TC NES SUBGROUP ON IDENTIFICATION OF PBT AND VPVP SUBSTANCES

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

Substance name: Tall-oil rosin

EC number: 232-484-6

CAS number: 8052-10-6

Molecular formula: not applicable (substance is a UVCB)

Structural formula: not applicable (substance is a UVCB)

Summary of the evaluation:

Tall-oil rosin is considered to be a UVCB substance. Based on screening data it is not fulfilling the PBT/vPvB criteria.

A test on ready biodegradation is available with tall-oil rosin showing ready biodegradation of the test substance. The P-screening criterion is therefore not fulfilled. Regarding the B-criterion, an experimentally determined log Kow of 3.6 at pH 7 is available. Based on this value a BCF of 56 was calculated with QSAR. The B-screening criterion is therefore not fulfilled. Based on acute aquatic toxicity results with L/EC50 above 100 mg/L the screening T-criterion is not fulfilled.

Data on individual constituents are not available. Based on QSAR there is no clear picture regarding persistence, bioaccumulation and toxicity because the constituents have pKa values around environmentally relevant pH values. However, no further testing is considered necessary as tall-oil rosin is readily biodegradable.

JUSTIFICATION

1 Identification of the Substance and physical and chemical properties

Table 1.1: Identification of tall-oil rosin

Name	Tall-oil rosin
EC Number	294-866-9
CAS Number	8052-10-6
IUPAC Name	-
Molecular Formula	not applicable
Structural Formula	not applicable
Molecular Weight	not applicable
Synonyms	Colophony Colofonia Kolophonium Rosin Résine, Tall-oil, Tallharz Tallharz, Mäntyhartsi, Talloljaharts, OULU 331

1.1 Purity/Impurities/Additives

Tall-oil resin (CAS no. 8052-10-6) is a UVCB (Substance of Unknown, Variable Composition, or of Biological Origin), which consists mainly of rosin acids, fatty acids and neutrals. Tall-oil rosin is derived as a by-product from the process for wood pulping, and the composition varies with age, species and geographical location of the raw material (wood).

The major constituents of tall-oil rosin are resin acids as shown in the following table (according to HARPA's environmental test program, 1998). The values given are examples.

Table 1.2 Composition of tall-oil rosin according to HARPA's Environmental Test Program, 1998.

Trivial name	CAS-no.	Content %
Abietic acid	514-10-3	38.8
Dehydroabietic acid	1740-19-8	16.5
Palustric acid	1945-53-5	10.0
Isopimaric acid	5835-26-7	4.4
Neoabietic acid	471-77-2	4.3
Pimaric acid	127-27-5	2.6
Levopimaric acid	79-54-9	2.6
Sandaracopimaric acid	471-74-9	2.0
Unidentified	-	18.8
Total		100

The following substances can be considered as corresponding substances:

Table 1.3 CAS numbers to be considered as corresponding substances to tall-oil rosin acids.

CAS number	EINECS	Name
8050-09-7	232-475-7	Rosin
94114-23-5	302-657-1	Resin acids and rosin acids, tall-oil
73138-82-6	277-299-1	Resin acids and rosin acids
65997-05-9	NLP:500-163-2	Rosin, polymd., Rosin oligomer
65997-06-0	266-041-3	Rosin, hydrogenated
1740-19-8	217-102-8	Dehydrogenated rosin

1.2 Physico-Chemical properties

Physico-chemical properties are available in IUCLID (European Commission, 2000) for tall-oil rosin.

