TC NES SUBGROUP ON IDENTIFICATION OF PBT AND VPVP SUBSTANCES

RESULTS OF THE EVALUATION OF THE PBT/VPVB PROPERTIES OF:

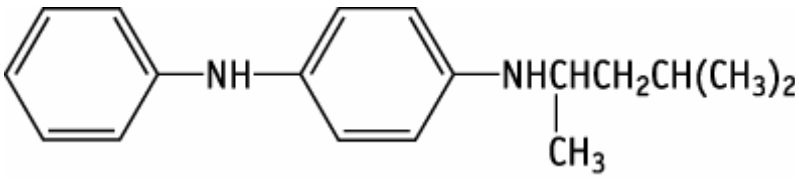
Substance name: N-1,3-Dimethylbutyl-N'-phenyl-p-phenylenediamine (6PPD)

EC number: 212-344-0

CAS number: 793-24-8

Molecular formula: $C_{18}H_{24}N_2$

Structural formula:



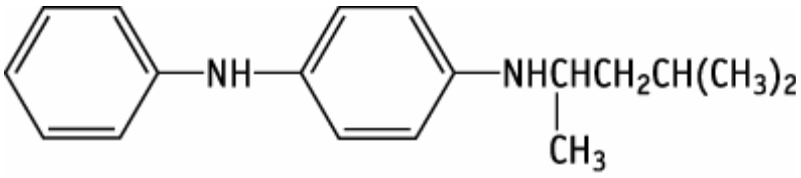
Summary of the evaluation:

The substance is not considered to be a PBT substance. It does not meet the P criterion. It does meet the screening criteria for B and T.

JUSTIFICATION

1 IDENTIFICATION OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

Name: N-1,3-Dimethylbutyl-N’-phenyl-p-phenylenediamine (6PPD)
EC Number: 212-344-0
CAS Number: 793-24-8
IUPAC Name: N-(4-Methyl-2-pentyl)-N-phenyl-1,4-diaminobenzene
Molecular Formula: $C_{18}H_{24}N_2$
Molecular Weight: 268.5
Structural formula:



Synonyms: N-Dimethylbutyl-N'-phenyl-p-phenylendiamine

N-(4-Methyl-2-pentyl)-N-phenyl-1,4-diaminobenzene (IUPAC)

N-(4-Methyl-2-pentyl)-N-phenyl-1,4-benzenediamine

1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N´-phenyl- (CA-index)

4-(Dimethylbutylamino)diphenylamine

Wingstay 300

Flexozone 7F

Santoflex 13

Vulkanox 4020

The abbreviation 6PPD will be used in this assessment.

1.1 Purity/Impurities/Additives

Purity: > 98 % w/w (industrial grade substance)

Impurities:

N,N- bis-(4-N'-(1',3'-Dimethylbutyl)aminophenyl)-N-phenylamine

N-3'(2',6',8'-Trimethylnonyl)-N'-phenyl-1,4-phenylenediamine (= N-(1´-(2´-

Methylpropyl)-3´,5´-dimethylhexyl)-N´-phenyl-1,4-phenylene diamine)

N-(4-aminophenyl)-aniline

(OECD, 2004).

1.2 Physico-Chemical properties

Table 1 Summary of physico-chemical properties

REACH ref Annex, §	Property	Value	Comments
V, 5.1	Physical state at 20 C and 101.3 KPa	Brown solid	
V, 5.2	Melting / freezing point	50 °C	
V, 5.3	Boiling point	ca. 370 °C	calculated
V, 5.5	Vapour pressure	6.85 × 10-3 Pa	calculated
V, 5.7	Water solubility	1 mg/l at 20 °C	
V, 5.8	Partition coefficient n-octanol/water (log value)	4.68	Calculated by KOWWIN v1.66
VII, 5.19	Dissociation constant	Not available	

2 MANUFACTURE AND USES

Not relevant.

3 CLASSIFICATION AND LABELLING

6PPD is not currently classified as dangerous for the environment under the Dangerous Substances Directive (67/548/EEC). Manufactures apply the classification R43 May cause sensitization by skin contact and R50-53 Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment (OECD, 2004).

