TC NES SUBGROUP ON IDENTIFICATION OF PBT AND VPVB SUBSTANCES

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

Substance name: Paraffin waxes and Hydrocarbon waxes, chloro

EC number: 264-150-0

CAS number: 63449-39-8

Molecular formula: not applicable

Structural formula: not applicable

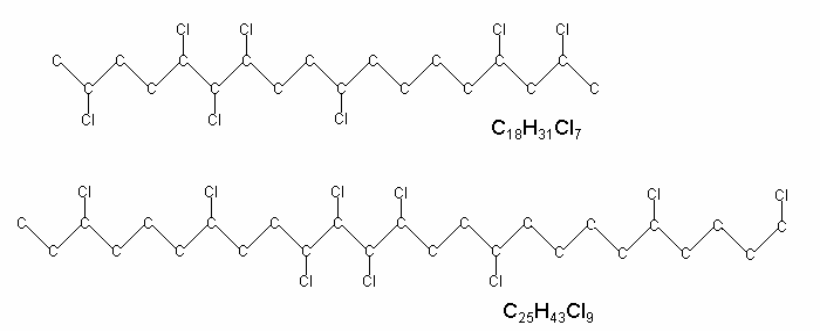
Summary of the evaluation:

Paraffin waxes and hydrocarbon waxes, chloro is not considered as a PBT substance. It is not likely to meet the B criterion. The T criterion is not met as a borderline case. The substance may meet the P/vP criteria according to the available experimental data.

JUSTIFICATION

1 IDENTIFICATION OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

Name:	Paraffin waxes and Hydrocarbon waxes, chloro
EC Number:	264-150-0
CAS Number:	63449-39-8
IUPAC Name:	
Molecular Formula:	$C_nH_{2n+2-y}Cl_y$, where n=18 to 32 and y = ~4 to ~30
Structural Formula:	Not applicable. Two structure examples of this multi-constituent substance are provided below.



(Environment Agency, 2006)

Molecular Weight:	Not applicable
Synonyms:	Hydrocarbon waxes, chlorinated; chloroparaffin; chlorinated paraffins; Alkanes, C_{18-30}, chloro; ; long-chain chlorinated paraffins; LCCP (abbreviation). For more synonyms, see Environment Agency (2006)

1.1 Purity/impurities/additives

The substance belongs to a group of long-chain chlorinated paraffins (LCCPs), which are also sold under other CAS numbers (e.g. CAS 85422-92-0). The substance contains chlorinated alkanes with a chain length C18 to C50. The products in liquid form consist of C18-C20 alkyl chains with chlorine content of 40-50% w/w whereas the solid products mainly contain > C20 alkyl chains with a chlorination content of approximatley 70% w/w (source: confidential IUCLID, company specific data sets) . According to Environment Agency (2006), chlorinated alkyl chains with a length of C16, C19 and C20 are expected to be present in LCCPs in a concentration of < 1%, 0% and < 0.2%, respectively. A typical concentration of 17% (with a possible range of 10-20%) is reported for C17-constituents.

1.2 Physico-chemical properties

Table 1 Summary of physico-chemical properties of the constituents groups. For details and references, see Environment Agency (2006).

REACH ref Annex, §	Property	C_{18-20} liquids	$C_{>20}$ liquids	$C_{>20}$ solids	Comments
V, 5.1	Physical state at 20 C and 101.3 Kpa	Liquid	Liquid	Solid	
V, 5.2	Melting / freezing point	-30°C [a] 0°C [b]	-30°C [a] 0°C [b]	100°C [c]	
V, 5.3	Boiling point	> 210°C (decomp.)	> 210°C (decomp.)	> 210°C (decomp.)	
V, 5.5	Vapour pressure	2.5×10^{-4} Pa (at 25°C)	2.5×10^{-5} Pa (at 25°C)	1.5×10^{-14} Pa (at 25°C)	
V, 5.7	Water solubility	5 µg l^{-1} (at ca. 20°C)	5 µg l^{-1} (at ca. 20°C)	5 µg l^{-1} (at ca. 20°C)	
V, 5.8	Partition coefficient n-octanol/water (log value)	9.7	10.3	17	
VII, 5.19	Dissociation constant	-	-	-	

a) For products with chlorine contents of 42-48% by weight.

b) For products with chlorine contents of 50-52% by weight.

c) For products with chlorine contents of around 70% by weight.

