TC NES SUBGROUP ON IDENTIFICATION OF PBT AND VPVP SUBSTANCES

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

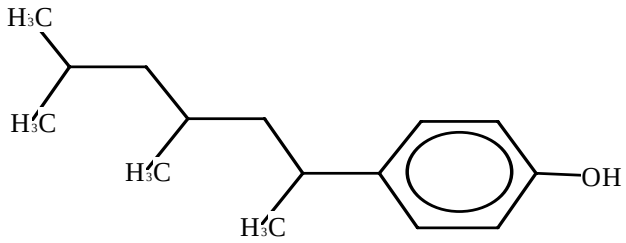
Substance name: Phenol, 4-nonyl-, branched (NP); Nonylphenol

EC number: 284-325-5; 246-67-0

CAS number: 84852-15-3; 25154-52-3

Molecular formula: $C_{15}H_{24}O$

Structural formula (idealised structure):



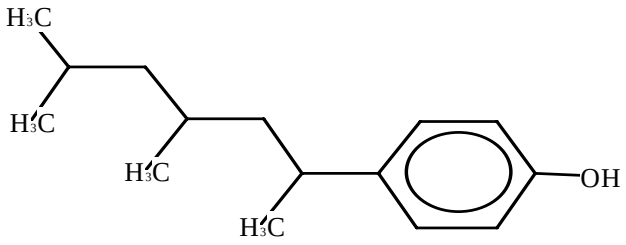
Summary of the evaluation:

Nonylphenol is not considered to be a PBT substance. It is very toxic to aquatic organisms (LC/EC_{50} < 1 mg/l) and fulfils the T criterion. The BCF of NP is in the range of 1300, therefore the B criterion is not fulfilled. The substance is inherently biodegradable and should not be considered as potentially persistent, therefore it does not meet the P criterion.

JUSTIFICATION

1 IDENTIFICATION OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

Name: Phenol, 4-nonyl-, branched; Nonylphenol
EC Number: 284-325-5; 246-67-0
CAS Number: 84852-15-3; 25154-52-3
IUPAC Name: 4-Nonylphenol, branched; Nonylphenol
Molecular Formula: $C_{15}H_{24}O$
Structural Formula:
(idealised structure)



Molecular Weight: 220.34 g/mole
Synonyms: NP, Nonylphenol, para-Nonylphenol, Monoalkyl (C3-9) phenol

1.1 PURITY/IMPURITIES/ADDITIVES

The purity of commercial nonylphenol is reported as 90% w/w with the following impurities; 2-nonylphenol (5% w/w) and 2,4-dinonylphenol (5% w/w). No additives are reported.

1.2 PHYSICO-CHEMICAL PROPERTIES

A risk assessment has been carried out for 4-nonylphenol (branched) and nonylphenol, CAS Nos. 84852-15-3 and 25154-52-3 (EU RAR, 2002). The physico-chemical properties summarised in Table 1 are taken from the risk assessment. The varied degree of branching in the nonyl group may be a factor in the variability of the 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	Clear to pale-yellow viscous liquid	Slightly phenolic odour
V, 5.2	Melting / freezing point	ca. -8°C (pour point measured according to DIN ISO 3016)	May vary according to the production process used
V, 5.3	Boiling point	290-300°C (commercially available material)	Undergoes thermal decomp before it reaches its boiling pt
V, 5.5	Vapour pressure	ca. 0.3 Pa at 25°C	Extrapolated value
V, 5.7	Water solubility	6 mg/l at 20°C	May be pH dependent
V, 5.8	Partition coefficient n-octanol/water (log value)	4.48	Measured value
VII, 5.19	Dissociation constant	~ 10 (could be higher)	Based on pKa of 9.9 for phenol

2 MANUFACTURE AND USES

One of the principal uses of NP in the past was the production of NP-ethoxylates which had a wide range of dispersive uses. A major use of NP-ethoxylates was in industrial and institutional cleaning. Under some conditions, NP can be one of the breakdown products of NP-ethoxylates. Following the risk assessment under the Existing Substances Regulation, most uses of NP-ethoxylates were prohibited under Directive 2003/53/EC, with only a small number of exemptions either for specific uses or where the waste waters are recycled or incinerated.