Table 1.4 Physico-chemical properties for Tall-oil rosin

REACH ref Annex, §	Property	Value	Source
VII, 7.1	Physical state	Solid or bulk liquid at 160°C	Union Camp Chemicals Durham
VII, 7.2	Melting point	73 °C	Mare S.p.A. Ossona/Fraz. Asmonte
VII, 7.3	Boiling point	230 °C at 0.66 hPa	Union Camp Chemicals Durham
VII, 7.4	Relative density	Relative density: 1.05 kg/m^3 at 25°C Density: 1050 kg/m^3 at 25 °C	Mare S.p.A. Ossona/Fraz. Asmonte Union Camp Chemicals Durham
VII, 7.5	Vapour pressure	< 0.0013 hPa at 20 °C < 0.00013 hPa at 20 °C	Mare S.p.A. Ossona/Fraz. Asmonte Union Camp Chemicals Durham
VII, 7.7	Water solubility	“insoluble”	Mare S.p.A. Ossona/Fraz. Asmonte Union Camp Chemicals Durham
VII, 7.8	Partition coefficient n-octanol/water (log value)	3.6 ay pH 7.5 (OECD 117) 4.4-7.2 at pH 2	Mare S.p.A. Ossona/Fraz. Asmonte Union Camp Chemicals Durham
VII, 7.16	Dissociation constant	No data available	-

No experimental data on the individual constituents of the mixture (as presented in Table 1.2) are available and therefore water solubility and log Kow have been estimated with QSAR.

Table 1.5 Water solubility and logKow of the constituents of tall-oil rosin

QSAR	Water solubility	Water solubility	log Kow
	(WATERNT, v1.0)	(WSKOWWIN v1.41)	(KOWWIN, v1.67)
Abietic acid	0.28 mg/l	0.09 mg/l	6.46
Dehydroabietic acid:	0.13 mg/l	0.08 mg/l	6.52
Palustric acid:	0.44 mg/l	0.02 mg/l	7.27
Isopimaric acid:	0.19 mg/l	0.09 mg/l	6.44
Neoabietic acid:	0.44 mg/l	0.07 mg/l	6.59
Pimaric acid:	0.19 mg/l	0.09 mg/l	6.45
Levopimaric aicd:*	0.28 mg/l	0.09 mg/l	6.46
Sandaracopimaric acid:	0.19 mg/l	0.09 mg/l	6.45

In QSAR there is an experimental value available for water solubility of abietic acid, which is 48.4 mg/L. This is considerably higher than the calculated value and may be a result of the pH dependency of the water solubility of abietic acid. Abietic acid and the other constituents have pKa values at environmentally relevant pH values; however, no experimental data are available.

Several pKa values have been found in the scientific literature:

- Luong et al. 1999 quotes that ”At pH below their pKa (< 5.7-6.4) the resin acids were virtually unionized and insoluble”
- In Kamaya et al. 2005 for dehydroabietic acid pKa values between 5.7 and 7.25 and 6.4-7.15 for abietic acid are given
- In Nyren and Back 1958 pKa values for abietic and dehydroabietic acid are 6.4 and 5.7, respectively, were reported
- Cited by Hall and Liver 1996 were pKa values for abietic and dehydroabietic acid of 7.15 and 7.25, respectively

PKa values for the constituents of tall-oil rosin were also predicted using the SPARC software (Version 1.4, released January 2008). Values of 4.7 to 4.8 were predicted and these are considered consistent with expectations for a carboxylic acid functional group. The predicted values are considered reliable as the method has been validated with a number of carboxylic acids. Predicted pKa values for 9 carboxylic acids (pKa 4.0-4.8) have been compared with measured pKa values for these acids obtained from the literature (pKa 4.2-5.0).

2 Manufacture and uses

Eight companies have notified the substance under Regulation 93/793 EEC according to IUCLID (European Commission, 2000). The substance is used in quantities between 100,000 – 500,000 tons per year (European Commission, 2000).

The substance is a UVCB. Tall-oil is derived as a by-product from the Kraft-process for wood pulping. It is a resinous material that consists mainly of rosin acids, fatty acids and neutrals. The chemical composition of tall-oil varies with age, species and geographical location of the coniferous trees. The resin acids are diterpene carboxylic acids based on an alkyl-substituted perhydrophenanthrene ring structure and the fatty acids are predominantly 18-carbon, straight-chain mono- or diunsaturated fatty acids. Essentially all of the crude tall-oil produced today is refined by fractional distillation, and these fractionation products are used in a wide variety of applications.

3 Classification and labeling

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

4 Environmental fate properties

4.1 Degradation (P)

4.1.1 Abiotic degradation

No data available.