2 MANUFACTURE AND USES

Eleven companies have notified the substance under Regulation 93/793/EEC. According to European Commission (2000), production and import volume is 10,000-50,000 tpa. Environment Agency (2006) estimated, that approximately 5,000 – 10,000 tons of long-chain chlorinated paraffins were used in the EU annually between 1998 and 2004.

A variety of uses has been reported by Environment Agency (2006) and European Commission (2000). These included, i.a., use as plasticiser in PVC, as flame retardant in rubber and textiles, as well as the use as plasticiser, binder and flame retardant in paints, coatings and sealants. LCCPs are also used in metalworking fluids and in fat liquors for leather treatment.

3 CLASSIFICATION AND LABELLING

The substance is not classified under Directive 67/548/EEC.

4 ENVIRONMENTAL FATE PROPERTIES

4.1 Degradation (P)

4.1.1 Abiotic degradation

Indirect photochemical degradation in the atmosphere has been calculated for several constituents from $C_{18}H_{33}Cl_5$ to $C_{30}H_{35}Cl_{27}$ by Environment Agency (2006). Half-lives between 30 and 112 hours were obtained for the reaction with OH-radicals using AOP v1.91 (24 h day^{-1}; $5*10^5$ OH^- cm^{-3}).

Long-chain chlorinated alkylchains are not expected to undergo abiotic degradation in aqueous media.

4.1.2 Biotic degradation

No standard ready or inherent biodegradation test results are available for the substance. The available biodegradation data has been evaluated by Environment Agency (2006). A brief overview of the reviewed information is provided below.

There is evidence that some microorganisms may be capable of degrading LCCPs in the environment in acclimatised or co-metabolic systems. In a 25-day biochemical oxygen demand (BOD) test, acclimatised microorganisms showed approximately 23% biodegradation of a $C_{20\text{-}30}$ (42% chlorinated) product, compared with 7.5% biodegradation using a non-acclimatised inoculum (Madeley and Birtley, 1980). The same authors also showed 11% mineralisation ($^{14}CO_2$ evolution) of centrally labelled ^{14}C-pentacosane (42% chlorinated), mixed with the same $C_{20\text{-}30}$ product, by non-acclimatised microorganisms after 8 weeks. Under anaerobic conditions, using several bacterial species isolated from soil, chlorinated $C_{24.5}$ (average) products showed up to 33% degradation, as measured by chloride release, after 36 or 48 hours incubation (Omori et al., 1987). The highest level of degradation was obtained for a 40.5% chlorinated substance in the presence of n-hexadecane as a co-metabolite. Other studies have shown, the potential for biodegradation appeared to decrease with increasing chlorine content, although up to 15% degradation was observed for a 70% chlorinated product. Allpress and Gowland (1999) isolated a bacterium (*Rhodococcus* sp.) from stream water that was able to utilise various chlorinated paraffins as the sole source of carbon and energy, with up to 14% degradation (measured as released chloride) after 71 days for a $C_{>20}$ (42% chlorinated) product.

It is not possible to derive rate constants for biodegradation in soil, surface water, marine water or sediment systems from the available data.

4.1.3 Other information [1]

No data available.

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

4.1.4 Summary and discussion of persistence

No standard ready or inherent biodegradation test results are available for long-chain chlorinated paraffins. From the available data, long-chain chlorinated paraffins can be considered to be not biodegradable in such systems. A biodegradation rate constant of 0 day^{-1} has been used for all types of long-chain chlorinated paraffins in the risk assessment of Environment Agency (2006).

4.2 Environmental distribution

Data not reviewed for this report.

4.2.1 Adsorption

4.2.2 Volatilisation

4.2.3 Long-range environmental transport

4.3 Bioaccumulation (B)

4.3.1 Screening data

LogKow values as summarised by Environment Agency (2006) in **Table 1** are 9.7-17. The alkyl chain length has the most impact on the logKow -value.

4.3.2 Measured bioaccumulation data

The available studies on bioconcentration and dietary accumulation cited below have been evaluated in detail by Environment Agency (2006).

