TC NES SUBGROUP ON IDENTIFICATION OF PBT AND VPVP SUBSTANCES

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

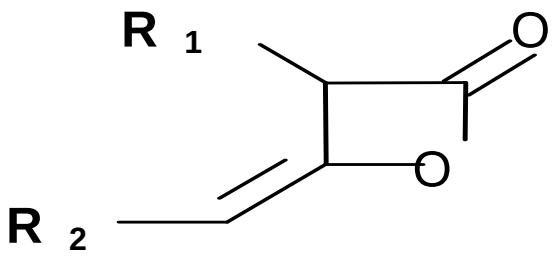
Substance name: Alkyl ketene dimer (AKD)

EC number: 284-932-5

CAS number: 84989-41-3

Molecular formula: $C_{28}H_{52}O_2$ to $C_{36}H_{68}O_2$

Structural formula:



Where R1 = $C_{12\text{-}16}$ and R2 = $C_{12\text{-}16}$

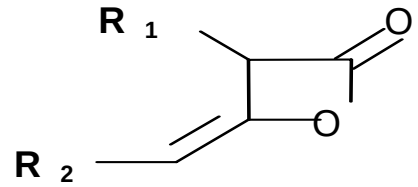
Summary of the evaluation:

AKD is not considered to be a PBT or a vPvB substance. The high predicted log K_{ow} and BCF values indicate that AKD has the potential to bioaccumulate. However, the substance does not meet the P criterion or the T criterion.

JUSTIFICATION

1 IDENTIFICATION OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

Name: Alkyl ketene dimer
EC Number: 284-932-5
CAS Number: 84989-41-3
IUPAC Name: 2-Oxetanone, 3-C12-16-alkyl-4-C13-17-alkylidene derivatives
Molecular Formula: $C_{28}H_{52}O_2$ to $C_{36}H_{68}O_2$
Structural Formula:



Where R1 = C_{12-16} and R2 = C_{12-16}

Molecular Weight: 420.73 to 532.94
Synonyms: AKD, Alkylketendimers, Alkyl ketene dimer wax

1.1 PURITY/IMPURITIES/ADDITIVES

Purity ranges from 80 to 95% alkyl ketene dimer. Typical impurities include; unreacted fatty acid (~ 2-5%), hydrolysed alkyl ketene dimer (~ 1-5%) and alkyl ketene trimers and tetramers (~ 2-10%).

1.2 PHYSICO-CHEMICAL PROPERTIES

The physico-chemical properties summarised in Table 1 are taken from the SIDS Initial Assessment Report for AKD prepared for SIAM 20, April 2005.

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	Solid	
V, 5.2	Melting / freezing point	43.6 – 56.4°C	Determined
V, 5.3	Boiling point	–	Decomposes above 200°C without boiling
V, 5.5	Vapour pressure	5.85×10^{-11} – 6.12×10^{-8} Pa	Calculated
V, 5.7	Water solubility	4.805×10^{-11} – 5.64×10^{-7} mg/l at 25°C	Calculated
V, 5.8	Partition coefficient n-octanol/water (log value)	> 6 (11.25 – 15.18)	Calculated
VII, 5.19	Dissociation constant		

Note: Data have been reported for a structurally related new chemical notified in the EU. Water solubility measured using the turbidimetric method is 0.3 mg/l (may not be particularly accurate) and log K_{ow} is 5.5.

2 MANUFACTURE AND USES

The only alkyl ketene dimer products currently available commercially are manufactured from mixtures of technical grade palmitic (C16) and stearic fatty acids (C18). The CAS number 84989-41-3 is considered to cover all of the commercial products of this type. The dominant product on the market, Aquapel® 364 is also manufactured from technical grade palmitic- and stearic acid and was chosen as the test sample because it is representative of what is available commercially.

All AKD produced is used in the paper and board industry as a paper sizing agent, to improve the resistance of the paper to water.

3 CLASSIFICATION AND LABELLING

This substance is not classified in the Annex I of Directive 67/548/EEC.

