment and cleaning up:** Absorb spillages onto sand, earth or any suitable adsorbent material. Leave to react for at least 30 minutes. Do not absorb onto sawdust or other combustible materials. Shovel into open-top drums for further decontamination. Wash the spillage area with water.
6.3.1. **Appropriate containment techniques:** Test atmosphere for MDI vapour.
6.3.2. **Appropriate clean-up procedures:** The compositions of liquid decontaminants are (percentages by weight or volume):
Decontaminant 1:
- sodium carbonate: 5 - 10 %
- liquid detergent: 0.2 - 2 %
- water: to make up to 100 %.

Decontaminant 2:
- concentrated ammonia solution: 3 - 8 %
- liquid detergent: 0.2 - 2 %
- water: to make up to 100 %.

Decontaminant 1 reacts slower with diisocyanates but is more environmentally friendly than decontaminant 2. Decontaminant 2 contains ammonia. Ammonia presents health hazards.
6.4. **Reference to other sections:** n/a.

7. HANDLING AND STORAGE

7.1. **Precautions for safe handling**
7.1.1. **Protective measures:** Provide sufficient air exchange and/or exhaust in work rooms. In all workplaces or parts of the plant where high concentrations of isocyanate aerosols and/or vapors may be generated (e.g. during pressure release, mold venting or when cleaning mixing heads with an air blast), appropriately located exhaust ventilation must be provided in order to prevent occupational exposure limits from being exceeded. The air should be drawn away from the personnel handling the product. The efficiency of the ventilation system must be monitored regularly because of the possibility of blockage. Atmospheric concentrations should be minimised and kept as low as reasonably practicable below the occupational exposure limit.
7.1.2. **Advice on general occupational hygiene:** No eating, drinking, smoking or tobacco use at the place of work. Contact with skin and eyes and inhalation of vapors must be avoided under all circumstances. Keep equipment clean. A basic essential in sampling, handling and storage is the prevention of contact with water. Keep stocks of decontaminant readily available.
7.2. **Conditions for safe storage, including any incompatibilities:** Store in accordance with local regulations. Store in original container protected from direct sunlight in a dry, cool and well-ventilated area, away from incompatible materials and food and drink. Keep container tightly closed and sealed until ready for use. Containers that have been opened must be carefully resealed and kept upright to prevent leakage. Do not store in unlabelled containers. Use appropriate containment to avoid environmental contamination. Suitable containers: steel, stainless steel. Unsuitable containers: copper, copper alloy and galvanised surfaces.
7.3. **Specific end use(s):** n/a.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Significant routes of exposure:
Human exposure: by inhalation.
Environmental exposure: air.
Pattern of exposure: accidental/infrequent.
The recommended control strategies:
1. Employ good industrial hygiene practice
2. Use local exhaust ventilation

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3. Enclose the process
4. Seek the advice of a specialist

8.1. **Control parameters**

Substance: 4,4-methylenediphenyldiisocyanate
CAS No. 101-68-8

Countries	Limit value (8 hours)		Limit value (short term)	
	ppm	mg/m^3	ppm	mg/m^3
Austria	0.005	0.05	0.01	0.1
Belgium	0.005	0.052		
Denmark	0.005	0.05	0.01	0.1
France	0.01	0.1	0.02	0.2
Germany		0.05		0.05(1)
Hungary		0.05		0.05
Poland		0.05		0.2
Spain	0.005	0.052		
Sweden	0.002	0.03	(0.005)	(0.05)

(1) 15 minutes average value

Source: http://bgia-online.hvbg.de/LIMITVALUE/WebForm_gw.aspx

8.1.1. **DNEL/PNEC-values:**

Workers:

Acute/short-term exposure- systemic effects (dermal):	DNEL 50 mg/kg bw/day
Acute/short-term exposure- systemic effects (inhalation):	DNEL 0.1 mg/ m^3
Acute/short-term exposure- local effects (dermal):	DNEL 28.7 mg/cm^2
Acute/short-term exposure- local effects (inhalation):	DNEL 0.1 mg/ m^3
Long-term exposure - systemic effects (inhalation):	DNEL 0.05 mg/ m^3
Long-term exposure - systemic effects (dermal):	Not applicable.
Long-term exposure - local effects (inhalation):	DNEL 0.05 mg/ m^3
Long-term exposure - local effects (dermal)	Not applicable.

