

## **Annex XV Report**

### **Proposal for identification of a substance as a CMR, PBT, vPvB or a substance of an equivalent level of concern**

**Substance Name:** Coal tar pitch, high temperature

**EC Number:** 266-028-2

**CAS number:** 65996-93-2

**Submitted by:** European Chemicals Agency (ECHA)

**Version:** August 2009

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## FOREWORD

This Annex XV report has been prepared in order to provide in its Part I the relevant information on the identity of Coal Tar Pitch, High Temperature (CTPHT) and on its properties as a basis for its identification as a substance of very high concern (SVHC) in accordance with Article 57 of the REACH Regulation. In Part II of this report the available information on manufacture, uses, releases of and alternatives to CTPHT is presented.

Coal tar pitch, high temperature, CTPHT, is an UVCB substance (substance of unknown or variable composition, complex reaction products or biological materials) characterised by a variable and high content of polycyclic aromatic hydrocarbons (PAHs), heterocyclic compounds and benzocarbazoles.

Relevant for the PBT/vPvB assessment of an UVCB substance are those of its constituents which are present in individual concentrations equal to or above 0.1% (weight/weight). The content of polycyclic aromatic hydrocarbons is the main concern regarding CTPHT as these constituents are among the major constituents of CTPHT and many of them proved to be animal carcinogens.

Having regard of this and of the fact that data availability for other constituents of CTPHT is even more limited than for its PAH-constituents, it has been decided to follow the approach pursued for risk assessment in the Annex XV Transitional Dossier on CTPHT prepared by The Netherlands and base the SVHC assessment of CTPHT on the SVHC properties of its PAH-constituents. The data on environmental fate and behaviour and on toxicity documented in the Annex XV Transitional dossier served therefore as the primary source of information and data basis for this Annex XV report.

As however only for the 16 EPA homocyclic PAHs sufficient data on hazard and exposure exist, these 16 PAHs are regarded as being representative for the effects and emissions of CTPHT. This approach implies therefore a possible underestimation of the hazard of CTPHT.

As out of the 16 PAHs, naphthalene and acenaphthylene were not detected in CTPHT, and both acenaphthene and fluorene were detected in concentrations below 0.1 %, the present dossier focuses on the following 12 PAHs considered relevant for the SVHC and exposure assessment of CTPHT: anthracene, phenanthrene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, dibenzo(a,h)anthracene, and indeno(1,2,3-cd)pyrene.

Whereas in the effects assessment part of the Annex XV Transitional dossier on CTPHT the PAH-constituents are addressed with focus on deriving PNEC-values for the environment and DNELs/DMELs for human health, the effects assessment in the present Annex XV dossier targets at comparison with the T-criteria set out in Annex XIII of the REACH Regulation. Hence, the judgment on which are the key data differs between the risk assessment, requiring selection of the lowest reliable and relevant effect-values, and the PBT/vPvB assessment, requiring selection of reliable data suitable for comparison with the T-criteria. Therefore, the data chosen for T-assessment in this report do in some instances differ from the data used for effects assessment in the Annex XV Transitional Dossier.

As regards Part II of this report, i.e. the Information on Manufacture, Import, Export, Uses, Exposure and Alternatives, an approach was chosen that involved a review of the relevant literature and consultation with the relevant industry stakeholders in the EU. As part of the consultation process, manufacturers, suppliers and downstream users of CTPHT were asked by means of questionnaires for:

- tonnage and market information on CTPHT (i.e. manufacture, import, export, supply volumes and economic values);
- information on the ID of CTPHT and its major constituents;
- information on emissions and releases of CTPHT (throughout the lifecycle); and
- information on potential alternatives to CTPHT and their suitability (in terms of their technical, environmental and health aspects).

Based on the responses, follow-up through direct contact was undertaken with a number of respondents. The reasons for such follow-up included the wish to gather information beyond the scope of the questionnaire, to obtain clarification on responses or to discuss particular aspects in more detail.

Consultation with companies for this study has relied mainly on contacts with the relevant industry associations, although in some cases, individual companies were approached directly to seek additional information. In general, the response/feedback obtained from industry has been variable in quantity and quality.

Much of the underlying work for the development of this Annex XV dossier was carried out under contract by DHI\*, in co-operation with Risk & Policy Analysts Limited\*\*, NCEC (AEA)\*\*\*, and Milieu Ltd\*\*\*\*.

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## ABBREVIATIONS / ACRONYMS

<b>AC</b>	Article Category
<b>ASTM</b>	American Society for Testing and Materials
<b>B</b>	Bioaccumulation
<b>BaP</b>	Benzo(a)pyrene
<b>BAT</b>	Best Available Technique
<b>BCF</b>	Bioconcentration factor
<b>CAS</b>	Chemical Abstracts Service
<b>CAT</b>	Category
<b>CCSG</b>	Coal Chemicals Sector Group
<b>CEFIC</b>	European Chemical Industry Council
<b>CLP</b>	Classification, Labelling and Packaging
<b>CMR</b>	Carcinogenic, mutagenic or toxic to reproduction
<b>CTP</b>	Coal Tar Pitch
<b>CTPHT</b>	Coal Tar Pitch, High Temperature
<b>CTPV</b>	Coal Tar Pitch Volatiles
<b>CVR</b>	Continuous Vertical Retorts
<b>DIN</b>	Deutsche Industrie Norm
<b>DNA</b>	Deoxyribonucleic Acid
<b>EAF</b>	Electric Arc Furnaces
<b>EC</b>	Effective Concentration
<b>EC<sub>10</sub></b>	Effective Concentration 10%
<b>EC<sub>50</sub></b>	Effective Concentration 50%
<b>ECHA</b>	European Chemicals Agency

<b>ELS</b>	Early Life Stage
<b>EPA</b>	Environmental Protection Agency
<b>EU</b>	European Union
<b>EURAL</b>	European list of waste products
<b>EUSES</b>	European Union System for the Evaluation of Substances
<b>IARC</b>	International Agency for Research on Cancer
<b>IPCS</b>	International Programme on Chemical Safety
<b>ISO</b>	International Standards Organization
<b>IUCLID</b>	International Uniform Chemical Information Database
<b>IUPAC</b>	International Union of Pure and Applied Chemistry
<b>Koc</b>	Organic carbon-water partitioning coefficient
<b>Kow</b>	Octanol-water partitioning coefficient
<b>LC<sub>10</sub></b>	Lethal Concentration 10%
<b>LC<sub>50</sub></b>	Lethal Concentration 50%
<b>LT<sub>50</sub></b>	Median Lethal Time
<b>LWS</b>	Liquid Waterproofing Systems
<b>NACE</b>	Nomenclature statistique des Activites economiques dans la Communaite Europeenne
<b>nd</b>	No publication date
<b>NOEC</b>	No Observed Effect Concentration
<b>OECD</b>	Organisation for Economic Co-operation and Development
<b>OH</b>	Hydroxyl radical
<b>P</b>	Persistence
<b>PAHs</b>	Polycyclic Aromatic Hydrocarbons

<b>PARCOM</b>	Paris Commission under the Convention for the Prevention of Marine Pollution from Land-Based Sources (" <i>Paris Convention</i> ")
<b>PBT</b>	Persistent, Bioaccumulative and Toxic
<b>PC</b>	Chemical product category
<b>PNA</b>	Polynuclear Aromatic
<b>PROC</b>	Process Category
<b>QI</b>	Quinoline Insoluble
<b>RAP</b>	Reclaimed Asphalt Pavement
<b>RAR</b>	Risk Assessment Report
<b>REACH</b>	Registration, Evaluation, Authorisation and Restriction of Chemicals
<b>SME</b>	Small and Medium sized Enterprise

<b>SVHC</b>	Substance of Very High Concern
<b>SU</b>	Sector of Use
<b>T</b>	Toxicity
<b>TOXNET</b>	Toxicology Data Network
<b>UCN</b>	Use code Nordic
<b>US</b>	United States
<b>UV</b>	Ultra-Violet
<b>UVCB</b>	Substances of Unknown or Variable composition, Complex reaction products or Biological materials
<b>vPvB</b>	Very Persistent and very Bioaccumulative

## PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CMR CAT 1 OR 2, PBT, vPvB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN

**Substance Name:** Coal tar pitch, high temperature

**EC Number:** 266-028-2

**CAS number:** 65996-93-2

- *It is proposed to identify the substance as a CMR (Carc. cat. 2) according to Article 57 (a).*
- *It is proposed to identify the substance as a PBT according to Article 57 (d).*
- *It is proposed to identify the substance as a vPvB according to Article 57 (e).*

### **Summary of how the substance meets the CMR (Cat 1 or 2), PBT or vPvB criteria, or is considered to be a substance giving rise to an equivalent level of concern**

Information on the persistence, potential for bioaccumulation and aquatic toxicity was not available for CTPHT itself. Therefore, the PBT assessment of CTPHT focused on the assessment of its PAH-constituents having been identified in concentrations above or equal to 0.1 % (indicator PAH-constituents). For 10 of these 12 indicator PAH-constituents assessed in total, half-lives in soil have been reported to be in the range of 5.7 to 9.1 years under field conditions. As these half-lives observed in soil exceed the P- and vP-criteria (half lives of 120, respectively 180 days), it is concluded that the vP criterion is fulfilled by all 10 PAH-constituents. Experimentally obtained BCF values higher than 5,000 are reported in fish, mollusks, or crustaceans for 9 indicator PAH-constituents of CTPHT. As these BCF values exceed the B- and vB criteria (measured BCF values in aquatic species > 2000, respectively > 5000), it is concluded that the vB-criterion is fulfilled by the respective 9 substances. BCF values > 2000 have been reported for anthracene, which is a further indicator PAH-constituent of CTPHT and thus fulfills the B-criterion. Long-term data for marine or freshwater species showing no effect concentrations (NOEC/EC<sub>10</sub>) < 0.01 mg/l are available for 9 of the indicator PAH-constituents of CTPHT. Furthermore, 6 of the indicator PAHs found in CTPHT are classified as carcinogen, mutagen or as toxic to reproduction in Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation). Based on the available experimental aquatic toxicity data and the data on classification, it is concluded that 11 of the 12 indicator PAH-constituents for the assessment of CTPHT fulfil the T-criteria of Annex XIII of the REACH Regulation.

On the basis of the available data, it is concluded that 7 of the 12 indicator PAH-constituents identified in CTPHT in concentrations equal to or above 0.1 % are to be considered as both vPvB and PBT substances (fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, benzo(k)fluoranthene, and benzo(ghi)perylene), one (phenanthrene) as vPvB, and one (anthracene) as PBT. For coal tar pitch, high temperature (CTPHT), the above conclusion on the PBT/vPvB properties of its indicator PAH-constituents has the consequence that this substance needs as well

be considered as a substance meeting both the criteria of Article 57(d) and of Article 57(e) of the REACH Regulation.

As, in addition, CTPHT is classified as a carcinogen (Carc. Cat.2, respectively 1B) in Annex VI of Regulation (EC) No 1272/2008, CTPHT is as well a substance meeting the criteria of Article 57 (a) of the REACH Regulation.

**Registration number(s) of the substance or of substances containing a given constituent/impurity or leading to the same transformation or degradation products:**

No registration dossier for the substance was submitted to ECHA by the publication date of this dossier (31 August 2009).

# **Part I**

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## **JUSTIFICATION**

# 1 IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

## 1.1 Name and other identifiers of the substance

<b>EC number:</b>	266-028-2
<b>EC name:</b>	Pitch, coal tar, high-temp.
<b>CAS number (in the EC inventory):</b>	65996-93-2
<b>CAS number:</b>	65996-93-2
<b>CAS name:</b>	Pitch, coal tar, high-temp.
<b>IUPAC name:</b>	not applicable
<b>Synonyms:</b>	anode pitch, binder pitch, clay pigeon binder, electrode pitch, hard pitch, impregnating pitch, soft pitch, vacuum pitch
<b>Index number in Annex VI of the CLP Regulation</b>	648-055-00-5
<b>Molecular formula:</b>	not applicable
<b>Molecular weight range:</b>	not applicable
<b>Structural formula:</b>	not applicable

Coal tar pitch, high temperature (CTPHT) is the residue from the distillation of high temperature coal tar (CAS no. 65996-89-6)<sup>1</sup> under vacuum in closed systems. The EINECS description is as follows: “*The residue from the distillation of high temperature coal tar. A black solid with an approximate softening point from 30°C to 180°C. Composed primarily of a complex mixture of three or more membered condensed ring aromatic hydrocarbons*”. The composition of CTPHT includes a large variety of polynuclear aromatic constituents, including heterocyclic derivatives.

## 1.2 Composition of the substance

CTPHT is a complex hydrocarbon mix consisting of three- to seven-membered condensed ring aromatic hydrocarbons, high molecular weight compounds, heterocyclic compounds and benzocarbazoles (The Netherlands, 2008b). Among its constituents also (poly)methylated derivatives of PAHs are found (Steinhauser, 1997, cited in The Netherlands, 2008).

In general, coal tars and coal tar pitches have variable compositions due to variation in source materials and in manufacturing processes. CTPHT is an UVCB substance characterised by a variable and high content of polycyclic aromatic hydrocarbons (PAHs) and heterocyclic compounds. Its exact composition varies due to its variable and complex nature, as well as due to

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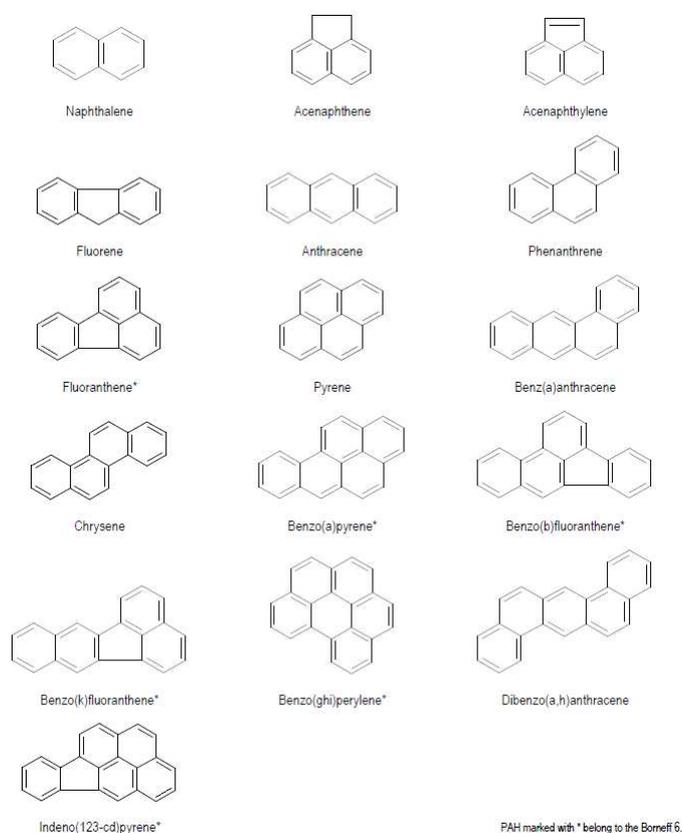
<sup>1</sup> Coal tars are produced as a by-product of the carbonisation of coal, by cooling and condensing the gases evolved in this process. Coal tars are composed of a complex mix of hydrocarbons and may contain as many as 10,000 constituents, of which approximately 400 have been identified (Franck, 1963). The composition of coal tars may vary greatly, depending on the type of coking coal employed, the coking process and the distillation process used.

variations in the distillation temperature. CTPHTs of different composition may be named with different synonyms hinting to their intended use, e.g. binder pitch or impregnating pitch. Differences in the composition of these two CTPHTs are shown in Table 1.1.

In the Annex XV Transitional Dossier on CTPHT (The Netherlands, 2008), the EPA 16 homocyclic PAHs (structural formulae in Figure 1) are regarded as being representative for the PAH emissions from CTPHT and the risk assessment is based on exposure and effect data available for these PAHs (addressed as ‘indicator PAHs’ in the following).

Information on the content of the 16 indicator PAHs and other organic constituents in CTPHT is available for CTPHT either used for impregnating or for binding (Table 1.1). As the main use of CTPHT is as binder pitch for the production of anodes and electrodes (see Part II of this dossier and The Netherlands, 2008), the data on composition available for binder pitch is therefore chosen as reference for the content of PAHs in the substance.

The present dossier focuses on indicator PAH-constituents that are considered relevant for the PBT assessment of CTPHT, i.e. those 12 PAHs confirmed to be contained in the substance in concentrations equal to or higher than 0.1 %. In total, those 12 PAHs represent approx. 10% of the matter of CTPHT. According to the information on binder pitch shown in Table 1.1 this includes the following 12 PAHs: anthracene, phenanthrene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, dibenzo(a,h)anthracene, and indeno(1,2,3-cd)pyrene. It should be noted that the selection of indicator PAHs for PBT assessment would be almost identical on the basis of composition data of impregnating pitch and the 0.1 % threshold (it would differ only with respect to anthracene, with a concentration of 0.074% in impregnating pitch).



**Figure 1:** Structural formulae of the 16 PAHs listed in Table 1.1

<b>Table 1.1: Indicative data on composition of CTPHT (The Netherlands, 2008)</b>								
Chemical name	EINECS Number	CAS Number	Molecular Formula	Molecular Weight	Concentration in Impregnating pitch		Concentration in Binder pitch	
					(mg/kg)	% *	(mg/kg)	% *
<b>Polycyclic Aromatic Hydrocarbons (PAHs)<sup>2</sup></b>								
Naphthalene	202-049-5	91-20-3	C <sub>10</sub> H <sub>8</sub>	128.17	n.d.	<b>n.d.</b>	n.d.	<b>n.d.</b>
Acenaphthylene	205-917-1	208-96-8	C <sub>12</sub> H <sub>8</sub>	152.20	n.d.	<b>n.d.</b>	n.d.	<b>n.d.</b>
Acenaphthene	201-469-6	83-32-9	C <sub>12</sub> H <sub>10</sub>	154.21	390	<b>0.039</b>	432	<b>0.043</b>
Fluorene	201-695-5	86-73-7	C <sub>13</sub> H <sub>10</sub>	166.22	144	<b>0.014</b>	472	<b>0.047</b>
Phenanthrene	201-581-5	85-01-8	C <sub>14</sub> H <sub>10</sub>	178.23	3874	<b>0.387</b>	6299	<b>0.630</b>
Anthracene	204-371-1	120-12-7	C <sub>14</sub> H <sub>10</sub>	178.23	737	<b>0.074</b>	1311	<b>0.131</b>
Fluoranthene	205-912-4	206-44-0	C <sub>16</sub> H <sub>10</sub>	202.25	17389	<b>1.739</b>	10789	<b>1.079</b>
Pyrene	204-927-3	129-00-0	C <sub>16</sub> H <sub>10</sub>	202.25	14849	<b>1.485</b>	9449	<b>0.945</b>
Benz(a)anthracene **	200-280-6	56-55-3	C <sub>18</sub> H <sub>12</sub>	228.29	15008	<b>1.501</b>	7715	<b>0.772</b>
Chrysene	205-923-4	218-01-9	C <sub>18</sub> H <sub>12</sub>	228.29	14041	<b>1.404</b>	8053	<b>0.805</b>
Benzo(b)fluoranthene **	205-911-9	205-99-2	C <sub>20</sub> H <sub>12</sub>	252.31	17408	<b>1.741</b>	12131	<b>1.213</b>
Benzo(k)fluoranthene **	205-916-6	207-08-9	C <sub>20</sub> H <sub>12</sub>	252.31	8704	<b>0.870</b>	6065	<b>0.607</b>
Benzo(a)pyrene **	200-028-5	50-32-8	C <sub>20</sub> H <sub>12</sub>	252.31	12924	<b>1.292</b>	10021	<b>1.002</b>
Dibenzo(a,h)anthracene **	200-181-8	53-70-3	C <sub>22</sub> H <sub>14</sub>	278.35	2209	<b>0.221</b>	1749	<b>0.175</b>
Benzo(ghi)perylene	205-883-8	191-24-2	C <sub>22</sub> H <sub>12</sub>	276.33	9945	<b>0.995</b>	8664	<b>0.866</b>
Indeno(1,2,3cd)pyrene **	205-893-2	193-39-5	C <sub>22</sub> H <sub>12</sub>	276.33	11106	<b>1.111</b>	9061	<b>0.906</b>
<b>Other Aromatic Hydrocarbons</b>								
1-Methylfluorene	217-048-5	1730-37-6	C <sub>14</sub> H <sub>12</sub>	180.26	n.d.	<b>n.d.</b>	61	<b>0.006</b>
2-Methylfluorene	215-853-6	1430-97-3	C <sub>14</sub> H <sub>12</sub>	180.26	50	<b>0.005</b>	112	<b>0.011</b>
Cyclopenta(def)phenanthrene **	205-905-6	203-64-5	C <sub>15</sub> H <sub>10</sub>	190.25	918	<b>0.092</b>	821	<b>0.082</b>
Acephenanthrylene **	205-911-9	205-99-2	C <sub>20</sub> H <sub>12</sub>	252.32	828	<b>0.083</b>	386	<b>0.039</b>

<sup>2</sup> The 16 PAHs regarded as being representative for the emissions of CTPHT in the Annex XV Transitional Dossier (The Netherlands, 2008).

<b>Table 1.1: Indicative data on composition of CTPHT (The Netherlands, 2008)</b>								
Chemical name	EINECS Number	CAS Number	Molecular Formula	Molecular Weight	Concentration in Impregnating pitch		Concentration in Binder pitch	
					(mg/kg)	% *	(mg/kg)	% *
Benzo(a)fluorene **	205-944-9	238-84-6	C <sub>17</sub> H <sub>12</sub>	216.29	4509	<b>0.451</b>	1974	<b>0.197</b>
Benzo(b)fluorene **	205-952-2	243-17-4	C <sub>17</sub> H <sub>12</sub>	216.29	4306	<b>0.431</b>	2456	<b>0.246</b>
Benzo(e)pyrene **	205-892-7	192-97-2	C <sub>20</sub> H <sub>12</sub>	252.32	11891	<b>1.189</b>	8976	<b>0.898</b>
Perylene	205-900-9	198-55-0	C <sub>20</sub> H <sub>12</sub>	252.32	5014	<b>0.501</b>	3167	<b>0.317</b>
Anthanthrene	205-884-3	191-26-4	C <sub>22</sub> H <sub>12</sub>	276.34	4581	<b>0.458</b>	3464	<b>0.346</b>
<b>Tar Bases / Nitrogen-containing Heterocycles</b>								
Acridine	205-971-6	260-94-6	C <sub>13</sub> H <sub>9</sub> N	179.21	242	<b>0.024</b>	264	<b>0.026</b>
Carbazole	201-696-0	86-74-8	C <sub>12</sub> H <sub>9</sub> N	167.2	1556	<b>0.156</b>	1664	<b>0.166</b>
<b>Sulfur-containing Heterocycles</b>								
Dibenzothiophene	205-072-9	132-65-0	C <sub>12</sub> H <sub>8</sub> S	184.26	269	<b>0.027</b>	438	<b>0.044</b>
<b>Oxygen-containing Heterocycles / Furans</b>								
Dibenzofuran	205-071-3	132-64-9	C <sub>12</sub> H <sub>8</sub> O	168.19	n.d	<b>n.d.</b>	215	<b>0.022</b>

\* n.d. = not detected (detection limit 50 mg/kg)

\*\* EC names reported in EINECS: for Benz(a)anthracene → Benz[a]anthracene; for Benzo(b)fluoranthene → Benzo[e]acephenanthrylene; for Benzo(k) → Benzo[k]fluoranthene; for Benzo(a)pyrene → Benzo[def]chrysene; for Dibenzo(ah)anthracene → Dibenzo[ah]anthracene; for Benzo(ghi)perylene → Benzo[ghi]perylene; for Indeno(1,2,3cd)pyrene → Indeno[1,2,3-cd]pyrene; for Cyclopenta(def)phenanthrene → 4H-Cyclopenta[def]phenanthrene; for Acephenanthrylene → Benzo[e]acetophenanthrylene; for Benzo(a)fluorene → Benzo[a]fluorene; for Benzo(b)fluorene → Benzo[b]fluorene; for Benzo(e)pyrene → Benzo[e]fluorene

### 1.3 Physico-chemical properties

<b>Table 1.2: Summary of physico-chemical properties of CTPHT (The Netherlands, 2008)</b>			
<b>REACH ref Annex, §</b>	<b>Property</b>	<b>Value</b>	<b>Comment/reference</b>
VII, 7.1	Physical state at 20°C and 101.3 kPa	Black solid	
VII, 7.2	Melting/freezing point	65 - 150 °C	Softening range; CCSG 2006 <sup>3</sup>
VII, 7.3	Boiling point	>360 °C	At 1013 hPa
VII, 7.5	Vapour pressure (Pa)	< 10 < 1000	At 20 °C; At 200 °C; OECD 104; CCSG 2006 <sup>2</sup>
VII, 7.7	Water solubility (mg/l)	~0.040	16 EPA PAHs, at a loading of 10 g/L at 22 °C; RÜTGERS VFT 1999
VII, 7.8	Partition coefficient n-octanol/water (log value)		Not applicable
	Density (g/m <sup>3</sup> )	1.15 – 1.40	At 20 °C; ASTM D 71; CCSG 2006 <sup>2</sup>
VII, 7.9	Flash point (°C)	>250	ISO 2719; CCSG 2006 <sup>2</sup>
VII, 7.12	Auto flammability (°C)	>450	Ignition point at 101.3 kPa; DIN 51794 ; CCSG 2006 <sup>2</sup>
VII, 7.11	Explosive properties	Not explosive	CCSG 2006 <sup>2</sup>
VII, 7.13	Oxidizing properties	Not oxidizing	CCSG 2006 <sup>2</sup>

<sup>3</sup> CCSG 2006: Internal communication, Coal Chemicals Sector Group/CEFIC 2006 (The Netherlands, 2008)

### 1.3.1 Physico-chemical properties of indicator constituents of CTPHT relevant for PBT/vPvB assessment

Table 1.3: Physico-chemical Properties of the 12 PAHs present in CTPHT in concentrations above or equivalent to 0.1% (The Netherlands, 2008)										
Substance	CAS no	Molecular formula	Molecular weight (g.mol <sup>-1</sup> )	Melting point (°C)	Boiling point (°C)	Water solubility (µg.l <sup>-1</sup> )	Log Kow (-)	Vapour pressure (Pa at 25 °C)	Density (kg.l <sup>-1</sup> )	Henry's constant (Pa m <sup>3</sup> /mol at 25 °C)
Anthracene	120-12-7	C <sub>14</sub> H <sub>10</sub>	178.2	216.4	342 <sup>e</sup>	47 <sup>a</sup>	4.68 <sup>d</sup>	9.4 x 10 <sup>-4i</sup>	1.283	4.3 <sup>l</sup>
Phenanthrene	85-01-8	C <sub>14</sub> H <sub>10</sub>	178.2	100.5	340	974 <sup>a</sup>	4.57 <sup>d</sup>	2.6 x 10 <sup>-2i</sup>	0.980	3.7 <sup>l</sup>
Fluoranthene	206-44-0	C <sub>16</sub> H <sub>10</sub>	202.3	108.8	375	200 <sup>a</sup>	5.20 <sup>d</sup>	1.2 x 10 <sup>-3h</sup>	1.252	1.1 <sup>o</sup>
Pyrene	129-00-0	C <sub>16</sub> H <sub>10</sub>	202.3	156	360	125 <sup>a</sup>	4.98 <sup>e</sup>	1.0 x 10 <sup>-3i</sup>	1.271	1.4 <sup>n</sup>
Benz(a)anthracene	56-55-3	C <sub>18</sub> H <sub>12</sub>	228.3	160.7	435	10.2 <sup>a</sup>	5.91 <sup>d</sup>	7.6 x 10 <sup>-6i</sup>	1.226	0.81 <sup>p</sup>
Chrysene	218-01-9	C <sub>18</sub> H <sub>12</sub>	228.3	253.8	448	1.65 <sup>a</sup>	5.81 <sup>d</sup>	5.7 x 10 <sup>-7j</sup>	1.274	0.079 <sup>q</sup>
Benzo(a)pyrene	50-32-8	C <sub>20</sub> H <sub>12</sub>	252.3	175	496	1.54 <sup>a</sup>	6.13 <sup>d</sup>	7.3 x 10 <sup>-7j</sup>	1.35	0.034 <sup>o(20 °C)</sup>
Benzo(b)fluoranthene	205-99-2	C <sub>20</sub> H <sub>12</sub>	252.3	168.3	481	1.28 <sup>a</sup>	6.12 <sup>f</sup>	3.3 x 10 <sup>-6k</sup>	-	0.051 <sup>o(20 °C)</sup>
Benzo(k)fluoranthene	207-08-9	C <sub>20</sub> H <sub>12</sub>	252.3	217	480	0.93 <sup>a</sup>	6.11 <sup>d</sup>	1.3 x 10 <sup>-7k</sup>	-	0.043 <sup>o(20 °C)</sup>
Benzo(ghi)perylene	191-24-2	C <sub>22</sub> H <sub>12</sub>	276.3	277	545 <sup>i</sup>	0.14 <sup>a</sup>	6.22 <sup>d</sup>	1.4 x 10 <sup>-8j</sup>	1.329	0.027 <sup>o(20 °C)</sup>
Dibenzo(a,h)anthracene	53-70-3	C <sub>22</sub> H <sub>14</sub>	278.4	266.6	524	0.82 <sup>b</sup>	6.50 <sup>e</sup>	3.7 x 10 <sup>-10j</sup>	1.282	1.3.10 <sup>-4q</sup>
Indeno(1,2,3-cd)pyrene	193-39-5	C <sub>22</sub> H <sub>12</sub>	276.3	163.6	536	0.1 <sup>c</sup>	6.58 <sup>f</sup>	1.7 x 10 <sup>-8k</sup>	-	0.046 <sup>q</sup>

The data presented above were taken from Mackay *et al.* (1992). The selected values for water solubility were preferably based on generated column methods (a) and if absent, on shake-flask methods (b) using geometric means ((c) for indeno(1,2,3-cd)pyrene, no data were available, a default value of 0.1 µg/l was used). The selected values for log Kow were preferably based on slow-stirring/generator column (c) or slow-stirring methods (d) using average values. If absent the log Kow values were based on the shake-flask method (e), or in absent of data calculated using ClogP model (f). The selected values for vapour pressure were based on manometry/gas saturation (g), gas saturation (h), gas saturation/effusion (i), effusion method (j) using geometric means or estimated using EPIWIN (k). The selected values for the Henry's constant were based on batch/gas stripping/wetted-wall column (l), batch/gas stripping (n), gas stripping (o), batch column (p) using geometric means or when no data were available, constants were calculated using EUSES 2.0 (q).

## 2 CLASSIFICATION AND LABELLING

### Classification in Annex VI of Regulation (EC) No 1272/2008

CTPHT has index number 648-055-00-5 in Annex VI, part 3, Tables 3.1 and 3.2 of Regulation (EC) No 1272/2008.

CTPHT is classified as carcinogen (Carc. Cat.2 ; R45) according to Annex VI, part 3, Table 3.2 (the list of harmonised classification and labelling of hazardous substances from Annex I to Directive 67/548/EEC) of Regulation (EC) No 1272/2008. According to the same Regulation, some of the indicator PAH-constituents relevant for the PBT/vPvB assessment of CTPHT are classified as carcinogen, mutagen or as toxic to reproduction. The full classification of CTPHT and its indicator PAH-constituents according to Annex VI, part 3, Table 3.2 of Regulation (EC) No 1272/2008) is provided in Table 2.1.