4 ENVIRONMENTAL FATE PROPERTIES

4.1 DEGRADATION (P)

4.1.1 Abiotic degradation

Model calculations (AOP v1.51) for indirect photolysis in air predicted 50% degradation after 3.7 hours. This suggests rapid photodegradation in air. However, given the use and physico-chemical properties of AKD, photodegradation is not seen as a relevant degradation pathway.

AKD is readily hydrolysed under neutral and alkaline conditions to form the dialkyl ketone. Hydrolysis studies are not available for the substance itself, but are available for the alkyl ketene dimer component of commercial AKD preparations. These showed half lives of between 23 and 140 hours at pH8 and 30°C.

The results of a study on the hydrolysis of a structurally related alkyl ketene dimer (notified as a new chemical in the EU under directive 92/32/EEC) indicate that AKD could be considered to hydrolyse under environmental conditions; pH 7 (half-life 10.4 hours at 30°C) and pH 9 (half-life 4.4 hours at 30°C).

A stability study carried out on an AKD dispersion at pH 3 over 4 weeks showed AKD losses of 4.5% and 16% at 25°C and 32°C, respectively. This indicates that the substance is more stable to hydrolysis at low pH.

4.1.2 Biotic degradation

AKD is poorly soluble in water and only marketed and used (in paper mills) as dispersions. The results of an OECD 301 B (Sturm) test and a MITI test for biodegradation indicate that dispersions of AKD are readily biodegradable (96%, > 60% within a 10 day window and > 94%, respectively over 28 days). The emulsifier used in these tests was naphthalene sulfonic acid, polymer with formaldehyde, sodium salt (CAS No. 9084-06-4).

More than 90% degradation (CO_2 evolution) was observed in a combination test for both biodegradation and elimination of AKD. The degradation observed in this test was attributed to

AKD since the contribution of the emulsifier cannot exceed its concentration in the test material (1.5% of TOC). In addition, the emulsifier is not readily biodegradable.

Less than 10% biodegradation over 28 days was seen in a manometric respirometry test carried out without an emulsifier. This is considered to be due to the substance separating from the aqueous phase and so not being in intimate contact with the bacteria.

The results of an OECD 302 A test on a structurally related alkyl ketene dimer (notified as a new chemical) indicate that this substance is inherently biodegradable showing 31% degradation in 28 days. Furthermore, this related substance has been clearly demonstrated to hydrolyse under neutral and alkaline conditions.

4.1.3 Other information [1]

4.1.4 Summary and discussion of persistence

Based on the available data, AKD is expected to hydrolyse readily under neutral and alkaline conditions in the environment. It is assumed to be more stable to hydrolysis at acidic pHs.

Due to the low solubility of AKD in water, standard test conditions in biodegradation studies are not applicable. Testing for biodegradation of insoluble substances may be facilitated by the admixture of small amounts of emulsifiers. Without an emulsifier, AKD separates from the aqueous phase preventing contact between the bacteria and the test material. When tested in the presence of small amounts of emulsifier, which increases the availability of the substance to micro-organisms, AKD has been shown to be readily biodegradable (>94% in 28 days). AKD is marketed and used only as a dispersion. A structurally related alkyl ketene dimer has been shown to be inherently biodegradable (31% in 28 days).

It is therefore concluded that AKD does not meet the P/vP criterion.

4.2 ENVIRONMENTAL DISTRIBUTION

4.2.1 Adsorption

A K_{oc} of 1.51×10^{7} – 2.0×10^{9} (PCKOCWIN v1.66) indicates that AKD will adsorb strongly to soil and sediment (SIAR, 2002).

4.2.2 Volatilisation

Henry's Law Constant was calculated as 0.643 – 6.2 atm m^3/mol using EPIWIN v3.10. This indicates that AKD could partition from water into the atmosphere. However, due to the low water solubility of AKD, this is unlikely to be an important route of transport in the environment.

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

4.3 BIOACCUMULATION (B)

4.3.1 Screening data[2]

The predicted log K_{ow} values of AKD range from 11.25 to 15.18, which suggests a high bioaccumulation potential. BCF values between 14 and 6×10^{15} were predicted using the polynomial QSAR given in the EU TGD for substances with log K_{ow} > 6. However, such QSAR estimations may not accurately represent true bioaccumulation potential and there is considerable uncertainty in these predicted BCF values.