3.1 Degradation (P)

3.1.1 Abiotic degradation

Hydrolysis

Several studies indicate that 6PPD undergoes abiotic degradation in water. The reaction is dependent on the presence of oxygen and heavy metals, pH-value, temperature, and irradiation. The major degradation products are 4-hydroxydiphenylamine, N-phenyl-p-benzoquinone monoimine and 1,3-dimethylbutylamine.

A study investigated the degradation of several rubber chemicals in aerated water (Monsanto 1979a). Within 25 h, 60 % of the initial 1 mg/l 6PPD solution was degraded yielding a half life of less than 1 day at 24 °C. A later Monsanto (1981) study on the biodegradation of 6PPD also examined the stability of 6PPD in aqueous test solutions under aerobic conditions. The half lives of 6PPD were 6.8 h (at 24 °C) in sterile, deionized water, 3.9 h in sterile Mississippi river water containing traces of heavy metals (at 24 °C) and 2.9h (at 24 °C) in biologically active Mississippi river water. Kretzschmar and Neyen (1992) report that 6PPD is stable for at least 4 weeks in aqueous solutions at pH 2 in the cold, but will be degraded at neutral or basic pH within a few hours.

Degradation of 6PPD in buffered aerobic solution and environmental water was examined in a study similar to OECD TG 111 (Bayer Industry Services 2003). 6PPD degradation in aerobic solutions is dependent on the temperature and on heavy metals. In buffered aerobic solution at 50°C the half life of 6PPD is 5 h, which is increased to about 14h at 26 °C. To simulate environmental conditions, 6PPD was dissolved in algae nutrient medium containing traces of ions of heavy metals such as Mn, Co, Cu, Mo, and Zn. Compared to buffered aerobic solution, in algae medium the half life period was significantly decreased to 8 h at 26 °C. 4-Hydroxydiphenylamine was identified as the major aromatic intermediate of 6PPD degradation under all conditions (Bayer Industry Services 2003). From the time course of 4-hydroxydiphenylamine formation and degradation at 50 °C, it is apparent that 4-hydroxydiphenylamine is not stable in aerobic media.

Photodegradation

In the atmosphere, 6PPD is expected to be photodegraded rapidly by OH-radicals. The calculated half-life of 6PPD in air due to indirect photodegradation is 1 h. Since 6PPD absorbs UV-B radiation it is expected that 6PPD will undergo direct photolysis due to absorbance of UV light (OECD, 2004).

3.2 Biotic degradation

In an OECD 301C ready biodegradability test (based on BOD) only ca. 2 % of 6PPD was biodegraded. Based on HPLC, ca. 92 % of 6PPD was removed within 28 d indicating that 6PPD was transformed. About two-thirds of the theoretical amounts of the transformation products 4-hydroxydiphenylamine and N-phenyl-p-benzoquinone monoimine, and 97 % of the 1,3-dimethylbutylamine were recovered. Although the 2-ring intermediates were degraded further, neither aniline nor p-benzoquinone, were recovered in significant quantities (CERI 1994).

In another respirometry test according to OECD 301C, 13 - 40 % of 6PPD were mineralized within 28 d. The difference between the results of 2 replicates was explained by the poor solubility of 6PPD (Bayer AG 1984).

In an insufficiently described shake flask test comparable to an US EPA 40 CFR method, measuring biodegradation from CO2 release, only part of 6PPD (7 %) was completely degraded after 32 d. However, primary degradation was also checked with aerated water, and a rapid 6PPD decline (60% primary degradation in 25 h) of a 1 mg/l solution was observed (Monsanto 1979a). It is not excluded that abiotic degradation occurred during these tests.

In conclusion, 6PPD is not readily biodegradable but primary degradation has been shown to occur in biodegradation tests with the formation of 4- hydroxydiphenylamine, N-phenyl-p-benzoquinone monoimine and 1,3-dimethylbutylamine.

3.2.1 Other information [1]

3.2.2 Summary and discussion of persistence

6PPD is not readily biodegradable but it is degraded rapidly in water. The reaction is dependent on the presence of oxygen and heavy metals, pH-value, temperature, and irradiation. A half-life for 6PPD of 6.8 h at 24 °C has been determined in sterile, deionized water and a half-life of 2.9h at 24 °C in biologically active Mississippi river water. The major degradation products are 4-hydroxydiphenylamine, N-phenyl-p-benzoquinone monoimine and 1,3-dimethylbutylamine.