A bioconcentration factor (BCF) of 8 to 16 was obtained for a C_{18-26} (49% chlorinated) substance after a 14-day exposure of bleak (*Alburnus alburnus*) to a concentration of 0.125 mg l^{-1} in brackish water (7% salinity) (Bengtsson et al., 1979). In rainbow trout (*Oncorhynchus mykiss*), a maximum BCF of 9 (measured as parent compound) was observed after 60 days exposure to a C_{22-26} (43% chlorinated) material, mixed with similarly chlorinated n-pentacosane-13-^{14}C; the corresponding BCF based on radiolabel measurement was 38, suggesting some metabolism within the fish tissues (Madeley and Maddock, 1983a). The measured exposure concentrations in water were 0.97 and 4.0 mg l^{-1}. For a $C_{>20}$ (70% chlorinated) material, mixed with 70% chlorinated n-pentacosane-13-^{14}C, the maximum BCFs were 43 and 54, based on parent compound and radiolabel measurements, respectively (Madeley and Maddock, 1983b). The measured exposure concentrations in water were 0.84, 1.9 and 3.8 mg l^{-1}. Although the exposure concentrations used for both of these LCCPs were above the solubility limit, in each case the highest BCFs were obtained at the highest exposure levels, suggesting that adsorption of undissolved material to the external surfaces of the fish may have contributed to the measured body burdens.

The same two substances, with corresponding radiolabels, as used for the rainbow trout studies above, were also tested in 60-day exposures to marine mussels (*Mytilus edulis*) (Madeley and

Thompson, 1983a and 1983b). The maximum BCFs obtained, by parent compound analysis, were 1,000 and 157 for the 40.5% and 70% chlorinated materials, respectively; by radiolabel the corresponding BCFs were 1158 and 341. It is possible that the filter feeding activity of the mussels may have resulted in the ingestion of particles of undissolved test substance, which may account for the higher BCFs than observed for fish.

Although the measured fish BCFs (above) were obtained using exposure concentrations in excess of the water solubility of the substances, they are consistent with the results of reliable studies for short-chain and medium-chain chlorinated paraffins that were obtained by testing below the solubility limit. BCFs of 7,816 and 1,087 were determined for short-chain (^{14}C-C_{11}) and medium-chain (^{14}C-C_{15}) chlorinated paraffins, respectively (Madeley and Maddock, 1983c; Thompson et al, 2000). Thus, based on a comparison with the available data for other chlorinated paraffins, the fish BCF for long-chain chlorinated paraffins would be expected to further reduce with increasing carbon chain length.

This trend of declining BCF with increasing chain length is further confirmed by QSAR estimation based on the octanol-water partition coefficient (Kow). Using a QSAR for substances of log Kow > 6 (EU Technical Guidance Document, 2003), the estimated BCFs in fish for the three types of LCCP are as follows:

$C_{18\text{-}20}$ liquid LCCP	BCF = 1,096
$C_{>20}$ liquid LCCP	BCF = 192
$C_{>20}$ solid LCCP	BCF <1

There is evidence from feeding studies that LCCPs can be taken up via the diet. The accumulation of a C_{18}, 49% chlorinated paraffin has been studied in juvenile rainbow trout (*Oncorhynchus mykiss*) by Fisk et al. (2000). The uptake and accumulation of a $C_{20\text{-}30}$, 42% chlorinated product has been investigated using both rainbow trout (*Oncorhynchus mykiss*) and mussel (*Mytilus edulis*) (Madeley and Birtley, 1980). Zitko (1974) looked at the uptake of two long-chain chlorinated paraffins in the diet of juvenile Atlantic salmon (*Salmo salar*) over 181 days. A further feeding study with fish has been carried out by Bengtsson and Baumann Ofstad (1982). In this experiment, bleak (*Alburnus alburnus*) were exposed to a $C_{18\text{-}26}$, 49% chlorinated product via food for 91 days, followed by a 316-day depuration period. Dietary uptake in rats has been reviewed in BUA (1992) and WHO (1996). In all dietary studies the concentrations reached in the animals were less than those in the diet. This indicates that although uptake of the substance can occur via the food, the levels do not increase through the food chain.

4.3.3 Other supporting information[2]

No data available.

[2]For example, measured concentrations in biota

4.3.4 Summary and discussion of bioaccumulation

Environment Agency (2006) summarises the data on bioaccumulation as follows:

the available bioconcentration results on long-chain chlorinated paraffins are not reliable as much of the data were obtained using exposure concentrations well in excess of the water solubility of the substance and it is generally not clear if the length of the studies was sufficient for steady state to be reached. Therefore, although these studies show that uptake does occur, it is not possible to obtain a reliable BCF value from them. As a result, the estimated data for the fish bioconcentration factor will be considered in the assessment as a precautionary approach. The following values will be used for the fish bioconcentration factor.