4.3.2 Measured bioaccumulation data[3]

A bioaccumulation test is available for a structurally related alkyl ketene dimer (notified as a new chemical) and indicates that the test substance has a fish BCF < 100 (OECD 305). However, this result should be treated with caution since the test was carried out above the water solubility limit in the presence of a dispersant. There are inherent difficulties in testing the bioaccumulation of poorly soluble substances and this may not be the most appropriate method. Also, the water phase may not be the primary exposure route for a substance of low solubility.

BCFs predicted using a measured log K_{ow} of 5.5 for the same substance range from 3.2 to 343 respectively for C12:C12 AKD and C16:C16 AKD using BCFWIN v2.15. However, the BCF is predicted to be 9440 when the QSAR given in the EU TGD for substances with log K_{ow} < 6 is used. This also suggests that AKD has the potential to bioaccumulate.

4.3.3 Other supporting information[4]

4.3.4 Summary and discussion of bioaccumulation

Although there is uncertainty in the BCF values (14 – 6×10^{15}) predicted using the calculated log K_{ow} values of 11.25 to 15.18, high bioaccumulation potential of AKD cannot be excluded. A BCF of 9440 predicted using a measured log K_{ow} of 5.5 for the structurally related new chemical notification also suggests that AKD has the potential to bioaccumulate.

Therefore, it is concluded that AKD meets the screening B/vB criteria.

4.4 SECONDARY POISONING

5 HUMAN HEALTH HAZARD ASSESSMENT

Data are not reviewed for this report.

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

3 For example, fish bioconcentration factor

4For example, measured concentrations in biota

6 ENVIRONMENTAL HAZARD ASSESSMENT

6.1 AQUATIC COMPARTMENT (INCLUDING SEDIMENT)

Acute and chronic toxicity data are available for fish, invertebrate and algae species for this substance. These data have been taken from the SIDS Initial Assessment Report for AKD prepared for SIAM 20, April 2005.

6.1.1 Toxicity test results

6.1.1.1 Fish

Acute toxicity

LC_{50} (96-hour) > 10,000 mg/l (nominal) for *Danio rerio* (OECD 203, static system, pH 7.7 – 8.0). No effects were seen at the solubility limit of the test solution. No analysis of the test concentrations was carried out and the test substance could have hydrolysed. The presence of undissolved test material throughout the test suggests that a saturated solution had been prepared.

6.1.1.2 Aquatic invertebrates

Acute toxicity

EC_{50} (48-hour) > 500 mg/l (nominal) for *Daphnia magna* (Directive 79/831 EEC, C2, static system, pH 7.98 – 8.08). Hydrolysis of AKD may have occurred, but the presence of undissolved test material suggests that a saturated solution had been prepared. Although the actual test concentrations of AKD in the test are not known, the results of this study indicate that AKD is of low acute toxicity to Daphnia. This conclusion is supported by the results of the long-term Daphnia reproduction test.

Long-term toxicity

A 21-day Daphnia reproduction study was carried out on a dispersion of AKD prepared in acetone with analysis. No effects were seen at the highest concentration tested (mean measured concentration of 0.8 mg/l). The absence of effects in this test indicates that the long-term NOEC is above the water solubility limit.

EC_{50} (21-day) >0.8 mg/l (mean measured) for *Daphnia magna* (OECD 211, mortality);

NOEC (21-day) =0.8 mg/l (mean measured) for *Daphnia magna* (OECD 211, reproduction and body length).

6.1.1.3 Algae and aquatic plants

Acute toxicity

$Er(b)C_{50}$ (72-hour) >0.17 mg/l (mean measured) for *Selenastrum capricornutum* (OECD 201). At the end of the algal growth inhibition test, concentrations were below the detection limit < 0.073 mg/l. It is thought that hydrolysis may have occurred since the pH had risen to 9.7.

A test carried out on a structurally related new notification showed no effects up to the water solubility limit ($Er(b)C_{50}$ (72-hour) > 0.46 mg/l, NOEC (72-hour) = 0.46 mg/l (growth rate and biomass) which supports the conclusion that AKD is of low acute toxicity to algae.

