TC NES SUBGROUP ON IDENTIFICATION OF PBT AND VPVB SUBSTANCES

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

Substance name: Sulfonyl chlorides, C16-34-alkane, chloro

EC number: 293-744-2

CAS number: 91082-32-6

Molecular formula: not applicable

Structural formula: not applicable

The assessment covers also the following substance identity:

Substance name: Paraffin waxes and Hydrocarbon waxes, chloro, sulfonated

EC number: 269-145-7

CAS number: 68188-19-2

Molecular formula: not applicable

Structural formula: not applicable

Summary of the evaluation:

Sulfonyl chlorides, C16-34-alkane, chloro is an UVBC considered as a substance, which may contain PBT/vPvB minor constituents and / or impurities. It has not been shown, that the concentration of such constituents / impurities would be < 0.1 % w/w (each).

The substance may meet the P/vP criteria based on screening data of its main constituents, impurities and hydrolysis products. The main constituents do not fulfil the screening B/vB criteria but the substance contains impurities, which may fulfil the B/vB criteria. The same conclusions apply to the hydrolysis products as to their corresponding parent compounds according to screening data. Ecotoxicity could be modelled only for hydrolysis products of certain potentially occurring constituents / impurities and they seem to fulfil the T criterion based on screening data. The assessment of the long-chain chlorinated fraction is presented in PBT summary no. 110.

Further PBT evaluation of this complex substance is not warranted because of its current production and use within the EU, which indicates only very limited environmental release. Further PBT assessment may in future be necessary, if future production and/ or use indicate significant environmental release.

JUSTIFICATION

1 IDENTIFICATION OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

Name:	Sulfonyl chlorides, C16-34-alkane, chloro
EC Number:	293-744-2
CAS Number:	91082-32-6
IUPAC Name:	
Molecular Formula:	not applicable
Structural Formula:	not applicable
Molecular Weight:	not applicable
Synonyms:	C16-C34-chloralkansulphochloride; CSC (abbreviation)

Alternative identity, which is also covered by this assessment:

Name:	Paraffin waxes and Hydrocarbon waxes, chloro, sulfonated
EC Number:	269-145-7
CAS Number:	68188-19-2
IUPAC Name:	
Molecular Formula:	not applicable
Structural Formula:	not applicable
Molecular Weight:	not applicable
Synonyms:	not available

1.1 Purity/Impurities/Additives

Sulfonyl chlorides, C16-34-alkane, chloro belongs to the group of UVCBs.

The composition as described by Clariant (2003):

Consituent	Concentration (% w/w)
C19-C24-chloroalkane-	2
C25-C27-chloroalkane-	32
C28-C30-chloroalkane-	46
C31-C34-chloroalkane-	18
> C34-chloroalkane-	2
Long-chain chlorinated paraffins (LCCPs; CAS 63449-39-8)	< 10 %

The average degree of chlorination is 4 chlorine atoms per molecule. According to the information on the raw material, 30 % of the alkanes are branched. Figure 1 presents a possible impurity.

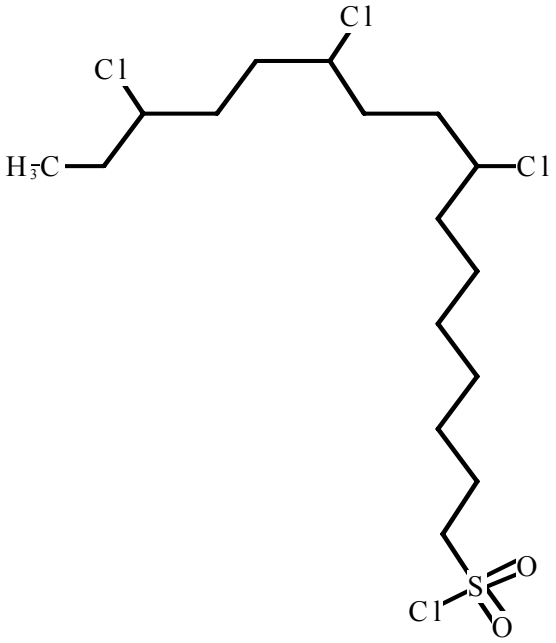

Figure 1 Structural formula of a possible impurity sulfhonyl chloride, hexadecane, trichloro.