$C_{18\text{-}20}$ liquid	BCF = 1,096
$C_{>20}$ liquid	BCF = 192
$C_{>20}$ solid	BCF <1

For the marine environment, there are data available on the accumulation of long-chain chlorinated paraffins by mussels in salt water and fish in brackish water. These show similar patterns of uptake as found for freshwater species. Again, no reliable BCF can be derived from the data, and so the estimated BCFs are considered the most relevant for the marine environment as a precautionary approach.

In addition to bioconcentration, the TGD also provides methods to take into account biomagnification in the assessment of secondary poisoning. The method requires a biomagnification factor (BMF) for fish, preferably expressed on a lipid normalised basis. According to the TGD, an appropriate BMF for long chain chlorinated paraffins would be 1 for all three types considered based on the fish BCF being < 2,000 and the log Kow being > 9.

There is evidence from feeding studies that the long-chain chlorinated paraffins can be taken up via the diet, but in all cases the concentrations reached in the animals were less than those in the diet. This indicates that although uptake of the substance can occur via the food, the levels should not increase through the food chain. These findings support the default BMF of 1 determined above. Uptake via diet or the undissolved phase may also explain some of the uptake seen in the available bioconcentration studies.

5 HUMAN HEALTH HAZARD ASSESSMENT

Data not reviewed for this report.

6 ENVIRONMENTAL HAZARD ASSESSMENT

6.1 Aquatic compartment (including sediment)

The ecotoxicity data cited below have been evaluated in more detail by Environment Agency (2006).

6.1.1 Toxicity test results

6.1.1.1 Fish

Acute toxicity

For fish, numerous 96-hour LC_{50} studies show no mortality at the highest concentrations tested, in many cases giving 96-hour LC_{50} values >300 mg l^{-1} (see e.g., European Commission, 2000).

Long-term toxicity

No mortalities or other symptoms of toxicity have been observed in the long-term exposures of fish in the bioaccumulation studies. These provide the following NOEC values, all showing no effects at concentrations well in excess of the solubility level of ≤ 0.005 mg l^{-1}:

Species	Substance	Duration (days)	NOEC (mg l^{-1})
Alburnus alburnus	C_{18-26}, 49% Cl	14	≥0.125
Oncorhynchus mykiss	C_{22-26}, 43% Cl	60	≥4
Oncorhynchus mykiss	$C_{>20}$, 70% Cl	60	≥3.8

6.1.1.2 Aquatic invertebrates

Acute toxicity

For the marine crustacean, *Nitocra spinipes*, for both a C_{22-26}, 42% chlorinated substance and a C_{18-26}, 49% chlorinated substance, the 96-hour LC_{50}s were greater than the highest concentrations tested, which were 1,000 and 10,000 mg l^{-1}, respectively (Tarkpea et al., 1981).

Acute toxicity to *Daphnia magna* has been determined for a C_{18-27} (60% chlorinated) product, with and without stabiliser, using both acetone and an emulsifier to prepare the test solutions (BUA, 1992). All the 24-hour EC_{50} values obtained were above 100 mg l^{-1}.

The 48-hour EC_{50} to *Daphnia magna* of a C_{18-20}, 52% chlorinated material was found to be greater than the maximum solubility achieved as a "water-accomodated fraction" (WAF) (Frank, 1993 and Frank and Steinhauser, 1994).

Long-term toxicity

For invertebrates, there were no mortalities in the long-term mussel (*Mytilus edulis*) bioaccumulation studies available (see Section 4.3). Effects were observed on the particle filtration rate at the higher exposure level for each substance but these effects were attributed to the physical effects of undissolved test substance. No such effects were seen at the lower exposure concentrations, which provide 60-day NOECs of 0.12 and 0.46 mg l^{-1} for the C_{22-26}, 43% Cl and $C_{>20}$, 70% Cl substances, respectively, both in excess of solubility.

The effects of C_{18-27} (60% chlorinated) on *Daphnia* reproduction were also determined, with a 21-day NOEC of 4.2 mg l^{-1}, well in excess of solubility. Inhibition observed above this level were

most probably due to the physical effects of undissolved material interfering with the organisms filter-feeding activity (BUA, 1992).

Frank (1993) and Frank and Steinhauser (1994) found no effects of the substance on survival and growth of *Daphnia* over 21 days at a nominal concentration of 1 mg l^{-1}, but reported effects of various dilutions of a WAF prepared at a loading rate of 10,000 mg l^{-1}. However, there are a number of reasons to doubt the validity of this result (Environment Agency, 2001). These include a failure of the temperature control system and a serious error in the statistical analysis that are not apparent from the published papers. The use of such a high loading when preparing the WAF is also likely to have preferentially dissolved any toxic impurities in the test substance that were more soluble than the LCCP. This may account for the apparent measured concentration of approximately 0.5 mg l^{-1} in the filtered WAF, well in excess of LCCP solubility, since the analytical method was non-specific (adsorbable organic halogen determination). If these procedural problems are ignored, but correcting the statistical analysis, the 21-day NOEC from this study was 0.029 mg l^{-1}.