4.1.2 Biotic degradation

According to IUCLID maximum 38 % biodegradation after 28 days is indicated in a closed bottle test according to OECD 301D (1981). A newer biodegradation study from 1991 with tall-oil rosin (OECD 301D) resulted in a biodegradation of 71 % after 28 days. The study is valid as the reference compound sodium acetate was degraded by 69 % of its theoretical oxygen demand after 14 days. Oxygen concentration was > 0.5 mg/L in all bottles during the test period. However, the study was performed for the whole mixture and does not give information whether (smaller) fractions of persistent substances are present in the mixture.

To assess biodegradation of the constituents QSAR predictions have been conducted.

Table 4.1 Persistency of possible constituents in CAS no. 8052-10-6

	BIOWIN 2 v4.10	BIOWIN 3 v4.10	BIOWIN 6 v4.10
Abietic acid	0.0165	2.4711	0.044
Dehydroabietic acid	0.0518	2.326	0.0561
Palustric acid	0.0165	2.4711	0.0606
Isopimaric acid	0.003	2.259	0.0907
Neoabietic acid	0.0165	2.4711	0.0589
Pimaric acid	0.003	2.259	0.0907
Levopimaric acid	0.0165	2.4711	0.044
Sandaracopimaric acid	0.003	2.259	0.0907

4.1.3 Other information [1]

No data available.

4.1.4 Summary and discussion of persistence

Two standard ready biodegradability test results are available for tall-oil rosin. In the first test tall-oil rosin was found not to be readily biodegradable. However, results from the second closed bottle test from 1999 are considered most reliable and showed that tall-oil rosin is readily biodegradable (71% by day 28).

Biodegradation has been predicted by QSAR for the respective constituents of the mixture. According to the predictions, the constituents behave very similarly and can be considered a borderline case between being readily and not readily biodegradable. According to the TGD a substance can be considered to be not readily biodegradable when the non-linear model prediction is <0.5 or the MITI non-linear model prediction is < 0.5 and the ultimate biodegradation timeframe prediction is < 2.2. Biowin 3 predictions show values between 2.3-2.5. This would mean that all constituents can be considered as being readily biodegradable when looking at the figures in table 4.1. However, according to REACH RIP 3.3 (Guidance on information requirements) a substance can be regarded as borderline case with respect to the ready biodegradation if the estimate of the ultimate degradation time (Biowin 3) gives a result in the range 2.2 to 2.7.

In conclusion, a valid biodegradation test with the mixture is available and showed ready biodegradation. The known constituents comprise of about 80% of the mixture and therefore the mixture can be considered readily biodegradable. However, minor fractions of persistent substances might be present in the mixture.

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

4.2 Environmental distribution

No data available.

4.2.1 Adsorption

4.2.2 Volatilisation

4.2.3 Long-range environmental transport

4.3 Bioaccumulation (B)

4.3.1 Screening data

According to IUCLID the log Kow of tall-oil rosin is 3.6 at pH 7.5 (OECD 117) and 4.4-7.2 at pH 2 (OECD 117). The QSAR estimation gives a BCF value of 56 (BCFwin v2.17), when calculating with a log Kow of 3.6.

The B-criterion of the constituents has been assessed using two different QSAR-programs:

Table 4.2 Log BCF values of constituents

Constituent	BCFwin v2.17 Log BCF	Bintein* Log BCF
Abietic acid	1.75	4.16
Dehydroabietic acid	1.75	-
Palustric acid	1.0	3.59
Isopimaric acid	1.75	4.17
Neoabietic acid	1.75	4.1
Pimaric acid	1.75	4.17
Levopimaric acid	1.75	4.16
Sandaracopimaric acid	1.75	4.17

* Bintein's model included in "OECD (Q)SAR Application Toolbox, Beta version v 0.6. September 2007."

Bintein's model (Bintein et al. 1993) gives log BCF values > 4 for all constituents apart from palustric acid (3.59), while BCFwin gives results < 2. The reason for this difference is most likely that the constituents are ionisable substances and that the pKa values might be around environmentally relevant pH values. Bintein's model is only based on non-ionic substances (Pavan et al. 2006), while BCFwin gives results for ionic substances.

4.3.2 Measured bioaccumulation data

Experimentally derived BCF values are not available for tall-oil rosin or the constituents.