General population:

Acute/short-term exposure- systemic effects (dermal):	DNEL 25 mg/kg bw/day
Acute/short-term exposure- systemic effects (inhalation):	DNEL 0.05 mg/ m^3
Acute/short-term exposure- systemic effects (oral):	DNEL 20 mg/kg bw/day
Acute/short-term exposure- local effects (dermal):	DNEL 17.2 mg/cm^2
Acute/short-term exposure- local effects (inhalation):	DNEL 0.05 mg/ m^3
Long-term exposure - systemic effects (inhalation):	DNEL 0.025 mg/ m^3
Long-term exposure - systemic effects (dermal):	Not applicable.
Long-term exposure - systemic effects (oral):	Not applicable.
Long-term exposure - local effects (inhalation):	DNEL 0.025 mg/ m^3
Long-term exposure - local effects (dermal)	Not applicable.
Long-term exposure - local effects (oral)	Not applicable.

PNEC aqua (freshwater): 1 mg/l
PNEC aqua (marine water): 0.1 mg/l
PNEC aqua (intermittent releases): 10 mg/l
PNEC STP: 1 mg/l

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PNEC sediment: As MDI is a reactant with water, access of water to MDI and vice versa is strictly controlled. Furthermore, MDI polymerizes in the presence of water and thus exposure of MDI to sediment is highly likely to be negligible. Therefore, PNEC sediment cannot be derived for MDI.
PNEC soil: 1 mg/kg soil dw (dry weight)
PNEC oral: There are no data on effects of oral MDI to birds. Exposure to birds is not expected and data from experimental animals show MDI to be of low oral toxicity.

8.2. **Exposure controls**
8.2.1. **Appropriate engineering controls:** Provide suitable exhaust ventilation at the processing machines.
8.2.2. **Personal protection equipment**
8.2.2.1. **Eye / Face protection:** safety glasses with side-shields (frame goggles) (e.g. EN 166).
8.2.2.2. **Skin protection:**
Hand protection: chemical resistant protective gloves (EN 374).
Examples of gloves materials that might provide suitable protection include:
Butyl rubber (BR): thickness >=0.5mm; breakthrough time >=480min.
Chlorinated polyethylene
Polyethylene
Ethyl vinyl alcohol copolymers laminated (EVAL)
Polychloroprene (Neoprene) (CR): thickness >=0.5mm; breakthrough time >=480min.
Nitrile/butadiene rubber (NBR): thickness >=0.35mm; breakthrough time >=480min.
Polyvinyl chloride (PVC)
Frequently repeated contact: Gloves with protection class 5 or higher is recommended.
Body protection: safety shoes (e.g. according to EN 20346) and closed work clothing.
8.2.2.3. **Respiratory protection:** Breathing apparatus, full face mask respirator. Respirators type protection can be used in combination with an organic vapour filter type A and where dusts or aerosols could be present with a minimum of A/P2 filter.
8.2.2.4. **General safety and hygiene measures**: Do not breath vapours/spray. Keep away from drink, food and animal feeding stuffs. No eating, drinking, smoking or tobacco use at the place of work. Hands and face should be washed before breaks and at the end of shift. At the end of the shift the skin should be cleaned and skin-care agents applied.
8.2.3. **Environmental exposure controls**: In accordance with local and national regulations.