3 CLASSIFICATION AND LABELLING

The classification and labelling of NP is listed in Annex I to Directive 67/548/EEC (28th ATP; 2001) as follows:

R 62 (Repr. Cat 3) – Possible risk of impaired fertility;

R 63 (Repr. Cat 3) – Possible risk of harm to the unborn child;

Xn;R22 – Harmful if swallowed;

C; R34 – Causes burns;

N; R50-53 – Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

4 ENVIRONMENTAL FATE PROPERTIES

4.1 DEGRADATION (P)

4.1.1 Abiotic degradation

NP released to the atmosphere is likely to be degraded by reaction with hydroxyl radicals. The half-life for the reaction of hydroxyl radicals with nonylphenol has been calculated as 0.3 days from a rate constant of 5.4×10^{-11} cm^3 $molec^{-1}$ s^{-1} which was estimated using AOP programme, Syracuse, 1991 (EU RAR, 2002). However, NP is not very volatile and is unlikely to enter the atmosphere in large amounts. NP is not thought to contribute to low-level ozone formation.

Hydrolysis and photolysis are thought to be negligible removal processes for this substance in the aquatic environment.

4.1.2 Biotic degradation

Ready biodegradation test results are available for nonylphenol. A limited number of studies from non-standard tests are also available.

In a modified Sturm test, NP achieved a degradation level of 0% within 32 days, with and without emulsifier. In a second study, again using a modified Sturm test, NP without emulsifier achieved a degradation level of 0% within 40 days. With emulsifier, a degradation level of 78% was achieved within 40 days. Although not readily biodegradable, these results indicate the NP may undergo biodegradation with adapted microorganisms and could be considered to be inherently biodegradable (EU RAR, 2002).

Two other ready biodegradation tests have been carried out using a commercial form of NP containing a highly branched alkyl chain. In an OECD 301 B test, ~ 10% biodegradation was seen after 10 days, rising to 53% after 28 days. In an OECD 301 F test (manometric respirometry), 19% degradation of NP was seen after 10 days rising to 62% in 28 days. Although NP shows significant biodegradation, it fails to meet the criteria for ready biodegradability (10-day window). These results indicate inherent biodegradability rather than ready biodegradability (EU RAR, 2002).

4.1.3 Other information [1]

The available data indicate that NP undergoes biodegradation in sediment and soil systems (EU RAR, 2002). Results of the studies indicate that NP undergoes microbial degradation after a period of induction of the microorganisms. A half life of 100 days for mineralisation of a straight chain NP in soil was reported, although a branched chain isomer would have a longer half-life than this. Different isomers of NP were found to degrade more easily than others. In general, increased branching in alkyl chains leads to a reduction in biodegradability.

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

4.1.4 Summary and discussion of persistence

Although NP does not meet the stringent criteria for ready biodegradability (10 day window), significant biodegradation was seen after 28 days (53 and 62%) in two ready biodegradation tests. It was concluded that NP is inherently biodegradable and therefore should not be regarded as potentially persistent. There is evidence from other tests that NP will undergo substantial biodegradation in surface water and soil, possibly after a period of adaptation. Half-lives for biodegradation in soil of 300 days and surface water of 150 days have been estimated. The estimated half-lives are thought to be representative of the worst case for mineralization of NP. However, given that biodegradation of NP depends on several factors, actual half-lives could be different than the estimated values depending on the actual conditions present.

It is concluded that nonylphenol does not meet the P criterion.

4.2 ENVIRONMENTAL DISTRIBUTION

4.2.1 Adsorption

4.2.2 Volatilisation

A low value of Henry's Law Constant of 11.02 Pa m^3 mol^{-1} indicates that volatilization is unlikely to be a significant removal mechanism of NP from water and the substance is unlikely to be transported very far in the atmosphere (EU RAR, 2002).

4.3 BIOACCUMULATION (B)

4.3.1 Screening data[2]

NP just fails to meet the screening B criterion based on a measured log K_{ow} of 4.48. The fish BCF used in the risk assessment (1280) was calculated using this value of log K_{ow} and is below the cut-off level for fulfilling the B/vB criterion. This value is in good agreement with the measured BCF values reported in the risk assessment.