Substance	CAS no	Index Number	Classification [concentration limits]
CTPHT	65996-93-2	648-055-00-5	Carc. Cat. 2; R45
Anthracene	120-12-7	*, **	*, **
Phenanthrene	85-01-8	*	*
Fluoranthene	206-44-0	*	*
Pyrene	129-00-0	*	*
Benz(a)anthracene	56-55-3	601-033-00-9	Carc. Cat. 2; R45 N; R50-53
Chrysene	218-01-9	601-048-00-0	Carc. Cat. 2; R45 Muta. Cat. 3; R68 N; R50-53
Benzo(a)pyrene	50-32-8	601-032-00-3	Carc. Cat. 2; R45 [C ≥ 0.01%] Muta. Cat. 2; R46 Repr. Cat. 2; R60-61 R43 N; R50-53
Benzo(b)fluoranthene	205-99-2	601-034-00-4	Carc. Cat. 2; R45 N; R50-53
Benzo(k)fluoranthene	207-08-9	601-036-00-5	Carc. Cat. 2; R45 N; R50-53
Benzo(ghi)perylene	191-24-2	*	*
Dibenzo(a,h)anthracene	53-70-3	601-041-00-2	Carc. Cat. 2; R45 [C ≥ 0.01%] N; R50-53
Indeno(1,2,3-cd)pyrene	193-39-5	*	*

**Key:**  
 \*: No classification in the context of Regulation (EC) No. 1272/2008  
 \*\*: Xi; R38 N;R50-53 (in the context of Directive 67/548/EEC) proposed in the draft risk assessment report on anthracene (Greece, 2008)  
 Carc.: carcinogenic; Muta: mutagenic; Repr.: toxic for reproduction  
 R43: May cause sensitisation by skin contact  
 R45: May cause cancer  
 R46: May cause heritable genetic damage  
 R50: Very toxic to aquatic organisms, and  
 R53: May cause long-term adverse effects in the aquatic environment  
 R60: May impair fertility  
 R61: May cause harm to the unborn child  
 R68: Possible risk of irreversible effects.  
 N: Dangerous for environment

Substance	CAS no [Index No]	Classification		Labelling	
		Hazard Class and Category Code(s) [specific concentration limits]	Hazard statement Code(s)	Pictogram, Signal Word Code(S)	Hazard statement Code(s)
CTPHT	65996-93-2 [648-055-00-5]	Carc. 1B	H350	GHS08 Dgr	H350
Anthracene	120-12-7	*,**	*,**	*,**	*,**
Phenanthrene	85-01-8	*	*	*	*
Fluoranthene	206-44-0	*	*	*	*
Pyrene	129-00-0	*	*	*	*
Benz(a)anthracene	56-55-3 [601-033-00-9]	Carc. 1B Aquatic Acute 1 Aquatic Chronic 1	H350 H400 H410	GHS08 GHS09 Dgr	H350 H410
Chrysene	218-01-9 [601-048-00-0]	Carc. 1B Muta. 2 Aquatic Acute 1 Aquatic Chronic 1	H350 H341 H400 H410	GHS08 GHS09 Dgr	H350 H341 H410
Benzo(a)pyrene	50-32-8 [601-032-00-3]	Carc. 1B [C ≥ 0.01%] Muta. 1B Repr. 1B Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1	H350 H340 H360-FD H317 H400 H410	GHS08 GHS07 GHS09 Dgr	H350 H340 H360FD H317 H410
Benzo(b)fluoranthene	205-99-2 [601-034-00-4]	Carc. 1B Aquatic Acute 1 Aquatic Chronic 1	H350 H400 H410	GHS08 GHS09 Dgr	H350 H410
Benzo(k)fluoranthene	207-08-9 [601-036-00-5]	Carc. 1B Aquatic Acute 1 Aquatic Chronic 1	H350 H400 H410	GHS08 GHS09 Dgr	H350 H410
Benzo(ghi)perylene	191-24-2	*	*	*	*
Dibenzo(a,h)anthracene	53-70-3 [601-041-00-2]	Carc. 1B [C ≥ 0.01%] Aquatic Acute 1 Aquatic Chronic 1	H350 H400 H410	GHS08 GHS09 Dgr	H350 H410
Indeno(1,2,3-cd)pyrene	193-39-5	*	*	*	*

**Key:**  
\*: No classification in the context of Regulation (EC) No. 1272/2008  
\*\*: Xi; R38 N;R50-53 (in the context of Directive 67/548/EEC) proposed in the draft risk assessment report on anthracene (Greece, 2008) [translated according to Table 1.1 of Annex VII of Regulation (EC) No. 1272/2008 into: Skin Irrit. 2; Aquatic Acute 1; Aquatic Chronic 1]  
N: Dangerous for environment; R50-53: Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.  
Carc.1B: Carcinogen; Muta 2, 1B: Germ cell mutagen; Repr.1B: Toxic to reproduction  
Aquatic acute 1, Aquatic chronic 1: Hazardous to the aquatic environment  
Skin Sens.1: Skin sensitizing  
H317: May cause an allergic skin reaction; H341: Suspected of causing genetic defects  
H350: May cause cancer; H360-FD: May damage fertility. May damage the unborn child  
H400: Very toxic to aquatic life; H410: Very toxic to aquatic life with long lasting effects.  
GHS07: exclamation mark; GHS08: health hazard; GHS09: environment; Dgr: Danger

The harmonised classification and labelling as hazardous substances according to Regulation (EC) No 1272/2008 (Annex VI, part 3, Table 3.1 (list of harmonised classification and labelling of hazardous substances)) for CTPHT and its 12 indicator PAH-constituents relevant for the PBT/vPvB assessment is presented in Table 2.2.

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## 3 ENVIRONMENTAL FATE PROPERTIES

### 3.1 Overview

The data presented here were retrieved from the Annex XV Transitional Dossier on coal tar pitch, high temperature (CTPHT) (The Netherlands, 2008).

According to the approach followed herein (see Section 1.2), the evaluation of the fate properties is based on available data for the 12 indicator PAHs considered relevant for the PBT/vPvB assessment of CTPHT. No information on the environmental fate of CTPHT itself was found.

### 3.2 Degradation

#### 3.2.1 Abiotic degradation

##### 3.2.1.1 Hydrolysis

In general, PAHs are hydrolytically stable in aqueous systems. Under environmental conditions, therefore, hydrolysis does not contribute to the degradation of PAHs (Howard *et al.* (1991) cited in The Netherlands, 2008).

##### 3.2.1.2 Atmospheric degradation

In the atmosphere, the PAHs are either gas phase or particle-associated. It has been shown that the 2-4 ring PAHs with vapour pressure higher than or equal to  $10^{-4}$  Pa are mostly gas phase-related and PAHs of 4 rings or more with vapour pressure below  $10^{-4}$  Pa are particle-associated. In the gas phase PAHs are oxidized by atmospheric hydroxyl (OH) and nitrate radicals and ozone, whereas the particle-associated PAHs are expected to be degraded by direct photolysis and by reaction with ozone (The Netherlands, 2008).

Atmospheric half-lives are given in the Annex XV Transitional Dossier on CTPHT. For the 2-4 ring PAHs, representative lifetimes with respect to gas-phase reactions range from 2 hours to 9 days for reactions with OH. Few data indicate half-lives from 4.8 hours to 340 days for gas phase nitrate and ozone reactions. Under environmental conditions, PAHs of higher molecular mass are almost completely adsorbed onto fine particles. Studies indicate that the degradation rate depends on the particle material, with PAHs being more stable when adsorbed to particles of higher carbon content. Representative lifetimes of the particle-associated PAHs are in the range of 15 minutes to 6-8 days with respect to photolysis (The Netherlands, 2008).

##### 3.2.1.3 Phototransformation in water and soil

PAHs are photo-degraded by two processes, direct photolysis by light with a wavelength  $< 290$  nm and indirect photolysis (photo-oxidation) by at least one oxidizing agent (Volkering and Breure (2003) cited in The Netherlands, 2008). Singlet oxygen is the main oxidant, but also reactions with nitrite and to a lesser extent with nitrate may take place (Suzuki *et al.*, (1987) cited in The Netherlands, 2008). The degradation rate depends on the content of dissolved oxygen, and may be increased in the presence of humic acid, while it increases exponentially with the temperature (Moore and Ramamoorthy, 1984 cited in The Netherlands, 2008). When PAHs are adsorbed to suspended particles, the accessibility for photochemical reactions will depend on the nature of the particles.

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Photodegradation in natural waters takes normally place only in the upper few centimetres of the water-column and is therefore not considered to have significant impact on the overall persistency of PAHs in the aquatic environment. As exposure to light is even more limited in soils, photodegradation is as well not considered a relevant degradation process in terrestrial environments.

### **3.2.2 Biodegradation**

#### **3.2.2.1 Biodegradation in water**

Standard tests for biodegradation in water have demonstrated that PAHs with up to four aromatic rings are biodegradable under aerobic conditions, but that biodegradation rates of PAHs with more aromatic rings are very low (The Netherlands, 2008). In general, the biodegradation rates decrease with increasing number of aromatic rings. This correlation has been attributed to factors like the bacterial uptake rate and the bioavailability. The bacterial uptake rate has been shown to be lower for the higher molecular weight PAHs as compared to the PAHs of lower molecular weight. This may be due to the size of high molecular weight members, which limits their ability to cross cellular membranes. In addition, bioavailability is lower for higher molecular PAHs due to adsorption to organic matter in water and sediment. It has further been shown that half-lives of PAHs in estuarine sediment are proportionally related to the octanol-water partition coefficient ( $K_{ow}$ ) (Durant *et al.*, (1995) cited in The Netherlands, 2008).

#### **3.2.2.2 Biodegradation in sediments**

In general, PAHs are considered to be persistent under anaerobic conditions (Neff (1979); Volkering and Breure (2003) cited in The Netherlands, 2008). Aquatic sediments are often anaerobic with the exception of a few millimetre thick surface layer at the sediment-water interface, which may be dominated by aerobic conditions. The degradation of PAHs in aquatic sediments is therefore expected to be very slow.

#### **3.2.2.3 Biodegradation in soil**

Biodegradation rates of PAHs in soil depend on several factors related to the soil type, including pH, moisture content, nutrients, oxygen, and the diversity of the soil microbial population. Various species (bacteria, fungi, yeasts and algae) are known to degrade PAHs in soil (The Netherlands, 2008). It has been shown that the number of PAH-degrading microorganisms and the degradation capacity is higher in PAH-contaminated soils than in pristine soils, something explained by the development of an adapted soil microbial community. Several studies have also been demonstrated enhanced PAH-degradation rates when the soil had been enriched with isolated PAH-degrading microorganisms (Davis *et al.* (1993); Grosser *et al.* (1995); Schneider *et al.* (1996) cited in The Netherlands, 2008).

On the basis of a comparison between two studies (Wild *et al.* 1991 and Wild and Jones, 1993) it was illustrated that the half-lives observed under laboratory conditions can be much shorter than those obtained from long-term field studies. This was attributed by the authors to the more optimal conditions (temperature, moisture content, nutrient and oxygen supply) applied in the laboratory tests.

Wild and Jones (1993) and Wild *et al.* (1991) studied the biodegradation of PAHs in soil amended with sewage sludge under laboratory and field conditions, respectively. The half-lives for PAHs determined in the two experiments are presented in Table 3.1. Whereas the half-lives obtained in the laboratory soil microcosms were in the range of days, those representing the field conditions were in the range of years.

<b>PAH (number of rings)</b>	<b>Half lives obtained from soil microcosms (days) Wild &amp; Jones (1993)</b>	<b>Half lives obtained from long term field experiment (years) Wild <i>et al</i> (1991)</b>
Phenanthrene (3)	83-193	5.7
Anthracene (3)	48-120	7.9
Fluoranthene (4)	110-184	7.8
Pyrene (4)	127-320	8.5
Benz(a)anthracene and Chrysene (4)	106-313	8.1
Benzo(b)fluoranthene (5)	113-282	9.0
Benzo(k)fluoranthene (5)	143-359	8.7
Benzo(a)pyrene (5)	120-258	8.2
Benzo(ghi)perylene (6)	365-535	9.1

No experimental data on half-lives for dibenzo(a,h)anthracene (5 rings) and indeno(1,2,3-cd)pyrene (6 rings) were found.

### 3.2.3 Summary and discussion on degradation

According to Annex XIII of the REACH Regulation, the definitive P criterion is based on half-lives in (fresh, estuarine or marine) water, soils or (fresh, estuarine or marine water) sediments. The degradation kinetics of PAHs in the different environmental compartments are influenced by a number of factors, and to a great extent determined by their very low water solubility and tendency to adsorb to particles and organic matter in the environment. Their low bioavailability (especially of PAHs with more than two aromatic rings) is one of the limiting factors for their biodegradation.

‘Aging’ is a phenomenon associated with increased residence time of PAHs in soil, which can further decrease the bioavailability of PAHs in the terrestrial environment. Freshly spiked PAHs are more readily desorbed and thus more bioavailable than PAHs that have been in soil or sediment for a longer period of time (The Netherlands, 2008). This means that studies involving artificially added PAHs (e.g. <sup>14</sup>C-labelled) often result in biodegradation rates much higher than rates observed for the same substances present in soil as part of a contamination by coal tar.

In the assessment for persistence of the PAHs representing CTPHT, half-lives obtained under realistic conditions, i.e. field conditions, are given priority, as Annex XIII of the REACH Regulation requires the data to be collected under the adequate conditions. The study by Wild *et al.* (1991) reports half-lives in soil for 10 of the 12 PAHs addressed in the present assessment [anthracene, phenanthrene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(ghi)perylene] above the P and vP criteria set in the Annex XIII, and it is selected as the key study for the P assessment of CTPHT. Experimental data on half-lives for dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene are lacking in this study.

Mackay *et al.* (1992) estimated half-lives in the different environmental compartments based on model calculations and literature search. On the basis of the results of this study, dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene are expected to be as well persistent in soil and sediment: the estimated half-lives for the two PAHs were in soil in the range of 420 to 1250 days, and in sediments longer than 1250 days.

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### 3.3 Environmental distribution

#### 3.3.1 Adsorption/desorption

The octanol-water coefficients of the indicator PAH-constituents of CTPHT are shown in Table 3.2. A linear relationship between  $K_{ow}$  and the organic carbon-water partitioning coefficient  $K_{oc}$  has been demonstrated for PAHs in sediments and soil. The Log  $K_{ow}$  values from 4.6 to 6.6 can be translated as a high potential for partitioning to soils and sediments. Partitioning processes like adsorption to airborne particulate matter, as well as accumulation in sludge during wastewater treatment, have been demonstrated especially for high molecular weight PAHs (The Netherlands, 2008).

Substance	Log $K_{ow}$
Anthracene	4.68
Phenanthrene	4.57
Fluoranthene	5.20
Pyrene	4.98
Benz(a)anthracene	5.91
Chrysene	5.81
Benzo(a)pyrene	6.13
Benzo(b)fluoranthene	6.12
Benzo(k)fluoranthene	6.11
Benzo(ghi)perylene	6.22
Dibenzo(a,h)anthracene	6.50
Indeno(1,2,3-cd)pyrene	6.58

#### 3.3.2 Volatilisation

With their low vapour pressures in the range of  $10^{-2}$ - $10^{-10}$  Pa, the PAHs contained in CTPHT are expected to volatilise very slowly. In the Annex XV Transitional Dossier on CTPHT it is concluded that, under field conditions, volatilisation of PAHs is insignificant (The Netherlands, 2008).

### 3.4 Bioaccumulation

#### 3.4.1 Aquatic bioaccumulation

Bioconcentration in aquatic organisms can be determined at steady state conditions as the concentration in the organism divided by the concentration in the water, or as the ratio between the rates of uptake and depuration at non steady state conditions. The bioconcentration factor (BCF) is linearly correlated with the  $K_{ow}$  up to log  $K_{ow}$  values in the range of 5 - 6. At higher log  $K_{ow}$  values, the BCF tends to stay constant or may even decrease with increasing log  $K_{ow}$  (The Netherlands, 2008). This is explained by characteristics like lipid solubility variations, slow desorption, low bioavailability, and reduced membrane passage due to the molecular size, usually associated with molecules having a very high  $K_{ow}$ . As for PAHs, this trend has been observed in studies of bioaccumulation potential in fish but not in studies with molluscs or crustaceans.

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Potential for biotransformation of substances in exposed species is also an important factor in assessing bioaccumulation. BCF values may be higher in early life stages of an organism than in the adult stage. Whereas fish, and to some extent also molluscs, have the ability to metabolise PAHs, no evidence of metabolism of PAHs has been observed in algae, or oligochaeta.

As part of the Annex XV Transitional Dossier on CTPHT (The Netherlands, 2008), data from studies on bioaccumulation of the 16 representative PAHs were collected. The quality of the studies was evaluated and each study was given a reliability score. Only studies evaluated as reliable and relevant are included for the 12 PAHs addressed in this report (valid without restrictions or valid with restriction; see Tables 3.3 & 3.4).

For each substance, a key study representative for the bioaccumulation potential has been selected. The studies preferred as key studies are equilibrium studies performed with fish and with chemical analysis of the substance in water and in the organism, showing high bioconcentration. However, in addition to data on fish, BCF values for molluscs and crustaceans are considered in the assessment of the bioaccumulation potential of the PAHs as well. In Tables 3.3 and 3.4 the selected key studies are highlighted by bold font of the reference. Justification for choosing the highlighted studies is provided in the notes to the tables.

Bioaccumulation and the role of biotransformation in the bioaccumulation process of PAHs were studied in a static experimental set-up with fathead minnows (*Pimephales promelas*) (De Maagd, 1996). The results indicated that biotransformation did influence the bioaccumulation of benz(a)anthracene, but had no effect on the accumulation of phenanthrene and anthracene. The uptake of fluoranthene, however, could be better modelled if biotransformation was taken into account. The calculated BCF values when biotransformation was inhibited were 6,800 for phenanthrene and anthracene, 3,400 for fluoranthene, and 200 for benz(a)anthracene.

In a second study by De Maagd *et al.* (1998), with fathead minnows, benz(a)anthracene was tested in a flow-through study resulting in BCF values of 262-265.

In another study with fathead minnows (Weinstein and Oris, 1999), juvenile fish (48 hours post-hatching) were exposed in a static system to four concentrations of fluoranthene. The determined BCF value was  $9,054 \pm 555$ .

A regular semi-static (renewal) bioaccumulation test was carried out by De Voogt *et al.* (1991). The BCF was determined by dividing the final concentration in fish by the average concentration in water during the last renewal period. The BCF values determined were 4,550 for anthracene and 11,300 for pyrene.

De Voogt *et al.* (1991) also performed a static experiment. The BCF value determined for anthracene as the concentration in fish divided by the concentration in water at the end of the static experiment was 6000.

Jonsson *et al.* (2004) exposed the fish *Cyprinodon variegatus* for 36d to phenanthrene and pyrene in a continuous flow system with seawater, followed by 8d of depuration. BCFs ranged from 700 to 2,229 for phenanthrene, and from 50 to 145 for pyrene.

**Table 3.3: Experimentally obtained BCF values of PAHs in fish or mollusks**

Substance	Species	BCF (L/kg)	Val	Test system	Type	Chem. analysis	References
Anthracene	<u>Mollusca</u> <i>U. imbecilis</i> (larv.)	345 (highest 420)	2	R	Equi (parent)		Weinstein & Polk (2001)
	<u>Fish</u> <i>L. macrochirus</i>	900	2	S	k <sub>1</sub> /k <sub>2</sub> (total)	<sup>14</sup> C	Spacie <i>et al.</i> , 1983
	<i>P. promelas</i>	6760	2	S	k <sub>1</sub> /k <sub>2</sub> (parent)	HPLC	De Maagd <i>et al.</i> , 1996
	<i>P. reticulata</i>	4550 (pref)*	2	R	Equi (parent)	HPLC	<b>De Voogt <i>et al.</i>, 1991</b>
	<i>P. reticulata</i>	6000	2	S	Equi (parent)	HPLC	<b>De Voogt <i>et al.</i>, 1991</b>
Phenanthrene	<u>Mollusca</u> <i>M. edulis</i>	1240	1	F	k <sub>1</sub> /k <sub>2</sub> (parent)	HPLC	McLeese & Burridge, 1987
	<i>M. arenaria</i>	1280	1	F	k <sub>1</sub> /k <sub>2</sub> (parent)	HPLC	McLeese & Burridge, 1987
	<u>Fish</u> <i>P. promelas</i>	6760	2	S	k <sub>1</sub> /k <sub>2</sub> (parent)	HPLC	<b>De Maagd <i>et al.</i>, 1996</b>
	<i>C. variegatus</i>	810 (le)	1	CF	k <sub>1</sub> /k <sub>2</sub> (parent)	GCMS	Jonsson <i>et al.</i> , 2004
	<i>C. variegatus</i>	2229 (he)	1	CF	k <sub>1</sub> /k <sub>2</sub> (parent)	GCMS	Jonsson <i>et al.</i> , 2004
	<i>C. variegatus</i>	700 (le)	1	CF	Equi (parent)	GCMS	Jonsson <i>et al.</i> , 2004
	<i>C. variegates</i>	1623 (he)	1	CF	Equi (parent)	GCMS	Jonsson <i>et al.</i> , 2004
Fluoranthene	<u>Mollusca</u> <i>M. edulis</i>	5920	1	F	k <sub>1</sub> /k <sub>2</sub> (parent)	HPLC	McLeese & Burridge, 1987
	<i>M. arenaria</i>	4120	1	F	k <sub>1</sub> /k <sub>2</sub> (parent)	HPLC	McLeese & Burridge, 1987
	<u>Fish</u> <i>P. promelas</i>	9054	2	S	Equi (parent)	HPLC	<b>Weinstein &amp; Oris, 1999</b>
	<i>P. promelas</i>	3388	2	S	k <sub>1</sub> /k <sub>2</sub> (parent)	HPLC	De Maagd <i>et al.</i> , 1996
Pyrene	<u>Mollusca</u> <i>M. arenaria</i>	6430	1	F	k <sub>1</sub> /k <sub>2</sub> (parent)	HPLC	McLeese & Burridge, 1987
	<i>M. edulis</i>	4430	1	F	k <sub>1</sub> /k <sub>2</sub> (parent)	HPLC	McLeese & Burridge, 1987
	<i>D. polymorpha</i>	16000 (21h)	2	S	k <sub>1</sub> /k <sub>2</sub> (total=parent)	LSC	Bruner <i>et al.</i> , 1994
	<i>D. polymorpha</i>	13000 (21h)	2	S	k <sub>1</sub> /k <sub>2</sub> (total=parent)	LSC	Bruner <i>et al.</i> , 1994
	<i>D. polymorpha</i>	35000 (15)	2	S	k <sub>1</sub> /k <sub>2</sub> (total=parent)	LSC	Bruner <i>et al.</i> , 1994
	<i>D. polymorpha</i>	43000 (Av1)	2	S	k <sub>1</sub> /k <sub>2</sub> (total=parent)	LSC	Gossiaux <i>et al.</i> , 1996
	<i>D. polymorpha</i>	37000 (Av2)	2	S	k <sub>1</sub> /k <sub>2</sub> (total=parent)	LSC	Gossiaux <i>et al.</i> , 1996
	<u>Fish</u> <i>Poecilia reticulata</i>	11300 (pref)	2	R	Equi (parent)	HPLC	<b>De Voogt <i>et al.</i>, 1991</b>
	<i>Poecilia reticulata</i>	2700*	2	S	Equi (parent)	HPLC	<b>De Voogt <i>et al.</i>, 1991</b>
	<i>C. variegatus</i>	145 (le)	1	CF	k <sub>1</sub> /k <sub>2</sub> (parent)	GCMS	Jonsson <i>et al.</i> , 2004

**Table 3.3: Experimentally obtained BCF values of PAHs in fish or mollusks**

Substance	Species	BCF (L/kg)	Val	Test system	Type	Chem. analysis	References
	<i>C. variegatus</i>	97 (he)	1	CF	k <sub>1</sub> /k <sub>2</sub> (parent)	GCMS	Jonsson <i>et al.</i> , 2004
	<i>C. variegatus</i>	50 (le)	1	CF	Equi (parent)	GCMS	Jonsson <i>et al.</i> , 2004
	<i>C. variegatus</i>	53 (he)	1	CF	Equi (parent)	GCMS	Jonsson <i>et al.</i> , 2004
Benz(a)anthracene	<u>Fish</u> <i>P. promelas</i>	200-265	2	S	k <sub>1</sub> /k <sub>2</sub> (parent)	HPLC	De Maagd <i>et al.</i> , 1996, 1998
Benzo(a)pyrene	<u>Mollusca</u> <i>D. polymorpha</i>	84000 (21h)	2	S	k <sub>1</sub> /k <sub>2</sub> (total=parent)	LSC	Bruner <i>et al.</i> , 1994
	<i>D. polymorpha</i>	41000 (211)	2	S	k <sub>1</sub> /k <sub>2</sub> (total=parent)	LSC	Bruner <i>et al.</i> , 1994
	<i>D. polymorpha</i>	77000 (15)	2	S	k <sub>1</sub> /k <sub>2</sub> (total=parent)	LSC	Bruner <i>et al.</i> , 1994
	<i>D. polymorpha</i>	133000 (Av3)	2	S	k <sub>1</sub> /k <sub>2</sub> (total=parent)	LSC	<b>Gossiaux <i>et al.</i>, 1996</b>
	<i>D. polymorpha</i>	142000 (Av4)	2	S	k <sub>1</sub> /k <sub>2</sub> (total=parent)	LSC	Gossiaux <i>et al.</i> , 1996

S. static exposure system; C: Continuous; F, flow-through system; R, static renewal system; k<sub>1</sub>/k<sub>2</sub>, kinetic: uptake rate/deposition rate. Equi: equilibrium, Val = Validity (1: Reliable without restrictions, 2: Reliable with restrictions, 3: Not reliable, 4: Not assignable); dw = based on dry weights; pref = preferred by the author; lw = based on lipid weights; le: low exposure concentration; he: high exposure concentration; HPLC: High Performance Liquid Chromatography; GCMS: Gas Chromatography Mass Spectrometry; LSC: Liquid Scintillation Counting

21h = 21 mm size class with high lipid content

211 = 21 mm size class with low lipid content

15 = 15 mm size class

Av1 = average BCF obtained from 4 experiments at ambient field temperatures (individual BCFs were 33000, 22000, 77000, and 39000)

Av2 = average BCF obtained from 6 experiments after acclimatisation to lab temperatures (individual BCFs were 32000, 48000, 41,000, 39000, 24000, and 39000)

Av3 = average BCF obtained from 11 experiments at ambient field temperatures (individual BCFs were 77000, 49000, 191000, 167000, 132000, 165000, 150000, 197000, 40000, 24000, and 273000)

Av4 = average BCF obtained from 12 experiments after acclimatisation to lab temperatures (individual BCFs were 190000, 83000, 61000, 197000, 220000, 116000, 40000, 147000, 215000, 270000, 107000, and 62000)

\* The BCF value of 4550 is considered the preferable one by de Voogt *et al.* (1991) as it was determined in a semi-static test by dividing the final concentration in the fish by the average concentration in water during the last renewal period whereas the other BCF (6000) was determined based on a static test (i.e. calculated from the concentration in the fish divided by the concentration in the water at the end of the test).

**Marked in bold:** Key study. The study by de Voogt *et al.*, 1991 was selected as key study for anthracene and pyrene as this was the most reliable one on fish showing BCF > 2000. For phenanthrene the study by de Maagd *et al.*, 1996 was the most reliable one with BCF > 2000. The study by Weinstein & Oris, 1999 was chosen as key study as it reports a reliable equilibrium BCF for fluoranthene. For benzo(a)pyrene the study by Gossiaux *et al.*, 1996 was chosen among studies on the same organisms and of same validity as key study because it was performed at ambient field temperatures compared to laboratory temperatures.

<b>Table 3.4: Experimentally obtained BCF values of PAHs in Crustaceans</b>						
<b>Substance</b>	<b>Species</b>	<b>BCF (L/kg)</b>	<b>Test System</b>	<b>Type</b>	<b>Chem. analysis</b>	<b>References</b>
Anthracene	<i>D. magna</i>	511	S	k <sub>1</sub> /k <sub>2</sub>	<sup>14</sup> C	McCarthy <i>et al.</i> , 1985
	<i>D. pulex</i>	917	S	Equi	FS	Southworth <i>et al.</i> , 1978
	<i>D. magna</i>	970	S	Equi	HPLC	Newsted & Giesy, 1987
Phenanthrene	<i>D. pulex</i>	325	S	Equi	FS	Southworth <i>et al.</i> , 1978
	<i>D. magna</i>	324	S	Equi	HPLC	Newsted & Giesy, 1987
Fluoranthene	<i>D. magna</i>	1742	S	Equi	HPLC	Newsted & Giesy, 1987
Pyrene	<i>D. pulex</i>	2702	S	Equi	FS	Southworth <i>et al.</i> , 1978
	<i>D. magna</i>	2702	S	Equi	HPLC	Newsted & Giesy, 1987
Benz(a)-anthracene	<i>D. magna</i>	2920	S	k <sub>1</sub> /k <sub>2</sub>	<sup>14</sup> C	McCarthy <i>et al.</i> , 1985
	<i>D. pulex</i>	10109	S	Equi	FS	Southworth <i>et al.</i> , 1978
	<i>D. magna</i>	10226	S	Equi	HPLC	<b>Newsted &amp; Giesy, 1987</b>
Chrysene	<i>D. magna</i>	6088	S	Equi	HPLC	<b>Newsted &amp; Giesy, 1987</b>
Benzo(a)pyrene	<i>D. magna</i>	12761	S	Equi	HPLC	Newsted & Giesy, 1987
Benzo(k)-fluoranthene	<i>D. magna</i>	13225	S	Equi	HPLC	<b>Newsted &amp; Giesy, 1987</b>
Benzo(ghi)-perylene	<i>D. magna</i>	28288	S	Equi	HPLC	<b>Newsted &amp; Giesy, 1987</b>
Dibenzo(a,h)-anthracene	<i>D. magna</i>	50119	S	Equi	HPLC	<b>Newsted &amp; Giesy, 1987</b>
S. static exposure system; k <sub>1</sub> /k <sub>2</sub> , kinetic: uptake rate/depuration rate. Equi: equilibrium FS: Fluorescence Spectrophotometry; HPLC: High Performance Liquid Chromatography <b>Marked in bold:</b> Key study. The study by Newsted & Giesy, 1987 was chosen as the key study for benz(a)anthracene, chrysene, benzo(k)fluoranthene, benzo(ghi)perylene and dibenzo(a,h)anthracene as the most reliable equilibrium study with BCF >2000.						

In a well documented study McLeese and Burridge (1987) determined PAH accumulation in the clam *Mya arenaria* and the mussel *Mytilus edulis* in flow through systems. Concentrations in water and animals were used to calculate k<sub>u</sub> and k<sub>e</sub>, which were subsequently used to calculate BCFs. The resulting BCFs for phenanthrene were 1,280 and 1,240, for fluoranthene 4,120 and 5,920, and for pyrene 6,430 and 4,430, with the first number representing the value for the mussel and the second for the clam.

Bruner *et al.* (1994) exposed the zebra mussel (*Dreissena polymorpha*) in a static system to <sup>3</sup>H-labelled benzo(a)pyrene and pyrene. BCFs were calculated using kinetic rate constants and ranged from 13,000 to 35,000 for pyrene, and 41,000 to 84,000 for benzo(a)pyrene.

Gossiaux *et al.* (1996) exposed the zebra mussel (*Dreissena polymorpha*) in a static system to radio-labelled benzo(a)pyrene in combination with pyrene. In total a number of 23 experiments with benzo(a)pyrene and 10 experiments with pyrene were conducted under either ambient field temperatures or laboratory temperatures. BCFs were calculated using kinetic rate constants and ranged from 37,000 to 43,000 for pyrene, and 133,000 to 142,000 for benzo(a)pyrene.

Experimental BCF values for crustaceans are presented in Table 3.4. Bioaccumulation in *Daphnia magna* has been studied by McCarthy *et al.* (1985) and Newsted & Giesy (1987). In the study by

McCarthy the BCF value for benz(a)anthracene was reported as 2,920, determined as the ratio between uptake rate and depuration rate. In the study by Newsted & Giesy (1987) the BCF was determined at steady state in a static system. Bioconcentration was determined for a range of PAHs, with the resulting BCFs being below 2,000 for anthracene, phenanthrene and fluoranthene, and above 2,000 for pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, benzo(k)fluoranthene, benzo(ghi)perylene, and dibenzo(a,h)anthracene.

In a study by Southworth (1978) the potential for bioaccumulation in *Daphnia pulex* was studied for PAHs in a static system. The bioconcentration factor was determined at steady state conditions and as the ratio between the rates of uptake and elimination at non steady state conditions. The study indicated that the PAH content of *Daphnia* lipid was in equilibrium with the aqueous PAH concentration. The reported BCF was above 2,000 for pyrene and benz(a)anthracene, and below 2,000 for anthracene and phenanthrene.

### 3.4.2 Summary and discussion of bioaccumulation

An overview of the BCF values of the selected PAH-constituents of CTPHT determined in the key studies is provided in Table 3.5.

A range of valid experimental fish data were available for phenanthrene, fluoranthene and pyrene, showing BCF values >5,000, and for anthracene above 2,000<sup>4</sup>, whereas experimental fish data for benz(a)anthracene and benzo(a)pyrene indicated BCFs below 2,000. Measured BCF values in molluscs were >5,000 for fluoranthene, pyrene and benzo(a)pyrene.

Experimental data from studies on other aquatic organisms, i.e. crustaceans, were considered for the PAHs for which no studies were available with fish or molluscs. For *Daphnia* experimental data for benz(a)anthracene, chrysene, benzo(a)pyrene, benzo(k)fluoranthene, benzo(ghi)perylene, and dibenzo(a,h)anthracene indicated BCF values > 5,000 and above 2,000 for pyrene. In studies with *Daphnia* the obtained BCFs for anthracene, phenanthrene and fluoranthene were below 2,000.