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9. PHYSICAL AND CHEMICAL PROPERTIES

9.1. **Information on basic physical and chemical properties**
9.1.1. **Appearance:**
Physical state: liquid (at 20°C, 1013 hPa)
Colour: slightly yellow
Odour: aromatic
Odour threshold: no data
9.1.2. **Basic data:**

pH (20 °C):	Data waiving. Not required by REACH annexes.
Melting range:	-17.0 to -4.7°C
Boiling point:	decomposes at 201°C
Flash point (closed cup):	min.200°C
Evaporation rate:	No data.
Flammability :	Not generate flammable gases in contact with water.
Auto flammability:	> 464°C
Vapour pressure:	0.0059 Pa (at 20°C)
Vapour density (air=1):	No data.
Density:	1.21 g/cm^3 (at 25°C)
Water solubility:	5.17 E- 08 g/L (estimated value)
Partition coefficient n-octanol/water(Log Pow):	8.56 (at 20°C, estimated value)
Viscosity:	30-90 mPa.s (25°C, dynamic)
Explosive properties:	Non explosive.

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Oxidising properties: Data waiving. In accordance with column 2 of REACH Annex VII the oxidising properties study need not be conducted if the substance is incapable of reacting exothermically with combustible materials on the basis of chemical structure.

9.2. **Other information**

Granulometry: Not applicable. In accordance with column 2 of REACH Annex VII the granulometry study does not need to be conducted as the substance is marketed or used in a non solid or granular form.
Solubility in organic solvents / fat solubility: Data waving. Not required by REACH annexes.
Surface tension: Not applicable. In accordance with column 2 of REACH Annex VII the surface tension study need not be conducted as, based on structure, surface activity is not expected or predicted, nor is it a desired property of the substance.
Oxidation reduction potential: Data waiving. Not required by REACH annexes.
Dissociation constant: Dissociation constans estimation is not feasible.

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10. STABILITY AND REACTIVITY

10.1. **Reactivity:** Reacts with water, acids, alcohols, amines, bases and oxidants.
10.2. **Chemical stability**
The main removal mechanism of MDI in the environment is hydrolysis. MDI reacts quickly with water to form predominantly solid, insoluble polyureas. Under conditions typical of many types of environmental contact, i. e. with relatively poor dispersion of the denser isocyanate, the interfacial reaction leads to the formation of a solid crust encasing partially or unreacted material. This crust restricts ingress of water and egress of amine, and hence slows and modifies hydrolysis.
Stability in organic solvents: All MDI isomers and forms are highly unstable in dimethylsulhpoxide solvent, water content of the DMSO increasing breakdown. The corresponding diamine is identified as one of the breakdown products. MDI is more stable in EGDE (ethyleneglycoldimethylether) as solvent.
10.3. **Possibility of hazardous reactions:** Reaction is slow with cold or warm water (<50°C), with hot water or steam the reaction is faster, producing carbon-dioxide causing pressure increase.

Acids, alcohols, amines, bases and oxidants cause fire and explosion hazard.
10.4. **Conditions to avoid:** High temperature, moisture, strong light.
10.5. **Incompatible materials:** Water, acids, alcohols, amines, bases and oxidants.
10.6. **Hazardous decomposition products:** No hazardous decomposition products if stored and handled as prescribed/indicated.

11. TOXICOLOGICAL INFORMATION

11.1. **Acute toxicity**
Acute toxicity – oral: Not classified. Based on available data, the classification criteria are not met.
Rat (female) LD50 > 5000 mg/kg bw
Acute toxicity –inhalation: Category 4
Rats LC50 > 2.24 mg/L (1h)
(Read-across based on 4,4'-methylenediphenyl diisocyanate - CAS 101-68-8)
Acute toxicity – dermal: Not classified. Based on available data, the classification criteria are not met.
Rabbit LD50 > 9400 mg/kg bw (24h)
(Read-across based on polymer MDI - CAS 9016-87-9.)
11.2. **Irritation / corrosion:** Summarized the results of the studies together with human occupational case reports support the official classification.
Skin corrosion / irritation: Category 2
Irritating in rabbits
(Read-across based on 4,4'-methylenediphenyl diisocyanate - CAS 26447-40-5.)
Eye damage / irritation: Category 2B
Not irritating to eyes in rabbits
(Read-across based on 4,4'-methylenediphenyl diisocyanate - CAS 26447-40-5.)