It is noted, that the PBT assessment of the LCCP –fraction is presented in the PBT summary no. 110.

1.2 Physico-Chemical properties

Table 1 Summary of physico-chemical properties. For details and references, see European Commission (2000).

REACH ref Annex, §	Property	Value	Comments
VII,7.1	Physical state at 20 C and 101.3 Kpa	liquid, solid	
VII, 7.2	Melting / freezing point		
VII, 7.3	Boiling point		
VII, 7.5	Vapour pressure		
VII, 7.7	Water solubility	"not soluble"	Hoechst AG (1989; data not evaluated)
VII, 7.8	Partition coefficient n-octanol/water (log value)		
	Dissociation constant	-	

Water solubility and logKow predicted for some constituents and impurities are presented in Table 4.2, chapter 4.3.1.

2 MANUFACTURE AND USES

Three companies have provided information on the substance under Regulation 93/793/EEC. According to industry, one manufacturer is operating at the present in Europe and has one downstream user. The market volume in Europe is currently < 500 t/a (Clariant, 2003). The substance is used as fat liquoring agent for leather treatment.

3 CLASSIFICATION AND LABELLING

The substance does not have a harmonised EU hazard classification and it does not appear in the Annex I of Directive 67/548/EEC ("The List of Dangerous Substances").

4 ENVIRONMENTAL FATE PROPERTIES

4.1 Degradation (P)

4.1.1 Abiotic degradation

A hydrolysis test carried out by Olivannan and Nayudamma (1973) resulted 1.42 % hydrolysis in 48 h. 90:10 (vol.) H_20:acetone was used as the test solution for 250 mg substance at a temperature of 30 ºC. The result relates to the hydrolysis reaction of the sulfonyl chloride fragment to sulfonate. The authors observed considerably faster hydrolysis in alkaline conditions (NaOH and Na_2CO_3 – buffers resulted 81.9 % and 34.9 % hydrolysis in 48 hours, respectively). They also observed, that the hydrolysis rate was dependent on the chain length of the alkyl chain to which the sulfonyl chloride was attached (the longer the chain, the more stabile the substance).

Before its use as fat liquoring agent, the substance is neutralized in alkaline water. This leads to a hydrolysis of the sulfonyl chloride fragment to sulfonate. Hence chlorinated alkylsulfonates (ionised form of sulfonic acids) are also relevant for the PBT-assessment.

4.1.2 Biotic degradation

A modified MITI test on ready biodegradability according to Directive 84/449/EEC C.7 has been conducted by Hoechst AG (1986). Predominantly domestic sludge was employed and in 28 days a degradation level of 68 % was reached. It is noted that the study report was not available to the Rapporteur for evaluation. According to the test, the multi-constituent substance (as a complex mixture) seems to be readily biodegradable. Due to the variety of constituents and impurities, a test with the whole substance is nevertheless not appropriate to conclude on its persistency, because if readily biodegradable components are present in high fractions, their behaviour dominates the result.

Persistency of some expected constituents, impurities and sulfonic acids (hydrolysis products) have been predicted by BIOWIN of Episuite 3.10 (see Table 4.1).

Table 4.1 Predicted persistency of some constituents, impurities and hydrolysis products.

	BIOWIN 2	BIOWIN 3	BIOWIN 6	Screening (v)P criteria of TGD fulfilled?
Sulfonylchloride alkanes:				
C16, 1 Cl (not branched) Smiles: CLS(=O)(=O)CCCCCCCC(CL)CCCCCCCC	0.1	2.5	0.07	Borderline*
C16, 4 Cl (fully branched Smiles: CLS(=O)(=O)C(C)(CL)C(C)(C)C(C)(CL)C(CL)(C)C(C)(C)C(C)(CL)CC	0	0.21	0.07	Yes
C16, 16 Cl (fully branched) Smiles: CLS(=O)(=O)C(CL)(CL)C(CL)(CL)C(CL)(CL)C(CL)(CL)C(CL)(CL)C(CL)(CL)C(CL)(CL)C(CL)(CL)C(CL)(CL)C(CL)(CL)C(CL)(CL)C(CL)(CL)C(CL)(CL)C(CL)(CL)C(CL)(CL)C(CL)(CL)C(CL)(CL)	0	-8.7	0	Yes
Alkane sulfonic acids**				
C16 2 Cl	0.93	2.51	0.02	Borderline*
C16, 3 Cl	0.57	2.26	0	Borderline*
C16, 4 Cl	0.31	2.02	0	Yes
C19, 3 Cl	0.42	2.17	0	Yes
C27, 3 Cl	0.13	1.92	0	Yes
C34, 3 Cl	0.03	1.71	0	Yes