4.3.2 Measured bioaccumulation data[3]

A measured fish BCF of 1300 (based on a fresh weight basis) was reported for NP. However, it may overestimate the BCF since fish are known to metabolise NP. More reliable BCFs with a mean of 741 have been measured and are of a similar order of magnitude (EU RAR, 2002). These values imply that the substance is not bioaccumulative within the PBT criteria.

No BMFs are available from fish studies in the assessment.

BCFs of around 2000-3000 (based on a fresh weight basis) have been measured for mussels (EU RAR, 2002). These values are above the cut-off level (BCF > 2000) and may result in the

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

3 For example, fish bioconcentration factor

B criterion being met. However, BCFs of around 340 have also been reported using caged mussels. The use of BCFs from species other than fish in assessing the risk of secondary poisoning has been established in risk assessments. However, there is a difference between using BCFs from mussels in estimating exposure concentrations for secondary poisoning and using them against this criterion where the thresholds were set using almost entirely log K_{ow} and fish BCFs. The aim of the B criterion is to identify substances which have the potential to accumulate through the marine food chain and the possibility of metabolism should be considered. Mussels or shellfish are more likely to take up a substance in non-dissolved, particulate form than fish who tend to eat food rapidly before it has chance to absorb much from the water. Food for mussels on the other hand may remain in the water for longer. Uptake with food or in particulates is a potentially relevant route, but this type of uptake in mussels is not comparable to that in fish. Also in the case of mussels it is not clear what to compare the level of substance in the organism with, for example water concentration or food. Therefore, the scale of threshold values for mussels ought to be different.

4.3.3 Other supporting information[4]

P-*tert*-octylphenol (OP) (CAS No. 140-66-9) is chemically very closely related to NP. OP has recently been evaluated and it was concluded that it does not fulfil the EU PBT criteria. A fact sheet for OP refers to the BCF value as evaluated in the NP risk assessment and the log K_{ow} values for both substances are comparable.

4.3.4 Summary and discussion of bioaccumulation

Available data indicate that NP accumulates to a significant extent in aquatic organisms with BCFs of up to 1,300 in fish based on a fresh weight basis. It should be noted that this value may over estimate the BCF since fish are known to metabolise NP and more reliable values with a mean of 741 have been measured. However, a BCF in the range of 1,300 is below the cut-off level for bioaccumulation (BCF > 2,000). Based on the log K_{ow} of 4.48, NP just fails to meet the screening B criterion, and the BCF estimated using this value of log K_{ow} is 1,280 which is in good agreement with the measured value of 1,300. The use of BCF values for mussels is not considered appropriate when considering the B criterion. It is concluded that this substance does not to meet the B criterion.

4.4 SECONDARY POISONING

5 HUMAN HEALTH HAZARD ASSESSMENT

Data are not reviewed for this report.

[4]For example, measured concentrations in biota

6 ENVIRONMENTAL HAZARD ASSESSMENT

6.1 AQUATIC COMPARTMENT (INCLUDING SEDIMENT)

Acute and chronic toxicity data for NP are available for fish, invertebrate and algae species. These data have been taken from the EU risk assessment for 4-nonylphenol (branched) and nonylphenol, CAS Nos. 84852-15-3 and 25154-52-3. The lowest results for fish, invertebrates and algae are summarised in the relevant sections.

A chronic NOEC of 0.0033 mg/l was reported for NP in a 72-hour toxicity test with the freshwater alga *Scenedesmus suspicatus*. Endocrine effects have been confirmed for this substance.

On the basis of the available data for this substance, the T-criterion is considered to be fulfilled.

6.1.1 Toxicity test results

6.1.1.1 Fish

Acute toxicity

LC_{50} (96-hour) = 0.128 mg/l for *Pimephales promelas*, freshwater species;

LC_{50} (96-hour) = 0.017 mg/l for *Pleuronectes americanus*, seawater species, result should be used with care as only a summary report is available;

LC_{50} (96-hour) = 0.310 mg/l for *Cyprindon variegatus*, seawater species.

Long-term toxicity

LOEC (33-day) = 0.014 mg/l, NOEC(33-day) = 0.0074 mg/l for *Pimephales promelas* embryos (survival);

LOEC (28-day) = 0.193 mg/l, NOEC(28-day) = 0.0775 mg/l for *Pimephales promelas* (mortality).