In the open literature Niimi and Lee (1992) reported experimental BCF values for abietic, dehydroabietic, neoabietic, palustric, pimaric, isopimaric and sandaracopimaric acid. Rainbow trout were exposed to waterborne acids for 20 days to estimate BCF values, followed by a 10 day acid-free period to estimate the elimination rate. The highest BCF found in the study was 220 for neoabietic acid after 10 days. This value declined to 129 at day 20. However, the study has some deficiencies. Fish were exposed to several substances simultaneously and the exposure period was only 20 days. Given the fact that the pH in the study was around 8 (8.0-8.3) and that these acids might have pKa values around or below 7, it can be assumed that the undissociated acids have not been tested but that the measured BCF values refer to their respective ionic forms.

4.3.3 Other supporting information[2]

No data available.

4.3.4 Summary and discussion of bioaccumulation

Experimental data on bioaccumulation are not available for tall-oil rosin or the constituents. The screening B-criterion based on a measured log Kow of tall-oil rosin of 3.6 is not fulfilled. The screening B-criterion based on calculated BCF values might be fulfilled dependant on the model used. According to BCFwin the screening B-criterion is not fulfilled, using Bintein's model it is fulfilled.

Theoretically, testing could hence be necessary to determine the actual bioaccumulation potential for the mixture/the constituents. However, testing of the substance as a whole might not be appropriate for this assessment due to variations in the composition of the mixture and the probably large concentration range of the anticipated constituents and impurities.

In conclusion, as tall-oil rosin does not fulfil the P-screening criterion further testing on the B-criterion is not considered necessary.

5 Human health hazard assessment

Data not reviewed for this report.

[2] For example, measured concentrations in biota

6 Environmental hazard assessment

6.1 Aquatic compartment (including sediment)

6.1.1 Toxicity test results

Acute aquatic ecotoxicity studies with tall-oil rosin are available with fish, daphnids and algae (see 6.1.1.1, 6.1.1.2 and 6.1.1.3).

The toxicity of the constituents has been evaluated with QSAR as no data on ecotoxicity of the constituents are available.

Table 6.1 QSAR values for EC50/LC50 in mg/L for fish, *daphnia magna* and algae.

	OECD Toolbox / Ecosar v0.99h	OECD Toolbox / Ecosar v0.99h	OECD Toolbox / Ecosar v0.99h
	Fish*	Daphnia magna*	Algae*
Abietic acid	0.44 / 0.144	0.01 / 0.21	9.8 / 0.17
Dehydroabietic acid	- / 0.126	- / 0.184	- / 0.149
Palustric acid	0.44 / 0.025	0.01 / 0.038	27.6 / 0.038
Isopimaric acid	0.53 / 0.147	0.01 / 0.214	9.86 / 0.173
Neoabietic acid	0.36 / 0.109	0.01 / 0.160	8.93 / 0.130
Pimaric acid	0.53 / 0.147	0.01 / 0.214	9.86 / 0.173
Levopimaric acid	0.44 / 0.144	0.01 / 0.210	9.79 / 0.170
Sandaracopimaric acid	0.53 / 0.147	0.01 / 0.214	9.86 / 0.173

* E/LC_{50} values in mg/L

6.1.1.1 Fish

Acute toxicity

According to IUCLID the 96 hours LC_{50} values for resin acids and rosin acids, sodium salts to Zebra fish were 100-200 mg/L (OECD 203).

Long-term toxicity

No data available.

Endocrine disruption

Extensive research has been conducted for several decades to elucidate the mechanisms of action of endocrine disrupters from pulp and paper mill effluents. While it is acknowledged that paper and pulp mill effluents exhibit endocrine disrupting potential, little information is available to directly link the reported effects observed in fish exposed to these effluents to individual fractions or specific substances.

Although some mechanisms have been identified, the causal agents are poorly characterised. It is, however, suggested that compounds such as terpenoidbased wood components and flavonoids in Kraft effluents are estrogenic, whereas terpenoids and stilbenes may be responsible for effects on the reproductive system of fish exposed to pulp mill effluents (Belknap et al., 2006). An Environment Canada report (McMaster *et al.*, 2004) suggests that that abietic acid and similar compounds may affect endocrine processes in vivo. It is also suggested that the endocrine disrupting compounds in these effluents are biodegradable and poorly bioaccumulative, thus suggesting attained exposure to cause effects. Little if any information is available to verify that these compounds are causing endocrine disrupting effects in vivo.