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Summarized the available animal data would not support classification of MDI as an eye irritant. But together with human occupational case reports in which symptoms of eye irritation were reported the legal classification as eye irritant should be applied.
11.3**. Sensitisation:** Animal data as well as studies in humans provide evidence of possible skin sensitisation, and of respiratory sensitisation due to MDI. Animal studies indicate that MDI is a strong allergen. Human case reports describe the occurrence of allergic contact dermatitis due to MDI exposure.
Skin sensitization: Skin sensitiser 1
Sensitizing in guinea pig.
Respiratory sensitization: Respiratory sensitiser 1
Sensitizing in guinea pig
(Read-across based on 4,4'-methylenediphenyl diisocyanate - CAS 101-68-8)
11.4. **Mutagenicity:** Not classified. Based on available data, the classification criteria are not met.
11.5. **Carcinogenicity**: Carc. Cat. 2
Rats (inhalation) NOAEC = 0.2 mg/ m³ (toxicity)
NOAEC = 1 mg/m³ (carcinogenicity)
LOAEC = 6 mg/m³ (carcinogenicity)
(Read-across based on polymer MDI – CAS 9016-87-9.)
11.6**. Reproductive toxicity:** Not classified. Based on available data, the classification criteria are not met.
Effects on fertility: No fertility nor multigeneration studies are available for MDI.
Developmental toxicity: MDI is not a developmental toxicant.
Rats NOAEL = 4 mg/m³ (maternal and foetal toxicity)
NOAEL = 12 mg/m³ (teratogenicity)
(Read-across based on polymer MDI – CAS 9016-87-9.)
11.7**. STOT-single exposure**: STOT SE 3
Rats (inhalation) NOAEL = 1 mg/m³
(Read-across based on polymer MDI – CAS 9016-87-9.)
11.8. **STOT-repeated exposure:** STOT RE 2
Rats (inhalation) NOAEC = 0.2 mg/m^3 (2 years)
LOAEC = 1.0 mg/m^3
Target organs: respiratory – lung.
(Read-across based on polymer MDI – CAS 9016-87-9.)
11.9. **Aspiration hazard**: Not classified due to lack of data.
11.10**. Toxicokinetics** (absorption, metabolism, distribution and elimination):
Oral exposure: No information is available on the toxicokinetics of MDI following oral exposure in animals.
Dermal exposure: No radioactivity was absorbed through human skin during a 54h continuous exposure, and only small amounts (maximally 0.23% of applied dose) were absorbed through rat and guinea pig skin. The majority of applied MDI equivalents were found to be associated with the skin.
Inhalation exposure: With respect to inhalation exposure, there is good and reliable data regarding distribution/excretion in experimental animals. Most of the systemically available dose was excreted via bile, and a slightly lower amount via urine.
11.11. **Genetic toxicity**: Not classified. Based on available data, the classification criteria are not met.

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12. ECOLOGICAL INFORMATION

12.1. **Toxicity**
12.1.1. **Aquatic toxicity**
Short-term toxicity to fish:
Freshwater fish LC50 >1000 mg/L(96h)
(Read-across based on polymer MDI - CAS 9016-87-9.)
Long-term toxicity to fish: Data waiving. In accordance with column 2 of REACH Annex IX the long-term toxicity testing on fish shall be proposed if the chemical safety assessment according to Annex I indicates the need to investigate further the effects on aquatic organisms. MDI is rapidly hydrolysed in aqueous solution. However, MDI is hydrophobic and

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poorly soluble in water and thus the heterogeneous reaction with water or soil is less rapid. The major product of such a reaction is a solid, insoluble polyurea. All methylenediphenyl isocyanates are produced in closed systems. Formation of insoluble polyurea due to the presence of water would cause abrasion problems and blockage of valves and pipes. Therefore, production plant releases of MDI to effluents are expected to be non-existent. Releases to soil and sediment are also expected to be negligible. Furthermore, the EUSES program has been used to calculate PEC values based on measured emission data provided by MDI producers and processors, including polyurethane producers. The corresponding PEC/PNEC ratios would be less than 1. Taking into account the scientific and exposure arguments, it appears appropriate to waiver the long-term fish/plant/soil and sediment toxicity studies.