3.3 Environmental distribution

3.3.1 Adsorption

3.3.2 Volatilisation

3.4 Bioaccumulation (B)

3.4.1 Screening data[2]

The calculated log Kow value of 4.68 for 6PPD indicates that the screening criterion for B is met. The BCF has been calculated to be 801 using the BCF-Program v2.14. However, given the abiotic degradation of 6PPD in water, the bioaccumulation potential of its degradation products should be considered. For 4-hydroxydiphenylamine a BCF of 30 has been calculated using the measured log Kow of 2.82 with BCFWIN v2.14 (OECD, 2004). Fish BCFs have been experimentally determined for N-Phenyl-p-benzoquinone monoimine and for 1,3-Dimethylbutylamine, as discussed below.

3.4.2 Measured bioaccumulation data[3]

No measured BCFs are available for 6PPD itself. However, fish BCFs have been determined in Cyprinus carpio for two of the degradation products of 6PPD (OECD, 2004). The measured BCF for N-Phenyl-p-benzoquinone monoimine in fish is < 1.2 – 23 and for 1,3-Dimethylbutylamine is < 1.7 – 17.

3.4.3 Other supporting information[4]

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1 For example, half life from field studies or monitoring data

2 For example, log K_{ow} values, predicted BCFs

3 For example, fish bioconcentration factor

4For example, measured concentrations in biota

3.4.4 Summary and discussion of bioaccumulation

Although 6PPD meets the screening criterion for B, with a calculated log Kow value of 4.68, the bioaccumulation potential of its degradation products is more relevant since it degrades rapidly in water:

4-hydroxydiphenylamine - a BCF of 30 has been calculated using the measured log Kow of 2.82 with BCFWIN v2.14 (OECD, 2004).Thus the screening criterion for B is not met.

N-Phenyl-p-benzoquinone monoimine – the measured BCF in fish is < 1.2 – 23. Thus the criterion for B/vB is not met.

1,3-Dimethylbutylamine – the measured BCF in fish is < 1.7 – 17. Thus the criterion for B/vB is not met.

3.5 Secondary poisoning

4 HUMAN HEALTH HAZARD ASSESSMENT

The mammalian toxicity for 6PPD has been reviewed as part of the OECD SIDS programme and a summary of the main findings of this review is given below in Table 2.

Table 2 Summary of mammalian toxicity data

Test	Species	Results
Acute oral (single dose) studies	Rat	LD50 500-1000 mg/kg bw (females) and 1000-2000 mg/kg bw (males)
Repeated dose studies – oral exposure via feed	Rat	13 week NOAEL 75mg/kg bw/day (anaemia)
Developmental toxicity/ teratogenicity	Rat & Rabbit	No indications for effects up to oral doses of 250 mg/kg bw/day in rats (highest dose tested). Exposure during the gestation period demonstrated the absence of a fetotoxic or teratogenic potential and of maternal toxicity in rabbits for doses up to 30 mg/kg bw/day (highest dose tested).

5 ENVIRONMENTAL HAZARD ASSESSMENT

5.1 Aquatic compartment (including sediment)

5.1.1 Toxicity test results

5.1.1.1 Fish

Acute toxicity

The available toxicity data for 6PPD have been reviewed and validated under the OECD SIDS programme (OECD, 2004). The following value was reported for acute toxicity to Oryzias latipes in a flow-through test: 96 h LC50 of 0.028 mg/l based on the geometric mean of measured concentrations. From the robust study summary, the 96h NOEC appears to be 0.008 mg/l, although this value is not reported in the SIAR.

Long-term toxicity

No data available.

5.1.1.2 Aquatic invertebrates

Acute toxicity

The available toxicity data for 6PPD have been reviewed and validated under the OECD SIDS programme (OECD, 2004). The following values were reported for acute toxicity to Daphnia magna: 48h EC50 0.23 mg/l, 48h NOEC 0.05 mg/l (flow-through test), 48h EC50 0.82 mg/l, 48h NOEC 0.56 mg/l (static test).