Substance	Value	Key study endpoint
Anthracene	4550	Fish: Equi (parent), <i>P. reticulata</i>
Phenanthrene	6760	Fish: $k_1/k_2$ (parent), <i>P. promelas</i>
Fluoranthene	9054	Fish: Equi (parent), <i>P. promelas</i>
Pyrene	2700-11300	Fish: Equi (parent), <i>P. reticulata</i>
Benz(a)anthracene	10226	Crustaceans: Equi, <i>Daphnia magna</i>
Chrysene	6088	Crustaceans: Equi, <i>Daphnia magna</i>
Benzo(a)pyrene	133000	Mollusca: $k_1/k_2$ (total=parent), <i>D. polymorpha</i>
Benzo(b)fluoranthene	-	No experimental data available
Benzo(k)fluoranthene	13225	Crustaceans: Equi, <i>Daphnia magna</i>
Benzo(ghi)perylene	28288	Crustaceans: Equi, <i>Daphnia magna</i>
Dibenzo(a,h)anthracene	50119	Crustaceans: Equi, <i>Daphnia magna</i>
Indeno(1,2,3-cd)pyrene	-	No experimental data available

<sup>4</sup> The question whether anthracene fulfils both the B and vB criteria or should only be considered as fulfilling the B-criterion was discussed at the Member State Committee meeting in October 2008 in the context of reaching an agreement on the identification of anthracene as a SVHC. Due to uncertainties on the validity of the highest reported BCF values (see as well section 3.4.1 of this report) it was concluded to consider anthracene only fulfilling the B-criterion but not the vB-criterion (MSC, 2008).

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No experimental data on the bioaccumulation potential of benzo(b)fluoranthene and indeno(1,2,3-cd)pyrene were found. On the basis of similarities of their Kow values and molecular sizes with other PAHs for which BCFs above the Annex XIII bioaccumulation criteria have been experimentally confirmed, it is nevertheless anticipated that BCF values for these two substances will be >2000 as well.

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## **4 HUMAN HEALTH HAZARD ASSESSMENT**

Information on hazard to human health relevant for the PBT/vPvB assessment of CTPHT and its PAH-constituents is provided in section 2 of this report (classification information).

Supplementary information on the toxicological properties of CTPHT and its PAH-constituents which could be relevant for risk assessment, comparative assessment of alternative substances, or for priority setting in the context of recommending substances for the 'Authorisation List' (Annex XIV of the REACH Regulation) can be found in Annex 1 to this report and the Annex XV Transitional Dossier on CTPHT (The Netherlands, 2008).

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## 5 ENVIRONMENTAL HAZARD ASSESSMENT

As regards environmental toxicity in the context of the PBT assessment in accordance with Annex XIII of the REACH Regulation, the toxicity criterion (T-criterion) refers to effects on aquatic organisms. Therefore, in this section, the toxicity of CTPHT and its PAH-constituents is considered for the aquatic environment only.

### 5.1 Aquatic compartment (including sediment)

#### 5.1.1 Overview

No information on the environmental hazard of CTPHT is available.

According to the approach followed (see section 1.2), the assessment is based on aquatic toxicity data available for the 12 indicator PAHs considered relevant for the PBT assessment of CTPHT.

PAHs can be toxic via different modes of action, such as non-polar narcosis and phototoxicity. Phototoxicity is caused by the ability of PAHs to absorb UVA radiation, UVB radiation, and in some instances, visible light. It may occur as the result of the production of singlet oxygen, which is highly damaging to biological material, or as result of the formation of new, more toxic compounds from the photomodification (usually oxidation) of PAHs (Lampi et al., 2006). Phototoxic effects can be observed after a short period of exposure, which explains why for PAHs like anthracene, fluoranthene and pyrene, where phototoxicity is most evident, the acute toxicity values under simulated solar radiation may be lower than the chronic toxicity values determined under less harsh radiation.

The phototoxicity of PAHs is relevant where the PAHs are exposed to light and UV radiation, and considered to be most important for upper layers of aquatic and terrestrial environments. Although UV penetration depths may vary among PAH-contaminated sites, it is not unlikely that significant portions of the aquatic community may be exposed to UV levels sufficient to induce phototoxicity, as UV levels occurring under normal sun light conditions have been shown to elicit these effects. There is growing evidence which suggests that phototoxic PAHs may be degrading aquatic habitats, particularly those in highly contaminated areas with shallow or clear water. Photo-induced chronic effects have been reported for anthracene at UV intensities occurring at depths of 10-12 m in Lake Michigan (Holst & Giesy, 1989). Phototoxicity of PAHs may also be initiated in aquatic organisms which have accumulated PAHs from the sediment and subsequently are exposed to sun light closer to the surface (The Netherlands, 2008). Phototoxic effects of PAHs are therefore considered relevant in this hazard, respectively T- assessment.

For data on toxicity to aquatic organisms, reference is made to the Annex XV Transitional Dossier on CTPHT (The Netherlands, 2008).

Studies selected as key studies in the Annex XV Transitional Dossier are those providing the lowest reliable value for the most critical effect and endpoint. Therein, due to the high phototoxic potential of some of the PAHs, key studies for derivation of PNEC values have for some of the substances been short term studies rather than long term studies. Nevertheless, for comparison with the environmental T-criterion of Annex XIII of the REACH Regulation (long-term no effect concentration for marine or freshwater organisms less than 0.01 mg/l), only long term studies have been selected as key studies for PBT assessment. The selected key studies are marked in bold in the Tables 5.1 – 5.11 below.

Sediment toxicity of the PAH-constituents could also be considered in the assessment of CTPHT toxicity. Sediment toxicities are normally expressed as mg/kg of dry weight of the sediment and in order to be able to compare sediment toxicity with the T-criterion for the aquatic environment, sediment toxicity values have to be transformed into aquatic toxicity values. This may be done by involving equilibrium considerations for partitioning between aqueous and non-aqueous phases in the sediment compartment. However, for this transformation, information on specific characteristics of the sediment concerned is needed. As this information is not available, the sediment toxicities of PAH-constituents of CTPHT are not considered in this dossier.

## 5.1.2 Toxicity data

### 5.1.2.1 Anthracene

Anthracene is very phototoxic and acute phototoxic effects are observed after relatively short periods of time (approximately half an hour) upon exposure of test systems to sunlight or artificial light containing UV radiation. Results of studies investigating the aquatic toxicity of anthracene are shown in Table 5.1. The strongest phototoxic effects have been observed in the presence of natural sunlight (The Netherlands, 2008). The results from the acute toxicity studies show a high acute toxicity of anthracene, with EC<sub>50</sub> values as low as 1 µg/l. Chronic toxicity is comparable with lowest NOECs or EC<sub>10</sub>s for reproduction of daphnids or growth of the alga *Pseudokirchneriella subcapitata* in the range of 1.4- 2 µg/l. As the EC<sub>10</sub>s and NOECs for growth of algae have not been obtained in tests of standard duration (72h), the 21 day study with *Daphnia magna* by Holst & Giesy (1989) is the study providing the lowest reliable long term NOEC and therefore has been chosen as the key study for T-assessment.

<b>Table 5.1: Aquatic Toxicity of Anthracene</b>					
<b>Species</b>	<b>Duration</b>	<b>Endpoint</b>	<b>Value</b>	<b>Comment</b>	<b>References</b>
<i>Freshwater organisms, acute</i>					
<i>Daphnia pulex</i>	24.5 h	EC <sub>50</sub> for immobility	1 µg/l	Dark for 24 h, then exposed to sunlight for 0.5 h	Allred & Giesy, 1985
<i>Freshwater organisms, chronic</i>					
<i>Pimephales promelas</i>	6-w cont. flow	NOEC for hatching	6.7 µg/l	16:8 h light:dark, fluorescent light and UV-A+B radiation	Hall & Oris, 1991
<i>Daphnia magna</i>	21-d static renewal	Lowest NOECs or EC <sub>10</sub> for reproduction	1.5-1.9 µg/l	16:8 h light:dark and UV-A+B radiation	<b>Holst &amp; Giesy, 1989</b> Foran <i>et al.</i> , 1991
<i>Pseudokirchneriella subcapitata</i>	34-36 hours static renewal	NOEC or EC <sub>10</sub> for growth rate or primary production	1.4-1.5 µg/l	UV-A radiation	Gala & Giesy, 1992
<i>Marine organisms, acute</i>					
<i>Artemia salina</i>	10 hours	EC <sub>10</sub>	1.7 µg/l	In the dark for 2 h, then exposed to sunlight for 8 h	Peachy & Crosby, 1996

### 5.1.2.2 Phenanthrene

The lowest chronic toxicity of phenanthrene has been observed by Halling-Sørensen *et al.* (1996) in a growth test with the alga *Pseudokirchneriella subcapitata* (resulting EC<sub>10</sub> 10 µg/l). However, this test was by far the lowest in a test series in which the authors tested several different experimental set-ups (see Table 5.2) and the result was obtained in a test of only 2-d duration (standard is 72 h). In another recent study the EC<sub>10</sub> for growth rate of *Pseudokirchneriella subcapitata* was also higher (23 µg/l: Bisson *et al.*, 2000). Therefore, the *Ceriodaphnia dubia* study by Bisson *et al.*, 2000 is chosen as the key study as it resulted in the lowest reliable long term EC<sub>10</sub>. The value of this EC<sub>10</sub> is 13 µg/l and is based on measured concentrations.

<b>Table 5.2: Aquatic Toxicity of Phenanthrene</b>					
<b>Species</b>	<b>Duration</b>	<b>Endpoint</b>	<b>Value</b>	<b>Comment</b>	<b>References</b>
<b><i>Freshwater organisms, chronic</i></b>					
<i>Pseudokirchneriella subcapitata</i>	2-d	EC <sub>10</sub> for growth	10 – 720 µg/l	Fluorescent light of 4000 – 8000 lux; to some of the air tight flasks HCO <sub>3</sub> <sup>-</sup> was added to control pH	Halling-Sørensen <i>et al.</i> , 1996
<i>Pseudokirchneriella subcapitata</i>	72 h	EC <sub>10</sub> for growth	23 µg/l	Light intensity 6000 – 8000 lux	Bisson <i>et al.</i> , 2000
<i>Ceriodaphnia dubia</i>	7-d	EC <sub>10</sub> for reproduction	13 µg/l	Photoperiod 16:8 h light:dark at less than 500 lux	<b>Bisson <i>et al.</i>, 2000</b>
<b><i>Marine organisms, acute</i></b>					
<i>Neanthes arenaceodentata</i>	96-h	LC <sub>50</sub>	51 µg/l		Emery & Dillon, 1996
<b><i>Marine organisms, chronic</i></b>					
<i>Neanthes arenaceodentata</i>	8 weeks	reproduction	20 µg/l	Some effects, only one sublethal concentration tested – limited validity of test	Emery & Dillon, 1996

### 5.1.2.3 Fluoranthene

Fluoranthene appears to be extremely phototoxic when organisms are exposed in parallel to ultraviolet radiation, such as in sunlight. The acute L(E)C<sub>50</sub>s of fluoranthene are comparable to the obtained chronic NOEC or L(E)C<sub>10</sub> values (see Table 5.3).

Numerous long term studies with a range of species representing various taxonomic groups report NOEC or EC<sub>10</sub> values for fluoranthene below 10 µg/l. Spehar *et al.*, 1999 studied both acute and chronic effects of fluoranthene in the presence and absence of UV radiation with different species. The 31d *Mysidopsis bahia* study by Spehar *et al.* (1999) was chosen as key study, as it provided the lowest reliable NOEC (0.6 µg/l).

<b>Table 5.3: Aquatic Toxicity of Fluoranthene</b>					
<b>Species</b>	<b>Duration</b>	<b>Endpoint</b>	<b>Value</b>	<b>Comment</b>	<b>References</b>
<b>Freshwater organisms, acute</b>					
<i>Utterbackia imbecilis</i>	24-h	LC <sub>50</sub>	2.45 µg/l	UV-A radiation	Weinstein and Polk, 2001
<i>Lumbriculus variegatus</i>	96-h	LC <sub>50</sub>	1.2 µg/l	12:12 h light:dark UV-A+B radiation	Spehar <i>et al.</i> , 1999
<i>Hydra americana</i>	96-h	LC <sub>50</sub>	2.2 µg/l	12:12 h light:dark UV-A+B radiation	Spehar <i>et al.</i> , 1999
<i>Daphnia magna</i>	48-h	LC <sub>50</sub>	1.6 µg/l	12:12 h light dark UV-A+B radiation	Spehar <i>et al.</i> , 1999
<b>Freshwater organisms, chronic</b>					
<i>Ceriodaphnia dubia</i>	7-d	EC <sub>10</sub> reproduction	1.2 µg/l	Photoperiod 16:8 h light:dark at less than 500 lux	Bisson <i>et al.</i> , 2000
<i>Hyaella azteca</i>	10-d	LC <sub>10</sub>	1.1 µg/l	16:8 h light:dark UV-A+B radiation	Wilcoxon <i>et al.</i> , 2003
<i>Daphnia magna</i>	21-d	NOEC growth	1.4 µg/l	12:12 h light:dark UV-A+B radiation	Spehar <i>et al.</i> , 1999
<i>Pimephales promelas</i>	32-d ELS test	NOEC growth	1.4 µg/l	12:12 h light:dark UV-A+B radiation	Spehar <i>et al.</i> , 1999
<i>Rana pipiens</i> larvae		NOEC hatching	>25 µg/l	Full sunlight	Hatch & Burton Jr., 1998
<i>Rana pipiens</i> larvae			100 % mortality at 5, 25, and 125 µg/l	Full sunlight	
<b>Marine organisms, acute</b>					
<i>Mulinia lateralis</i>	96-h	LC <sub>50</sub>	2.8 µg/l	16:8 hours light:dark, laboratory UV A and B light	Spehar <i>et al.</i> , 1999
<i>Mysidopsis bahia</i>	96-h	LC <sub>50</sub>	1.4 µg/l		
<i>Arbacia punctulata</i>	96-h	LC <sub>50</sub>	3.9 µg/l		
<i>Pleuronectes americanus</i>	96-h	LC <sub>50</sub>	0.1 µg/l		
<b>Marine organisms, chronic</b>					
<i>Mysidopsis bahia</i>	31-d	NOEC reproduction	11.1 µg/l	16:8 hours light:dark, laboratory fluorescent light	Spehar <i>et al.</i> , 1999
<i>Mysidopsis bahia</i>	31-d	NOEC reproduction	0.6 µg/l	16:8 hours light:dark, laboratory UV A and B light	

#### 5.1.2.4 Pyrene

With regard to acute effects, the most sensitive freshwater organism appears to be *Daphnia magna*, with EC<sub>50</sub> values of 1.38 - 20 µg/l (Table 5.4). The lowest acute effect concentrations for embryos/larvae of marine molluscs and neonates/nauplii of crustaceans are reported in the range 0.23-36 µg/l and hence are similar to those observed for fresh water species in the presence of UV-radiation.

Chronic toxicity data are reported for fresh water species with EC<sub>10</sub> values of 1.2-2.1 µg/l and for one marine oyster (*Crassostrea*) with a NOEC for shell development of 0.5 µg/l (Lyons *et al.*, 2002). As this latter NOEC value was the lowest one from a reliable study, it was chosen as the key study.

<b>Table 5.4: Aquatic Toxicity of Pyrene</b>					
<b>Species</b>	<b>Duration</b>	<b>Endpoint</b>	<b>Value</b>	<b>Comment</b>	<b>References</b>
<b><i>Freshwater organisms, acute</i></b>					
<i>Daphnia magna</i>	27 h	EC <sub>50</sub> immobility	1.38 µg/l	neonates 16:8 hour light:dark for 24 hours UV radiation for 2 hours and 1 h recovery	Wernersson, 2003
<i>Daphnia magna</i>	48 hours	EC <sub>50</sub> for immobility	2.7 to 20 µg/l	neonates UV-B radiation four times two hours	Nikkilä <i>et al.</i> , 1999
<i>Utterbackia imbecilis</i>	24-h	LC <sub>50</sub>	2.63 µg/l	UV-A radiation	Weinstein & Polk, 2001
<b><i>Freshwater organisms, chronic</i></b>					
<i>Pseudokirchneriella subcapitata</i>	72-h	EC <sub>10</sub> growth	1.2 µg/l	Light intensity 6000 – 8000 lux	Bisson <i>et al.</i> , 2000
<i>Ceriodaphnia dubia</i>	7-d	EC <sub>10</sub> reproduction	2.1 µg/l	Photoperiod 16:8 h light:dark at less than 500 lux	Bisson <i>et al.</i> , 2000
<b><i>Marine organisms, acute</i></b>					
<i>Artemia salina</i>	3-h	LC <sub>50</sub>	8 µg/l	2 hours in the dark UV-radiation for one hour	Kagan <i>et al.</i> , 1985, 1987
<i>Artemia salina</i>	10-h	LC <sub>50</sub>	36 µg/l	2 hours in the dark followed by eight hours with UV-radiation	Peachy & Crosby, 1996
<i>Artemia salina</i>	10-h	EC <sub>50</sub>	3.4 µg/l	2 hours in the dark followed by eight hours with sunlight	Peachy & Crosby, 1996
<i>Mysidopsis bahia</i>	48-h	LC <sub>50</sub>	0.89 µg/l	16:8 hour light:dark UV-A B radiation	Pelletier <i>et al.</i> , 1997
<i>Mulinia lateralis</i>	48-h 96-h	LC <sub>50</sub>	0.23 µg/l 1.68 µg/l	Embryos/larvae Juveniles 16:8 hour light:dark UV-A B radiation	Pelletier <i>et al.</i> , 1997
<b><i>Marine organisms, chronic</i></b>					
<i>Crassostrea gigas</i>	48 h	NOEC shell development	0.5 µg/l	Embryos/larvae 12:12 hour light:dark UV-A B radiation	Lyons <i>et al.</i> , 2002

### 5.1.2.5 Chrysene

The water solubility of chrysene is about 1.6 µg/l, with a range between 1.0 and 3.3 µg/l (Mackay *et al.*, 2000). Around or below this value, no significant effects were observed for any species in a regular toxicity experiment, although chronic toxicity studies were performed with algae,

crustaceans (including *Daphnia*) and fish. The only study, that showed a considerable effect of chrysene, was a determination of the median lethal time of neonates of *Daphnia magna* (Newsted & Giesy, 1987). In this experiment, the daphnids were exposed to one concentration of chrysene (measured concentration of 0.7 µg/l). After 24 hours of exposure with a 16:8 h light:dark photoperiod, the animals were exposed to a mix of UV A , UV B and visible light. The median lethal time after UV-radiation started was 24 hours. Thus, after 48 hours, of which the last 24 hours were with UV irradiation, 50% mortality of the daphnids occurred at 0.7 µg/l. This type of study is however not designed to determine dose-response relationships and hence quantitative data on toxicity or toxicity threshold values cannot be derived from the result.

Species	Duration	Endpoint	Value	Comment	References
<i>Freshwater organisms, acute</i>					
<i>Daphnia magna</i>	Until 50 % of the test animals died	LT <sub>50</sub>	24 h (after commencement of irradiation and exposure to 0.7 µg/l chrysene)	Static renewal test: exposure to 0.7 µg/l chrysene After 16:8 hours light:dark photoperiod irradiation with UV A and B + visible light	<b>Newsted &amp; Giesy, 1987</b>

#### 5.1.2.6 Benz(a)anthracene

Data on acute toxicity of benz(a)anthracene are available for algae, crustaceans and amphibians. Effects within the water solubility of the substance have been observed for the crustacean *Daphnia pulex* upon exposure to mixed fluorescent and natural light and for larvae of the amphibian *Pleurodeles waltl* irradiated throughout the experiment with UV-A light (see Table 5.6). The lowest chronic toxicity has been observed for the alga *Pseudokirchneriella subcapitata* with an EC<sub>10</sub> of 1.2 µg/l for growth inhibition. This study was therefore chosen as key study. For the crustacean *Ceriodaphnia dubia* no effects were observed at the highest test concentration of 8.7 µg/l (Bisson *et al.*, 2000). Studies showed that UV irradiation increases the toxicity of benz(a)anthracene (The Netherlands, 2008).

Species	Duration	Endpoint	Value	Comment	References
<i>Freshwater organisms, acute</i>					
<i>Daphnia pulex</i>	96 h	EC <sub>50</sub>	10 µg/l	12:12 h photoperiod to mixed fluorescent and natural light	Trucco <i>et al.</i> , 1983
<i>Daphnia magna</i>	48 h	EC <sub>50</sub>	>9.1 µg/l	Dark	Bisson <i>et al.</i> , 2000
<i>Pleurodeles waltl</i> (larvae)	6 d	LC <sub>50</sub>	at 3.1 µg/l 100% survival; at 6.3 µg/l 100% mortality	Irradiation with UV-A light throughout experiment	Fernandez & L'Haridon, 1992)
<i>Freshwater organisms, chronic</i>					
<i>Pseudokirchneriella subcapitata</i>	72-h	EC <sub>10</sub> growth	1.2 µg/l	Light intensity 6000 – 8000 lux	<b>Bisson <i>et al.</i>, 2000</b>

### 5.1.2.7 Benzo(b)fluoranthene

No effects have been observed at concentrations within the water solubility of benzo(b)fluoranthene, i.e. up to 1.1 - 1.5 µg/l (Mackay et al. 2000 in The Netherlands 2008). An acute study with *Daphnia magna* in the dark showed no effects at the tested concentration of 1.1 µg/l (Bisson et al., 2000). In a 24-h study with the same organism and a photoperiod of 16:8 h light:dark, extended by 2 hours of irradiation with UV light followed by 2 hours of recovery, the EC<sub>50</sub> for immobilisation was determined as 4.2 µg/l, which is above the water solubility of benzo(b)fluoranthene (Wernersson & Dave, 1997).

### 5.1.2.8 Benzo(ghi)perylene

Only in a small number of studies effects have been observed at test concentrations within the water solubility limit of benzo(ghi)perylene (Table 5.7). The EC<sub>50</sub> obtained in the *Daphnia* test is above the water solubility of 0.14 µg/l. As regards chronic toxicity of benzo(ghi)perylene, no effects were observed in an early life stage study with *Brachydanio rerio* up to concentrations of 0.16 µg/l (Hooftman & Evers-de-Ruiter, 1992). However, effects on the reproduction of the crustacean *Ceriodaphnia dubia* were reported by (Bisson et al., 2000) with a resulting EC<sub>10</sub> value of 0.082 µg/l. This study was chosen as the key study for T-assessment.

Species	Duration	Endpoint	Value	Comment	References
<i>Freshwater organisms, acute</i>					
<i>Daphnia magna</i>	48 h	EC <sub>50</sub>	>0.2 µg/l	Dark	Bisson et al., 2000
<i>Pimephales promelas</i> (7-d old larvae)	120 h	LC <sub>20</sub>	0.15 µg/l	First 24h of exposure to substance without UV radiation in parallel, followed by 96 h exposure with concomitant UV radiation	Oris & Giesy, 1987
<i>Freshwater organisms, chronic</i>					
<i>Ceriodaphnia dubia</i>	7-d	EC <sub>10</sub> reproduction	0.082 µg/l	Photoperiod 16:8 h light:dark at less than 500 lux	Bisson et al., 2000

### 5.1.2.9 Benzo(k)fluoranthene

In the available studies on acute toxicity to *Daphnia magna* no effects were observed, which might be attributable to the low water solubility of the substance (The Netherlands 2008).

As regards chronic toxicity, a 7-d reproduction test with *Ceriodaphnia dubia* did not reveal effects either (Bisson et al., 2000) and in a test with the alga *Pseudokirchneriella subcapitata* the EC<sub>10</sub> for growth was larger than 1 µg/l (Bisson et al., 2000), which is above the water solubility of the substance (about 1 µg/l; Mackay et al. 2000, cited in The Netherlands 2008). However, an early life stage study performed with *Brachydanio rerio* revealed length as the most sensitive endpoint, with an EC<sub>10</sub> value of 0.17 µg/l (Hooftman & Evers-de Ruiter, 1992; Table 5.8). Due to the good fit of the log-logistic equation, this EC<sub>10</sub> estimate has a low uncertainty. The study was chosen as the key study for T-assessment.

Table 5.8: Aquatic Toxicity of Benzo(k)fluoranthene					
Species	Duration	Endpoint	Value	Comment	References
<i>Freshwater organisms, chronic</i>					
<i>Brachydanio rerio</i>	28 d	LC <sub>52</sub>	0.58 µg/l	ELS	Hooftman & Evers-de Ruiter, 1992
<i>Brachydanio rerio</i>	42 d	LC <sub>50</sub>	0.65 µg/l	ELS	
		EC <sub>10</sub> weight EC <sub>10</sub> length	0.31 µg/l 0.17 µg/l		

### 5.1.2.10 Benzo(a)pyrene

Table 5.9: Aquatic Toxicity of Benzo(a)pyrene					
Species	Duration	Endpoint	Value	Comment	References
<i>Freshwater organisms, acute</i>					
<i>Daphnia magna</i>	27 h	EC <sub>50</sub>	1.2 µg/l	16:8 hour light:dark followed by 2 hour UV-A B radiation and 1 hour recovery	Wernersson, 2003
<i>Freshwater organisms, chronic</i>					
<i>Pseudokirchneriella subcapitata</i>		EC <sub>10</sub> growth	0.78 µg/l	Light intensity 6000 – 8000 lux, cool white fluorescent lamps	Bisson <i>et al.</i> , 2000
<i>Oncorhynchus mykiss</i>	36 d	NOEC EC <sub>10</sub> * abnormalities	1.5 µg/l (2.9 µg/l, calculated, above WS)	ELS * determined from presented data with log-logistic dose-response relationship (The Netherlands 2008)	Hannah <i>et al.</i> , 1982
<i>Ceriodaphnia dubia</i>	7-d	EC <sub>10</sub> reproduction	0.5 µg/l	Laboratory light Photoperiod 16:8 h light:dark at less than 500 lux	Bisson <i>et al.</i> , 2000
<i>Marine organisms, chronic</i>					
<i>Crassostrea gigas</i>	48 h	NOEC shell development EC <sub>10</sub>	1 µg/l 1.1 µg/l	Embryos 12:12 hour light:dark fluorescent light without UV rad.	Lyons <i>et al.</i> , 2002
<i>Crassostrea gigas</i>	48 h	NOEC shell development EC <sub>10</sub>	0.5 µg/l 0.22 µg/l	Embryos 12:12 hour light:dark UV-A B radiation	Lyons <i>et al.</i> , 2002

Only acute toxicity studies with exposure to UV-light result in effects at concentrations near the water solubility of 1.2 -1.8 µg/l (Mackay *et al.* 2000, cited in The Netherlands 2008). Results from studies on the aquatic toxicity of benzo(a)pyrene are shown in Table 5.9. The lowest acute toxicity of benzo(a)pyrene was observed in a test with *Daphnia magna* under exposure to UV radiation.

Chronic toxicity of benzo(a)pyrene was reported for the alga *Pseudokirchneriella subcapitata* with an EC<sub>10</sub> of 0.78 µg/l, and for reproduction of *Ceriodaphnia dubia* with an EC<sub>10</sub> of 0.5 µg/l in a 7-d study when exposed to laboratory light without UV (Bisson *et al.*, 2000). In a 28-d early life stage (ELS) study with *Brachydanio rerio* no effects were observed up to the highest test concentration of 4.0 µg/l, which is already above the water solubility of benzo(a)pyrene (Hooftman & Evers-de Ruiter, 1992). In another ELS study with *Oncorhynchus mykiss* a NOEC of 1.5 µg/l was obtained

for developmental abnormalities as endpoint (Hannah *et al.*, 1982). Evaluation of the data presented by Hannah *et al.* with a log-logistic relationship resulted in the derivation of an EC<sub>10</sub> of 2.9 µg/l (The Netherlands 2008), which again is above the water solubility of benzo(a)pyrene.

Furthermore, it has been shown that UV radiation increases the long term toxicity of benzo(a)pyrene. For shell development of *Crassostrea gigas*, when exposed to UV radiation, the calculated EC<sub>10</sub> was 0.22 µg/l whereas under UV-lacking fluorescent laboratory lighting conditions the resulting EC<sub>10</sub> was 1.1 µg/l (Lyons *et al.* 2002).

As the study on shell development of the marine mollusc *Crassostrea gigas* resulted in the lowest reliable chronic EC<sub>10</sub> value (0.22 µg/l) it was chosen as key study for T-assessment.

#### 5.1.2.11 Dibenzo(a,h)anthracene

Results of studies of the aquatic toxicity of dibenzo(a,h)anthracene are provided in Table 5.10. Chronic toxicity studies with fresh water species are available for crustaceans, aquatic plants, and algae. For *Lemna gibba* no effects at concentrations near the water solubility were observed (Huang *et al.*, 1997). No effect was observed at concentrations up to 0.032 µg/l in a 7-d study with *Ceriodaphnia dubia* (Bisson *et al.*, 2000). The 72-h EC<sub>10</sub> for the growth rate of *Pseudokirchneriella subcapitata* was 0.14 µg/l (Bisson *et al.*, 2000). In both the test with *C. dubia* and *P. subcapitata* concentrations were measured. As the study with *Pseudokirchneriella subcapitata* resulted in the lowest reliable chronic EC<sub>10</sub> value it was chosen as the key study.

Table 5.10: Aquatic Toxicity of Dibenzo(a,h)anthracene					
Species	Duration	Endpoint	Value	Comment	References
<i>Freshwater organisms, acute</i>					
<i>Daphnia magna</i>	27 h	EC <sub>50</sub>	1.8 µg/l	16:8 hour light:dark followed by 2 hour UV-A B radiation and 1 hour recovery	Wernersson, 2003
<i>Daphnia magna</i>	28 h	EC <sub>50</sub>	4.6 µg/l	16:8 hour light:dark followed by 2 hour UV-A B radiation and 2 hour recovery	Wernersson & Dave, 1997
<i>Freshwater organisms, chronic</i>					
<i>Pseudokirchneriella subcapitata</i>	72 h	EC <sub>10</sub> growth	0.14 µg/l	Light intensity 6000 – 8000 lux	Bisson <i>et al.</i> , 2000

#### 5.1.2.12 Indeno(1,2,3-cd)pyrene

Table 5.11: Aquatic Toxicity of Indeno(1,2,3-cd)pyrene					
Species	Duration	Endpoint	Value	Comment	References
<i>Freshwater organisms, chronic</i>					
<i>Pseudokirchneriella subcapitata</i>	72 h	EC <sub>10</sub> growth	1.5 µg/l	Light intensity 6000-8000 lux	Bisson <i>et al.</i> , 2000
<i>Ceriodaphnia dubia</i>	7-d	EC <sub>10</sub> reproduction	0.27 µg/l	Photoperiod 16:8 h light:dark at less than 500 lux	

For indeno(1,2,3-cd)pyrene, a chronic EC<sub>10</sub> value of 1.5 µg/l is reported for growth of the algae *Pseudokirchneriella subcapitata* in a study of 72h duration. The 7-d EC<sub>10</sub> for reproduction of the crustacean *Ceriodaphnia dubia* was 0.27 µg/l (Bisson *et al.*, 2000; see Table 5.11). In both studies

concentrations were measured. The study with the lowest EC<sub>10</sub>, i.e. reproduction of *Ceriodaphnia dubia*, was chosen as key study for T-assessment.

### 5.1.3 Summary and discussion on aquatic toxicity

An overview on the aquatic toxicity obtained in the key studies selected for the PAH-constituents of CTPHT is provided in Table 5.12.

Substance	Value	Key study endpoint
Anthracene	1.5 µg/l	EC <sub>10</sub> reproduction, <i>Daphnia magna</i> , 21-d
Phenanthrene <sup>5</sup>	13 µg/l	EC <sub>10</sub> reproduction, <i>Ceriodaphnia dubia</i> , 7-d
Fluoranthene	0.6 µg/l	NOEC reproduction, <i>Mysidopsis bahia</i> , 31-d
Pyrene	0.5 µg/l	NOEC shell development, <i>Crassostrea gigas larvae</i> , 48-h ELS
Benz(a)anthracene	1.2 µg/l	EC <sub>10</sub> growth, <i>Pseudokirchneriella subcapitata</i> , 72-h
Chrysene <sup>6</sup>	-	No significant effects up to the water solubility of the substance detected in any regular toxicity test. Only study in which considerable effects were detected was a median lethal time (LT <sub>50</sub> ) study with <i>Daphnia magna</i>
Benzo(a)pyrene	0.22 µg/l	EC <sub>10</sub> shell development, <i>Crassostrea gigas larvae</i> , 48-h ELS
Benzo(b)fluoranthene	-	No toxicity has been observed up to the water solubility limit of the substance
Benzo(k)fluoranthene	0.17 µg/l	EC <sub>10</sub> growth (length), <i>Brachydanio rerio</i> , 42-d
Benzo(ghi)perylene	0.082 µg/l	EC <sub>10</sub> reproduction, <i>Ceriodaphnia dubia</i> , 7-d
Dibenzo(a,h)anthracene	0.14 µg/l	EC <sub>10</sub> growth, <i>Pseudokirchneriella subcapitata</i> , 72-h
Indeno(1,2,3-cd)pyrene	0.27 µg/l	EC <sub>10</sub> reproduction, <i>Ceriodaphnia dubia</i> , 7-d

The experimental data indicate a high chronic and acute toxicity of the PAH constituents of CTPHT for aquatic organisms. NOEC/EC<sub>10</sub> values <10 µg/l have been observed for the following PAHs: anthracene, fluoranthene, pyrene, benz(a)anthracene, benzo(a)pyrene, benzo(k)fluoranthene, benzo(ghi)perylene, dibenzo(a,h)anthracene, and indeno(1,2,3-cd)pyrene. For phenanthrene, the EC<sub>10</sub> value of the selected key study with *Ceriodaphnia dubia* is > 10 µg/l, but for the algae *Pseudokirchnerella subcapitata* a two days growth inhibition study (i.e. exposure time shorter than required according to the guideline) showed EC<sub>10</sub> values down to 10 µg/l.