Short-term toxicity to aquatic invertebrates:
Freshwater invertebrates EC50/LC50 >1000 mg/L (24h)
(Read-across based on polymer MDI - CAS 9016-87-9.)

Long-term toxicity to aquatic invertebrates:
Freshwater invertebrates EC10/LC10 or NOEC = 10 mg/L (21 day)
(Read-across based on polymer MDI - CAS 9016-87-9.)

Toxicity to aquatic algae and cyanobacteria:
Freshwater algae EC50/LC50 >1640 mg/L (72h)
(Read-across based on polymer MDI - CAS 9016-87-9.)

Toxicity to aquatic plants other than algae: Data waiving. Not required by REACH annexes. However, a mesocosm study with PMDI exists in which the toxicity towards macrophytes (Potamogeton crispus and Zannichellia palustris) was assessed. No toxicity was observed at a loading of 1000 and 10,000 mg/l, approximately 100% of the substance was found in the sediment as hardened material.
(Read-across based on polymer MDI - CAS 9016-87-9.)

Toxicity to microorganisms:
Microorganisms EC50/LC50 >100 mg/L (3h)
(Read-across based on polymer MDI - CAS 9016-87-9.)

Toxicity to other aquatic organisms: This information is not available, but not required under REACH.

12.1.2. **Sediment toxicity**: Data waiving. Annex X states that this study need not be conducted if the chemical safety assessment does not indicate a need to further investigate the effects on sediment organisms.

12.1.3. **Terrestrial toxicity**

Toxicity to soil macroorganisms except arthropods:
Eisenia fetida EC50 > 1000 mg/kg soil dw (14 days)
(Read-across based on polymer MDI - CAS 9016-87-9.)

Toxicity to terrestrial arthropods: Data waiving. Based on the chemical safety assessment and the risk assessment, there is no need to further investigate the terrestrial arthropods toxicity as there is no risk for the terrestrial environment as indicated by the PEC/PNEC ratio being < 0.239. Direct/indirect exposure to soil is unlikely.
(Read-across based on polymer MDI - CAS 9016-87-9.)

Toxicity to terrestrial plants:
Avena sativa EC50 > 1000 mg/kg soil dw (14 days)
Lactuca sativa EC50 > 1000 mg/kg soil dw (14 days)
(Read-across based on polymer MDI - CAS 9016-87-9.)

Toxicity to soil microorganisms: Data waiving. Annex X states that this study need not be conducted if the chemical safety assessment does not indicate a need to further investigate the effects on sediment organisms.
(Read-across based on polymer MDI - CAS 9016-87-9.)

Toxicity to other above-ground organisms: Data waiving. Not required by REACH annexes.

12.1.4. **Atmospheric toxicity**: This information is not available.

12.1.5. **Microbiological activity in sewage treatment systems**

Toxicity to aquatic micro-organisms:
EC50/LC50 100 mg/l (3h)
(Read-across based on polymer MDI - CAS 9016-87-9.)