6.1.1.3 Algae and aquatic plants

No data are available on the toxicity of LCCPs to freshwater algae. Craigie and Hutzinger (1975) investigated the toxicity of a $C_{>20}$ (50% chlorinated) product to three species of marine algae (*Dunaliella tertiolecta, Olisthodiscus* sp. *and Thalassiosira fluviatilis*). The substance was added to the test flasks as a solution in acetone to give nominal concentrations of 1 mg l^{-1} and 100 mg l^{-1} (in duplicate) and the acetone evaporated to dryness. A natural seawater medium was added to the flasks which were then sterilised by autoclaving and inoculated with the algae. No effects on algal biomass were seen in any of the exposed populations after 6 days growth at 20^{o}C (within 96-105% of the control values). Although no analytical measurements of the exposure concentrations were carried out, it is likely that, at least at the higher nominal concentration, there was sufficient excess material present to ensure that the dissolved concentration was at or near the solubility limit. Therefore, although a precise NOEC cannot be determined, the results strongly indicate that the substance was not toxic to these algal species.

6.1.2 Sediment organisms

No data available.

6.1.3 Other aquatic organisms

Data not evaluated for this report.

6.2 Terrestrial compartment

No data available.

6.3 Atmospheric compartment

No data available.

7 PBT AND vPvB

7.1 PBT, vPvB assessment

Persistence: based on the laboratory studies and other data available, long-chain chlorinated paraffins are considered to be unlikely readily or inherently biodegradable. Although there is some evidence that long-chain chlorinated paraffins may biodegrade in the environment it is considered likely that the rate will be sufficiently slow that long-chain chlorinated paraffins may meet the P/vP criteria.

Bioaccumulation: although the bioconcentration of long-chain chlorinated paraffins has been investigated in laboratory studies, none of the available data are considered sufficiently robust to allow a reliable BCF to be determined for long-chain chlorinated paraffins. Based on estimates of BCF (calculated using the available logKow –values), and consideration of the known accumulation properties of structurally similar substances (short and medium chain chlorinated paraffins), the BCF for long-chain chlorinated paraffins is considered to be < 2,000. In addition, the results of dietary uptake studies provide evidences that no accumulation in the food chain is expected. Thus it is concluded that long-chain chlorinated paraffins are unlikely to meet the B criterion.

Toxicity: the majority of acute and chronic aquatic toxicity studies with LCCPs show that no lethal or sublethal effects are observed up to and substantially above the solubility limit, other than probable physical effects of undissolved material at concentrations two or more orders of magnitude in excess of solubility. This absence of aquatic toxicity is consistent with the evidence of low bioaccumulation potential indicating low bioavailability. Only one study, on the chronic toxicity of a C_{18-20}, 52% chlorinated material to *Daphnia magna*, reports any toxic effects at levels potentially close to the solubility level (NOEC 0.029 mg l^{-1}). Based on the experimental data, long-chain chlorinated paraffins do not meet the toxicity criterion/are considered as not to fulfil the T criterion as a borderline case.

Summary: paraffin waxes and hydrocarbon waxes, chloro is not likely to fulfil the B criterion. The substance may meet the P/vP criteria according to the screening data. Concerning the T criterion, the substances (esp. shorter chain constituents) may be regarded as a borderline case. It is concluded that these substances are not considered as PBT substances.

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INFORMATION ON USE AND EXPOSURE

Not relevant as the substance is not identified as a PBT.

OTHER INFORMATION

The information and references used in this report were taken from the following sources:

BUA (1992) Chlorinated Paraffins. GDCh-Advisory Committee on Existing Chemicals of Environmental Relevance (BUA). BUA Report 93, June 1992.

Environment Agency (2006) Environmental Risk Evaluation Report: long-chain chlorinated paraffins. Authors: Brooke, D.N. and Crookes, M.J.

European Commission (2000). IUCLID Dataset, Paraffin waxes and Hydrocarbon waxes, chloro, CAS 63449-39-8, 18.2.2000.

WHO (1996) Environmental Health Criteria 181. Chlorinated Paraffins. International Programme on Chemical Safety (IPCS).