No toxicity to aquatic organisms has been observed within the water solubility limit of benzo(b)fluoranthene. The same is the case for chrysene, with the exception that in one study aimed at determining the mean lethal time (LT<sub>50</sub>) of *Daphnia magna* upon exposure to 0.7 µg/l chrysene considerable toxic effects have been observed. This type of study is however not designed to determine dose-response relationships and hence quantitative data on toxicity like EC<sub>10</sub> or EC<sub>50</sub> values or toxicity threshold values like long-term no effect levels cannot be derived from the results. Therefore, the result of this study is not a suitable basis for comparison with the T-criteria of Annex XIII of the REACH Regulation.

<sup>5</sup> The lowest chronic values reported are EC<sub>10</sub> for *Pseudokirchneriella subcapitata* of 10 µg/l (Halling-Sørensen *et al.*, 1996)

<sup>6</sup> No results from toxicity studies available that could be used for comparison with the T-criteria of REACH Annex XIII.

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## 6 CONCLUSIONS ON THE SVHC PROPERTIES

### 6.1 PBT / vPvB assessment

#### 6.1.1 Assessment of PBT/vPvB properties – comparison with the criteria of Annex XIII

No information on persistence, potential for bioaccumulation and aquatic toxicity was found for CTPHT itself. Therefore, the PBT assessment for CTPHT focuses on the assessment of its PAH-constituents present in concentrations  $\geq 0.1\%$  (see Section 1.2).

##### 6.1.1.1 Persistence

Half-lives in soil for the following 10 PAH-constituents of CTPHT have been reported to be in the range of 5.7 to 9.1 years under field conditions:

Anthracene	Chrysene
Phenanthrene	Benzo(a)pyrene
Fluoranthene	Benzo(b)fluoranthene
Pyrene	Benzo(k)fluoranthene
Benz(a)anthracene	Benzo(ghi)perylene

As these half-lives observed in soil exceed the P- and vP-criteria (half lives of 120, respectively 180 days in soil), it is concluded that the vP criterion is fulfilled by all 10 above listed PAH substances.

No experimental data on persistence were found for dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene. A final conclusion on the P- or vP-properties of these substances can therefore not be drawn. Estimated half-lives  $> 400$  days in soil for dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene (Mackay *et al.*, 1992) indicate however that the two PAHs are presumably persistent in sediments and soils as well.

##### 6.1.1.2 Bioaccumulation

Experimentally obtained BCF values above 5,000 are reported for the following 10 PAH-constituents of CTPHT:

Matrix: <b>fish</b>	
Fluoranthene	Pyrene
Phenanthrene	
Matrix: <b>molluscs:</b>	
Fluoranthene	Benzo(a)pyrene
Pyrene	
Matrix: <b>crustaceans:</b>	
Benz(a)anthracene	Benzo(k)fluoranthene
Chrysene	Benzo(ghi)perylene
Benzo(a)pyrene	Dibenzo(a,h)anthracene

As the BCF values of the above PAH substances exceed the B- and vB criteria (measured BCF values in aquatic species > 2000, respectively > 5000), it is concluded that the vB-criterion is fulfilled by all 9 substances .

Furthermore, experimentally obtained BCF value above 2000 have been reported for anthracene and it has already been agreed by the Member State Committee (MSC, 2008) that anthracene fulfills the PBT-criteria and, hence, the B-criterion.

No experimental data on the bioaccumulation potential of benzo(b)fluoranthene and indeno(1,2,3-cd)pyrene were found. A final conclusion on the B- or vB-properties of these substances can therefore not be drawn. However, on the basis of similarities of their Kow values and molecular sizes with other PAHs for which BCFs above the Annex XIII bioaccumulation criteria have been experimentally confirmed, it is anticipated that these two substances will at least fulfill the B-criterion (i.e. BCF >2000) as well.

### 6.1.1.3 Toxicity

Experimental data of aquatic species referring to chronic toxicity endpoints (NOEC/EC<sub>10</sub>) < 0.01 mg/l) are available for 9 of the PAH-constituents of CTPHT, namely:

Anthracene	Benzo(a)pyrene
Fluoranthene	Benzo(k)fluoranthene
Pyrene	Benzo(ghi)perylene
Benz(a)anthracene	Dibenzo(a,h)anthracene
	Indeno(1,2,3-cd)pyrene

For phenanthrene the reported values for chronic toxicity are > 10 µg/l. For benzo(b)fluoranthene no toxicity was observed within the limits of its water solubility. The same applies for chrysene with the exemption of one study, which however is not suitable to determine a (no)effect level (see sections 5.1.2.5 and 5.1.3).

Some of the PAH-constituents of CTPHT are classified as a carcinogen, mutagen or as toxic to reproduction in Annex VI of Regulation (EC) No 1272/2008.

<b>Substance</b>	<b>Carcinogen (Category 2, Respectively 1B)</b>	<b>Mutagen (Category 2, Respectively 1B)</b>	<b>Toxic To Reproduction (Category 2, Respectively 1B)</b>
Benz(a)anthracene	X		
Chrysene	X	X	
Benzo(a)pyrene	X	X	X
Benzo(b)fluoranthene	X		
Benzo(k)fluoranthene	X		
Dibenzo(a,h)anthracene	X		

Based on the available experimental aquatic toxicity data and the data on classification, it is concluded that 11 of the 12 indicator PAH-constituents relevant for the assessment of CTPHT (apart phenanthrene) fulfil the T-criteria of Annex XIII of the REACH Regulation [long term NOEC for aquatic organisms < 0.01 mg/l or substance classified as carcinogenic (cat. 1 or 2),

mutagenic (cat. 1 or 2) or toxic to reproduction (cat. 1, 2 or 3) or there is evidence of chronic toxicity as identified by the classifications T, R48 or Xn, R48 according to Directive 67/548/EEC<sup>7</sup>].

### 6.1.2 Summary and overall conclusions on the PBT, vPvB or equivalent level of concern properties

An overview on the conclusions drawn on persistence, potential for bioaccumulation and toxicity to human health and the environment based on comparison of the data presented for the 12 indicator PAH-constituents of CTPHT with the PBT/vPvB criteria of Annex XIII of the REACH Regulation is provided in Table 6.2.

Substance	Persistence	Bioaccumulation	Toxicity Human health	Toxicity Aquatic Environment	Conclusion
Anthracene	vP	B	-	T	PBT
Phenanthrene	vP	vB	-	-	vPvB
Fluoranthene	vP	vB	-	T	PBT/vPvB
Pyrene	vP	vB	-	T	PBT/vPvB
Benz(a)anthracene	vP	vB	T	T	PBT/vPvB
Chrysene	vP	vB	T	-	PBT/vPvB
Benzo(a)pyrene	vP	vB	T	T	PBT/vPvB
Benzo(b)fluoranthene	vP	No experimental data	T	- (No signs of toxicity up to limit of water solubility)	-
Benzo(k)fluoranthene	vP	vB	T	T	PBT/vPvB
Benzo(ghi)perylene	vP	vB	-	T	PBT/vPvB
Dibenzo(a,h)anthracene	No experimental data	vB	T	T	-
Indeno(1,2,3-cd)pyrene	No experimental data	No experimental data	-	T	-

Based on the data available, it is concluded that 7 of the 12 PAH-constituents present in CTPHT in concentrations equal to or above 0.1% are to be considered as both vPvB and PBT substances. These are: fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, benzo(k)fluoranthene and benzo(ghi)perylene.

Phenanthrene fulfils the vPvB criteria, but not the PBT criteria. Anthracene fulfils the PBT criteria, but not the vPvB criteria.

<sup>7</sup> In the CLP Regulation (1272/2008), classifications [T, R48] and [Xn, 48] have been replaced by [STOT RE 1, H372] and [STOT RE 2, H373] ([Hazard Class, Hazard statement]) respectively. No one of the PAHs addressed in this PBT assessment is classified as such.

STOT RE 1,2: Specific target organ toxicity – repeated exposure; H372: Causes damage to organs through prolonged or repeated exposure; H373: May cause damage to organs through prolonged or repeated exposure.

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For benzo(b)fluoranthene, dibenzo(a,h)anthracene, and indeno(1,2,3-cd)pyrene no definitive conclusion on their PBT/vPvB properties is possible, due to lack of data relevant for P/vP and/or B/vB assessment in accordance with Annex XIII of the REACH Regulation.

For coal tar pitch, high temperature, the above conclusion on the vPvB and PBT properties of its PAH-constituents has the consequence that the substance needs to be considered as a substance with both vPvB and PBT properties. It is concluded that CTPHT is a substance containing at least 5 to 10 % of PAH-constituents with both vPvB and PBT properties.

This assessment relies only on the indicator PAH-constituents of CTPHT. It should however be considered that residual constituents of CTPHT may have similar structure with the indicator PAHs selected and, therefore, fractions of these residual constituents may have PBT and / or vPvB properties as well.

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# **Part II**

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## **INFORMATION ON MANUFACTURE, USES, EXPOSURE, AND ALTERNATIVES**

## 7 INFORMATION ON MANUFACTURE, IMPORT/EXPORT AND USES – CONCLUSIONS ON EXPOSURE

### 7.1 Information on manufacture, import and export of CTPHT

#### 7.1.1 Manufacture, import and export of CTPHT

##### 7.1.1.1 Manufacturing sites

CTPHT is the residue from the distillation of high temperature coal tar (see Annex 4 for further details about CTPHT manufacturing process).

Within the European Union (EU), coal tar distillation currently occurs at 11 manufacturing sites, owned by seven different companies, in nine Member States. These sites have a total distillation capacity of around 2,475 kilotonnes per year (kt/yr) (see Table 7.1); the actual manufacture (distillation) of coal tar derivatives is however around 2,000 kt/yr (Jacobs, 2006; Stompel, 2008).

No	Company	Location	Country	Capacity (kt/yr)
1	Company A	Castrop Rauxel	Germany	500
2	Company A	Zelzate	Belgium	240
3	Company A	Blachownia	Poland	90
4	Company B	Nyborg	Denmark	225
5	Company B	Scunthorpe	UK	90
6	Company B	Port Clarence	UK	160
7	Company C	Trubia	Spain	370
8	Company D	Luchana	Spain	100
9	Company E	Valasske Mezirici	Czech Republic	460
10	Company F	Uithoorn	Netherlands	140
11	Company G	Galati	Romania	100
<b>Total distillation capacity</b>				<b>2,475</b>
<i>Source: Stompel (2008)</i>				

##### 7.1.1.2 Manufacture, import, export and use of CTPHT

Table 7.2 sets out the manufacturing capacity and actual manufacture of CTPHT manufacturing sites in 2005 (Jacobs, 2006).

More recent figures indicate a total manufacture of 1,000 kt/yr of CTPHT within EU (Stompel, 2008).

With regard to the import/export balance of CTPHT, the EU Risk Assessment Report (RAR, 2008) notes that in 2004 import and export of CTPHT from/into EU were respectively around 92 kt/yr and 355 kt/yr; the RAR estimated the total EU use of CTPHT to be around 554 kt/yr (RAR, 2008). More recent information by Stompel (2008) suggests that around 300 kt/yr and 50 kt/yr are respectively exported and imported. In either case, EU total use is generally around 65 - 75% of EU manufacture.

No	Company	Location	Country	Capacity (kt/yr)	Manufacture (kt/yr)
1	Company A	Castrop Rauxel	Germany	250	200
2	Company A	Zelzate	Belgium	120	90
3	Company A	Blachownia**	Poland	80	47.5
4	Company B	Nyborg	Denmark	120	76
5	Company B	Scunthorpe	UK	50	28.8
6	Company B	Port Clarence	UK	90	51.2
7	Company C	Trubia	Spain	180	125
8	Company D	Luchana	Spain	55	47.5
9	Company E	Valasske Mezirici	Czech Republic	230	220
10	Company F	Uithoorn	Netherlands	70	50
11	Company G*	Galati	Romania		
<b>Total EU-27 capacity / manufacture</b>				<b>1,245</b>	<b>936</b>

*Source: Jacobs (2006)*

*\* Latest information suggests that this plant is now idle and unlikely to be active before 2012 - bearing in mind the current economic conditions and attempts to temporarily reduce steel production by 50% (there was, however, some prior discussion relating to expanding the tar distillation plant's capacity).*

*\*\* This tar distillation unit shut down in November 2007 and restarted March 2008. It is now understood that this site has now been shut down, possibly permanently. There is, however, a pitch upgrading plant (a simple vacuum distiller) and pitch solidification plant which is still in operation adjacent to this site. No significant activity has occurred there this year (2009) and with the closure of the Blawchonia site, this site can only work if CTP is brought in from other plants within or outside Europe.*

Table 7.3 provides a summary of the market figures for CTPHT in EU, for years 2004 (RAR) and 2008 (Stompel):

	2004 (RAR)	2008 (Stompel)	2004 (RAR)	2008 (Stompel)
<b>EU total manufacture</b>	817 kt	1,000 kt	<b>100%</b>	<b>100%</b>
Export outside EU	355 kt	300 kt	43%	30%
EU sales	462 kt	700 kt	57%	70%
Import into EU	92 kt	50 kt	11%	2 - 5%
<b>EU total consumption (Import + EU sales)</b>	<b>554 kt</b>	<b>750 kt</b>	<b>68%</b>	<b>75%</b>

### **7.1.1.3 Estimated future trends**

In the years leading up to 2008, there had been an increase in the use of coal tar (since a historical minimum in 2002) and in the first part of 2008, a steady demand for coal tar products with the price of coal tar going down was observed (Stompel, 2008). Information received from a number of producers and downstream users of CTPHT-based electrodes confirms that the consumption of CTPHT during the three years (prior to 2009) was steady. However, the recent economic downturn has resulted in changes to the current trend, as well as, future projections.

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In terms of manufacture, the total volume rises from around 817 kt/yr in 2004 (RAR) to around 936 kt in 2006 (Table 7.2, Jacobs, 2006) and then further to 1,000 kt (Stompel, 2008). This suggests a steady increase in the use of coal tar pitch over the last four years, but is also due to adhesion of Romania to EU in 2007. Similarly, in terms of manufacturing capacity, the total EU manufacturing capacity of CTPHT in 2004 was 1,127 kt while, in 2005, it was estimated at around 1,245 kt/yr (Jacobs, 2006).

As far as imports are concerned, Stompel (2009) notes that, a few years ago, it was estimated that around 50 kt of CTPHT were imported into the EU from Ukraine; but, more recently, Ukraine has been exporting more to Russia which may suggest a decrease in Ukrainian exports into the EU.

In terms of downstream uses of CTPHT, the aluminium industry is the largest single downstream user sector for CTPHT; aluminium manufacture is, therefore, a key factor on the demand side (as is steel production, on the supply side) for the amount of CTPHT manufactured (as noted in Annex 3 all coal tar products are produced in relatively fixed proportion to CTP). For instance, in 2007, the demand of CTPHT was expected to grow as a function of growth in aluminium manufacture. However, the recent economic downturn has resulted in lower sales of carbon pitch as smelter closures and curtailments and overall lower demand in end markets have impacted on customer volumes. CTPHT manufacturers have in turn taken steps to reduce such impacts, including temporary plant shutdowns at some sites (Koppers, 2008a).

Downstream users of CTPHT have also confirmed that, in 2009, due to the general economic situation, a significant decrease in CTPHT consumption is expected; after the economic recovery, a slight increase in the use (compared to 2008) is expected over the next five years. The impacts of this downturn may vary from company to company depending on their end markets and extent of exposure; for instance, one manufacturer of CTPHT supplies over 90% of its CTPHT to the aluminium industry, typically under long-term contracts ranging from three to five years.

However, discussing the trends on demand of CTPHT, it is important to note that in the event that there is a total lack of demand for CTPHT (e.g. for regulatory or market reasons), coal tar will continue to be manufactured as a by-product of the coal carbonisation process and alternative uses (or treatment) would have to be found for CTPHT from the distillation process. In this regard, Stompel (2009) notes that coal tar can be utilised in a number of different ways (for instance, in a total downturn in demand in the end markets) including:

- use as a substitute for pulverised coal injection (this technology is applied in certain steelworks on the condition that the water content (in tar) is below a certain level);
- use as a fuel in other industrial applications;
- being returned to the coke making process (when coal tar is mixed with coal, it improves the quality of the coke); and
- use as carbon black feedstock (this is a major use in Japan and China where more than 2 million tonnes are utilised in this way).

Prior to the economic downturn, Koppers (2008) indicated that the future expansion of the CTPHT market will be in Asian and Middle Eastern countries; however, this may no longer be the case as a three to four year delay on new aluminium projects in the Middle East is now expected (Stompel, 2009). It is also worth noting that (due to process synergies, as described earlier), when the demand for steel increases, there is a general correlation with the supply of metallurgical coke and thus more coal tar is produced. In this context, the decision by a major international steel company to reduce operations and temporarily lower production by 50% (Standard, 2008) could mean lower supplies

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of coal tar. Stompel (2009) notes that there is actually a world over-supply of coal tar of some six to seven million tonnes/year. Even if the entire EU coke making industry is removed, there will still be sufficient coal tar although some EU tar processing companies will be affected economically and could go out of business.

With regard to the position of EU manufacturing in the global market, it is worth noting that in 1975, Western Europe alone had 19 coal tar producing units with a distillation capacity of 3,000 kt/yr, Eastern Europe had 11 units with a distillation capacity of around 1,700 kt/yr and the old Soviet Union had 15 units with a production capacity of around 3,300 kt/yr. Between 1975 and 2005, around 3,400 kt of distillation capacity disappeared from the European tar industry and China has replaced Europe as the main producer and processor of coal tar accounting for over 50% of the global market (Stompel, 2008). Furthermore, Ukraine alone has nine coal tar processing plants with a capacity of 1,350 kt/yr while Russia has eight plants with a production capacity of 1,850 kt/yr (Stompel, 2008). Europe (Western and Eastern) is now thought to account for around 12% of world coal tar production (Jacobs, 2006; Stompel, 2008).

### **7.1.2 Releases from manufacture of CTPHT**

No information on releases from manufacturing sites has been provided by manufacturers of CTPHT during the development of this dossier. IUCLID (2000), however, indicates that, as CTPHT is manufactured under vacuum in closed systems, there are only two possible point sources of exposure to CTPHT:

- a) dust generated while handling solid pitch; and
- b) fumes evolved when pitch is stored as liquid.

Both are controlled by using exhaust ventilation systems or anti-dust oil sprayed on the products (for dust) and by scrubber systems (for fumes) (IUCLID, 2000).

The RAR for CTPHT considers releases of polycyclic aromatic hydrocarbons (PAHs) relevant to CTPHT. According to the RAR (2008), at coal tar processing facilities (where CTPHT is manufactured), many other (coal-tar related) products are produced and all these different activities contribute to the total release of PAHs by a given facility. As CTPHT is the final product that remains after several distillation steps, it is difficult to consider it separately from all the other production steps in coal tar processing. Any reported figures in the RAR do not, therefore, represent emissions from the production of CTPHT per se, but the whole process of coal tar processing (RAR, 2008).

However, it appears to be the case that there are emission management measures in place at the production sites of CTPHT. It appears that for all the sites indicated in the RAR gaseous emissions from process point sources are collected to some extent and treated either through incineration or via scrubbers. Similarly, for all the sites, waste water is either treated in an off-site municipal sewage treatment plant, an off-site industrial waste water treatment plant or on-site and emitted to the local receiving water (RAR, 2008).

## 7.2 Information on uses and releases from uses of CTPHT

### 7.2.1 Uses of CTPHT

Taking into account the information obtained from a literature review and provided during consultation, this section:

- describes the uses (and functions) of CTPHT in different applications;
- estimates the total quantities of CTPHT being used in each application;
- provides the past and future trends for the uses (where known); and
- describes the structure of the supply chain (and any inter-linkages between processes, where known).

#### 7.2.1.1 Summary

CTPHT is mainly used as a binding agent (ca. 95 %). Smaller volumes are used as heavy duty corrosion protection agent (ca. 1 %) and, e.g. in medicinal preparations. The use of CTPHT mainly involves industrial and to a lower extent professional users; according to the information available, consumer uses of CTPHT are limited to very specific uses (clay target shooting, medicinal preparations and, perhaps, roofing and heavy duty corrosion protection products).

At the global level, it appears that CTPHT is used (Jacob, 2006):

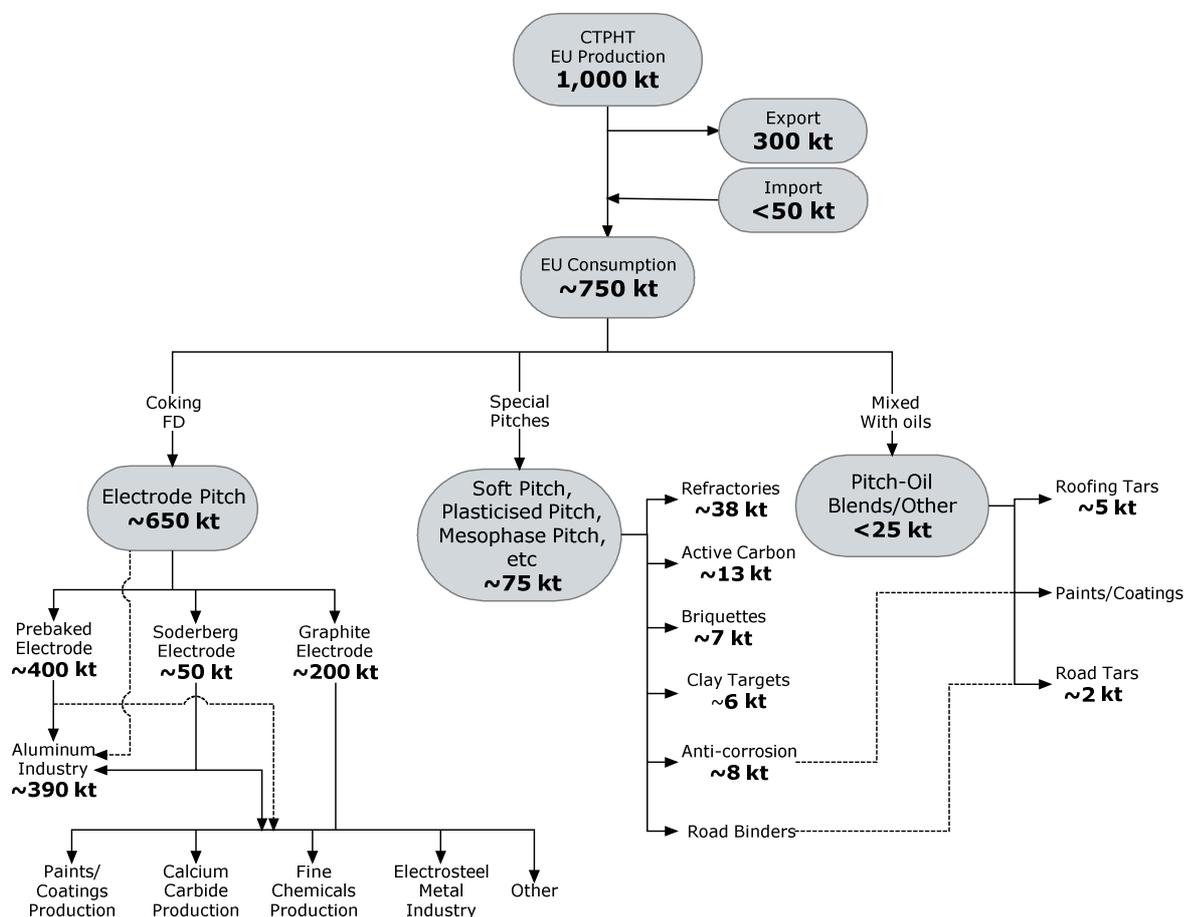
- in the production of electrodes, for around 85% of the total quantities used in EU;
- in a variety of other applications, for the remaining ~15 % CTPHT used in EU.

Use application	Function of CTPHT	Annual quantity used (in kilotonnes - kt)	% of total use
Electrodes			
• Prebaked anodes	Binding agent	400.0	53.3%
• Carbon and graphite electrodes (including carbon and graphite products other than electrodes)	Binding agent	200.0 (other products: 23.0)	26.7% (other products: 3.1%)
• Søderberg electrodes	Binding agent	50.0	6.7%
Refractories	Binding agent	37.5*	5.0%
Active carbon/carbon fibres	Starting material / Binding agent	12.8*	1.7%
Paints and coatings	Anti-corrosion	7.5*	1.0%
Briquettes	Binding agent	6.8*	0.9%
Clay targets	Binding agent	6.0	0.8%
Roofing	Coating (waterproofing) / Adhesive agent	5.3*	0.7%
Road construction	Binding/Sealing agent	1.5*	0.2%
Other (including medicinal) **		22.7	3.0%
<b>Total EU Consumption</b>		<b>750</b>	<b>100%</b>

\* Tonnages derived from percentages given for EU CTPHT sales in 2003 in the RAR (2008)  
 \*\* This also reflects the possibility that, for some of the use applications where no up-to-date data has been received, there may have been more significant upward changes in the tonnages used since 2003

Table 7.4 provides a comprehensive summary of all the applications in which CTPHT is used and the relevant tonnages.

Figure 2 summarizes in a graphical way the mass flow for the uses of CTPHT in the EU:



**Figure 2:** Mass flow diagram of the uses of CTPHT

Key points to bear in mind relating to Figure 2:

- anti-corrosion and paint/coatings are discussed together in Section 7.2.1.2.4 (as are road binders and road tars in Section 7.2.1.2.7); however, different types of pitch may be used in these applications. This is the reason for the joining dotted lines in Figure 2; and
- electrode pitch may either be supplied directly to the aluminium industry (shown by dotted lines) or as prebaked electrodes.

To enable manufacturers and importers of substances to produce and use standardised generic exposure scenarios under REACH, a standardised use descriptor system has been published by ECHA (Guidance on Information Requirements and Chemical Safety Assessment, Chapter R.12.). The use description is based on four elements:

- sector of use (SU);
- chemical product category (PC), supplemented by NACE and UCN codes as appropriate;

- 
- process category (PROC); and
  - article category (AC), with separate lists for articles with intended release of substances and for those without such release, supplemented by TARIC codes as appropriate.

For each of the uses of coal tars identified in the following sub-sections, Annex 5 provides the four use descriptors described above and an indication of whether or not these entail consumer exposure (to the coal tars).

### **7.2.1.2 Detailed description of uses**

#### **7.2.1.2.1 Production of electrodes**

##### **a) Function and applications**

CTPHT is mainly used as a binding agent in the production of electrodes (whether anodes, cathodes or graphite electrodes) which are mainly used in the production of primary metals, ferro-alloys, non-ferrous metals, metal alloys, calcium carbide and silicon carbide (RAR, 2008).

There are three main types of electrodes, which are produced using different processes, contain different levels of CTPHT, and are used in varying applications (RAR, 2008):

- Söderberg electrodes are manufactured by heating green paste (which itself is produced from coal coke or petroleum coke and up to 28% of CTPHT) to a temperature between 100°C and 150°C, after which it is pressed into the desired form and allowed to cool;
- prebaked electrodes are produced using the same green paste (in this case, with around 15% CTPHT); however, the green electrodes are baked in large furnaces at a temperature of about 1,100°C in the absence of air for up to four weeks in open or closed top ring furnaces; open furnaces account for 60% of prebaked anodes produced. During the baking process the coal tar is converted into coke, making the material electrically conductive. There is a 5% loss in weight due to loss of volatiles in the tar<sup>8</sup>; and
- graphite electrodes are obtained after additional impregnation with pitch, followed by re-baking and consecutive graphitisation at temperatures of around 2,800°C for several days, usually carried out in Acheson or Castner furnaces. Graphite electrodes are produced from an average of 20 - 30% coal tar pitch and 70 - 80% of petroleum coke. Single chamber, pit and closed ring furnaces are used for the baking process. Tunnel furnaces are used for small-scale production of speciality carbon.

In terms of downstream use:

- Söderberg electrodes are commonly used in submerged electric arc furnaces (e.g. for production of ferro-alloys) and in the electrolysis process for primary aluminium production<sup>9</sup>;

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<sup>8</sup> When CTPHT is heated, coal tar pitch volatiles are released. The volatiles and particulates are kept in the ovens (under pressure compared to outside the ovens) where they are burned as fuel, with the remainder being removed and passed through a filter system (The Netherlands, 2008b).

<sup>9</sup> It is estimated that ( Jacobs, 2006):

- 
- prebaked electrodes are mainly used as anodes in primary aluminium production<sup>9</sup>; and
  - baked graphite electrodes are used in electric arc furnaces for the production of a variety of products such as ferro-alloys, silicon carbide and calcium carbide and phosphorous. Graphite electrodes are used in electric arc furnaces for the production of steel<sup>10</sup>.  
It is important to note that other specialist carbon and graphite products than electrodes are produced in a similar way than graphite electrodes. These are used in many, primarily high temperature, processes including: moulds, furnace parts, seals and brushes, silicon manufacture, oil drilling, metallurgical processes, etc. (ECGA, 2009). Due to the similarities in the manufacturing processes and the subsequent difficulties in finding separate detailed data for these two applications, the uses of CTPHT in baked graphite electrodes and other carbon and graphite products have always been treated together in the rest of this report; however, when it was possible, more precise information on these applications have been included.

### b) Volumes

The RAR estimates that the manufacture of electrodes (including anodes) accounts for 87% of EU total sales of CTPHT. Applying these percentage (85 - 87%) to the current EU consumption figure (~750 kt) of CTPHT suggests that around **650 kt** of CTPHT is actually used in the EU in the production of electrodes.

The largest single application of CTPHT is its use in the production of anodes for the aluminium industry. The RAR (2008) estimates that this use accounts for around 322 kt of EU sales of CTPHT (excluding imports). More recent information provided by the European Aluminium Association (EAA, 2009) indicates that aluminium plants in the EEA currently account for around 390 kt/yr of CTPHT (including imports, which account for around 5% (or ~20 kt)) used in the manufacture of around 5 million tonnes of primary aluminium.

In terms of repartition between the different technologies, EAA (2009) estimates that, for the anodes consumed by the aluminium industry, prebaked anodes account for around 95% of EU production, while Söderberg accounts for the remaining 5%. Prebaked anodes can, therefore, be calculated to account for around **370 kt/yr** while Söderberg electrodes for around **20 kt/yr**.

The second largest use of CTPHT is in the manufacture of carbon/graphite electrodes used for the production of a variety of products, such as steel, ferro-alloys, silicon carbide, calcium carbide and phosphorous. The RAR (2008) estimates that this use accounts for around 81 kt of EU sales of CTPHT (excluding imports). However, responses received from individual companies during a consultation made for the purpose of this report accounted for around 177 kt of CTPHT being used in this application; table 7.5 below summarizes the information from the mentioned consultation:

- 
- depending on which aluminium smelting technology is used, around 450 kg to 500 kg of anodes are consumed for every tonne of primary aluminium metal produced;
  - CTPHT consumption using the Söderberg process is around 156 kg/t of aluminium manufactured and 100 kg/t of aluminium for prebaked anodes.