12.1.6. **Non compartment specific effects relevant for the food chain (secondary poisoning)**: Data waiving. Annex X states that this study needs to be considered taking into account the mammalian dataset that is usually available. Toxicity data in rats and dogs show no overt toxicity by the oral route. Oral PMDI to rats

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showed the LD50 to be in excess of 10,000 mg/kg body weight. Ingested PMDI forms mainly inert polyureas. Exposure to birds is not expected. There is no reason to suppose that PMDI will show significant oral toxicity to birds. Therefore no tests are deemed necessary.
(Read-across based on polymer MDI - CAS 9016-87-9.)
12.1.7. **Conclusion on classification:**
Hazardous to the aquatic environment (acute): Not classified. (EC/LC50 for fish, invertebrates and algae > 1000 mg/l)
Hazardous to the aquatic environment (chronic): Not classified. (NOEC for algae >1640 mg/l, NOEC for invertebrates > 10 mg/l)

12.2. **Persistence and degradability**
Phototransformation in air:
Half-life (DT50): 1 day
Hydrolysis: MDI reacts with water to form predominantly inert polyurea.
Half-life (DT50): 20 h (at 25°C)
Hydrolysis rate constant: 0.5-1h
(Read-across based on oligomeric MDI – CAS 32055-14-4.)
Phototransformation in water and soil: There are no phototransformation data in water and soil for the test substance.
Biodegradation in water: Under test conditions no biodegradation observed. (Read-across based on polymer MDI - CAS 9016-87-9.)
Biodegradation in water and sediment: Data waiving. In accordance with Annex XI, simulation biodegradation tests are technically not feasible as the test substance reacts quickly with water. MDI is rapidly hydrolysed in aqueous solution. However, MDI is hydrophobic and poorly soluble in water and thus the heterogeneous reaction with water or soil is less rapid. The major product of such a reaction is a solid, insoluble polyurea. All methylenediphenyl isocyanates are produced in closed systems. Formation of insoluble polyurea due to the presence of water would cause abrasion problems and blockage of valves and pipes. Therefore, production plant releases of MDI to effluents are expected to be non-existent. Releases to soil and sediment are also expected to be negligible. Furthermore, the EUSES program has been used to calculate PEC values based on measured emission data provided by MDI producers and processors, including polyurethane producers. The corresponding PEC/PNEC ratios would be less than 1. Taking into account the scientific and exposure arguments, it appears appropriate to waiver the long-term fish/plant/soil and sediment toxicity studies.
Biodegradation in soil: Data waiving. See at Biodegradation in water and sediment.
12.3. **Bioaccumulation**

Bioaccumulation - aquatic / sediment: Due to the high reactivity of the substances of the MDI category with water, bioaccumulation tests can in principle not be performed with these substances. However, one bioaccumulation test with 4,4'-MDI and a mesocosm study with PMDI with an indication of bioaccumulation potential have been performed. As no analytical measurements were done, it cannot be determined if the values are truely related to MDI. However, based on the available information and the reactivity of MDI substances of the category approach, no new bioaccumulation study is deemed necessary.
BCF (aquatic species) 200 (dimensionless)
Terrestrial bioaccumulation: No data is available on terrestrial bioaccumulation for the test substance, but it is not required under REACH.
12.4. **Mobility in soil**

Adsorption/desorption: Data waiving. According to Annex VIII the study need not be done if the test substance degrades rapidly. MDI is rapidly hydrolysed in aqueous solution. However, MDI is hydrophobic and poorly soluble in water and thus the heterogeneous reaction with water or soil is less rapid. The major product of such a reaction is a solid, insoluble polyurea. All methylenediphenyl isocyanates are produced in closed systems. Formation of insoluble polyurea due to the presence of water would cause abrasion problems and blockage of valves and pipes. Therefore, production plant releases of MDI to effluents are expected to be non-existent. Releases to soil and sediment are also expected to be negligible. Furthermore, the EUSES program has been used to calculate PEC values based on measured emission data provided by MDI producers and processors,

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including polyurethane producers. The corresponding PEC/PNEC ratios would be less than 1. Taking into account the scientific and exposure arguments, it appears appropriate to waiver the long-term fish/plant/soil and sediment toxicity studies.
Volatilisation: The estimated Henry's Law Constant, calculated from the measured vapour pressure and the calculated water solubility, is 2.263 x 10-7 atm-m^3/mole. Hence, volatilization is unlikely to be a significant removal mechanism for MDI substances of the category approach.
12.5. **Results of PBT and vPvB assessment**:

Conclusion for the P criterion: The results from the inherently biodegradation test indicate that PMDI is not biodegradable. Based on experimental hydrolysis and indirect photolysis half-lives, PMDI is not considered to be persistent in the environment and is identified as not P. Based on the justification in the category approach, it is assumed that all MDI analogues included in the category are not P.
Conclusion for the B criterion: Although MDI has a high measured log Kow value (4.51), a full bioaccumulation test with 4,4'-MDI indicated that the bioaccumulation potential is low. Due to the fast hydrolysis, exposure of the environment to the substance is unlikely or very low, there is no potential for significant bioaccumulation possible. Hence, 4,4'-MDI does not fulfil the requirements for the B criterion and is identified as not B. Based on the justification in the category approach, it is assumed that all MDI analogues included in the category are not B.
Conclusion for the T criterion: criteria. It was noted that the concentrations tested were far above the water solubility of the MDI substances (i.e. 7.5 mg/l). However, the water solubility limit of MDI is far above the criteria for T and on the basis of aquatic toxicity tests MDI is identified as not T. However, according to Annex I of 67/548/EEC MDI is classified as Xn, R48, which automatically triggers a T. Based on this classification MDI is identified as T.

12.6. **Other adverse effects**
It is not expected that MDI has an effect on global warming, ozone depletion in the stratosphere or ozone formation in the troposphere.
Secondary poisoning: Based on the available information, there is no indication of a bioaccumulation potential and, hence, secondary poisoning is not considered relevant.
Exposure to birds is not expected and data from experimental animals show MDI to be of low oral toxicity.

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13. DISPOSAL CONSIDERATIONS

13.1. **Waste treatment methods:** The products becoming useless and the contaminated containers not suitable for product storage must be handled as hazardous waste in accordance with EU and regional hazardous waste regulations.
13.2. **European Waste Catalogue code (EWC):** 08 05 01
13.2.1. **Product / Packaging disposal:** Contaminated packaging should be emptied as far as possible; than it can be passed on for recycling after being thoroughly cleaned. Wrappings cleaned from contamination with suitable cleaning process (e.g. by steaming, treating with washing fluid, etc.) must be considered as non hazardous waste.
13.2.2. **Waste treatment options:** Incinerate in suitable incineration plant, observing local authority regulations.

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14. TRANSPORT INFORMATION

Land transport (ADR/RID/GGVSE)
Sea transport (IMGD-Code/GGVSee)
Air transport (ICAO-IATA/DGR)
14.1. UN number: Not dangerous goods
14.2. UN proper shipping name: Not dangerous goods
14.3. Transport hazard class(es): Not dangerous goods
14.4. Packaging group: Not dangerous goods
14.5. Environmental hazards

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Marine pollutant: no
14.6. Special precautions for users
EmS number: Not dangerous goods
14.7. Transport in bulk according to Annex II of MARPOL73/78 and the IBC Code: Not relevant.

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15. REGULATORY INFORMATION

15.1. **Safety, health and environmental regulations/legislation specific for the substance Information regarding relevant Community safety, health and environmental provisions:**
4,4'-Methylenediphenyl diisocyanate, oligomers is not listed in Annex I of Directive 96/82/EC (Seveso II).
15.1.1. **EU regulations**

• COUNCIL DIRECTIVE of 27 June 1967 on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances (67/548/EEC).
• Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006.
• REGULATION (EC) No 1907/2006 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC.
• Council Directive 96/82/EC of 9 December 1996 on the control of major-accident hazards involving dangerous substances.