* "Borderline" fulfilling the P screening criteria because BIOWIN 2 and/ or 6 preditions are < 0.5 but BIOWIN 3 predictions are just above 2.2. (i.w.e in the range from 2.2 to 2.8)

**Sulfonic acids have a pKa of ca. 2. Hence, these compounds are present in environmentally relevant pH (ca. 4-9) in ionised sulfonate form. BIOWIN models are based on experimental data on biodegradation and therefore the predictions also refer to the environmentally relevant pH range or the pH range occurring in standard tests for ready biodegradability

4.1.3 Other information [1]

No data available.

4.1.4 Summary and discussion of persistence

Sulfonyl chlorides, C16-34-alkane, chloro is according to a standard modified MITI –test readily biodegradable (66 % degraded in 28 days; Hoechst, 1986). Due to the large variety of constituents and impurities in the substance, testing of the whole multi-constituent substance without any specific information on different fractions cannot be used to describe its degradation exhaustively enough. Some readily biodegradable main constituents may dominate the result.

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

No experimental data on degradation of constituents, impurities or hydrolysis products are available. According to the BIOWIN predictions, constituents containing 2 or more chlorine atoms are potentially persistent. Lower chlorinated constituents are probably not persistent, but for them the result is depending on the length and the degree of branching of the alkyl chain.

Testing of representative constituents and impurities would be necessary for making a thorough evaluation of the half-lives (persistency) of representative or "worst case" constituents to be able based on test data to conclude whether or not this multi-constituent substance should be considered as fulfilling the (v)P criteria.

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[2]

Water solubility, logKow and BCF of some expected constituents, impurities and sulfonic acids (hydrolysis products) have been predicted using EPIWIN 3.10 (see Table 4.2).

Table 4.2 Predicted water solubility, logKow and BCF of some constituents, impurities and hydrolysis products.

	Water solubility (mg l^{-1} at 25 ºC) WSKOW	LogKow (KOWWIN under EPIWIN 3.10)	BCF (BCFWIN under EPIWIN 3.10)	BCF ("recalculated Connell")
Sulfonylchloride chloroalkanes:				
C16, 1 Cl (not branched)	$1.6*10^{-4}$	8.8	7	7,733
C16, 4 Cl (fully branched)	$3.5*10^{-6}$	10	5	465
C16, 16 Cl (fully branched)	$2.7*10^{-27}$	27	3	0**
C23, 1 Cl (not branched)		12.3	3	0**
C23, 4 Cl (not branched)		12.8	3	0**
Alkane sulphonic acids				
C16 2 Cl (not branched)		5.35	71	16,387
C16, 3 Cl (not branched)		5.53	5.6 or 71	23,009

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

C16, 4 Cl (not branched)		5.71	71	25,375
C19, 3 Cl (not branched)		7.00	71	33,113
C27, 3 Cl (not branched)		10.93	3.16 or 71	21.6**
C34, 3 Cl (not branched)		14.37	3.16 or 71	0**

** domain limit for the model is exceeded (logKow > 10).

BCFWIN takes into account the alkyl chain length in its estimation and predicts therefore significantly lower values than the recalculated Connell model. Results of both models should be interpreted with caution because predictions for alkanes with very long chain lengths are not within the applicability domain of the models.