<sup>10</sup> It is estimated that 3 to 5 kg of electrode material is consumed to produce 1 tonne of steel (Franck & Stadelhofer, 1987)

**Table 7.5: Tonnages of CTPHT used in the manufacture of electrodes by Downstream User companies which responded to consultation**

Companies	Country**	Tonnage (kt)	End use application/sector for CTPHT
Company A	UK	0.6	Production of electrodes for fine chemicals production
Company B	Spain	3.5	Production of coal anthracite, calcined/graphite based electrodes
Company C	Norway	0.4	Production of carbide
Company D	Germany	18	Production of Söderberg, carbon/graphite electrodes and furnace linings
Company E	France	13.5	Production of graphite electrodes
Company F	France	31.2	Production of graphite electrodes and shapes
Company G	Slovakia	0.5	Production of carbon and artificial graphite
Company H*	Germany	0	Production of calcium carbide
Company I	Germany	9	Production of graphite electrodes
Company J	Switzerland	100	Production of carbon/graphite electrodes, cathodes and specialities
Company K	Sweden	0	Production of graphite electrodes
Company L	Germany	0.2	Production of calcium carbide
<b>TOTAL</b>		<b>176.9</b>	

\* Unknown content of CTPHT in electrodes

\*\* Note that for confidentiality reasons the countries have been scrambled and do not, therefore, match the corresponding tonnages

ECGA (2009) considers that this figure of 177 kt should be considered as ‘indicative’ (as opposed to ‘definitive’) of the amount of CTPHT used. It has to be noted that the above tonnage is still likely to be an underestimate of the total amount of electrodes used in the EU as no information has been received from the steel industry - where graphite electrodes are employed in electric arc furnaces.

The contribution of the production of other specialist carbon and graphite products (such as seals, brushes, etc.), which appear to be produced in the EU for an annual capacity of around 2 million tonnes, has also to be taken into account. Therefore, it is considered that around **200 kt** of CTPHT per year are currently used for carbon and graphite electrodes and other product applications.

In summary, it is estimated that:

- around 650 kt of CTPHT is used in electrode manufacture in the EU;
  - around 400 kt<sup>11</sup> of this is used in prebaked anodes;
  - around 200 kt is used in carbon and graphite electrodes and other products; and
  - around 50<sup>12</sup> kt is used in Söderberg electrodes;
- from the 400 kt used in prebaked anodes; around 370 kt is used in aluminium smelters, with the remaining 30 kt<sup>13</sup> going to other uses (e.g. steel production);
- from the 200 kt used in carbon and graphite electrodes, the 177 kt accounted for in Table 7.5 covers the majority of graphite electrodes used in the production of ferro-alloys, silicon/calcium carbide and phosphorous; the remainder (23 kt), however, covers other graphite products such as seals, brushes and similar products which are also produced in a similar way as graphite electrodes (and any other uses unaccounted for); and

<sup>11</sup> Estimation made on the basis of available figures for the use of prebaked anodes in aluminium industry.

<sup>12</sup> 650 kt/yr – (400 kt/yr + 200 kt/yr)

<sup>13</sup> 400 kt/yr – 370 kt/yr

- 
- from the 50 kt used in Söderberg electrodes, around 20 kt is used in aluminium smelters, with the remaining 30 kt going to other uses (e.g. for production of ferro-alloys and steel).

### c) Trends

With regard to the aluminium industry, the EAA (2009) indicates that there has been little change in the demand for/use of CTPHT over the past five years; however, they predict a possible downward trend over next five years due to capacity reduction in Europe.

For the carbon and graphite companies which responded (as listed in Table 7.5), they indicated that the consumption of CTPHT during the last three years was quite stable. In 2009, due to the general economic situation, a significant decrease is expected; however, after the economic recovery, a slight increase in the consumption (compared to 2008) is forecast over the next five years

The use of CTPHT in electrodes is, however, expected to continue for the foreseeable future as industry indicates that there are no suitable alternatives. All the responding companies (in Table 7.5) (as well as the EAA) stated that their end products depended on CTPHT and that in the event of a refused authorisation, they would have to shut down production and the required preparations (paste)<sup>14</sup> or articles (electrodes) would then be imported from India, China and Russia (where they are already today produced at lower costs). They expect the situation to be the same for steel and aluminium industries.

On the global front, analysts recently projected that aluminium prices are likely to stay strong over the next few years due to growth in Chinese demand and supply constraints from tight raw material and energy markets. By 2010, world aluminium production was expected to increase to 40 million tonnes (4.7% annual growth from 2005) and consequently, the demand for CTP would increase to 4.4 million tonnes (a 0.9 million tonnes increase) (Jacobs, 2006). However, it is likely that the current problems with world economies might affect these projections and consequently, demand for CTPHT.

### d) Structure of the supply chains involved in that use

The supply chain for electrodes would appear to flow from:

- the **manufacturer(s) of the CTPHT** (11 sites across the EU); to
- the **supplier(s)<sup>15</sup> of the CTPHT**: information provided by some downstream users indicates that the CTPHT is delivered directly (from the place of manufacture) to the manufacturers of the electrodes (anodes) using special trucks in a heated condition<sup>16</sup>. EAA (2009) indicates that there are nine such suppliers of CTPHT in Europe for primary aluminium production; to

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<sup>14</sup> Provided that this paste is a preparation in the sense of the REACH Regulation, then the authorisation requirement would also apply to placing on the market and use of CTPHT in the imported preparation.

<sup>15</sup> According to the available information, ‘suppliers’ are either the manufacturers of the CTPHT (or one of their dedicated subsidiaries) themselves or independent actors, which are ‘distributors’ in the sense of REACH.

<sup>16</sup> The RAR (The Netherlands, 2008b) notes that after distillation, the pitch is pumped into storage tanks and maintained at 200°C. Some of this pitch is delivered via tanker or exported as a molten liquid by either road tankers or ships. Other pitch is solidified into “pencils” in a pencilling plant. Using enclosed conveyor belts, these ‘pencils’ are transported to a storage warehouse or to a ship (using lorries or another conveyor belt).

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- the **formulator(s)/supplier(s) of the green paste** (or block): anode production consists of the three production steps: anode paste production, anode forming and anode baking (Fischer *et al*, nd). Although all three steps are likely to take place at any integrated site (or smelter); it is possible that paste production and forming can also take place at a separate ‘paste plant’ and the cooled green paste (or block) is then supplied to an anode baking plant; to
  - the **producer(s) of the electrodes or anodes (i.e. anode baking plants)**: some companies specifically produce and ship anodes to their customers (such as the aluminium production sites). On the other hand, some anode baking plants are directly linked to aluminium smelters (and are considered an integral part of the aluminium production process (JRC, 2008). The manufacture of graphite electrodes can also take place at sites where anode baking occurs. The number of such sites in the EU is currently unclear; to
  - users of the electrodes - where this includes all the production sites for aluminium, steel, carbide, etc. (although, some production sites may also undertake the formulation of green paste and manufacture of electrodes/anodes). According to JRC (2008), at the beginning of 1998, 22 primary aluminium smelters were operating in the EU and a further eight in the EEA. Some of these companies operate plants in different European countries or have subsidiaries or branches in other parts of the world, or are part of international co-operations. In Western Europe, Norway appears to be the largest producer of primary aluminium (1,190 kt in 2003) and other primary aluminium producing countries in the Western Europe are Iceland and Switzerland producing (266 and 44 kt primary aluminium respectively); altogether these three countries represent ~37% of Western Europe’s primary aluminium production (The Netherlands, 2008). There are around 200 European companies whose annual production of secondary aluminium is more than 1,000 tonnes per year (JRC, 2008). Norway also appears to be the largest ferro-alloy and non-ferrous metal producer in Western Europe; the majority of these ferro-alloys are produced in electric arc furnaces (EAF) applying Søderberg electrodes (The Netherlands, 2008); and
  - in a **recycling** step, some used anodes are returned to the manufacturers of the electrodes (for instance, to produce new prebaked anodes<sup>17</sup>). Carbon dusts from anode recovery and cleaning operations can also be re-used in steel furnaces as slag modifiers or as carburisers<sup>18</sup>; alternatively, these materials can find use in cement kilns as substitute fuels (Alcan, 2003);
  - **waste stage**: anodes which are not re-used are treated as waste and subject to waste legislation requirements (Alcan, 2003).

As far as production of other carbon and graphite products (such as seals, brushes, etc.) is concerned, it appears to involve 88 sites in EU (JRC, 2008).

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<sup>17</sup> Note that CTPHT used to manufacture graphite electrodes/shapes is converted to graphite in the processing step; there is, therefore no recovery step (ECGA, 2009). For prebaked anodes, the anodes in the electrolytic cells need to be changed when there is about 10 cm left of the anode. This is cleaned and returned to the anode plant, where it is crushed and mixed with petrol coke and pitch to make new anodes. All anodes for aluminium manufacture, therefore, contain a certain percentage of used anodes (EAA, 2009).

<sup>18</sup> Carburising is the addition of carbon (using a gaseous, liquid, solid source) to the surface of low-carbon steels at temperatures generally between 850 and 950°C.

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### **7.2.1.2.2 Refractories**

#### **a) Function and applications**

Refractories are materials that maintain sufficient physical and chemical stability to be used for structural purposes in high temperature environments encountered in the process industries (Ewais, 2004). They provide linings for high-temperature furnaces and other processing units and by definition are expected to be able to withstand physical wear, mechanic stress and strain, corrosion by chemical agents and high temperatures (above 500°C) (RAR, 2008; Schacht, 2004).

Most 'heavy' refractories are based on six base oxides (used individually or in combination): silicon, aluminium, magnesium, calcium, chromium and zirconium - in combination with carbon (Routschka, 2007).

CTPHT is used as a binder which, when added to a refractory mix, holds the various aggregates and matrix particles together (thereby contributing to the refractory products' strength) in a form that can be handled with minimum breakage (Schacht, 2004).

#### **b) Volumes**

According to the RAR (2008), refractories accounted for around 5% of EU sales of CTPHT in 2003. Applying this percentage to the current EU consumption of CTPHT (and assuming no significant change in consumption pattern has occurred) indicates that around 37.5 kt of CTPHT are currently used in the production of refractories.

#### **c) Trends**

The production of metals, cement, glass, etc. all depend on refractories, as do specialist applications in the aerospace industry (high temperature propulsion systems) and nuclear industry (Ewais, 2004). According to a market research report (MTP, 2007), total production of refractories in the EU-25 countries increased by an average of about 0.8% per year by weight between 2002 and 2006. The region now produces 5.3 million tonnes of refractory products, valued at approximately €3.4 billion which is 1.3 million tonnes more than it actually uses, making the EU a net exporter.

Iron and steel production is indicated to account for around 55% (or up to 70%, according to Moore, nd) of the total demand for refractories; therefore, the profitability of the refractories industry as a whole is strongly influenced by steel production levels and steel plant investments (Ewais 2004; MTP, 2007). Volume-wise, refractory consumption is, however, not necessarily increasing in line with steel demand. Improved operations (specifically in process control and hot gunning repair) and the increased use of modern steel process routes that require a shift from low-grade fireclays to high-grade products have resulted in a significant reduction in refractory consumption per tonne of steel (Ewais, 2004). Moore (nd) notes that 20 years ago, glass consumed around 12 kg/t of refractories, but this has dropped to around 5 kg/t today while steel has reduced consumption from 30 kg/t in 1980 to 10kg/t.

Furthermore, Routschka (2007) notes that, although hard coal pitch has the best performance/cost ratio of all coking binders, due to stricter environmental protection legislation, standard coal tar pitches have been almost completely substituted by petroleum pitches or pitches from a special high temperature vacuum treatment of coal tar pitch. This is broadly consistent with information in the RAR (2008) which indicates that the pitch industry is proposing to use pitches with a higher

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softening point resulting in a benzo(a)pyrene (B(a)P) content of 300 ppm compared to current levels in pitches ranging up to 20,000 ppm (RAR, 2008).

#### **d) Structure of the supply chains involved in that use**

The structure of the supply chain appears to flow from:

- **manufacturers of refractory metal:** who manufacture refractory metals, semi-finished as well as engineered/value added products. Most of these refractory producers are based outside Europe, as the scale of EU production (and natural endowment) of these refractory metals is often insufficient for meeting the entire European demand (for instance, only two major companies produce chromium metal in the EU); to
- **producers of refractories:** who manufacture the refractories using the CTPHT in combination with the refractory metals. Refractories are purchased by iron and steel companies mostly as articles, although occasionally as powders (preparations) (Eurofer, 2008). According to Cerame-Unie (nd), the main production capacity for refractories tends to be found in Germany, Italy, France and the United Kingdom. Austria is also an important producer and exporter of refractories. Overall, the EU refractories industry employs around 25,000 people; the exact number of refractory producers in the EU is, however, unknown; to
- **users:** which includes the steel, metals, cement and glass industries. In 2007, Germany was the largest consumer of refractories in the EU, with about 19% of the total, followed by Italy and Spain with 14% and 13% respectively (MTP, 2007). These downstream users may obtain their refractories directly from non-EU refractory suppliers. Moore (nd) notes that there is a clear trend towards more finished refractories coming from China and China's dominance in raw material supply has in fact increased hugely in the last ten years; and
- **recycling and waste stage:** in terms of their lifecycle, Alcan (2003) indicates that refractory materials from anode baking furnaces can be re-used following replacement with new bricks. Simple cleaning and sorting are often the only treatment necessary for re-use. More generally, Eurofer (2008) indicates that after their economical lifetime, refractories are discarded and as such become waste. They are dismantled and either:
  - taken back by the suppliers as waste within the scope of their supply contract;
  - put at the disposal of a waste treatment operator for sorting out, elimination and/or recovery; or
  - sorted out and partly eliminated as waste and partly recovered for placing on the market for reprocessing and future reuse.

#### **7.2.1.2.3 Active carbon/carbon fibres**

##### **a) Function and applications**

The RAR identifies the 'production of active carbon' as one of the uses of CTPHT. Information available in the literature indicates that coal tar pitch (or bituminous coals) can be used as a raw material for the production of active carbon (or activated carbon) (Gryglewicz *et al*, nd). Activated carbons are typically used as a solid adsorbent material and are produced specifically to achieve a

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large internal surface (500 - 1,500m<sup>2</sup>/g) which, in turn, makes it ideal for adsorption<sup>19</sup> (Lenntech, nd). Activated carbon can be found in a variety of applications including: air treatment, drinking water treatment, effluent water treatment, food processing, industrial processes (purification and catalysis), medical uses (charcoal cloth, masks), military and industrial respirators and a number of other applications (Chemviron, nd). Activated carbon is also available in special forms such as cloth and fibres.

Active carbon can also be agglomerated and formed into a variety of briquettes (Chemviron, nd). This latter use is referenced in the RAR (2008) which notes that, “*where active carbon has to be shaped, the raw material such as coal can be pulverised, briquetted using a binder [presumably coal tar pitch] and finally carbonised*”.

Carbon fibres are manufactured from coal tar pitch. In this process, coal tar pitch is first filtered to remove solids and then treated with heat, which results in a mesophase pitch. The mesophase pitch is then spun into monofilaments and the pitch monofilament is oxidised using oxygen. The oxidised fibre then undergoes carbonisation at temperatures of 1,000 - 1,500°C, followed by graphitisation at 2,500 to 3,000 °C for the production of high modulus fibres. Carbon fibres are used in the production of highly stressed construction materials and for the production of high-strength sports equipment (golf clubs, tennis racquets, skis) (Franck & Stadelhofer, 1987).

#### **b) Volumes**

According to the RAR (2008), active carbon accounted for around 1.7% of EU sales of CTPHT in 2003. Applying this percentage to the current EU consumption of CTPHT (and assuming no significant change in consumption pattern has occurred) indicates that around 12.8 kt of CTPHT are used in the active carbon (and carbon fibre) applications.

It should be noted that there may be some overlap between products described under ‘active carbon/carbon fibres’ and those for ‘specialist carbon and graphite products’ described earlier. JRC (2008) further notes that the biggest carbon producing plant in Europe is located in the Netherlands with a production capacity of 340 kt /yr, which will expand to 375 kt/yr.

#### **c) Trends**

According to the RAR, pitch-based active carbons are increasingly being produced outside the EU (RAR, 2008).

#### **d) Structure of the supply chains involved in that use**

The structure of the supply chain is not known.

It has not been possible to provide estimates of the number of producers of active carbon and/or carbon fibres or estimate the proportion of them using CTPHT.

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<sup>19</sup> Adsorption may be defined as the physical process which occurs when liquids, gases or suspended matter adhere to the surfaces of, or pores in, an adsorbent material (usually solid).

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#### **7.2.1.2.4 Paints and coatings**

##### **a) Function and applications**

CTPHT is used in coatings products for anti-corrosion protection. For heavy duty corrosion protection and application as sealing compounds, a further increase in the plasticity range is achieved by hot-mixing these pitches with extenders such as finely ground coal, minerals, diatomaceous earth, or fly ash. To meet especially high anti-corrosion requirements, coal tar pitches are combined with polymers. Such pitch-polymer combinations may consist of two-pack systems with epoxy or polyurethane or one-pack systems with other polymers or elastomers (RAR, 2008).

Special coal tar pitches are also used in the production of one-pack physically drying paints. Pitch paints have been used to protect concrete against aggressive water, for corrosion protection of steel constructions in industry, hydraulic steel structures, and underground pipelines. In one-pack, physically drying pitch polymer combination paints, pitch paints are mixed with thermoplastic polymers such as PVC, chlorinated rubber, polychloropyrene, polyacrylonitrile, or polystyrene (4-8% wt. % of polymer). They are superior to the conventional pitch paints, and are especially used to protect structures in the sewerage and effluent sector (RAR, 2008).

In two-pack chemically drying combination paints, pitch and solvent or high-boiling tar oils are mixed with reaction-curing resins such as epoxy resins and polyurethanes. These are widely used in hydraulic steel structures, ship building (antifouling) and harbour construction, sewerage sector, and pipeline construction (RAR, 2008).

##### **b) Volumes**

According to the RAR (2008), paints and coatings accounted for around 1% of EU sales of CTPHT in 2003. Applying this percentage to the current EU consumption of CTPHT (and assuming no significant change in consumption pattern has occurred) indicates that around 7.5 kt of CTPHT are currently used in paints and coatings applications.

Four companies in the paints and coatings industry provided responses to the questionnaire developed for the purpose of this report:

- the first company uses 1,200 tonnes of CTPHT;
- the second company uses only 0.3 tonnes of CTPHT;
- the third company uses 182 tonnes of CTPHT used in anti-corrosion epoxy paints (accounting for over 90% of company volume), anti-fouling tie coat and anti-corrosion vinyl, and these are all used in ship maintenance and repair; and
- the fourth company indicates that it stopped the use of coal tars in its end products a while back.

##### **c) Trends**

According to information provided by industry for the RAR, corrosion protection with pitch-based products is declining and phasing out of this use is predicted in the next few years. This appears to be consistent with information provided by the third company above, which indicates that the use of these coal tar substances has been stable for the last three years, although prior to that, production had decreased by 50% over three years due to a reshuffle to Asia. The current volume manufactured by this company is for the EU market and they forecast a decreasing demand for these coal tars in the future.

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It has also to be noted that, under the framework of the OSPAR Convention to which the European Community is party, it is recommended that inland ships are not treated with one-component coal tar coating systems (see PARCOM Recommendation 96/4 for the Phasing Out of the Use of One-Component Coal Tar Coating Systems for Inland Ships); the expected impact of this recommendation is a decrease of the use of CTPHT-based coatings within EU.

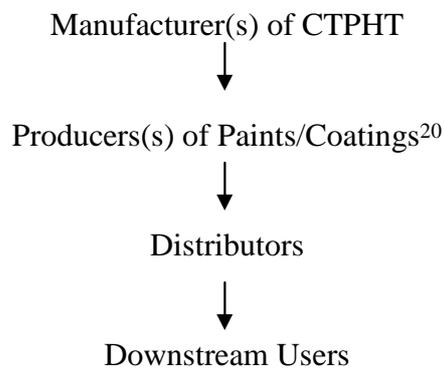
The RAR (2008), however, notes that subsequent information provided by industry contradicts this position that the use of CTPHT in heavy duty corrosion protection has been reduced significantly and that in the short term this application will be phased out.

#### **d) Structure of the supply chains involved in that use**

Information on supply chains provided by the consulted companies indicates that:

- the first company obtains its supplies from the Netherlands and France, and supplies to 10 - 20 customers in France and Belgium.
- the second company indicates that three products containing pitch are sold directly to 40-50 end users.
- the third company has two EU suppliers of the raw materials to their factories and the resulting products are distributed to over 50 customers across Europe.

The structure of the supply chain would therefore be:



#### **7.2.1.2.5 Briquettes**

##### **a) Function and applications**

CTPHT is a conventional binder used for making coal briquettes, where briquettes are essentially combustible fuel materials which can be used for domestic (e.g. heating and barbeques) or industrial heating.

Briquettes are essentially made up of:

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<sup>20</sup> The information provided by the 1<sup>st</sup> company which was consulted tends to indicate that, in certain cases, additional levels in the supply chain could appear, e.g. CTPHT distributors (between CTPHT manufacturers and paints and coatings producers) or specialisezd CTPHT-based paints and coating suppliers (between paint and coatings producers and distributors).

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- a base material (which could be coals of different properties, pre-treated coals, low- or high-temperature coke, peat, lignite, anthracite, charcoal and mixtures of these), and
  - a binder (in this case, CTPHT) to hold the material together when they are compressed into shape.

The shape and size of the briquettes depend essentially on their intended application (i.e. domestic or industrial); however, the binder may be around 5-12% of the overall mixture.

### **b) Volumes**

According to the RAR (2008), briquettes accounted for around 0.9% of EU sales of CTPHT in 2003. Applying this percentage to the current EU consumption of CTPHT (and assuming no significant change in consumption pattern has occurred) indicates that around 6.8 kt of CTPHT is currently used in the production of briquettes.

### **c) Trends**

In the early 1980's, capacities of 2,000 kt/yr of briquettes existed and these are now down to around 150 kt/yr (RAR, 2008). The overall trend in the use of briquettes appears to be downwards for technological, economic and environmental/legislative reasons.

Technology-wise, the increasing use of petroleum, gas and electricity for heating purposes has caused a reduction in the use of coal briquettes (Speight, 1994). It also appears to be the case that the coals used in the manufacture of briquettes are those normally considered of too low quality for use as a main component in coking blends. Thus, it would be expected that this industry would be most advanced in countries possessing large amounts of inferior coal, where fuel is high priced and/or where there is great supplies of coal tar pitch (binders). Essentially, to ensure a market for briquettes, the price has to be considerably lower than the market price for good coal (or other fuels).

The RAR (2008) also notes that the use of pitch bound coal briquettes is forbidden in some countries (e.g. Germany and Scandinavian countries; no legal references have been found however) and there is a general move towards using more environmental friendly binders like starch and molasses. Furthermore, this market appears to be linked to dedicated and captive users in mining countries (France and Belgium) where retired miners have rights on solid fuels provided by the former State owned companies (RAR, 2008), and it can be reasonably foreseen that it will progressively disappear in a rather near future.

However, the RAR (2008) notes that subsequent information provided by industry tends to contradict the assumption that the use of CTPHT in coal briquetting is being totally phased out.

### **d) Structure of the supply chains involved in that use**

The structure of the supply chain is unknown.

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#### **7.2.1.2.6 Clay targets**

##### **a) Function and applications**

As for that application, CTPHT is used as a binder.

Clay targets (previously known as “clay pigeons”) are designed as flying (saucer-shaped) targets for sports shooters and small game hunters to practice on, or in actual sports. The targets are flung into the air to create moving targets to shoot at; they must, therefore, be able to withstand the stress of transportation and being thrown from traps at very high speeds while also disintegrating readily when hit by a pellet (WIPO, 1995; RAR, 2008).

Clay targets usually consist of a filler (e.g. calcium carbonate (limestone)) and a binder (e.g. coal tar pitch). The filler and binder are made into a target by melting (using heat) and then pressing the mixture into a mould. Coal tar pitch (CTPHT) is indicated to make up to 30% by weight of the mix (AFEMS, 2009).

Clay targets are made to very exacting specifications with regard to their weight and dimensions and are required to conform to international standards..

##### **b) Volumes**

The RAR (2008) estimates that around 5.8 kt/yr of CTPHT are used in clay target manufacture. More recent information received from the European Association of Sporting Ammunition Manufacturers (AFEMS) indicates that around 6 kt/yr of CTPHT are currently used in clay target manufacture (2008 figures) (based on information provided by two clay target manufacturers-members of AFEMS). This is equivalent to around 0.8% of the total EU consumption of CTPHT. AFEMS (2009) also estimates that around 200 million CTPHT-based clay targets are consumed in Europe annually.

##### **c) Trends**

In general, the trend regarding the production and use of CTPHT-based clay targets over the next five years is expected to be downward.

Information provided by AFEMS (2009) suggests that around 12 kt/yr of CTPHT were used in the manufacture of around 400 million clay targets in the last two to three years. They, therefore, estimate that the use of CTPHT in clay target production in the EU has decreased by 50% (down to 6kt), as a result of extensive efforts made by companies in the search for alternatives. AFEMS, however, notes that a phasing out of this use in the EU is unlikely (as market conditions do not support such action) except if stipulated by legislation. AFEMS (2009) indicates that the alternatives to CTPHT are around four to five times more expensive than CTPHT increasing the cost of clay targets by around 220%. Thus, in countries where large reductions in the use of CTPHT-based clay targets have been achieved, this is due to legislative restrictions on use which result in a level playing field for sales made within that particular country.

Although a number of sources make reference to EU and national legislation which would restrict the use of CTPHT-based clay targets, it has not been possible to locate the legal text. CPC (nd) states that “*clays produced with CTPHT are already banned in many countries in Europe and these clays are likely to be banned in the UK, in the very near future*”. The RAR also references manufacturers claiming to apply petroleum pitch in order to meet “*EEC environmental protection*

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*directives*". CCI International (nd) notes that their clays are *designed to meet the toughest environmental regulations*" and *"the PAH levels being considerably lower than the mandatory figure"* (with approvals in Germany).

In the Netherlands, there is actually national legislation<sup>21</sup> which restricts the use of CTPHT-based clay targets. This legislation regulates the maximum content of a number of environmentally hazardous substances in clay targets and sets maximum permissible concentrations (in mg/kg dry substance) for the following substances: arsenic (29), barium, (160), cadmium (0.8), chromium (100), cobalt (9), copper (36), mercury (0.3), lead (85), molybdenum (3), nickel (35), zinc (140), and PAH<sup>22</sup> (10).

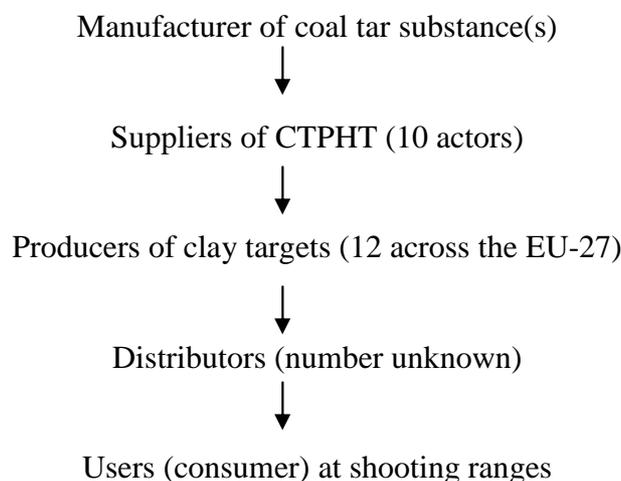
In countries with such legislation, a phasing out of use may have occurred; however, this does not apply in other regions without legislation. Thus, while the environmental effects as well as possible risk of ingestion by animals (feeding near shooting ranges) with subsequent health risks are key drivers in the 'search' for alternatives to CTPHT-based clay targets, the actual driver for introducing the alternatives may be said to be legislative pressures.

#### **d) Structure of the supply chains involved in that use**

Information provided by AFEMS (2009) suggests that:

- there are fewer than 10 companies supplying CTPHT to clay target manufacturers;
- there are around 12 companies using CTPHT in the manufacture of clay targets; and
- end-uses of the clay targets occur at around 20,000 shooting ranges across Europe.

The overall structure of the supply chain would therefore be:



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<sup>21</sup> Decree of 19 May 2004 (Stb. 237) promulgating rules concerning the limitation of the environmental consequences of clay pigeon shooting (Decree on clay pigeon shooting (Law on environmentally hazardous substances)).(Staatsblad van het Koninkrijk der Nederlanden, 2004, 12 pp.).

<sup>22</sup> 10 PAHs are included in the regulation, with the following CAS-numbers: 91-20-3 (naphthalene), 85-01-8 (phenanthrene), 120-12-7 (anthracene), 206-44-0 (fluoranthene), 56-55-3 (benz[a]anthracene), 218-01-9 (chrysene), 207-08-9 (benzo(k)fluoranthene), 50-32-8 (benzo[def]chrysene), 191-24-2 (benzo[ghi]perylene) and 193-39-5 (indeno[1,2,3-cd]pyrene).

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In terms of market share, information provided by AFEMS indicates that two companies located in Italy and Finland account for around 20 - 25% of clay targets produced in the EU.

### **7.2.1.2.7 Road construction and paving**

#### **a) Function and applications**

In road construction and paving applications, CTPHT is used as a binding/sealing agent.

It is important to clarify the meaning of three key terms - asphalt, bitumen and coal tars - as they all apply to road construction:

- ‘bitumen’ is a semi-solid hydrocarbon product produced by removing the lighter fractions (such as liquid petroleum gas, petrol and diesel) from heavy crude oil during the refining process. Bitumen is not in itself an end-product; its primary use is as a constituent of products used in paving and roofing applications. Approximately 85% of all the bitumen produced worldwide is used as the binder in asphalt for roads; 10% is used in roofing applications and the remaining 5% in sealing and insulating purposes in a variety of building materials (Eurobitume, 2009a).
- the term ‘asphalt’ refers to a mixture of bitumen and mineral aggregate designed for specific paving applications. It is typically composed of around 95% mineral aggregates mixed with 5% paving grade bitumen (the exact concentration of bitumen depending on the type of asphalt mix and end-use). The bitumen functions as the binder/glue that binds all the mineral aggregates in a cohesive mix. In addition to the construction and maintenance of major highways (motorways and trunk roads), asphalt is also used extensively for rural roads and urban streets, airport runways and taxiways, private roads, parking areas, bridge decks, footways, cycle paths and sports and play areas (EAPA, 2009).
- in the past, coal tar was used extensively in paving materials across Europe; it was always used as a mixture of petroleum-derived bitumen along with tar in all layers of pavement applications. O’Flaherty (2002) notes that these tar-bitumen blends seek to combine the best qualities of both binders. They have good weathering characteristics, a lower tendency to strip from aggregates (compared with pure bitumen) and are less brittle (compared with pure tars).

According to the European Asphalt Producers Association (EAPA, 2009), because of their similar appearance and technical effects, little distinction was made between bitumen and tar as a construction material. In practice their origin and consequently their chemical composition are however quite different: while bitumen is a product of the crude oil refining process, tar is a product of coal processing in a coking plant. As a result of the destructive distillation of coal, coal tar contains PAHs in considerable amounts – far higher than bitumen (EAPA, 2009).

According to EAPA, coal tar was used in the following European countries: Belgium (until 1992), Czech Republic (until 1999), Germany (until 1995) Denmark (until 1975), Finland (until 1960s), France (until 1970), Netherlands (until 1991), Norway (until 1960), Sweden (until 1974), Slovakia (until 1980), Turkey (until 1979) and UK (until 1999).

Thus, bitumen had replaced coal tar significantly in Europe during the 1970s and 1980s (except the UK where it was used only infrequently from 1980s to 1999 on specific contracts requiring an

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asphalt of high resistance to fuel contamination) – due to increasing oil production and declining coke usage and the related economic factors.

It also appears that most of the European countries (for instance the Netherlands) have banned the use of coal tar pitch in road construction by law or agreement between trade unions and road building companies (The Netherlands, 2008).

Overall, asphalt has been used extensively for paving and road construction owing to its excellent waterproofing and adhesive properties which are important for binding and holding the aggregates in the pavement together. However, asphalt has some drawbacks relating to its chemical makeup: because asphalt is a very complex mixture of chemicals which are predominantly open chain (aliphatic) in structure and also being a by-product of the petroleum distillation process, it can be attacked and disintegrated by other by-products derived from petroleum (e.g. automotive oils, petrols, fuels, etc). The actual rate of pavement deterioration (from simple corrosion to development of minor cracks which widen and deepen with time) depends upon the traffic volume as well as climatic conditions. These problems are associated primarily with parking lots, airport runways, service stations, etc (SGSC, nd).

The life of road pavements can, therefore, be extended by applying a protective coating that resists attack by the elements that destroy the asphalt. Information in the literature (mainly from the US) indicates that coal tar pitch (CTP) emulsions have been used (since the 1950s) as seal coatings for extending the life and lowering maintenance costs associated with asphalt pavements. They are the pavement sealers recommended for asphalt or tar surfaces where resistance to gasoline spillage is required (Whittier, nd). These CTP emulsions are indicated to be water-based and the finished product is a stable, homogeneous composition that is applied with ease (SGSC, nd). SGSC (nd) notes that unsealed pavements will require repairs starting with the second year and could require a one-inch overlay as often as every seven years.