6.1.1.2 Aquatic invertebrates

Acute toxicity

According to IUCLID 48 hours EC_{50} values for tall-oil rosin to *Daphnia magna* were in the range of 238 to 479 mg/L (OECD 202).

In the literature (Kamaya et al. 2005) measured 48 hours EC_{50} values for D*aphnia magna* for abietic acid (7.98 mg/L) and dehydroabietic acid (7.48 mg/L) are stated. These are considerably higher than the QSAR-estimates.

The difference in toxicity between data from literature and QSAR may be that toxicity of the substances is pH dependent. In the QSAR models calculations are based on non-dissociated molecules, while in toxicity tests, salts of the acids may be present. A good example for the pH dependence of toxicity of these compounds is dehydroabietic acid. For *Daphnia magna* the 48 h EC_{50} increases from 2.47 mg/L at pH 6.5 to 77 mg/L at pH 10 (Zanella 1983; http://smartech.gatech.edu/bitstream/1853/677/1/3355_005_081982.pdf).

Long-term toxicity

No data available.

6.1.1.3 Algae and aquatic plants

According to IUCLID the 72 hours ErC_{50} values for tall-oil rosin to *Selenastrum capricornutum* were 644-688 mg/L (OECD 201).

6.1.2 Sediment organisms

No data available.

6.1.3 Other aquatic organisms

No data available.

6.2 Terrestrial compartment

No data available.

6.3 Atmospheric compartment

No data available.

7 PBT and vPvB

7.1 PBT, vPvB assessment

Persistence

The screening P criterion is not fulfilled for tall-oil rosin based on the test result from a ready biodegradation test. Tall-oil rosin was shown to be readily biodegradable. As the test was conducted with the mixture, no information is available whether smaller fractions of persistent substances are present in the mixture. Therefore biodegradation of the constituents was predicted by QSAR. The results were quite similar for all constituents. According to the TGD a substance can be considered to be not readily biodegradable when the non-linear model prediction is <0.5 or the MITI non-linear model prediction is < 0.5 and the ultimate biodegradation timeframe prediction is < 2.2. Biowin 3 predictions show values between 2.3-2.5; however, the screening P-criterion might nevertheless be fulfilled for all constituents. According to REACH RIP 3.3 (Guidance on information requirements) a substance can be regarded as borderline case with respect to the screening P-criterion if the estimate of the ultimate degradation time (BIOWIN 3) gives a result in the range 2.2 to 2.7.

In conclusion, as the mixture is readily biodegradable based on experimental data and the known constituents comprise of about 80% of the mixture, it can be concluded that tall-oil rosin is readily biodegradable, therefore not fulfilling the P-criterion.

Bioaccumulation

According to IUCLID the log Kow of tall-oil rosin is 3.6 at pH 7.5 and 4.4-7.2 at pH 2. QSAR estimation gives a BCF value of 56 (BCFwin v2.17), when using 3.6 for calculations. Based on this data the B-criterion is considered not to be fulfilled.

Toxicity

Acute toxicity (L/EC_{50}) values for the aquatic studies are > 100 mg/l. The T-criterion is considered not to be fulfilled.

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:

Belknap, A. M., Solomon, K. R., MacLatchy, D. L., Dube, M. G. and Hewitt, L. M. (2006). Identification of compounds associated with testosterone depressions in fish exposed to bleached kraft pulp and paper mill chemical recovery condensates. Environ Toxicol Chem 25, 2322-2333.

Bintein, S., Devillers, J., Karcher, W. (1993). Nonlinear dependence of fish bioconcentration on n-Octanol/water partition coefficients. *SAR and QSAR in Environmental Research*, **1**, 29-39.