Chlorinated alkylsulfonic acids are the expected hydrolysis products of the substance when this is diluted in water buffered to keep the pH in neutral or alkaline range. Due to the pKa of ca. 2 (known for different sulfonic acid derivatives), these substances are present in ionised sulfonate form in the environmentally relevant pH range (4-9). BCFWIN predicts for this type of ionic substances having alkyl chains with ≥ 11 carbons a 1.85 ≤ log BCF (≤ ca. 2.2). For the latter, the corresponding BCF is 158. However, this method provides many underestimations of BCFs compared to measured values (see Meylan et al., 1999) and the model database for ionic substances with long alkyl chains is very limited (only 5 compounds included). Hence, BCFWIN should not be used to conclude on the bioaccumulation potential of such substances. In addition, logKow is not a good predictor of bioaccumulation potential of surfactants like alkyl sulfonates, because uptake to organisms may occur via other type of binding than binding to lipids. The use of any QSARs predictions of BCF or water solubility from logKow (as presented in Table 4.2) should therefore be considered with caution here.

It is noted, that the constituents/impurities having a logKow > 10 are presently expected to elicit only a limited uptake in biota.

4.3.2 Measured bioaccumulation data[3]

No experimental data on bioaccumulation are available for the substance, its constituents, impurities or their hydrolysis products.

Salts of strong acids like sulfonates are known to be poorly absorbed into cells because the charged species are hindered to cross membranes (Boethling and Mackay, 2000). Measurements for another sulphonate LAS (Linear Alkylbenzenesulfonate) with radiolabelled material gave BCF values of 16 to 66 depending on the chain length distribution (HERA, 2002).

4.3.3 Other supporting information[4]

No data available.

[3] For example, fish bioconcentration factor

[4] For example, measured concentrations in biota

4.3.4 Summary and discussion of bioaccumulation

No experimental data on bioaccumulation of the substance or its constituents, impurities and hydrolysis products (chlorinated alkylsulfonates) are available. The available models predicting BCF from logKow are not reliable for these substances. The BCFWIN and the recalculated Connel model provide contradictory BCF-predictions. Testing would be necessary to determine the actual bioaccumulation potential for these substances. Testing of the substance as a whole does not seem analytically feasible due to the multitude and the large concentration range of the constituents and impurities in this multi-constituent substance. The bioaccumulation potential of constituents, impurities or hydrolysis products (in the following referred to only as constituents) having alkyl-chains with more than 23 carbons is expected to be low due to a very high predicted logKow (> 10). Hence, the important candidates for testing in the frame of the bioaccumulation assessment would be the impurities with shorter alkyl-chains and their hydrolysis products.

5 HUMAN HEALTH HAZARD ASSESSMENT

Data not reviewed.

6 ENVIRONMENTAL HAZARD ASSESSMENT

Acute ecotoxicity data are available on sulfonyl chlorides, C16-34-alkane, chloro for fish and micro-organisms (European Commission, 2000). These data were not evaluated in this context. It is noted, that suspensions of the substance in water are strongly acidic (pH 1-2) and ecotoxicity tests can only be carried out after neutralisation of the sulfochloride to the sulfonate. For the main constituents no experimental data are available. Prediction of ecotoxicity for single constituents is reliable only for those with logKow lower than 6-8 (depending on the QSAR-model chosen). Hence, it was only possible to characterise excotoxicity of chlorinated C16-alkane sulfonates. As an example, ECOSAR predicts for the trichlorinated species an acute EC_{50} of 0.003 mg l^{-1} for shrimp and for fish an acute LC_{50} of 0.3 mg l^{-1}. For the tetrachlorinated constituents the predicted EC_{50} is 0.02 mg l^{-1} for shrimp and an acute fish LC_{50} of 0.25 mg l^{-1} have been calculated similarly. Constituents with 1-5 chlorine atoms all have similar ECOSAR predictions.

6.1 Aquatic compartment (including sediment)

6.1.1 Toxicity test results

6.1.1.1 Fish

Acute toxicity

Long-term toxicity

6.1.1.2 Aquatic invertebrates

Acute toxicity

Long-term toxicity

6.1.1.3 Algae and aquatic plants

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: Sulfonyl chlorides, C16-34-alkane, chloro may meet the P/vP criteria based on screening data of its main constituents and impurities. The main use of the substance is as liquoring agent for leather. In this use, the substance is neutralized before use and cause as consequence a hydrolysis of the sulfonyl chlorides to sulfonates. These are hence relevant for the PBT-assessment. Most of the main constituents, impurities and hydrolysis products may according to BIOWIN –predictions (see Table 4.1) be persistent or very persistent. Further testing would be necessary to fully assess their degradation rate and hence their status in relation to the P criteria.