A US Air Force Specification for thermoplastic coal tar emulsion slurry (Grip-flex, nd) specifies the following:

*“A cold applied, thermoplastic modified coal tar emulsion slurry, produced as a complete product in the manufacturing plant, to provide a jet fuel resistant, anti skid wearing surface for use on asphalt and concrete pavements warranted for a period of FOUR (4) years to be free from defects of material and workmanship and to not lose adhesion, dissolve, or wear away. Type I is installed on flightline operational areas; Type II is installed on milled surfaces, heavily oxidized pavements, parking lot and road surfaces.*

*The coal tar base shall provide chemical resistance to agents that destroy asphalt. The thermoplastic coal tar emulsion shall provide the elasticity to bond to the asphalt or concrete and the cohesive ability to hold the aggregate in place. A service life of 10 years is expected; a limited warranty, by the manufacturer to perform repairs for four years for defects in materials, workmanship, loss of adhesion, dissolution, or diminution by friction, use, time, elements, or constant wet exposure to petrochemicals, e.g., JP 4, hydraulic oils, gasoline, etc., for periods of seven (7) days or less.”*

At present, it is unclear whether this use of coal tar pitch as a seal coating is entirely outside the EU or not; however, this has been identified as a possible use, which should be taken into consideration (for authorisation process purposes) if it is confirmed.

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## b) Volumes

According to the RAR (2008), road construction accounted for around 0.2% of EU sales of CTPHT in 2003. Applying this percentage to the current EU consumption of CTPHT (and assuming no significant change in consumption pattern has occurred) indicates that around 1.5 kt of CTPHT are used in road construction applications.<sup>23</sup>

The accuracy of this estimate is however uncertain. Information provided by EAPA (2009), however, indicates that one company specialising in applying anti-skid layers at airports used around 500 tonnes in 2008 (EAPA, 2009).

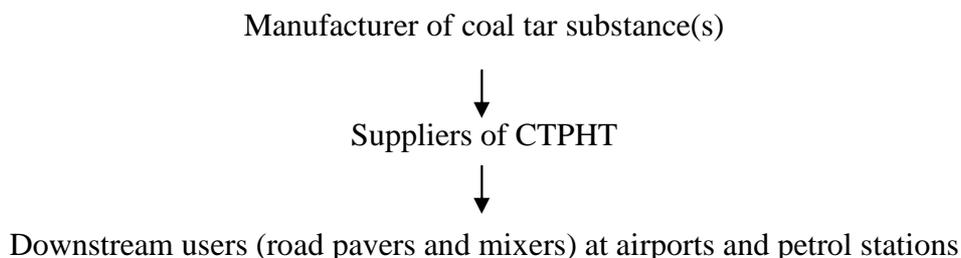
## c) Trends

As already mentioned above, there is information (EAPA, 2009) indicating that coal tar is no longer used for road construction or paving operations. The RAR (2008) notes that the amount of pitch used for road applications is decreasing as it is replaced by petroleum-based pitches (and sealers) on account of their lower PAH content. In some countries it is also legally allowed to rely on cold techniques with or without binders (emulsion, foam bitumen, and or hydraulic binders). SGSC (nd) also notes that, in recent years, asphalt emulsion-based seal coatings have been introduced with varying degrees of success as a replacement for CTP-based seal coatings

Therefore, it appears that only very particular applications such as anti-kerosene coatings for parking lots, airfields and fuel stations still use coal tar pitch emulsions (RAR, 2008).

## d) Structure of the supply chains involved in that use

Although no information was received on the structure of the supply chain, it is expected that the overall structure of the supply chain would be as follows:



### 7.2.1.2.8 Roofing

#### a) Function and applications

CTPHT is used as impregnating, coating and adhesive agent, mainly for waterproofing purposes.

Until the late 1970s, coal tar was the technology of choice for flat and low-slope commercial roofing. Its unique structure, with closed rings of atoms linked to form a stable molecular

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<sup>23</sup> By way of context, EAPA (2009) estimates that in 2007, around 435 million tons of asphalt was produced in Europe (including Russia) and more than 20 million tons of bitumen was used in the asphalt industry in 2007 to produce asphalt.

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configuration, made coal tar highly impermeable to moisture, UV rays, atmospheric oxygen and chemicals (e.g. salts and corrosive agents in urban pollution) (Younkin, nd).

The traditional coal tar system is a built-up roof that is manufactured on-site, with layers of felts adhered to the roof using hot-applied coal tar pitch. Coal tar pitch acts as the waterproofing agent that protects the roof from the elements, while the felts act as reinforcement. According to the RAR (2008a), during the laying down of a new roof, the CTP is heated and applied at approximately 191°C to 204°C. Coal tar's molecular structure provides the benefit of actually healing itself as it melts a little in the sun; thus any cracks formed by impact or rapid drops in temperature reseal when surface temperatures rise and the coal tar softens. For this reason, coal tar roofing cannot be used on greatly sloping roofs. To counteract its low softening point, coal tar roofing is used in combination with a gravel surface which adds additional benefits such as extra weight reducing wind uplift and protecting the roof from the sun (Younkin, nd; Koppers, 2003).

Advanced coal tar technologies are pre-manufactured, improving the proven durability of traditional coal tar with polymer modifiers in a quality-controlled factory environment (Younkin, nd). By using plasticised pitches or by adding extenders, the plasticity and temperature stability of roofing tars can be improved considerably (RAR, 2008).

#### **b) Volumes**

According to the RAR (2008), roofing accounted for around 0.7% of EU sales of CTPHT in 2003. Applying this percentage to the current EU consumption of CTPHT (and assuming no significant change in consumption pattern has occurred) indicates that around 5.3 kt of CTPHT are used in roofing applications.

#### **c) Trends**

Various studies show that the use of coal tar pitch in roofing was still relatively common in some EU countries in the 1950s, but decreased significantly in the 1960s. Coal tar and coal tar pitch were also used for waterproofing of building foundations and interior spaces in the 1950s, and in roof treatment products until the mid-1980s (FIOH, 2007).

It appears that coal tar's share of the roofing market has fallen in the last 20 years due to the discovered carcinogenicity of coal tar pitch volatiles.

#### **d) Structure of the supply chains involved in that use**

The structure of the supply chain is not known.

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#### 7.2.1.2.9 Medicinal preparations<sup>24</sup>

##### a) **Function and applications**

Coal tar preparations have been used for many years to treat various skin conditions, such as eczema, psoriasis, seborrheic dermatitis, dandruff, etc. These preparations may be applied directly to the skin, added to a bath, or used on the scalp and are available in a number of dosage forms (e.g. as liquids, ointments, shampoos<sup>25</sup>, soaps, gels/jellies, emulsions, etc) (Mayo, 2008).

Coal tar is refined by various methods to potentially obtain more aesthetically acceptable and pharmaceutically practical products (e.g. coal tar topical solution and coal tar distillate). Official compendial monographs (or pharmacopoeia) on coal tar do not, however, specify the composition of the coal tar, other than to require that not more than 2% of 100 mg of coal tar remain as a residue (ash) on ignition. Since coal tar is not a chemical entity and its therapeutic effect depends on a myriad of carbonised and volatile constituents, some experts believe that the degree of refinement of coal tar is responsible for variation in therapeutic effectiveness of different coal tar products (AHFS, 2008).

##### b) **Volumes**

Although a questionnaire was sent to the three main EU industry associations covering medicinal products, information on quantities used has been received from only two companies. While the first company confirmed uses of other coal tar derivatives than CTPHT in the manufacture of shampoos and emollients (moisturisers), the second company (a SME) indicated the use of 100 kg of CTPHT in the manufacture of medicated shampoo products.

If industry associations confirmed the use of coal tars in these applications, the specific coal tars and quantities appeared to be unknown (at the industry association level).

##### c) **Trends**

No information could be obtained regarding the specific use of CTPHT in these applications.

##### d) **Structure of the supply chains involved in that use**

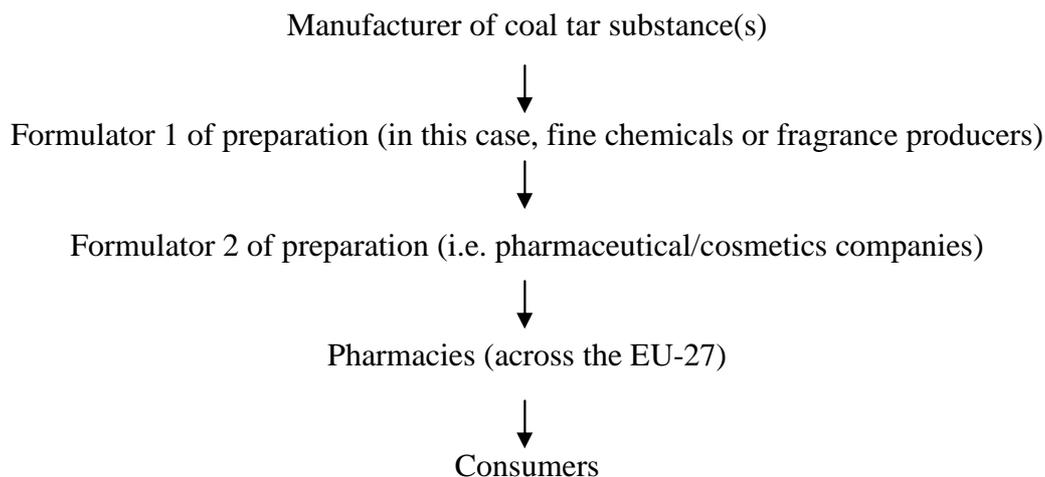
The available information indicates that coal tar can be purchased as a preparation (or more specifically, a “multi-component mixture of natural and/or synthetic raw materials”) which is then further formulated into various end-products (by the respondent) which are placed on the market.

The structure of the supply chain would therefore be:

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<sup>24</sup> It has not been possible to clarify if these “*medicinal preparations*” cover medicinal products and/or cosmetic products; it has to be noted that, if it would appear that part or all of these preparations are medicinal products in the meaning of the EU-legislation, these should not be subject to authorisation.

<sup>25</sup> Although soaps/shampoos may technically be considered to be (borderline) cosmetic products, the EU Cosmetics Directive (76/768/EEC) does not allow the use of coal tars in cosmetic products. This is stipulated in Annex II of the Directive (which lists all substances which must not form part of the composition of a cosmetic product). Entry 420 reads “crude and refined coal tars” - the ban is, therefore, general and is independent of the quality/level of refinement of these materials (as confirmed by the EU Cosmetic and Toiletries Association - COLIPA).



#### **7.2.1.2.10 Carbon black manufacture and tyres**

Information received from the European Tyre and Rubber Manufacturers Association (ETRMA, 2009) indicates that coal tar pitch is not a raw material in tyre or general rubber goods manufacturing. CTP is basically the major feedstock for carbon black production. ETRMA indicates that in any case, during carbon black production, most of the feedstock is dehydrogenated so only traces may remain in the final product.

#### **7.2.1.2.11 Manufacture of pyrene**

A possible use of CTPHT in the production of pyrene has been highlighted by industry; however, this use has not yet been confirmed (or validated).

## 7.2.2 Releases from the uses of CTPHT

### 7.2.2.1 Preliminary remarks

In considering releases of CTPHT (and its constituents) from the uses discussed in above sections, it should be borne in mind that each industry sector or application requires different physico-chemical characteristics relating to CTPHT.

In industry terminology, CTPHT is indeed known by many different names (or forms) such as: soft pitch, hard pitch, binder pitch, mesophase pitch, pulverised pitch (pitch powder), etc - depending on the users' industry background. As already discussed, these various pitch forms are also produced and applied in various uses, for instance:

- soft pitches are typically used in refractory binders and as road binding agents;
- mesophase pitches, produced by removing low molecular weight species from coal tar pitch, are used to make high technology products, such as carbon fibres;
- plasticised pitches, produced by digesting coal in pitch and high boiling coal tar distillate modified by inert material filler, are used in anti-corrosion coatings; and
- pitch-oil blends, produced by mixing CTPHT with (distillate) oils, are used in road tars, roofing tars, paints and coatings.

Table 7.6 provides an example of the different specifications for coal tar pitch for different industry sectors, which could again vary as per customer requirements.

	<b>Söderberg process</b>	<b>Prebaked smelter process</b>	<b>Graphite industry</b>	<b>Refractories industry</b>
Softening Point °C	90 - 105	101 - 113	95 - 110	80 - 90
Coking Value (Conerdom) (minimum %)	53	54	53	45
Toluene Insoluble (minimum %)	30	32	22	20
Quinoline Insoluble (%)	8 -12	7 (min)	10 - 16	8 (max)
Ash (maximum %)	0.30	0.25	0.30	0.30
Moisture (maximum %)	0.20	0.50	0.50	Nil
<i>Source: <a href="http://www.easterntarcoatings.com">www.easterntarcoatings.com</a></i>				

It should be noted that even within the same product different types of pitch may be used. In describing the process for producing graphite electrodes, Franck & Stadelhofer (1987) note that the coal tar pitch used as a binder is made from tars selected on the basis of their quinoline insoluble (QI) content. To increase the carbon density of the baked carbon product, it is further impregnated with low QI pitches in a vacuum/pressure process. While the binder pitches are produced exclusively from coal tar, impregnating pitches can be produced from low QI tar or by heat treatment of cat-cracker residues. Differences between the binder pitch and impregnating pitch are provided in Table 7.8.

Therefore, there appears to be no 'standard' pitch with a chemical composition which can be characterised within narrow margins. Each type of pitch will have a typical chemical composition or, more specifically, a PAH pattern; and within one type of pitch, some variation in the PAH pattern will occur. The PAH pattern and content of a particular pitch may also change considerably for certain uses (e.g. as a binding agent in a formulation with bitumen for road paving) as other PAH-containing components are added (RAR, 2008).

	<b>Binder Pitch</b>	<b>Impregnating Pitch</b>
Softening Point °C	95	60
Quinoline Insoluble (%)	10	2
Toluene Insoluble (%)	39	18
Coking Residue (Conradson)	56	38
Viscosity	1,200	55

*Source: Franck & Stadelhofer, 1987*

Following from the above, it has not been possible within the context of this report to obtain information from stakeholders within each of the use sectors on their emissions of CTPHT (and its constituents) or the PAH profile of emissions for each application. Companies responding to the consultation launched for the purpose of this report have indicated that data on the emission of coal tars during the service life of products is very difficult to estimate when one considers the particular end use of the products concerned (particularly those with consumer end-points, e.g. briquettes). On the other hand, in uses such as graphite electrodes, the coal tar pitch is not present in the final product and there is, therefore, no exposure to coal tar pitch or its constituents for the downstream user.

The discussion below, therefore, considers emissions controls which are applied in the various use sectors which possibly impact on releases of CTPHT (and its constituents).

### **7.2.2.2 Releases from uses of CTPHT and emission control measures**

#### **7.2.2.2.1 Production of electrodes**

Information relating to releases of CTPHT will focus on releases by **producer(s) of the electrodes or anodes** (at anode baking plants) and those by **downstream users** of the electrodes (i.e. production sites for aluminium, steel, carbide, etc).<sup>26</sup>

As already discussed, the largest single application of CTPHT is its use as a binding agent in the production of anodes (used in the electrolytic process) in the aluminium industry.

There are some key differences between the prebaked and Söderberg anodes when used in aluminium electrolysis. According to the European Aluminium Association (EAA):

- in prebaked, during the production process, the carbon anodes are mixed and baked at around 1,150°C in the anode baking plant. Hence, during the electrolytic process (involving downstream users), there are no PAH emissions from the prebaked anodes due to the earlier high temperature ‘coking’ and volatilisation of the PAHs. Emissions associated with prebaked electrodes are, therefore, limited to those arising from the anode baking plant. The anode baking process is, however, a closed operation; it is, therefore, easier to control and abate the emissions. Gases from these plants are treated with dry scrubbers and filtered or passed

<sup>26</sup> Releases by manufacturers of the CTPHT (are already considered in Section 1.2) and further information on emissions controls (e.g. for coke ovens) is available in the Draft Reference Document on Best Available Techniques for the Iron and Steel Industry (February 2008 Draft). Supplier(s) of the CTPHT also appear to have special delivery conditions (i.e. using special trucks in heated conditions, as discussed earlier). No further information is available on the recycling step beyond that already provided in Section 1.3.2.

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through regenerative thermal oxidation units resulting in very low emissions. For most anode plants, the emissions are in the region of 1 kg BaP/year or less and all plants are expected to adhere to the EU Ambient Air Quality Standard. Water is used to cool the green (unbaked) anodes before the baking process, and some plants release this to sea (with emissions no more than 40 kg PAHs as (Borneff6/year<sup>27</sup>) while others have closed cooling water systems (EAA, 2009). EAA notes that, in general, it is possible to install closed cooling water circuits, however, for existing plants this may be difficult due to space and process limitations (EAA, 2009);

- in Söderberg, the mixture of coal tar pitch and petrol coke is actually baked in place during the electrolysis process. This means that there are emissions of PAH (directly from the anodes) during the electrolysis process and these are more difficult to capture in the gas treatment systems. Some of the PAHs pass through the gas collection system round the lower part of the anode and are combusted in the burner, which is part of the gas suction system. The rest evaporates from the top of the anode and escapes to air.

There are three remaining operating Söderberg smelters in Europe, and these have modernised (or are in the process of doing it) the operation by including raised anode casings (to reduce the evaporation) or by installing extra gas suction systems on the top of the anode and a separate cleaning system for this. One of the plants which have completed this now has emissions of less than 500 kg BaP/year to air. The air flow here is normally around 15 million m<sup>3</sup>/hour for this type of plant and all plants are expected to adhere to the EU Ambient Air Quality target value for 2013 of 1 ng/m<sup>3</sup> BaP in the surrounding areas (EAA, 2009).

A key difference is, therefore, that in Söderberg plants, new anode paste is continuously added to the electrolytic cells and the emission as well as the emission profile is constant. For prebaked plants, however, there is no emission during electrolysis, the anodes are baked to pure carbon in the anode baking plant, and all the PAH emissions occur here during the baking process. In simple terms, compared with the Söderberg process, the PAH emissions are shifted to the anode baking plant in prebaked, where it is easier to control and there is insignificant residual PAH in anodes as these are baked at 1,150°C (EAA, 2009).

It is also worth noting that while the anodes used only in the primary smelters for aluminium electrolysis are consumed during the production process (based on their dual role as a source of heat required for melting the aluminium as well as a carbon source for reducing aluminium oxides to metallic aluminium) (EAA, 2009), the electrodes in electric arc steel manufacturing, while equally used up over time, are not used in a chemical reaction but provide thermal energy via the electric arc developed between the electrodes (Jacobs, 2006).

With regard to emissions, the EAA (responding on behalf of aluminium manufacturing sites) indicates that there has been a reduction in their emissions in the period since completion of the RAR (in 2008) (EAA, 2009). More specifically, compared with information in the RAR, plants S3 and S4 are closed, plant PA9 has significantly reduced emissions, plants S5 and S6 are being upgraded to new Söderberg and plant A1 is installing new scrubbers (EAA, 2009). EAA (2009) also notes that for paste and anode baking plants, dedicated extraction systems and scrubbers/filters systems to remove coal tar emissions and particles are used. Dust minimisation in transportation and storage activities and prevention of rain water contamination is also undertaken.

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<sup>27</sup> The Borneff 6 refers to a group of six PAHs selected on the basis of their ease of detection and used in a number of emissions inventories (e.g. UNECE POP). The six PAHs are: fluoranthene, benzo(b) fluoranthene, benzo(k) fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(ghi)perylene.

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In terms of emissions control, the EAA notes that the remaining Söderberg plants in Europe are either rebuilt to a modernised Söderberg or in the process of doing this, which will significantly reduce their emissions. For anode baking plants, the state of the art technology is regenerative thermal oxidising units for free standing anode baking plants or dry scrubbing units with alumina (Al<sub>2</sub>O<sub>3</sub>) for anode baking plants attached to primary smelters. In this case, the alumina used is returned to the smelter. For water, the best available technique (BAT) is closed circuit cooling water systems. For occupational exposures, current BaP exposures in anode baking plants and modernised Söderberg plants are below any existing national<sup>28</sup> OELs in EU Member States (EAA, 2009). EAA (2009) also notes that emissions of PAH from industry are a minor source for the total emissions of PAHs as shown in studies undertaken before the setting of Ambient Air Quality limits, and the aluminium industry is not among the major sources of PAH emissions from industry.

With regard to use in graphite electrodes, companies responding to consultation note that there is no more CTPHT material left in the finished and sold product (graphite electrode). Any fraction of the raw material CTPHT is converted into carbon or graphite during the different production process steps - with the exception of a very small quantity of fume gases that have to be treated by special air purification techniques. In effect, CTPHT is not present in the final product and customers do not receive any CTPHT-containing products. One company responding to consultation also indicated that due to the emission controls employed in their processes, the emission of harmful substances originating from coal tar pitch is very close to zero.

In any case, operational conditions, risk management and best practice in the production of anodes (and the relevant emissions and emissions controls) is covered in Chapters 4 (for aluminium) and 12 of the Draft Reference Document on Best Available Techniques for the Non-Ferrous Metals Industries (December 2008 Draft).

#### **7.2.2.2.2 Refractories**

At present, information on the emission of PAHs from the use of coal tar pitch as binder for refractories is very limited. As noted earlier, the industry is moving towards pitches with a higher softening point resulting in a lower BaP (or PAH) content.

#### **7.2.2.2.3 Active carbon**

According to the RAR, pitch-based active carbons are processed in closed vessels where the pitch is pyrolysed to pure carbon with controlled emissions (RAR, 2008)

#### **7.2.2.2.4 Briquettes**

As noted in RAR (2008a), when used as binding agent for barbecue briquettes, no exposure should happen during the use of the briquette in itself since, coal tar pitch will be totally transformed or volatilised during the briquettes' production process.

There is no information available on emissions from use of briquettes for heating

#### **7.2.2.2.5 Clay targets**

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<sup>28</sup> There is no EU-level OEL for the substance

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AFEMS (2009) estimates that around 6,000 tonnes of CTPHT are released to the environment, with 3,000 tonnes ending up in soil while 3,000 tonnes end up in waste. It is understood that the remains of the clay targets can be collected after the shoot but this is hard to organise and costly. In addition, the clay targets can take years to break down and, as such, regular shooting ground can become highly contaminated (CPC, nd). At the same time, as discussed earlier, some companies claim to produce clay targets with considerably low PAH levels.

#### **7.2.2.2.6 Road paving (/ Roofing)**

In countries where tar was used in the past, old existing roads can have layers that contain tar that was used in the past. Industry is, therefore, confronted with tar only in those situations where existing roads containing tar are maintained, reconstructed or demolished. In these situations, EAPA indicates that procedures are applied in respect of occupational health and protection of the environment in all phases of the process. These protective measures would include (EAPA, 2009):

- protective measures during milling to prevent emissions of, and exposure to, tar containing dust;
- separation of tar containing pavement layers from non-tar containing layers; the final end point of non-recycled tar containing materials is unknown;
- avoiding hot recycling of tar containing reclaimed asphalt pavement (RAP); and
- restricting re-use of tar containing RAP to cold techniques. In some countries, it is allowed to rely on cold techniques with or without binder (emulsion, foam bitumen and/or hydraulic binders) in road base applications.

As noted in the RAR (2008a), recycling of asphalt road surfaces started in Western Europe in 1980 and such recycling/resurfacing operations are often combined with road paving. In this process, the old layer of asphalt is stripped and mixed with new asphalt at the asphalt plant or at the paving site and re-applied to the road surface (RAR, 2008a). Asphalt that is reclaimed during maintenance operations (e.g. by milling) is in general re-used to produce new hot mix asphalt. However, reclaimed asphalt-containing tar is not re-used to produce hot-mix asphalt. In this case (of asphalt-containing tar), the waste is considered hazardous and the hot recycling is not allowed (EAPA, 2009).

According to information provided by EAPA (2009), if reclaimed asphalt contains PAHs and/or phenol over a certain limit value, it is considered to be ‘asphalt-containing tar’. In practice, however, the definition of ‘asphalt containing tar’ can differ from country to country as there are different limits in several European countries mentioned in the relevant national legislation. There is also a definition in the European list of waste products (EURAL) according to which ‘reclaimed asphalt containing more than 0.1 % coal tar should be regarded as hazardous waste’ (EAPA, 2004).

In the Netherlands, the re-use and the recycling of reclaimed asphalt containing tar is not allowed anymore by the government. The Dutch national policy is to remove it from the building chain and, as such, reclaimed asphalt containing tar is burned and the remaining clean aggregate can be re-used (EAPA, 2009).

Finally, the RAR (2008a) notes that people may be shortly exposed (1 day) as a result of road taring or roofing with a very low frequency (once every 10 years), and to concentrations in air much lower than workers as the distance to the source is larger and the concentration will consequently be reduced due to dilution (RAR, 2008a).

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#### 7.2.2.2.7 Medicinal products

The first company indicated that, during the formulation process, there is no waste product from the manufacturing process. All bulk containers containing residues are also treated by licensed agents. The second company indicated that manufacturing is undertaken in a clean room environment with air handling systems.

#### 7.2.2.2.8 Other uses

There is no information available relating to releases from other uses of CTPHT.

#### 7.2.2.3 *Sources of releases of PAHs, in particular from the use of CTPHT*

In order to get an overview of the spatial distribution of actual emissions, consideration needs to be given to all the possible sources of CTPHT as well as their constituents (i.e. PAHs) that may be released.

In that respect, the following sources would have to be taken into account (bold font highlights possible sources related to the use of CTPHT<sup>29</sup>):

- Coke ovens;
- Coal tar distillation plants (which may be part of the coke oven plant or operate independently at another site);
- Industrial (or point) sources, such as:
  - **Aluminium production sites (prebaked)**
  - **Anode baking sites (some of which takes place at aluminium production sites);**
  - **Iron and steel production sites (electric arc furnaces);**
  - **Non-ferrous metals production sites;**
  - **Fine chemicals and carbide production sites;**
  - Coke and solid smokeless fuel (**briquettes**) production sites;
  - Other sites where industrial combustion (e.g. coal, wood, etc.) occurs;
- The energy sector, including:
  - Petroleum refining plants;
  - Natural gas production sites;
  - Electricity production plants (oil, coal);
- Domestic sources, such as:
  - **Burning of briquettes;**
  - Wood burning;
  - Coal fires (stoves, fireplaces);

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<sup>29</sup> However, not all PAH emissions from the source may originate from CTPHT.

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- Localised diffuse sources, such as:
    - **Road paving;**
    - Wood preservation products<sup>30</sup>;
    - **Roofing;**
    - **Clay Targets;**
  
  - Mobile sources, such as:
    - Transport (fuel combustion);
    - Natural fires and open burning;
  
  - Waste disposal sites, such as:
    - Landfills;
    - Waste incineration sites (sludge, municipal waste, etc); and
  
  - Municipal waste (or sewage) treatment works.

It appears that many unintentional sources contribute to the total emission of PAHs into the environment which are not related to manufacture and use of CTPHT. Overall, it can be concluded that a consistent description of the emissions and emission sources of PAHs is not available.

As regards PAH emissions to air, it seems that the largest emission sources are non-industrial, like domestic combustion of solid fuels, the use of coal tar-based products (creosote) for wood preservation and road transport; the emissions of these three sources together can amount to 54%-89% of the total PAH emission to air, dependent on the references (The Netherlands, 2008).

For emission of PAHs to surface water even less data is available. Some industrial point sources can be large emission sources of PAHs. Compared to (industrial) point source data, the emission via atmospheric deposition seems more important (The Netherlands, 2008).

Overall, in the context of this report, it was not possible to undertake a quantification of the actual releases from the possible sources of emissions of CTPHT (and its constituents) as no respective detailed information was provided by the CTPHT industry (both manufacturers and users). In addition, it appears to be little relevant information on this topic available in the literature. For these reasons it was also not possible to undertake a comparison of releases of the constituents relevant for the PBT properties of CTPHT with those from unintentional processes.

Consequently, it was not possible to develop an EU-wide mass balance, for CTPHT and its relevant constituents. For that, quantitative information would be required on manufacture, import and export of CTPHT (and its constituents, where appropriate), as well as information on releases from manufacturing sites and all uses in the EU, including those from consumer uses, the waste phase or those resulting from unintentional formation in incineration and other processes. Information on import and export of articles containing the substance, conditions of use and the lifecycle of the substance would have also been required.

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<sup>30</sup> PAH emissions from wood preservation may decrease due to the entry into force of directive 2001/90/EC (The Netherlands, 2008)

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While every attempt has been made to obtain the necessary information, the absence of relevant data in the literature or from consultation made this exercise impossible.

### 7.2.3 Conclusions

#### Wide-dispersiveness of uses

As regards the characterization of the uses of CTPHT in terms of their release pattern, it is relevant to identify the wide dispersive uses as they are causing the most relevant exposures of humans and the bulk of PAH releases to the environment.

The term "wide dispersive use" is explained in Chapter R.16.2.1.6 of the Guidance on Information Requirements and Chemical Safety Assessment (ECHA, 2007b) as follows: "*Wide dispersive use refers to many small point sources or diffuse release by for instance the public at large or sources like traffic. ... Wide dispersive use can relate to both indoor and outdoor use*". In the Technical Guidance Document for Risk Assessment of new and existing substances and biocides (TGD, 2003) this term is defined as follows: "*Wide dispersive use refers to activities which deliver uncontrolled exposure. Examples relevant for occupational exposure: Painting with paints; spraying of pesticides. Examples relevant for environmental/consumer exposure: Use of detergents, cosmetics, disinfectants, household paints.*" In addition, the ECETOC Report No. 93 on Targeted Risk Assessment (Appendix B) states: "*A substance marketed for wide dispersive use is likely to reach consumers, and it can be assumed that such a substance will be emitted into the environment for 100% during or after use*" (ECETOC, 2004).

Wide dispersive uses are hence characterised by use(s) of a substance on its own, in a preparation or in an article at many places that may result in not insignificant releases and exposure to a considerable part of the population (workers, consumers, general public) and/or the environment. This means that uses taking place at many places, which however do not result in significant releases of a substance, may be considered only as 'widespread' but not as 'wide dispersive'.

In general, consumer use can be considered as wide dispersive if it can be reasonably assumed that this use results in non-negligible releases. Professional use can be wide dispersive as well if it takes place at many sites and is carried out by many workers and if it cannot be excluded that releases are negligible.

Depending on the information available, as many as possible of the following parameters have been used as indicators to assess whether a use (and the resulting releases) should be considered 'wide dispersive':

- Tonnage supplied to the use in question.
- The complexity of the supply chain and the number of actors in the chain. In how many settings/locations does the use take place? What are the typical sizes of these settings?
- In which form is the substance placed on the market (e.g. as such, as part of a preparation, in/on an article)?
- Can the substance be released (and to which extent) during the service life of an article or a preparation (e.g. paints, adhesives, detergents) or is it transformed (thereby losing its hazardous properties) or incorporated into a matrix (e.g. polymer) in a way preventing release?

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- Information on operational conditions and risk management measures.
  - Information on whether there is occupational exposure (quantitative or qualitative; e.g. approximate number of exposed workers, information on releases to the working environment, occupational exposure concentrations, health effects, OELs).
  - Information whether there is consumer exposure (quantitative or qualitative; e.g. possibility of consumer use, information on consumer exposure, health effects, limit values).
  - Releases to the environment (mainly for PBTs/vPvBs; e.g. t/y to the different compartments air, water, soil).
  - Possibility of releases during the waste phase.
  - Monitoring information for a substance in environmental compartments such as water, sediment, soil or in biota.

In table 7.9 conclusions on the wide-dispersiveness of the uses of CTPHT are summarised.

#### Complexity of supply chains

As far as the complexity of supply chains is concerned, it appears that, depending on the specific uses of CTPHT, they can be rather simple (i.e. with rather limited number of levels and/or of parallel supply strands and/or number of actors) to rather complex, mainly when involving either different industry sectors (e.g. medicinal products) or a high number of actors. In any case, all actors seem to be rather well identified and communication should not be, even though not well developed so far, a major issue.