6.1.1.2 Aquatic invertebrates

Acute toxicity

EC_{50} (96-hour) = 0.0207 mg/l for *Hyalella azteca*, freshwater amphipod;

EC_{50} (48-hour) = 0.085 mg/l for *Daphnia magna*, freshwater species;

LC_{50} (96-hour) = 0.043 mg/l for *Mysidopsis bahia*, marine invertebrate;

LC_{50} (96-hour) = 0.038 mg/l for *Mulinia lateralis*, marine invertebrate, use result with care as limited details given in test report.

Long-term toxicity

LOEC (20-day) = 0.091 mg/l, NOEC(20d) = 0.042 mg/l for *Chironomus tetans*, freshwater species (survival);

NOEC (21-day) = 0.024 mg/l for *Daphnia magna*, freshwater species (surviving offspring);

NOEC (21-day) = 0.0039 mg/l for *Mysidopsis bahia*, seawater species (length).

6.1.1.3 Algae and aquatic plants

EC_{50} (72-hour) = 0.0563 mg/l for *Scenedesmus subspicatus*, freshwater species (biomass);

EC_{50} (96-hour) = 0.027 mg/l for *Skeletonema costatum*, saltwater species (biomass);

EC_{10} (72-hour) = 0.0033 mg/l for *Scenedesmus subspicatus*, freshwater species (biomass).

Note, no long-term NOEC available, EC_{10} value taken to be equivalent to a long-term NOEC in accordance with the TGD guidance.

6.1.2 Sediment organisms

6.1.3 Other aquatic organisms

LC_{50} (30-day) = 260 mg/kg dw, EC_{50}(30d) = 220 mg/kg dw for *Rana catesbiana* (tadpole);

At 10, 20 and 30 days, LOEL = 390 mg/kg dw and NOEL = 155 mg/kg dw.

The authors of the study concluded that the levels of NP in water were high enough to cause toxicity and it was not possible to attribute the toxic effects to either water or sediment exposure.

6.2 TERRESTRIAL COMPARTMENT

For NP there are toxicity data available for terrestrial micro-organisms, plants and animals. Terrestrial invertebrates appear to be the most sensitive group.

EC_{50} (21-day) = 13.7 mg/kg, EC_{10} (21-day) = 3.44 mg/kg (reproduction) for *Apporec-todea calignosa* (earthworm).

The 21-day EC_{10} value for reproduction is taken as being equivalent to a NOEC.

6.3 ATMOSPHERIC COMPARTMENT

No data are available on the effects on NP through aerial exposure to non-mammalian organisms.

6.4 INDIRECT EXPOSURE VIA THE FOOD CHAIN

7 PBT AND VPVB

7.1 PBT, VPVB ASSESSMENT

Persistence: although NP does not meet the stringent criteria for ready biodegradability, it is inherently biodegradable and therefore should not be regarded as potentially persistent. It is concluded that NP does not fulfill the P criterion.

Bioaccumulation: available data indicate that the BCF for NP is in the range of 1,300 and therefore below the cut-off level for bioaccumulation. Nonylphenol just fails to meet the screening B criterion based on a measured log K_{ow} of 4.48. The fish BCF calculated using this value of log K_{ow} is 1,280, which is in good agreement with the measured values. The substance is considered not to meet the B criterion.

Toxicity: NP is very toxic to aquatic organisms (LC/EC_{50} < 1 mg/l) and fulfils the T criterion for the environment. A chronic NOEC of 0.0033 mg/l was reported for NP in a 72-hour toxicity test with the freshwater alga *Scenedesmus suspicatus*. Endocrine effects have also been confirmed for this substance.

Summary: although NP does not meet the criteria for readily biodegradable, it is inherently biodegradable and should therefore not be considered as potentially persistent. Thus the P criterion is not fulfilled. This substance does not meet the screening B criterion as the BCF is in the range of 1,300, which is below the cut-off level for bioaccumulation and the log K_{ow} is 4.48. Although the T criterion is fulfilled, the overall conclusion is NP does not meet the criteria for a PBT substance.

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:

European Union Risk Assessment Report, 4-Nonylphenol (branched) and nonylphenol, CAS Nos: 84852-15-3 and 25154-52-3. European Communities 2002, EUR 20387 EN.