16.OTHER INFORMATION

16.1. **Indication of changes**: This version replaces all previous versions.
16.2. **Abbreviations and acronyms**:

BCF: Bioconcentration factor
bw: bodyweight
Carc.: Carcinogenicity
CAS number: Chemical Abstracts Service number
CLP: Classification Labelling Packaging Regulation
CSR: Chemical Safety Report
DNEL: Derived No Effect Level
DMSO: dimethylsulhpoxide
dw: dry weight
EC: European Commission
EC number: EINECS and ELINCS number
EC50: Half maximal effective concentration
EINECS: European Inventory of Existing Commercial Chemical Substances
ELINCS: European List of Notified Chemical Substances
ERC: Enviromental Release Category
ES: Exposure scenario
Irrit.: Irritation
LC50: Lethal concentration, 50 %
LD50: Median Lethal dose
LOAEC: Lowest Observed Adverse Effect Concentration
MK value: Maximum Concentration value

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NOAEC: No Observed Adverse Effect Concentration
NOEC: No Observed Effect Concentration
OECD: Organisation for Economic Cooperation and Development
PBT: Persistent, Bioaccumulative and Toxic *Version 1.0 –30.11.2010 16 / 18* PMDI: Polymethylene polyphenyl poliisocyanate
PNEC: Predicted No Effect Concentration
PROC: Process category
REACH: The Registration, Evaluation, Authorisation and Restriction of Chemicals
Resp.: Respiratory
Sens.: Sensitisation
STEL value: Short Term Exposure Limit value
STOT: Specific Target Organ Toxicity
STOT SE: Specific target organ toxicity — single exposure
STOT RE: Specific target organ toxicity — repeated exposure
STP: Sewage Treatment Plant
SU: Sector of use
Tox.: Toxicity
TWA value: Time Weighted Average value
vPvB: Very Persistent and Very Bioaccumulative
16.3. **Key literature references and sources for data**: Registration dossier for MDI homopolymer (CAS 25686-28-6).

16.4. **Classification for mixtures and used evaluation method according to Regulation (EC) 1207/2008 (CLP):**

Classification according to Regulation (EC) 1207/2009	Classification procedure
Acute Tox. 4; H332	Read-across.
Skin Irrit. 2; H315	Read-across.
Eye Irrit. 2A; H319	Read-across.
Resp. Sens.1; H334	Read-across.
Skin Sens. 1; H317	On basis of test data.
Carc. 2; H351	Read-across.
STOT SE 3; H335	Read-across.
STOT RE 2; H373	Read-across.

16.5. **Relevant R-, S-, H- and P-phrases**

R-phrases:

R20	Harmful by inhalation.
R36/37/38	Irritating to eyes, respiratory system and skin.
R42/43	May cause sensitization by inhalation and skin contact.
R48/20	Harmful: danger of serious damage to health by prolonged exposure through inhalation.
R40	Limited evidence of a carcinogenetic effect.

S-phrases:

S38	In case of insufficient ventilation, wear suitable respiratory equipment.
S1/2	Keep locked up and out of reach of children.
S23	Do not breathe vapour.
S36/37	Wear suitable protective clothing and gloves.
S45	In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

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H-phrases:

H351	Suspected of causing cancer <state route of exposure if it is conclusively proven that no other routs of exposure cause the hazard>.
H332	Harmful if inhaled.
H319	Causes serious eye irritation.
H335	May cause respiratory irritation.
H315	Causes skin irritation.
H334	May cause allergy or asthma symptoms or breathing difficulties if inhaled.
H317	May cause an allergic skin reaction.
H373	May cause damage to organs <or state all organs affected, if known> through prolonged or repeated exposure <state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard>. Respiratory system. Inhalation.

P- phrases:

P260	Do not breathe dust/fume/gas/mist/vapours/spray.
P280	Wear protective gloves/protective clothing/eye protection.
P285	In case of inadequate ventilation wear respiratory protection.
P302+P352	IF ON SKIN: Wash with plenty of soap and water.
P304+P340	IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing.
P305+P351+P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P309+P311	IF exposed or if you feel unwell: Call a POISON CENTER or doctor/physician.

Annex 1. Exposure scenario (ES)

Approved by	:	Ümit ÇAKAZ
Approval date	:	10/12/2015
Supersedes	:	Not applicable, original version.
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