Table 7.9: Characterisation of the uses of CTPHT in terms of their release pattern		
Use application	Annual quantity used (in kilotonnes – kt)	Characterisation
Electrodes		
<ul style="list-style-type: none"> <li>• Prebaked anodes</li> </ul>	400.0	Production of prebaked anodes (formulation of electrode paste and baking of the anodes) appears to be the step in the life cycle that causes the most significant PAH emissions. The number of electrode baking plants and the number of workers potentially exposed during these processes is currently unknown. However, given the amount of CTPHT used and the fact that numerous plants for aluminum smelting and steel production are located all over the territory of the EU, it is concluded that neither the number of workers exposed during the manufacture of the anodes can be considered as insignificant nor the amount of PAHs released to the environment from anode baking plants spread all over the EU. Consequently, the use of CTPHT for prebaked anodes is considered as <b>wide-dispersive</b> .
<ul style="list-style-type: none"> <li>• Carbon and graphite electrodes (including carbon and graphite products other than electrodes)</li> </ul>	200.0 (other products: 23.0)	The same considerations as for prebaked anodes apply for carbon and graphite electrodes, including the production of other carbon and graphite products. There are plants for producing the electrodes in several EU-countries, and plants for producing other carbon and graphite products seem to be numerous and spread all over the EU territory. Therefore, the use of CTPHT for carbon and graphite electrodes (including its use for other carbon and graphite products) is considered as <b>wide-dispersive</b> .
<ul style="list-style-type: none"> <li>• Søderberg electrodes</li> </ul>	50.0	Around 20 kt of the CTPHT used in Søderberg electrodes is used in aluminum smelters and 30 kt is supplied to other applications such as production of ferro-alloys and steel. For Søderberg electrodes, the step in the lifecycle causing the most significant emissions appears to be the use of the electrodes in the smelting processes themselves. As regards aluminum smelting, there are still 3 smelters operating in Europe using Søderberg electrodes. Given the annual amount of CTPHT used for aluminum smelting, these plants can be considered as very large PAH point sources. However, in addition there are very many plants producing steel or ferro-alloys all over the EU, which consume 30kt CTPHT per year included in Søderberg electrodes. Hence, it can be assumed that a significant number of workers are exposed to PAH emissions resulting from the use of these electrodes and that environmental releases of PAH will as well be considerable and widespread all over the territory of the EU. Consequently, the use of CTPHT for Søderberg electrodes is considered as <b>wide-dispersive</b> .
Refractories	37.5	Refractories are used in many industrial applications such as production of metals, cement, glass etc. as well as in specialist applications in the aerospace and nuclear industry. The main production capacity for refractories seems to be located in Germany, Italy, France, United Kingdom and Austria. The EU refractories industry employs around 25,000 people. Although information on the releases of PAHs from the use of CTPHT as binder for refractories is at present very limited, it can be assumed that at least during the production of refractories and probably as well during their use and their waste phase exposure of workers and releases to the environment cannot be excluded. Given the number of workers employed by the refractory industry and its downstream users and considering the number of sites where refractories may be produced or used, it is concluded that the use of CTPHT for refractories should be considered as <b>wide-dispersive</b> .
Active carbon/carbon fibres	12.8	CTPHT appears to be used as an intermediate in the production of active carbon and carbon fibres. Its constituents are transformed during production of active carbon and carbon fibres to (forms of) carbon. The final material does not contain CTPHT anymore. Active carbon appears to be produced in closed

<b>Table 7.9: Characterisation of the uses of CTPHT in terms of their release pattern</b>		
<b>Use application</b>	<b>Annual quantity used (in kilotonnes – kt)</b>	<b>Characterisation</b>
		vessels with control of emissions. Although information about production of active carbon and carbon fibres is incomplete, it seems that these uses cannot be considered as wide dispersive.
Paints and coatings	7.5	CTPHT in paints and coatings is used for heavy duty corrosion protection of concrete and steel constructions and as sealing. Given the amount of CTPHT used for this application, the potential number of workers exposed and the potential number of sites of application of coatings and sealings, which are concomitantly sites of PAH release, it is concluded that the use of CTPHT in paints and coatings should be considered as <b>wide-dispersive</b> .
Briquettes	6.8	CTPHT is used as binder in briquettes. Briquettes are still a common heating material in many European countries. Workers in the briquette production plants as well as distributors and consumers may be exposed to PAHs emissions from briquettes (during handling). Although the major part of the PAHs contained in the CTPHT binder may be destroyed during incineration of briquettes, it cannot be excluded that a significant amount of PAHs is released undestroyed. Taking account of the use and release pattern, the use of CTPHT in briquettes is considered as <b>wide-dispersive</b> .
Clay targets	6.0	Approximately 200 million CTPHT-based clay targets are used at many shooting ranges all over Europe. It is assumed that 50% of the used targets are recovered and disposed of. However, 50% remain in the environment and cause PAH releases. This use is considered as <b>wide-dispersive</b> .
Roofing	5.3	For roofing, CTPHT is used in open applications as impregnating, coating and adhesive agent, mainly for waterproofing purposes. Supposed the figure of 5.3 kt/a supply of CTPHT to this use is correct, then very many roofs in European countries in which this use is not prohibited may be treated with CTPHT and many workers exposed to PAH emissions during its processing. Environmental releases of PAHs during CTPHT application and service life of the roofs occur as well. As recycling, respectively fate after service life is not clear, there may be further PAH emissions occurring in these life-cycle steps. Consequently, this use is considered as <b>wide-dispersive</b> .
Road construction	1.5	It is not clear to which extent CTPHT is still used for road construction, respectively surface sealing of special purpose areas, e.g. at airfields to render them kerosene resistant. In principle, CTPHT could be used at many sites for paving and sealing purposes and therefore the same considerations as for use of CTPHT for roofing apply. Therefore, use of CTPHT for paving and area sealing is considered as <b>wide-dispersive</b> .
Other	22.7	There are 3 further uses known about which not much information could be obtained regarding amounts of CTPHT supplied, sites, exposure and releases. In two of these uses, the production of carbon black and pyrene, CTPHT seems to be used as intermediate (starting material) and the uses appear to take place in (large) industrial settings. This information is hinting towards a conclusion that these uses do not appear to be wide-dispersive. The third use regards use of coal tar derivatives in medicinal or cosmetic products. It is not clear to which extent CTPHT (or certain fractions of it) is used for these purposes (confirmed is a volume of 100 kg/yr) and what the releases from these applications are.

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## 8 CURRENT KNOWLEDGE ON ALTERNATIVES<sup>31</sup>

### 8.1 Analysis of current knowledge on alternatives per use of CTPHT

#### 8.1.1 Production of electrodes

Information provided by industry (including aluminium industry and producers/downstream users of carbon/graphite electrodes) indicates that there are currently no viable alternatives to CTPHT-based electrodes.

With regard to the aluminium production process, the European Aluminium Association (EAA) claims that CTPHT is currently the only binder suitable for anode production and if CTPHT would happen to be not available for that application the European primary aluminium smelters would have to shut down. Other sources confirm that there are at present no known viable substitutes to CTPHT-based electrodes in the aluminium production process (Jacobs, 2006).

However, it appears that, in some particular cases, a small portion of petroleum-based products are combined with coal tar pitch in order to improve the environmental performance of the anode. This appears to be consistent with the literature review presented in Annex 6. A. to this report which presents several recent research efforts made with the purpose to develop petroleum-enhanced coal tar pitches and/or alternative binders.

It also appears from information in the literature (RAR, 2008) and confirmed by industry (EAA, 2009) that the main potential alternative to prebaked anodes is a new technology, which has been developed at laboratory scale and is based on inert anodes<sup>32</sup>. However, this technology appears to be still immature and costly. EAA (2009) indicates that although a major company announced around five years ago that they intended to start trials, this company is yet to install these at their own plants to date. EAA (2009) notes that it is currently impossible to state specifically when (and if) this technology will actually be available on the market. There is also an open question regarding whether there would be any advantage in installing these inert anodes in an existing smelter or if they could only be installed in a completely new type of design.

In summary, it appears that:

- over the last two decades, the electrode-manufacturing and use industry (including the aluminium industry) has undertaken (and continues to undertake) a number of research and development (R&D) projects aimed at identifying suitable alternatives to CTPHT-based electrodes. The potential use of petroleum-derived binders for producing anodes (with lower PAH emissions) has also been evaluated (see Annex 6. 1);

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<sup>31</sup> Note: it has to be reminded that the term “*alternatives*” refers to either the use of an alternative substance, or an alternative technique or technology, or a combination of them, including changes that make the process step involving the use of substance redundant; all of these solutions should lead to substitution of the substance in question.

<sup>32</sup> Inert anodes are electrodes that do not chemically react with the molten material in the furnace and therefore wear much less than graphite/carbon anodes because the carbon-material of this latter type of anodes reacts with oxygen from the metal oxides (ores) to be molten.

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- no suitable replacement for CTPHT-based electrodes has yet been found which is technically and commercially viable, and it cannot be predicted (if and) when this will occur. However, while economics drove hitherto efforts towards finding alternatives the future key drivers in the search for alternatives are likely to be raw material availability and environmental regulations;
  - there is information currently available and accessible on research efforts involving CTPHT manufacturers, aluminium smelters and various researchers discussing the results of various research efforts to find replacements to CTPHT. Although these efforts have been intense, many of the evaluations undertaken appear to have produced less than desirable (or acceptable) results. However, in some cases, the current trend is for a small portion of petroleum-based products to be combined with coal tar pitch to improve the environmental performance of the anode. For the aluminium industry, state-of-the-art emissions control technologies (e.g. regenerative thermal oxidising units) are being fitted on existing anode baking plants and existing Söderberg plants in Europe are being modernised; and
  - although, there are two main groups of actors (relevant to alternatives) in this supply chain (i.e. the anode baking plants and the downstream users of electrodes), concrete details regarding the current stage and extent of R&D efforts is not publicly available and co-operation between actors in the supply chain is likely to be mainly at the ‘field-testing’ phase of the R&D process (due to the potentially large market benefits relating to the discovery of a suitable alternative).

### 8.1.2 Refractories

By definition, ‘binders’ refer to the raw materials which are added to the refractory mixes to hold the various aggregates and matrix particles together.

Although there are many different types of binders available, the technical suitability of the binder (and type of bond formed) differs depending on the type of refractory. The refractory itself is designed and manufactured such that its properties are appropriate for the intended applications. For instance, in the production of iron in a blast furnace, the refractory should have sufficient abrasion and heat resistance to the molten iron and slag interface, while refractories used in the electric arc furnace should be able to tolerate the mechanical impingement of the scrap iron and the arcing (or hot spots) created from the electric current.

In other primary metal industries, such as aluminium, the refractory properties requirements are quite different from those used in steel making. Here, the temperatures of the refining and alloying processes are much lower than steel; however, there is the unique problem of penetration in the refractories. The refractories should, therefore, be designed so that it has a non-wetting characteristic (which is introduced using special additives) to molten aluminium (Schacht, 2004).

Information in the literature identifies two main groups of binders (Schacht, 2004):

- ***inorganic binders***: this group includes materials such as various clay minerals, soluble sulfates and sulphuric acid, sodium silicates, calcium aluminate cements, soluble phosphates, polyphosphates, borates, etc; and
- ***organic binders***: which includes materials such as pitches, resins, lignins and lignosulphonates, dextrans and starches, cellulose, polyvinyl alcohol, etc.

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More details about pitches and resins and the experience gained in their use in refractories applications is presented in Annex 6. 2. to this report.

In summary:

- according to some sources of information, phenolic resins, despite its drawbacks, appear to have already achieved extensive acceptance (and use) as alternatives to CTPHT-based refractories (Schacht, 2004; Ewais, 2004). Other sources indicate that standard coal tar pitches have been almost completely substituted by petroleum pitches or pitches obtained from a special high temperature vacuum treatment of coal tar pitch (Routschka, 2007);
- the extent to which this implies a phase out in the use of CTPHT (particularly in the EU) is unknown (no information was received from the refractories sector for this report);
- there is information currently available and accessible on the use of phenolic resins as refractory binders which can be drawn upon by various actors in the supply chain, if required. E.g. the European Phenolic Resin Association website provides information on various refractory applications in which phenolic resins may be used, including manufacture of carbon bonded brick, manufacture of iso-pressed products, tap hole clay resins and monolithic applications (EPRA, 2009);
- the level of co-operation between actors in the supply chain in the development and implementation of alternatives to the use of CTPHT in refractories applications is unknown.

### **8.1.3 Active carbon/Carbon fibres**

Active (or activated) carbon can be made from many substances with high carbon content (e.g. coal, wood and coconut shells). Davini (1999) indicates that active carbons can be prepared by suitable pyrolysis of petroleum pitches and subsequent activation of the obtained chars. However, the key point to be taken into consideration when discussing possible alternatives is that the raw material used has a very large influence on the characteristics and performance of the final 'active carbon' product (Chemviron, nd).

Similarly, carbon fibres can be obtained from different sources (e.g. rayon and polyacrylonitrile); however, the final properties are different. For instance, pitch fibres usually display higher density, higher elasticity and higher electrical conductivity, while polyacrylonitrile produces exceptionally high strength fibres. Fibres from different sources can, therefore, be used to complement each other in their properties. Also, the yield from different sources varies largely: the yield of carbon fibres from rayon is 20 - 25%, while that from polyacrylonitrile is around 45 - 50% and from pitch around 75 - 85%. This high yield from pitch was a key reason for the increased use of pitch as a precursor for carbon fibres (Franck & Stadelhofer, 1987).

In conclusion, alternatives appear to be available; however, there may be some performance trade-offs that could limit the technical suitability of certain alternatives for specific applications.

No further information has been obtained on how far the supply chain actors are in the process of replacement of CTPHT-based active carbon/carbon fibres, on their actual level of knowledge on and access to information on possible alternatives, and on their level of cooperation in the identification and implementation of alternatives.

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#### 8.1.4 Paints and coatings

Information on the availability of alternatives to paints and coatings was received from four companies which were consulted when developing this report:

- the first company indicated that the use of coal tars is not critical for its specific applications;
- the second company indicated that, so far, no suitable alternative has been proposed for its applications in the marine sector;
- the third company indicated that there are coal tar free alternatives with performance comparable to that of coal tar containing products but the current demand for coal tar products comes from the customer on the basis of cost effectiveness<sup>33</sup> and long successful performance history. According to this company, if the authorities would decide to ban the use of coal tar containing products for coatings purposes, then suppliers would have to comply and the current supply strategies (which are mainly based on the cost of the products) would disappear.
- the fourth company indicated that it had already stopped the use of coal tars in its products.

Furthermore, information found on internet suggests that replacement of coal tar-based paints and coatings is possible. The example of a US company which replaced coal tar epoxies in its products in 2006 due to concerns over VOC emissions and human health, although they accept that there will be some revenue losses initially, is given. In that case, the coal tar epoxies have been replaced by pure epoxy or modified epoxy products, which apparently have equal or better performance (Pipeline & Gas Journal, 2005).

While the above information could suggest a more general trend away from coal tar-based paints, it cannot be stated for certain if this is actually a trend as the use applications of the coal tar-based coatings appear to be quite specialist (or for professional applications). However, it appears to be the case that in some specialist applications a move away from coal tars has already occurred. For instance, with regard to ship building, Cardolite (nd) indicates that phenalkamines are curing agents of choice to replace coal tar epoxy systems. Another technology based on polyamide is indicated to be widely known but not as efficient as coal tar epoxy systems. The cost of phenalkamines is slightly higher than other technologies but as these systems cure very quick, application costs are also reduced. Colour could be a drawback if phenalkamines are used for pale coloured top coats; however this is not important for hull and ballast tank coating. The superstructures and the deck could be top coated with polyurethane or acrylic (Cardolite, nd).

In summary:

- it is unclear at which stage the paints and coatings industry is in terms of replacing CTPHT, due to the specialist and/or professional nature of its use. It is also unclear the extent to which the information provided on suitable alternatives applies to individual companies, as opposed to the sector, as a whole;
- information in the literature however suggests that replacement of coal tar-based paints and coatings is possible and, in certain cases, already on-going. On the other hand, there is no information on how long a complete phase out would take. It is also unclear if the producers of the paints and coatings are able to supply alternatives and whether these would be

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<sup>33</sup> coal tar free alternatives are estimated to be around 1.5 times more expensive on a per litre basis compared to coal tar based products

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technically suitable for the intended downstream uses (hence, the continued demand by customers as alluded to by the third company);

- no conclusions could be drawn on the level of co-operation in the supply chain as the information provided appears to apply to individual companies only.

## **8.1.5 Briquettes**

### **8.1.5.1 Alternative substances**

Although coal tar pitch is still widely used as a binder in the production of briquettes, it appears to be progressively replaced by petroleum-derived products.

However, it appears that petroleum-derived materials are indicated to have a lower content of coke forming components compared with coal tar pitch and this may be a disadvantage when they are used as the binders for non-caking coal briquettes (e.g. anthracites) (Speight, 1994). In a more recent study, Paul *et al* (2002) explored the use of petroleum residues as binders and the effects of feedstock, char and binder properties, as well as operating conditions were investigated. The study found that the interaction of oxygen with the binder can be beneficial in increasing the mechanical strength of formcoke briquettes. This interaction of oxygen with the binder can be effected through air-blowing and curing in air. The strength is also enhanced by the addition of asphaltene and increased coking temperature. Adding 20%wt asphaltene resulted in a maximum increase in strength, which made the petroleum residues of comparable strength with coal tar binders (Paul *et al*, 2002).

It appears that a number of other alternative substances have been investigated over the years, including the use of propane asphalt, phenolic resins, pre-gelling starches, organic acids, lignosulphate, magnesia cement and acetone as binders. Sulphite liquor (a by-product obtained from sulphite pulp process) has been found to possess significant adhesive properties. Starch also has substantial adhesive power and is used in the manufacture of charcoal briquettes used increasingly in barbeque grills. When added at 1- 3% w/w as a solid or in a suspension, starch is an effective binder for the production of coal briquettes (Speight, 1994).

### **8.1.5.2 Alternative techniques**

An alternative method for producing briquettes involves the use of no binders. This process consists of manufacturing briquettes from coal dust using pressure. However, the coal must contain 5-12% of water and have a high bitumen or resin content.

A binderless briquette can also be made by feeding coal particles into a hot gas stream in a flash dryer. This causes water to evaporate from the coal and the coal particles are then compressed into briquettes.

In summary:

- there appears to be suitable alternatives to the use of CTPHT in briquettes;
- the extent to which industry is in the process of replacing (or has replaced) CTPHT is however unknown;
- information on alternatives is currently available and accessible;
- the extent of co-operation between actors in the supply chain in searching for alternatives is unknown.

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### 8.1.6 Clay targets

The most widely used alternative to coal tar pitch in clay targets is petroleum bitumen/asphalt (CAS No 8052-42-4); other alternatives include polymeric substances, resins, starch and gypsum (AFEMS, 2009) or a mixture of several clays (with no binder) (RAR, 2008).

CPC (nd) indicates that the manufacturing process involved in using petroleum pitch is more difficult and complex compared with that required to manufacture CTPHT-based clay targets. However, it is suggested that these complications have been overcome.

Information provided by AFEMS (2009) also indicates that the use of petroleum bitumen requires little technical adjustment (compared to coal tars) and the resulting clay targets have equivalent quality to the coal tar-based clay targets. However, a limit to this alternative seems to be that the special types of bitumen required by the clay target industry are not easily available. Another main issue seems to be that this special petroleum bitumen is four to five times more expensive than CTPHT; the use of this special bitumen is indicated to consequently increase the cost of clay targets by around 220%.

Various other patents relating to different production methods and raw materials for making clay targets can also be found online from the World Intellectual Property Organisation website (WIPO, 1995). These include:

- compressing a mixture of gypsum (70%) and ash (30%) (both of which are waste products of various processes) in a mould which sets instantly due to a reaction of excess water in the gypsum with the calcium oxide in the ash. The final product is non-toxic, but the compressive force needed makes this option non-cost competitive;
- a slight variation on the above method, i.e. using by-product gypsum (40-70%), calcined gypsum (containing less water) (1-22%), a metal oxide to control the weight of the final product (2-15%), and water. Other fillers can be used to provide bulk and strength to the final product, such as waste slag, siliceous earths etc. Again, the liquid sets the mixture during compression, but only a moderate compressive force is required and setting continues after the product has been removed from the mould and all the excess water has been removed. This method creates a durable, non-toxic product based on low cost raw materials and manufacturing processes; and
- another option (discussed in a US Patent, see Patentstorm, nd) involving the use of common soil (70-80%), clay (15%) and a degradable, non-toxic, binder material (10-15%). In this case, the binder could be carbohydrate-based, sugar-based, starch-based, vegetable gum or polymer-based.

According to AFEMS (2009), most of the alternatives to coal tar mentioned above (i.e. polymeric substances, resins, or a mixture of several clays (with no binder)) are mainly theoretical efforts and none of these alternatives has reached the prototype stage. Also, some of these substances would not be environmentally acceptable (AFEMS, 2009).

In summary:

- there appear to be available alternatives to CTPHT-based binders in clay targets;
- these alternatives have already been adopted in countries where there are legislative restrictions on the use of CTPHT. For countries where there are no legal restrictions on the use of CTPHT-based clay targets, the price of these alternatives makes them non-viable;

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therefore, replacement of CTPHT has not yet occurred and is unlikely to occur in the absence of legislation;

- information on alternatives appears to be easily available and accessible, and co-operation between actors in the supply chain does not appear to be an issue.

### **8.1.7 Road construction and paving**

As indicated earlier, coal tar appears to be no longer used for road construction or paving operations. It is however indicated that an on-going and important use of coal tar is in anti-skid layers on runways in airports. EAPA (2009) indicates that, according to information provided by one company specialised in applying anti-skid layers at airports, there are three possible techniques for applying anti-skid layers, only one of these techniques involving coal tar. This company indicates that, while there are some alternatives, some airport authorities do specifically request for coal tar-containing anti-skid layers for their runway(s). This company used around 500 tonnes in 2008 across Europe and indicates that this use is decreasing and is expected to end in the near future (EAPA, 2009).

A US company (SGSC, nd) also notes that the US Federal Aviation Administration Specifications (P-625, 627 and 628) accepts only CTP-based seal coatings for use on airport projects, because the CTP-based seal coatings offer greater resistance to jet fuel. As noted by O'Flaherty (2002), the main advantage of coal tar is that it is much less vulnerable, compared to bitumen, to the dissolving action of petroleum solvents or distillates and is therefore important in locations where spillages of petrol, diesel and oil are likely (O'Flaherty, 2002).

In summary:

- there appears to be, in a limited number of specific cases (airports), a safety critical use of CTPHT-based road tars;
- while there are alternatives, there appear to be some airports in the EU which, so far, only accept CTPHT-based anti-skid layers; however, even though no calendar for substitution has been drawn at this point in time, it appears that this specific use of CTPHT is currently decreasing and expected to end in a foreseeable future;
- the extent of co-operation across the supply chain for the development and implementation of alternatives to CTPHT is not known.

### **8.1.8 Roofing**

Coal tar's share of the roofing market has fallen in the last 20 years due to the discovered carcinogenicity of coal tar pitch volatiles. In order to protect its market share, and to reduce the emissions, attempts were made to remove the carcinogens during processing but this led to increasing base costs of coal tar pitch (Mellott, nd). Research and development have now gone into altering coal tar pitch to maintain its waterproofing ability but remove the health hazards. By adding polymers, the coal tar pitch can now be laid hot or cold, to decrease volatiles, and it has now become elastomeric (Mellott, nd).

It also appears that a number of alternative roofing systems to coal tar pitch-based ones exist. Of particular relevance to the properties of coal tar-based roofs seems to be the liquid waterproofing systems (LWS): these are chemical compounds that can be applied to surfaces in liquid form and which quickly 'cure' or dry to form a solid waterproof membrane. Bitumen was the first form of

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liquid waterproofing and has been used for this purpose for thousands of years. It is claimed by industry that, in the last two decades, huge advances have been made in liquid waterproofing technology and there are now many other generic types of liquid systems available and most of these can be installed cold and are typically applied by brush, spray or roller (ELWA, nd).

High performance liquid systems are also claimed to be able to cope with extremes of temperature, movement, UV degradation, complex design features, maintenance traffic and wind uplift. It is suggested that there is currently an increasing acceptance for the use of liquid systems, which now would account for a substantial proportion and increasing part of the waterproofing market (ELWA, nd).

There appears to be a quite comprehensive amount of information on several possible alternative roofing systems, such as EPDM membrane, thermoplastic polyolefin, modified bitumen roofing, liquid-applied monolithic roof system, built-up asphalt roofs and metal sheeting; more details are given in Annex 6. 3. to this report.

In summary:

- there appears to be suitable alternatives to the use of CTPHT-based roofing systems;
- the extent to which industry is in the process of replacing (or has replaced) CTPHT is however unknown, even though it is claimed by some industrial actors that (some of ) these alternatives are ready for industrial/professional use, accepted by users and even, in certain cases, already implemented;
- information on alternatives is currently available and accessible; and
- the extent of co-operation between actors in the supply chain in searching for alternatives is unknown.

### **8.1.9 Medicinal products**

The available information on possible alternatives to CTPHT in medicinal products applications is very limited.

From the consultation launched for this report, a company indicated that without the coal tars it would be impossible to produce its medicinal products. A second company also indicated that no suitable alternatives have been identified so far.

The extent to which industry, as a whole, has researched suitable alternatives to CTPHT or is in the process of replacing (or has replaced) CTPHT is unknown.

## **8.2 Conclusions**

It appears that for most of the uses there is information on alternatives. For some uses of CTPHT, there have even been a lot of efforts in terms of research and development in order to identify possible alternative or, on the other hands, to confirm the limits to replacement. However, in the specific case of the use of CTPHT in medicinal products, the available information on possible alternatives appears to be very limited.

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According to the information available, most of the information on possible alternatives is available to actors in the supply chain and apparently readily accessible.

For most of its uses, CTPHT has started to be replaced for already a more or less long time, or its replacement seems to be possible, and even foreseeable, in a very short term. On the contrary, cases where replacement has not started yet because of a lack of available alternatives are clearly identified. This is in particular the case for CTPHT-based anodes, which represent a major part of the volume of CTPHT used.

In general, the extent of communication and/or co-operation across the supply chain for the identification, development and implementation of alternatives to CTPHT is not well known, but does not appear as an issue which could be the reason for major difficulties and request a lot of additional efforts in the development on authorisation applications.

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# **Other information**

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## REFERENCES

- AFEMS (2009): Information provided by the Association of European Manufacturers of Sporting Ammunition (AFEMS) in Response to Consultation, February - March 2009.
- AHFS (2008): Coal Tar (Crude) Misc - Detailed Monograph, AHFS Drug Information, Selected Revisions March 2006, American Society of Health-System Pharmacists (AHFS), Maryland, USA. Information downloaded from <http://www.medscape.com/druginfo>
- Alcan (2003): Thematic Strategy on the Prevention and Recycling of Waste, Letter from Alcan Primary Metal (Europe) to the European Commission, DG Environment, dated 25 November 2003.
- Allred PM, Giesy JP (1985): Solar radiation-induced toxicity of anthracene to *Daphnia pulex*. *Environ Toxicol Chem* 4: 219-226.
- Armstrong B., Hutchinson, E., Fletcher, T. (2003): Cancer risk following exposure to polycyclic aromatic hydrocarbons (PAHs): a meta-analysis. Rep No 068. Sudbury, UKL Health and safety Executive. Accessed at April 14, 2009. Available from <http://www.hse.gov.uk/research/rrpdf/rr068.pdf>
- ATSDR (2002): Toxicological profile for wood creosote, coal tar, coal tar pitch, and coal tar pitch volatiles. US Department of Health & Human Services. September 2002:1-354.
- Bisson M, Dujardin R, Flammarion P, Garric J, Babut M, Lamy M-H, Porcher J-M, Thybaud É, Vindimian É (2000): Complément au SEQ-Eau: méthode de détermination des seuils de qualité pour les substances génotoxiques. Verneuil-en-Halatte, France: Institut National de l'Environnement Industriel et des Risques (INERIS), Agence de l'eau Rhin-Meuse.
- Bruner KA, Fisher SW, Landrum PF (1994): The role of the Zebra Mussel, *Dreissena polymorpha*, in contaminant cycling: I. The effect of body size and lipid content on the bioconcentration of PCBs and PAHs. *J. Great Lakes Res.* 10(4): 725-734.
- Cardolite (nd): How to Replace Efficiently Coal Tar Epoxies in the Shipbuilding Industry? Paper by Dr Jean-Luc Dallons downloaded from the Cardolite Corporation website: <http://www.cardolite.com/Pdf/Marinecoaltarreplacement.pdf>
- Carneiro *et al* (nd): Activated Carbon Fibers for Environmental Applications, Publication by Veronica Carneiro, Lisa Huggins, Curtis Lee and Joel Harris, *Journal of Undergraduate Research in Engineering and Science*, Information downloaded from: <http://virtual.clemson.edu/caah/synergy/ISSUE-1ACFEA.htm>
- CCI International (nd): Environmentally Friendly Clays, Information downloaded from the CCI International website: [http://www.cci-international.com/english/\\_environment.htm](http://www.cci-international.com/english/_environment.htm)
- Cerame-Unie (nd): Refractories, Article downloaded from the European Ceramics Industries (Ceramic-Unie) website: <http://www.cerameunie.eu/refractories.html>

- 
- Chemviron (nd): What is Activated Carbon? Information downloaded from the Chemviron Carbon website: [www.chemvironcarbon.com/en/carbon/activated-carbon](http://www.chemvironcarbon.com/en/carbon/activated-carbon)
- CPC (nd): Clay Pigeons - Quality, Information downloaded from the Clay Pigeon Company website: <http://www.claypigeoncompany.co.uk/quality.html>
- CSIRO (nd): Wood Char shows Potential for Carbon Anode Production, Information downloaded from the Australian Commonwealth Scientific and Research Organisation (CSIRO) website: <http://www.csiro.au/science/Bioanodes.html>
- Davini (1999): Desulphurization Properties of Active Carbons Obtained from Petroleum Pitch Pyrolysis, by Paola Davini, Chemical Engineering Department of Pisa University, *Carbon*, Volume 37, Issue 9, 1999, Pages 1363-1371.
- De Maagd PGJ (1996): Polycyclic aromatic hydrocarbons: fate and effects in the aquatic environment. Academic Thesis, Rijksuniversiteit Utrecht, The Netherlands
- De Maagd PGJ, Sinnige TL, Schrap SM, Opperhuizen A, Sijm DTHM (1998): Sorption coefficient of polycyclic aromatic hydrocarbons for two lake sediments: influence of the bacteriocide sodium zide. *Environ. Toxicol., Chem* 17, 1899-1907,
- De Voogt P, Van Hattum B, Leonards P, Klamer JC, Govers, H (1991): Bioconcentration of polycyclic heteroaromatic hydrocarbons in the guppy (*Poecilia reticulata*). *Aquat. Toxicol.*, 20, 169-194
- EAA (2009): Information provided by the European Aluminium Association (EAA) in response to Consultation, 5 February, 2009.
- EAPA (2005): Industry Statement on the Recycling of Asphalt Mixes and Use of Waste of Asphalt Pavements, EAPA, May 2005.
- EAPA (2009): Information provided by the European Asphalt Producers Association (EAPA) in response to Consultation, 5 February, 2009.
- ECETOC (2004): Technical Report No. 93. Targeted Risk Assessment. ECETOC AISBL, Brussels, Belgium.
- ECGA (2009): Information provided by the European Carbon and Graphite Association (ECGA) in Response to Consultation, March 2009.
- ECHA (2007): Guidance for the preparation of an Annex XV dossier on the identification of substances of very high concern. European Chemicals Agency, June 2007. Available from: [http://guidance.echa.europa.eu/docs/guidance\\_document/svhc\\_en.pdf](http://guidance.echa.europa.eu/docs/guidance_document/svhc_en.pdf)
- ECHA (2007b). Guidance on information requirements and chemical safety assessment. Chapter R.16: Environmental Exposure Estimation. European Chemicals Agency, 2008. Available from: [http://guidance.echa.europa.eu/docs/guidance\\_document/information\\_requirements\\_r16\\_en.pdf?vers=20\\_08\\_08](http://guidance.echa.europa.eu/docs/guidance_document/information_requirements_r16_en.pdf?vers=20_08_08)

- 
- ELWA (nd): Liquid Waterproofing, Information downloaded from the European Liquid Waterproofing Association (ELWA) website [http://www.elra.org.uk/index.php?option=com\\_content&task=view&id=54&Itemid=71](http://www.elra.org.uk/index.php?option=com_content&task=view&id=54&Itemid=71)
- Emery Jr. VL, Dillon TM (1996): Chronic toxicity of phenanthrene to the marine polychaete worm, *Nereis (Neanthes) arenaceodentata*. Bull Environ Contam Toxicol 56: 265-270.
- EPRA (2009): Refractories, Information downloaded from the European Phenolic Resin Association (EPRA) website: <http://www.epra.eu/28.html>
- ETRMA (2009): Information provided by the European Tyre and Rubber Manufacturers Association (ETRMA) in response to Consultation, 27 February, 2009.
- Eurobitume (2009): Information provided by the European Bitumen Association (Eurobitume) in Response to Consultation, 21 February 2009.
- Eurobitume (2009a): What is Bitumen? Information downloaded from the Eurobitume website: [http://www.eurobitume.org/about/what\\_is\\_bitumen.html](http://www.eurobitume.org/about/what_is_bitumen.html)
- Eurofer (2008): EUROFER/PRE Joint Position on Spent Refractories, dated 4 November 2008.
- European Parliament and Council (2008): Regulation (EC) No 1272/2008 of the European Parliament and of the council of December 2008. On classification, labelling and packaging of substances and mixture, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2007.
- Ewais M (2004): Carbon Based Refractories, *Journal of the Ceramic Society of Japan*, 112 (10) 517-532 (2004)
- FIOH (2007): The BWA Confounder Study - Retrospective Assessment of Workers' Exposure to Carcinogenic Substances in Bitumen Waterproofing, Finnish Institute of Occupational Health (FIOH) - 2007.
- Fischer *et al* (nd): The Changing World of Anode Raw Materials: Can Today's Carbon Technology Cope with it? Paper by Werner K. Fischer, Felix Keller and Ulrich Mannweiler, R&D Carbon Ltd. Switzerland. Downloaded from the R&D Carbon website: <http://www.rd-carbon.com/pdf/changingworld.pdf>
- Foran JA, Holst LL, Giesy JP (1991): Effects of photoenhanced toxicity of anthracene on ecological and genetic fitness of *Daphnia magna*: A reappraisal. Environ Toxicol Chem 10: 425-427.
- Franck HG (1963): Presently Little Used But Potentially Important Coal\_Tar Chemicals, Symposium On Recovery, Purification And Utilization Of Coal Chemicals, Spring Cincinnati 07(1)
- Franck HG & Stadelhofer JW (1987): Industrial Aromatic Chemistry, Springer Verlag, 1987.
- Gala WR, Giesy JP (1992): Photo-induced toxicity of anthracene to the green alga, *Selenastrum capricornutum*. Arch Environ Contam Toxicol 23: 316-323.