In addition, a study was conducted with Daphnia magna to examine how the toxicity of 6PPD solutions changed with abiotic degradation and the formation of degradation products (OECD, 2004). Freshly prepared 6PPD solution exhibited a nominal 48 h LC50 of 0.51 mg/l and a 48 h NOEC of 0.25 mg/l. Stirring for 24 h in an open beaker at room temperature decreased the toxicity of the test solution significantly. The 48 h NOEC of aged 6PPD test solution was > 1 mg/l (highest exposure concentration; Monsanto 1984). This observed reduction in toxicity of the 6PPD solution is presumably due to oxidation and/or hydrolysis of 6PPD.

Long-term toxicity

No data available.

5.1.1.3 Algae and aquatic plants

The available toxicity data for 6PPD have been reviewed and validated under the OECD SIDS programme (OECD, 2004). A 96h EC50 of 0.6 mg/l and 96h NOEC of 0.2 mg/l were reported for 6PPD for the green alga Selenastrum capricornutum based on changes in chlorophyll a concentrations and cell density.

5.1.2 Sediment organisms

5.1.3 Other aquatic organisms

5.2 Terrestrial compartment

5.3 Atmospheric compartment

5.4 Indirect exposure via the food chain

6 PBT AND vPvB

6.1 PBT, vPvB assessment

Persistence: Ready biodegradability tests show that the substance is not readily biodegradable but that primary degradation occurs. Degradation is dependent on the presence of oxygen and heavy metals, pH-value, temperature, and irradiation. The major degradation products are 4-hydroxydiphenylamine, N-phenyl-p-benzoquinone monoimine, and 1,3-dimethylbutylamine. A half-life for 6PPD of 2.9h at 24°C has been determined in river water. Given the rapid degradation of 6PPD in water under environmental conditions and the lack of concern for the bioaccumulation potential of the major degradation products (see below), the P criterion is not met.

Bioaccumulation: Although 6PPD meets the screening criterion for B, with a calculated log Kow value of 4.68, the bioaccumulation potential of its degradation products is more relevant since it degrades rapidly in water:

4-hydroxydiphenylamine - a BCF of 30 has been calculated using the measured log Kow of 2.82 with BCFWIN v2.14 (OECD, 2004).Thus the screening criterion for B is not met.

N-Phenyl-p-benzoquinone monoimine – the measured BCF in fish is < 1.2 – 23. Thus the criterion for B is not met.

1,3-Dimethylbutylamine – the measured BCF in fish is < 1.7 – 17. Thus the criterion for B is not met.

Toxicity: The lowest LC50 is 0.028 mg/L for fish. No chronic ecotoxicity studies are available. The screening T criterion is met.

Summary: 6PPD does not meet the P criteria, and so is not considered a PBT substance according to the EU criteria.

INFORMATION ON USE AND EXPOSURE

Not relevant as substance is not identified as a PBT.

OTHER INFORMATION

The information used in this report was taken from the following sources:

Bayer AG (1984) Biologischer Abbau von Vulkanox 4020. Unpublished study WV-LE Umweltschutz/AWALU 1984-12-3

Bayer Industry Services (2003) Report on N-(1,3-Dimethylbutyl)-N´-phenyl-1,4-phenylenediamine(6PPD). Investigation on stability in aqueous test solutions (unpublished)

BUA (1996) GDCh-Advisory Committee on Existing Chemicals of Environmental Relevance (BUA) Report 208, N-(1,3-Dimethylbutyl)-N'-phenyl-1,4-phenylene diamine (6PPD). S Hirzel Wissenschaftliche Verlagsgesellschaft, Stuttgart

CERI (1994) Chemicals Evaluation and Research Institute (Kurume, Japan) Test 21203 (IUCLD data set)

Kretzschmar HJ, Neyen V (1992) HPLC-Analyse von N-Phenyl-N´-(1.3-dimethylbutyl)-pphenylenediamin (6PPD) im Migrat von Gummi-Bedarfsgegenstaenden. Deutsche Lebensmittel-Rundschau 88 (12): 387 - 390

Monsanto (1979a) Environmental persistence screening of selected rubber chemicals. Unpublished study ES-78-SS-28

Monsanto (1981) Degradation of N-(1,3-Dimethylbutyl)-N´-phenyl-1,4-phenylenediamine Unpublished study ES-81-SS-52

OECD (2004). OECD SIDS Dossier for N-(1,3-Dimethylbutyl)-N´-phenyl-1,4-phenylenediamine, CAS No. 793-24-8.