Long-term toxicity

A NOEC (biomass and growth rate) > 0.17 mg/l was obtained in the 72-hour test with *Selenastrum capricornutum*. No effects were observed in this test.

6.2 SEDIMENT ORGANISMS

6.2.1 Other aquatic organisms

EC_{20} (30-m) > 1,000 mg/l for activated sludge (OECD 209 – respiration inhibition test). It was concluded that AKD is not inhibitory to activated sludge micro-organisms.

6.3 TERRESTRIAL COMPARTMENT

An OECD 208 test was carried out to determine the effects of AKD on seed germination and plant growth of oat (*Avena sativa*), sunflower (*Helianthus annuus*) and mung bean (*Phaseolus aureus*). No dose related effects were seen in any of the species tested at any of the test concentrations.

28-day NOEC (vegetative growth) = 1,000 mg/kg; 28-day EC_{50} (vegetative growth) > 1,000 mg/kg;

28-day LOEC (vegetative growth) > 1,000 mg/kg; 14-day NOEC (emergence) = 100 mg/kg;

14-day EC_{50} (emergence) > 1,000 mg/kg; 14-day LOEC (emergence) = 1,000 mg/kg.

No mortality was observed at the highest dose tested in an acute toxicity test with earthworm *Eisenia foetida*. LC_{50} (14-day) > 1,000 mg/kg soil, NOEC = 1,000 mg/kg soil.

6.4 ATMOSPHERIC COMPARTMENT

No information reported in the literature.

6.5 INDIRECT EXPOSURE VIA THE FOOD CHAIN

7 PBT AND VPVB

7.1 PBT, VPVB ASSESSMENT

Persistence: commercial preparations of AKD have been shown to hydrolyse readily under neutral and alkaline conditions, but are more stable under acid conditions. Based on the available data, AKD is expected to hydrolyse under neutral and alkaline conditions in the environment and is assumed to be stable to hydrolysis at acidic pHs in the environment, pH 5-7. When tested in the presence of small amounts of emulsifier in order to increase the bioavailability of the substance to micro-organisms, AKD has been shown to be readily biodegradable with 94% biodegradation in 28 days. This is relevant to the form in which the substance is marketed and used. A structurally related new chemical notification has also been shown to be inherently biodegradable with 31% degradation in 28 days. It is concluded that the P criterion is not met for AKD.

Bioaccumulation: predicted log K_{ow} values of 11.25 to 15.18 (BCF values of 14 – 6×10^{15} predicted) suggest a high bioaccumulation potential. A BCF of 9440 predicted using a measured log K_{ow} of 5.5 for the structurally related new chemical notification also suggests that AKD has the potential to bioaccumulate. It is concluded that AKD meets the screening B/vB criteria.

Toxicity: no acute effects were seen up to the solubility limit of test substance and it was concluded that AKD is of low acute toxicity to fish, Daphnia and algae. AKD showed no toxicity up to its solubility limit in the long-term tests and is of low chronic toxicity to algae and aquatic invertebrates. It was also concluded that AKD is of low acute toxicity to plants and earthworms. The substance is therefore considered not to meet the T criterion.

Summary: the high log K_{ow} suggests that AKD has a high potential for bioaccumulation, thus the B/vB criterion is met. However, available data indicate the AKD is readily degradable by micro-organisms when tested in the presence of an emulsifier (1.5%). Furthermore, the substance hydrolyses under neutral and alkaline conditions in the environment. A structurally related new chemical notification has also been shown to hydrolyse under neutral and alkaline conditions and is considered to be inherently degradable. AKD is considered not to meet the P criterion. AKD shows low acute toxicity to aquatic organisms, plants and earthworm and low chronic toxicity to Daphnia and algae. It therefore does not fulfil the T criterion.

In conclusion, AKD is not considered to be a PBT or a vPvB 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:

SIDS Initial Assessment Report for Alkyl ketene dimer (AKD) prepared for SIAM 20, 19-22 April 2005. Sponsor Country UK.