Bioaccumulation: The substance does not meet the B/vB criteria based on screening data of its main constituents (with C-chain length > 23) and their foreseen hydrolysis products. The predicted logKow –values of these species are very high (> 10) (see Table 4.2) Some of the minor constituents, impurities and their hydrolysis products have a predicted $4.5 \leq \log Kow \leq 10$ and they might fulfil the B or vB criterion. Further assessment and testing would be necessary to determine more reliably / precisely the bioaccumulation potential of these constituents.

Toxicity: No experimental long-term ecotoxicity data are available for the constituents or impurities of the substance. QSAR-models cannot exhaustively predict ecotoxicity of the main constituents and impurities because predictions would be outside the applicability domain of the models. Ecotoxicity was hence only predicted with ECOSAR for possible sulfonate-impurities with chlorinated C16-alkyl chain. The calculated acute ecotoxicity is lower than 0.1 mg l^{-1} for the shrimp model. The fish model produced values slightly above this limit. Hence, ecotoxicity testing would be necessary to complete the assessment although it can be concluded that the hydrolysis products with chlorinated C16-alkyl chain may meet the T criterion based on screening data. In the frame of this assessment those impurities should be targeted for ecotoxicity testing, which fulfil the P/vP and B/vB criteria.

Summary: Sulfonyl chlorides, C16-34-alkane, chloro may meet the P/vP criteria based on screening data of its main constituents and impurities. The main constituents (about 98 %) and their hydrolysis products do not fulfil the screening B/vB criteria. The substance contains minor constituents and/or impurities, which may fulfil the B/vB criteria according to screening data. Also the hydrolysis products of minor constituent and/or impurities may fulfil the B/vB criteria according to screenign data. Ecotoxicity could be evaluated only for hydrolysis products of some impurities. These fulfil the T criterion based on screening data. The PBT assessment of the LCCP –fraction has been presented in PBT summary no. 110.

It is concluded that sulfonyl chlorides, C16-34-alkane, chloro is considered as an UVBC which may contain PBT/vPvB impurities. It has not been shown, that the concentration of these impurities is < 0.1 % w/w (each). Further PBT evaluation of this complex substance is not warranted because of its current production and use within the EU, which indicates only very limited environmental release. Further PBT assessment may in future be necessary, if future production and/ or use indicate significant environmental release.

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 source:

European Commission, 2000. IUCLID Dataset, Sulfonyl chlorides, C16-34-alkane, chloro, CAS 91082-32-6, 19.2.2000.

Other sources:

Boethling and Mackay 2000. Handbook of Estimation Methods for Chemicals, Ed. Boethling, R.S.; Mackay, D., Lewis Publisher, N.Y., 2000, ISBN 1-56670-456-1

Clariant, 2003. EU List of Potential PBTs & vPvBs among the IUCLID HPV Chemicals (Rev. 1, Nov. 21, 2002, 93 Listings); Clariant Proof Document for Delisting, C16-34 Chloroalkane sulfonylchlorides, CAS No. 91082-32-5; Update 2003-10-14 provided to ECB and the Rapporteur.

GDCh, 1996. BUA Report 181, Chloroalkane sulfonic acids, sodium salt, 1996. CDCh-Advisory Committee on Existing Chemicals (BUA). BUA Report 93, Chlorparaffine, VCH Verlag, Weinheim,1993, ISBN 3-527-28602-0

HERA, 2002. HERA Risk Assessment, Linear Alkylbenzensulfonate (LAS), CAS No. 68411-30-3, July 2002; http://www.heraproject.com/files/HERA_LAS_RA-final_draft_for_publication_August_4_.pdfMeylan, H., Howard, P.H., Boethling, R.S., Aronson, D., Printup, H. and Gouchie, S., 1999. Improved method for estimating bioconcentration/bioaccumulation factor from octanol/water partition coefficient. Env. Tox. Chem., 18(4), 664-672.