Cited by Hall, E.R. and Liver, S.F., 'Interactions of resin acids with aerobic and anaerobic biomass—II. Partitioning on biosolids', Water Research, Vol 30, Issue 3, March 1996, 672 – 678. Primary reference not known

Kamaya, Y, Tokita, N and Suzuki K. 2005: Effects of dehydroabietic acid and abietic acid on survival, reproduction and growth of the crustacean *Daphnia magna*. Ecotoxicology and Environmental Safety 61, 83-88.

Luong, J.H., Rigby, T., Male, K.B. and Bouvrette, P. 1999: Separation of resin acids using cyclodextrin-modified capillary electrophoresis. Electrophoresis 20 (7), 1546-1554.

Niimi, A.J. and Lee, H.B. (1992). Free and conjugated concentrations of nine resin acids in Rainbow trout (*Oncorhynchus mykiss*) following waterborne exposure. Environmental Toxicology and Chemistry 11, 1403-1407.

McMaster, M. E., Parrott, J. L. and Hewitt, L. M. (2004). A decade of research on the Environmental impacts of pulp and paper mill effluetns in Canada (1992-2002). National Water Research Institute, Environment Canada

Nyren, V. and Back, E., 'The ionization constants, solubility product and solubility of abietic acid and dehydroabietic acid', Acta Chemica Scandinavica, , 12(7), 1958, p 1816 – 1820

OECD (Q)SAR Application Toolbox, Beta version v 0.6. September 2007.

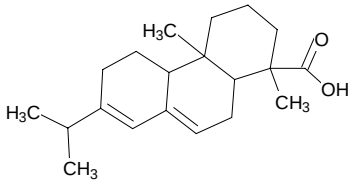
Pavan et al. 2006: Review of QSAR models for bioconcentration. European Commisssion. Directorate General. Joint Research Centre, Ispra. EUR 22327 EN.

SPARC; available at: http://ibmlc2.chem.uga.edu/sparc/

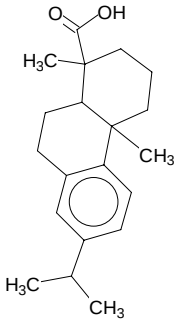
Zanella, E. (1983); Effect of pH on acute toxicity of dehydroabietic acid and chlorinated dehydroabietic acid to fish and Daphnia. Bull Environ Contam Toxicol 30, 133-140

ANNEX

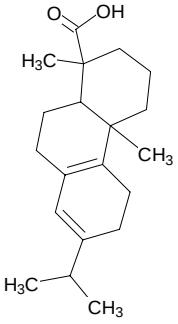
Structural formulas of the substances covered by this assessment. The CAS numbers refer here to the pure substances, not to tall-oil rosin fraction on the market.



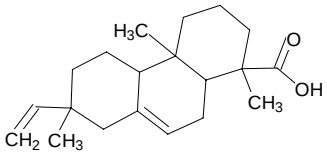
Abietic acid (CAS 514-10-3)



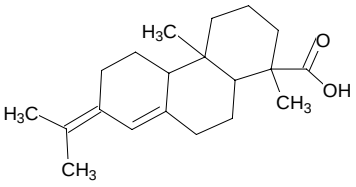
Dehydroabietic acid (CAS 1740-19-8)



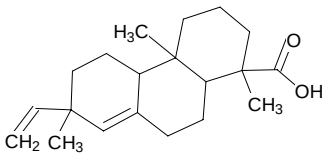
Palustric acid (CAS 1945-53-5)



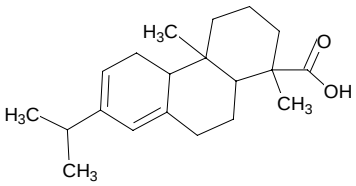
Isopimaric acid (CAS 5835-26-7)



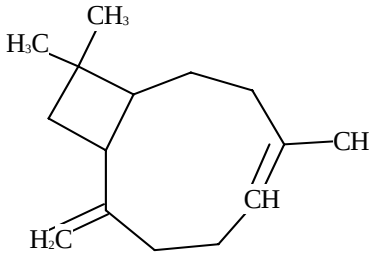
Neoabietic acid (CAS 471-77-2)



Pimaric acid (CAS 127-27-5)



Levopimaric acid (CAS 79-54-9)



Sandaracopimaric acid (CAS 471-74-9)