- 
- Gossiaux DC, Landrum PF, Fisher SW (1996): Effect of temperature on the accumulation kinetics of PAHs and PCBs in the Zebra Mussel, *Dreissena polymorpha*. J. Great Lakes Res. 22 (2): 379-388
- Greece (2008): Draft Risk Assessment Report on Anthracene. Rapporteur: Greece. Draft report of 01.04.2008
- Grip-flex (nd): U.S. Airforce Specifications for Thermoplastic Coal Tar Slurry Seal, Information downloaded from Grip-flex website: [http://www.grip-flex.com/images/US\\_Air\\_Force\\_Spec.doc](http://www.grip-flex.com/images/US_Air_Force_Spec.doc)
- Gryglewicz *et al* (nd): Suitability of Coal/Pitch – PET Mixture for Activated Carbon Production, Paper published by Ewa Lorenc-Grabowska, Grazyna Gryglewicz, Jacek Machnikowski, Maria-Antonia Díez and Carmen Barriocanal and available at: <http://digital.csic.es/bitstream/10261/5181/1/Suitability%20of%20Coal-Pitch%20DIEZ%20BARRIOCANAL.pdf>
- Hall AT, Oris JT (1991): Anthracene reduces reproductive potential and is maternally transferred during long-term exposure in fathead minnows. Aquat Toxicol 19: 249-264.
- Halling-Sørensen B, Nyholm N, Baun A (1996): Algal toxicity test with volatile and hazardous compounds in air-tight test flasks with CO<sub>2</sub> enriched headspace. Chemosphere 32: 1513-1526
- Hannah JB, Hose JE, Landolt ML, Miller BS, Felton SP, Iwaoka WT (1982): Benzo(a)pyrene-induced morphologic and developmental abnormalities in rainbow trout. Arch Environ Contam Toxicol 11: 727-734.
- Hatch AC, Burton Jr. GA (1998): Effects of photoinduced toxicity of fluoranthene on amphibian embryos and larvae. Environ Toxicol Chem 17: 1777-1785
- Holst LL, Giesy JP (1989): Chronic effects of the photoenhanced toxicity of anthracene on *Daphnia magna* reproduction. Environ Toxicol Chem 8: 933-942.
- Hooftman RN, Evers-de Ruiter A (1992): Early life stage tests with *Brachydanio rerio* and several polycyclic aromatic hydrocarbons using an intermittent flow-through system (draft OECD guideline). Delft, the Netherlands: TNO Environmental and Energy Research, TNO Institute of Environmental Sciences. TNO-report IMW-R 92/210.
- IARC (1985): Coal-tars and derived products. In: IARC Monographs on the evaluation of the carcinogenic risk of chemicals to humans. Polynuclear aromatic compounds, Part 4, Bitumens, Coal-tars and derived products, Shale Oils and Soots. Volume 35:83-159. Lyon:IARC.
- IARC (1998): IARCH monographs on the evaluation of carcinogenic risks to humans. Volume 32: Polynuclear aromatic compounds, Part 1: Chemical, environmental and experimental data.

- 
- IARC (2009): Information taken from the IARC webpage visited at April 3rd 2009. <http://monographs.iarc.fr/ENG/Classification> (IARC Monographs on the Evaluation of carcinogenic risks to humans).
- IPCS, (1998): Environmental Health Criteria 202. Selected non-heterocyclic polycyclic aromatic hydrocarbons. 1-883 p. World Health Organisation, Geneva, Switzerland.
- IUCLID (2000): IUCLID Dataset (for Pitch Coal Tar, High Temperature), created by the European Commission - European Chemicals Bureau, February 2000.
- Jacobs (2006): The Coal Tar Distillation Market Report, Jacobs Consultancy, 2006.
- Jonsson G, Bechmann RK, Bamber SD, Baussant T (2004): Bioconcentration, biotransformation, and elimination of polycyclic aromatic hydrocarbons in sheepshead minnows (*Cyprinodon variegatus*) exposed to contaminated seawater. *Environ Toxicol Chem* 23: 1538-1548
- JRC (2008): Draft Reference Document on Best Available Techniques for the Non-Ferrous Metals Industries, Integrated Pollution Prevention and Control, European Commission, Joint Research Centre (JRC), European IPPC Bureau, Draft December 2008.
- Kagan J, Kagan ED, Kagan IA, Kagan PA (1987): Do polycyclic aromatic hydrocarbons, acting as photosensitizers, participate in the toxic effects of acid rain? In: Zika RG, Cooper WJ, eds. Photochemistry of environmental aquatic systems. ACS Symposium Series 327. Washington, DC: American Chemical Society. pp (191-204).
- Kagan J, Kagan ED, Kagan IA, Kagan PA, Quigley S (1985): The phototoxicity of non-carcinogenic polycyclic aromatic hydrocarbons in aquatic organisms. *Chemosphere* 14: 1829-1834
- KEMI (1994): Information on Substances - Coal Tar, Information downloaded from the Swedish Chemicals Agency (KEMI) website: [http://apps.kemi.se/flodessok/floden/kemamne\\_eng/stenkolstjara\\_eng.htm](http://apps.kemi.se/flodessok/floden/kemamne_eng/stenkolstjara_eng.htm)
- Koppers (1998): Strategies for a Declining North American Coal Tar Supply, Light Metals 1998 Métaux Légers, Paper written by John T. Baron, Charles E. Kraynik, and Robert H. Wombles, Koppers Industries Inc., Technical Center, Pittsburgh.
- Koppers (2003): Coal Tar Pitch, Information downloaded from the Koppers website: [http://www.koppers.com/htm/PandS\\_Roof\\_CTPitch.html](http://www.koppers.com/htm/PandS_Roof_CTPitch.html).
- Koppers (2008): Form 10-K, Annual Report Pursuant to Section 13 or 15(D) of the Securities Exchange Act of 1934, for the Fiscal Year Ended December 31, 2007, United States Securities And Exchange Commission Washington, D.C. 20549, Commission File Number 1-32737 - Koppers Holdings Inc, Signed February 21, 2008.

- 
- Koppers (2008a): Koppers Holdings Inc Q4 2008 Earnings Call Transcript, Information downloaded from:  
<http://seekingalpha.com/article/121060-koppers-holdings-inc-q4-2008-earnings-call-transcript>
- Koppers (nd): Developing Coal Tar/Petroleum Pitches, Paper by Robert H. Wombles and Melvin D. Kiser
- Lampi MA, Gruska J, McDonald KIC, Xie F, Huang X-D, Dixon DG, Greenberg BM (2006): Photoinduced toxicity of polycyclic aromatic hydrocarbons to *Daphnia magna*: ultraviolet-mediated effects and the toxicity of polycyclic aromatic hydrocarbon photoproducts. *Environ Toxicol Chem* 25: 1079-1087.
- Lenntech (nd): Activated Carbon Adsorption, Information downloaded from the Lenntech website: [www.lenntech.com/adsorption.htm](http://www.lenntech.com/adsorption.htm)
- Lyons BP, Pascoe CK, McFadzen IRB (2002): Phototoxicity of pyrene and benzo(a)pyrene to embryo-larval stages of the pacific oyster *Crassostrea gigas*. *Mar Environ Res* 54: 627-631.
- Mackay, D, Shiu, WY, and Ma, KC (1992): *Illustrated Handbook of Physical–Chemical Properties and Environmental Fate of Organic Chemicals*. Lewis Publishers, Boca Raton, FL.
- Marzin *et al* (1997): Petroleum Pitch, A Real Alternative To Coal Tar Pitch As Binder Material For Anode Production, Paper prepared and presented by Roger Marzin, Carola Acuna; Maria de Oteyza, Maraven, S.A., Nuevos Desarrollos, Raymond C. Perruchoud. Information downloaded from:  
<http://www.tms.org/Meetings/Annual-97/Program/Sessions/TP230C.html>
- Mayo (2008): Coal Tar (Topical Route), Information (last updated Dec 1, 2008) downloaded from the Mayo Clinic website:  
<http://www.mayoclinic.com/health/drug-information/DR601911>
- McCarthy JF, Jimenez BD, and Barbee T (1985): Effect of dissolved humic material on accumulation of polycyclic aromatic hydrocarbons: Structure-activity relationships. *Aquat Toxicol*, 7, 15-24.
- McLeese DW and Burrige LE (1987): Comparative accumulation of PAHs in four marine invertebrates. In: Capuzzo IM & Kester DR ed. *Oceanic processes in marine pollution*. Malabar, Florida, Kirger RE, 109-118.
- Mellott, J. (nd): Coal Tar Pitch – Its Past, Present and Future in Commercial Roofing, Information downloaded from the Garland Company UK website:  
<http://www.garlandukltd.co.uk/educational/ytr/thinking-green-coal-tar.html>
- Moore (nd): The Changing Face of the Global Refractories Industry, Presentation by Paul Moore at the ACerSand TRI Joint Fall Meeting, Presentation downloaded from the International Minerals website:  
[http://www.mineralnet.co.uk/pdfs/697/52\\_refractoriespittsburgh.pdf](http://www.mineralnet.co.uk/pdfs/697/52_refractoriespittsburgh.pdf)

- 
- MTP (2007): European And International Refractories Industry: A Market/Technology Report, Materials Technology Publications, Nov 2007. Description downloaded from the Research and Markets website:  
<http://www.researchandmarkets.com/reports/652032>
- MSC (2008). Member State Committee Support Document for Identification of Anthracene as a Substance of Very High Concern. Adopted on 8 October 2008.  
[http://echa.europa.eu/doc/candidate\\_list/svhc\\_supdoc\\_anthracene\\_publication.pdf](http://echa.europa.eu/doc/candidate_list/svhc_supdoc_anthracene_publication.pdf)
- The Netherlands (2008): Annex XV Transitional Dossier. Coal Tar Pitch High Temperature (November 2008). Rapporteur: The Netherlands. Documentation of the work done under the Existing Substance Regulation (EEC) No 793/93 and submitted to the European Chemicals Agency according to Article 136(3) of Regulation (EC) No 1907/2006. Published by the European Chemicals Agency at:  
[http://echa.europa.eu/doc/trd\\_substances/pitch\\_coal\\_tar\\_high\\_temp/ann\\_xv\\_trd/trd\\_netherlands\\_pitch.pdf](http://echa.europa.eu/doc/trd_substances/pitch_coal_tar_high_temp/ann_xv_trd/trd_netherlands_pitch.pdf)
- The Netherlands (2008b): European Union Risk Assessment Report (RAR), Coal-Tar Pitch, High Temperature (CAS No: 65996-93-2, EINECS No: 266-028-2), Risk Assessment – Human Health, April 2008.
- Newsted JL, Giesy JP (1987): Predictive models for photoinduced acute toxicity of polycyclic aromatic hydrocarbons to *Daphnia magna*, Strauss (*Cladocera, crustacea*). Environ Toxicol Chem 6: 445-461.
- Nikkilä A, Penttinen S, Kukkonen JVK (1999): UV-B induced acute toxicity of pyrene to the waterflea *Daphnia magna* in natural freshwaters. Ecotoxicol Environ Saf 44: 271-279.
- O’Flaherty (2002): Highways: The Location, Design, Construction & Maintenance of Pavements, by C.A.O’Flaherty, 4<sup>th</sup> Edition, 2002.
- Oris JT, Giesy Jr. JP (1987): The photo-induced toxicity of polycyclic aromatic hydrocarbons to larvae of the fathead minnow (*Pimephales promelas*). Chemosphere 16: 1395-1404.
- Patent storm (nd):US Patent 5467998 - Non-Toxic, Edible, and Biodegradable Skeet and method of making the same, Information downloaded from:  
<http://www.patentstorm.us/patents/5467998/description.html>
- Partanen T and Boffetta P (1994): Cancer risk in asphalt workers and roofers: review and meta-analysis of epidemiologic studies. Am J Ind Med 26; (6): 721-740.
- Paul *et al* (2002): Use of asphalts for formcoke briquettes, Fuel Processing Technology, 76, pp.211-230.
- Peachey RL, Crosby DG (1996): Phototoxicity in tropical reef animals. Mar Environ Res 42: 359-362
- Pelletier MC, Burgess RM, Ho KT, Kuhn A, McKinney RA , Ryba SA (1997): Phototoxicity of individual polycyclic aromatic hydrocarbons and petroleum to marine invertebrate larvae and juveniles. Environ Toxicol Chem 16: 2190-2199

- 
- Pipeline & Gas Journal (2005): International Paint to Eliminate Coal Tar Epoxies, Information downloaded from: <http://www.allbusiness.com/mining/support-activities-mining-support-oil/460597-1.html>
- PSU (nd): Alternative Binder Pitches for Carbon Anode Production, Uthaiporn Suriyaphradilok, Colin Jennis-McGroarty, Adam Zel, and John M. Andresen, The Energy Institute, Pennsylvania State University.
- Ronneberg A and Langmark F (1992): Epidemiologic evidence of cancer in aluminium reduction plant workers. *Am J Ind Med* 22; (4): 573-590.
- Routschka, G (2007): Pocket Manual Refractory Materials, 2<sup>nd</sup> edition, McGrawHill.
- Schacht (2004): Refractories Handbook, by Charles A. Schacht (Editor), August 2004.
- SCHER, (2008): EU Scientific Committee on Health and Environmental Risks Coal tar pitch, high temperature Human Health Part CAS No: 65996-93-2 EINECS No: 266-028-2, The SCHER adopted this opinion at its 22<sup>nd</sup> plenary on 12 March 2008.
- SGSC (nd): Understanding how Sealcoating Works, Information downloaded from the South Georgia Sealcoating and Stripping LLC website: [http://www.sgasealcoating.com/how\\_sealcoating\\_works.htm](http://www.sgasealcoating.com/how_sealcoating_works.htm)
- Southworth GR, Beauchamp JJ, & Schmieder PK (1978): Bioaccumulation potential of polycyclic aromatic hydrocarbons in *Daphnia pulex*. *Water Res*, 12: 973-977.
- Spacie A, Landrum PF, & Liversidge GJ (1983): Uptake, depuration, and biotransformation of anthracene and benzo(a)pyrene in bluegill sunfish. *Ecotoxicol Environ Saf*, 7: 330-341.
- Spehar RL, Poucher S, Brooke LT, Hansen DJ, Champlin D, Cox DA (1999): Comparative toxicity of fluoranthene to freshwater and saltwater species under fluorescent light. *Arch Environ Contam Toxicol* 37: 496-502.
- Speight (1994): The Chemistry and Technology of Coal, James Speight, CRC, 2<sup>nd</sup> Edition, July 1994.
- Standard (2008): Arcelor Mittal Galati to Reduce Production Due to Fewer Orders, Information downloaded from: [http://www.standard.ro/articol\\_62806](http://www.standard.ro/articol_62806)
- Stansfield E (2008): Products and By-Products of Coal, Read Books, first published in 1915.
- Stompel (2008): The Past, The Present, And The Future of the European Coal Tar Industry: A Path To Where? Presentation by Dr. Zygmunt Stompel at the International Tar Association Annual Conference 2008, Kyoto, 12 – 14 May.
- Stompel (2009): Information provided by Dr. Zygmunt Stompel in response to Consultation, March 2009.

- 
- TGD (2003): Technical Guidance Document on Risk Assessment in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market. Part III, Chapter 5 – Use categories. European Communities, 2003.
- Trucco RG, Engelhardt FR, & Stacey B (1983): Toxicity accumulation and clearance of aromatic hydrocarbons in *Daphnia pulex*. Environ Pollut, A31: 191-202
- Weinstein JE, Oris JT (1999): Humic acids reduce the bioaccumulation and photoinduced toxicity of fluoranthene to fish. Environ. Toxicol. Chem., 18, 2087-2094.
- Weinstein JE, Polk KD (2001): Phototoxicity of anthracene and pyrene to glochidia of the freshwater mussel *Utterbackia imbecilis*. Environ Toxicol Chem 20: 2021-2028.
- Wernersson A-S (2003): Predicting petroleum phototoxicity. Ecotoxicol Environ Saf 54: 355-365.
- Wernersson A-S, Dave G (1997): Phototoxicity identification by solid phase extraction and photoinduced toxicity to *Daphnia magna*. Arch Environ Contam Toxicol 32: 268-273
- Whittier (nd): Cold Applied Coal Tar Paints, by Fred Whittier, Pittsburgh Chemical Company, Pittsburgh, Pennsylvania, Information downloaded from Argonne National Laboratory (ANL), a US Department of Energy Laboratory website: [http://www.anl.gov/PCS/acsfuel/preprint%20archive/Files/09\\_4\\_ATLANTIC%20CITY\\_09-65\\_0179.pdf](http://www.anl.gov/PCS/acsfuel/preprint%20archive/Files/09_4_ATLANTIC%20CITY_09-65_0179.pdf)
- Wilcoxon SE, Meier PG, Landrum PF (2003): The toxicity of fluoranthene to *Hyaella azteca* in sediment and water-only exposures under varying light spectra. Ecotoxicol Environ Saf 54: 105-117.
- Wild SR, Berrow ML, Jones, KC (1991): The persistence of polynuclear aromatic hydrocarbons (PAHs) in sewage sludge amended agricultural soils. Environ. Pollut., 72, 141-157.
- Wild SR, Jones, KC (1993): Biological and abiotic losses of polynuclear aromatic hydrocarbons (PAHs) from soils freshly amended with sewage sludge. Environ Toxicol Chem 12: 5-12.
- WIPO (1995): Method For Manufacturing Of Clay Target (WO/1995/003258), Information downloaded from the World Intellectual Property Organisation (WIPO) website: <http://www.wipo.int/pctdb/en/wo.jsp?IA=F11994000326&DISPLAY=DESC>
- Younkin, E (nd): Coal Tar Roofing – Taking a New Look at an Old Technology, Information downloaded from the Garland Company UK website: [http://www.garlandukltd.co.uk/files/modified\\_bur/CoalTarRoofing\\_RSIXtra206.pdf](http://www.garlandukltd.co.uk/files/modified_bur/CoalTarRoofing_RSIXtra206.pdf)

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# **Annexes**

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## **A1 ANNEX 1. SUPPLEMENTARY INFORMATION ON HUMAN HEALTH HAZARD ASSESSMENT**

### **A1.1 Overview**

In this annex, supplementary information is presented on human health hazards of CTPHT based on the Annex XV Transitional Dossier (The Netherlands, 2008). Due to the lack of sufficient data on CTPHT itself, information on PAH-constituents detected in CTPHT (and in particular on 14 of the EPA 16 PAHs with sufficient effect data available) is used, and reference is made to closely related compounds like coal tar pitch (CTP) and CTP volatiles (CTPV). More details can be found in the Annex XV Transitional Dossier. In this Annex some additional data on CMR properties of CTPHT or its constituents, from the PubMed and TOXNET online databases, have been furthermore provided.

### **A1.2 Mutagenicity**

#### **A1.2.1 In vitro data**

Pertinent data on CTP and CTP volatiles (CTPV) are used for this evaluation due to lack of data on CTPHT. CTP was found to be mutagenic in *S. typhimurium* strains TA98, TA100 both with and without metabolic activation (Solorzano *et al.*, 1993 cited in The Netherlands, 2008). In several other studies it also has been reported that CTP is mutagenic in bacteria (Machado *et al.*, 1993 cited in The Netherlands, 2008), yeast (IARC, 1985) and mammalian cells (IARC, 1985). On the other hand, although *in vitro* genotoxicity tests using mammalian cells mostly gave positive results, they were not conclusive (The Netherlands, 2008).

#### **A1.2.2 In vivo data**

No relevant animal (*in vivo*) data addressing potential genotoxicity of CTPHT, coal tar, coal tar waste, or coal tar products could be found.

#### **A1.2.3 Human data**

Although some human studies on the mutagenicity of CTP exist, there are not enough data to conclude on the mutagenicity of CTPHT for humans. The general observation is that urine of workers exposed to CTP or CTPV is not mutagenic in bacterial gene mutation tests (IPCS, 1998 cited in The Netherlands, 2008). Exceptions are urine samples of aluminium reduction plant workers (Heussner *et al.*, 1985 cited in The Netherlands, 2008), heavily exposed psoriasis patients, and coke oven and carbon plant workers (IPCS, 1998 cited in The Netherlands, 2008).

In the case of *in vivo* studies investigating effects on human blood cells, no conclusive study could be found, but few studies report increased genotoxicity in populations exposed to CTP or CTPV (e.g. IPCS, 1998, Arnould *et al.*, 1999 cited in The Netherlands, 2008).

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#### **A1.2.4 Other Relevant Information**

In a number of cases of occupational exposure to CTPHT, PAH-DNA adducts in blood cells were observed. According to these data, CTPHT should be regarded as genotoxic (SCHER, 2008).

### **A1.3 Carcinogenicity**

#### **A1.3.1 Carcinogenicity: Oral**

No studies were found on the potential carcinogenicity of CTPHT itself after oral exposure of animals. Few studies tested carcinogenicity of coal tar mixtures and BaP after oral exposure. One of these studies suggested that BaP in the coal tar diets causes fore stomach tumours in rodents, while other genotoxic components cause lung and liver tumours (Culp *et al.*, 1996 cited in The Netherlands, 2008). Furthermore, the occurrence of small intestine tumours were attributed to chemically-induced cell proliferation.

In another study, where BaP was administered by gavage to rodents, dose related carcinogenic effects were observed in the liver, fore stomach and epidermal structures (RIVM, 2001 cited in The Netherlands, 2008). Of these, the effects on liver are considered to be the most relevant for humans (The Netherlands, 2008).

#### **A1.3.2 Carcinogenicity: Inhalation**

Animal studies using female Wistar rats (Heinrich *et al.*, 1994 cited in The Netherlands, 2008), and newborn female mice (Schulte *et al.*, 1994 cited in The Netherlands, 2008) showed increased lung tumour growth after inhalation of CTPHT. No other organs developed exposure-related tumours besides the lungs. Therefore CTPHT was concluded to be definitively carcinogenic in rats and mice causing lung tumours after inhalation exposure (SCHER, 2008).

#### **A1.3.3 Carcinogenicity: Dermal**

While no information was found on the carcinogenicity of CTPHT after dermal exposure, dermal exposure to 40% solutions of CTP caused skin tumours as well as pulmonary adenomas, and squamous cell carcinoma of the stomach in white mice (Kireeva, 1968 cited in The Netherlands, 2008). In addition, when male mice were treated with a toluene solution of a CTP, they developed malignant and benign skin tumours (Emmett *et al.*, 1981, cited in The Netherlands, 2008).

#### **A1.3.4 Other Relevant Information**

Epidemiological data referring to different uses and exposures to CTPHT are summarised in Table A1.1 from the Annex XV Transitional Dossier (The Netherlands, 2008).

### **A1.4 Toxicity to Reproduction**

#### **A1.4.1 Effects on Fertility**

No relevant data were found on the toxicity to reproduction of CTPHT.

<b>Table A1.1: Epidemiological Data Relevant for the Different Human Exposure Cases</b>		
<b>Exposure Case</b>	<b>Reported Type of Cancers</b>	<b>Reference (cited in The Netherlands, 2008)</b>
Production of CTPHT in coal tar distillation plants	Lung and bladder (statistically non significant)	Armstrong <i>et al.</i> , 2003
Aluminium industry	Lung and bladder cancer; excess risk of stomach, kidney, prostate, pancreas, lymphatic and haemopoietic cancer and leukaemia	Ronneberg and Langmark, 1992
Use as a binder in asphalt industry and in roofing	No conclusive data	Partanen and Boffetta, 1994
Use in heavy-duty corrosion protection or as a binder for refractories, coal briquetting, and clay pigeons	Increased mortality due to bladder and prostatic cancer	IARC, 1985

#### **A1.4.2 Developmental Toxicity**

No relevant data were found on the developmental toxicity of CTPHT.

#### **A1.4.3 Human Data**

No relevant study was found on the toxicity for reproduction of CTPHT to humans. No impact on sperm counts was reported for workers exposed to CTPV (Ward, 1988 cited in ATSDR, 2002).

#### **A1.4.4 Other Relevant Information**

No other relevant information was found.

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## **A2 ANNEX 2. SUPPLEMENTARY INFORMATION ON ENVIRONMENTAL FATE PROPERTIES**

### **A2.1 Terrestrial bioaccumulation**

Very limited information on the potential for bioaccumulation in terrestrial organisms is included in the Annex XV Transitional Dossier (The Netherlands, 2008). Terrestrial bioaccumulation can be described as a hydrophobic equilibrium partitioning between the pore water and the internal concentration in organisms. According to the Technical guidance document the BCF can be estimated based on the  $K_{ow}$  and the density of the organism, by an equilibrium partitioning equation. This equation is applicable for estimating the BCF in earthworms, but not to isopods. In the Annex XV Transitional Dossier on CTPHT, bioaccumulation in earthworms was estimated by using the equilibrium partitioning equation, resulting in BCF values in the range of 450 to 46,000, with BCFs below 2,000 for anthracene, phenanthrene, fluoranthene and pyrene (The Netherlands, 2008).

### **A2.2 Secondary poisoning**

Based on the limited information on toxicity of the selected PAH to birds and mammals, no assessment of secondary poisoning can be made for CTPHT according to the Annex XV Transitional Dossier. Food web transfer of PAHs may theoretically occur in both aquatic and terrestrial environments. However, no indications of biomagnification have been identified. This is explained by relatively high rates of metabolism and excretion of PAHs in vertebrates and some invertebrates (The Netherlands, 2008). Accumulation of PAHs metabolites by predators is a further possible phenomenon, which though has received limited attention (The Netherlands, 2008).

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## A3 ANNEX 3. MANUFACTURING PROCESS OF CTPHT

Coal tar is manufactured as a by-product of the coking of coal (coal carbonisation) to produce metallurgical coke (used in steel production). In this process, coal is heated in a coke oven (found in coke plants or as part of steel works) to extreme temperatures (of 1,250 - 1,350°C) to produce coke (the primary product), high temperature coal tar (or coke oven tar) and other by-products which are collected outside the coke oven.

Historically, slightly lower temperatures (of 1,000 - 1,100°C) were applied in continuous vertical retorts (CVR) used in the manufacture of town gas to yield high temperature, coal tars (or CVR tars) (KEMI, 1994). Other processes capable of generating coal tar include the production of domestic coke and synthetic natural gas from coal which takes place under relatively mild conditions (at 600 - 750°C for 4 - 6 hours) yielding what is known as 'low temperature coal tar' (KEMI, 1994). Stompel (2009), however, indicates that, in the main, these low (and middle) temperature coal tars are no longer being produced as the production processes (which resulted in their production, i.e. gas making and coal carbonisation for gas production) have now ceased.

Crude coal tar from these processes is a complex mixture of over 350 aromatic compounds and further distillation is required to separate and purify the components of the coal tar. During the distillation process, which takes place at a refinery (which may be part of the coal tar producing plant or operate independently at another site), the coal tar is heated in a large closed vessel such that the lighter components boil off first, the heavier components boil off at higher temperatures and the various fractions are collected at different levels of the distillation tower. As shown in Figure 3, there are two main outputs from the distillation process:

- **distillates:** these are the volatile fractions which are captured as vapours and condensed to liquid and can also be mixed according to the specifications of the desired final end product. A 're-distillate' is the product of a repeat distillation process on a distillate, usually carried out to improve the purity of the product; and
- **pitch:** this refers to the least volatile residue not captured as a vapour and is essentially the 'distillate residue'. This is typically the largest by volume and most important product of the distillation process and the type of pitch required (e.g. softness) governs the end temperature of the distillation process (and vice versa).

The distillation process essentially separates the coal tar into fractions, which are either sold as is or further processed to achieve the required specifications. Most modern distilleries employ continuous stills with multiple columns and recirculation (Jacobs, 2006). Figure 3 overleaf provides a schematic description of the production process, while Figure 4 provides a flowchart of the typical primary products from coal tar distillation (as well as the primary end markets and end products).

For the particular company represented in Figure 3, during the distillation process, heat and vacuum are utilised to separate coal tar into three primary components: carbon pitch (~50%), creosote oils (~30%) and chemical oils (~20%) (Koppers, 2008). The chemical oils are essentially mixtures of light oils, carbolic oils, anthracene oils, naphthalene oils, etc. and these can be further refined to produce items such as naphthalene, tar acids, and solvent naphtha.

Probably more representative across companies are the typical proportions of the various distillates as described by Franck & Stadelhofer (1987): pitch (50 - 55%), anthracene oil (20 - 30%), naphthalene oil (10 - 12%), wash oil (7 - 8%), carbolic oil, flourene oil and methyl naphthalene (2 - 3% each). In practice, the exact mix produced will differ by company and depending on local

markets; for example, in Japan, increased value is placed on creosote, so pitch manufacturers attempt to produce as much of it as possible (Jacobs, 2006). Koppers (2008) does, however, note that because all coal tar products are produced in relatively fixed proportions to coal tar pitch (CTP), the level of CTP consumption generally determines the level of production of other coal tar products.

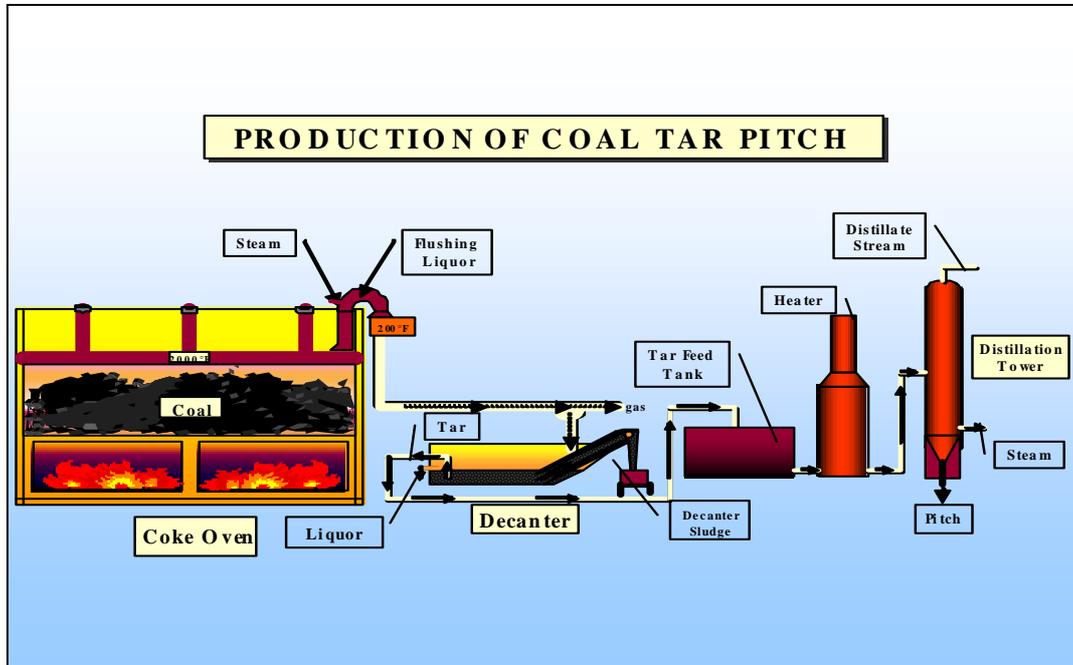


Figure 3: Coal tar production process (Koppers, 1998)

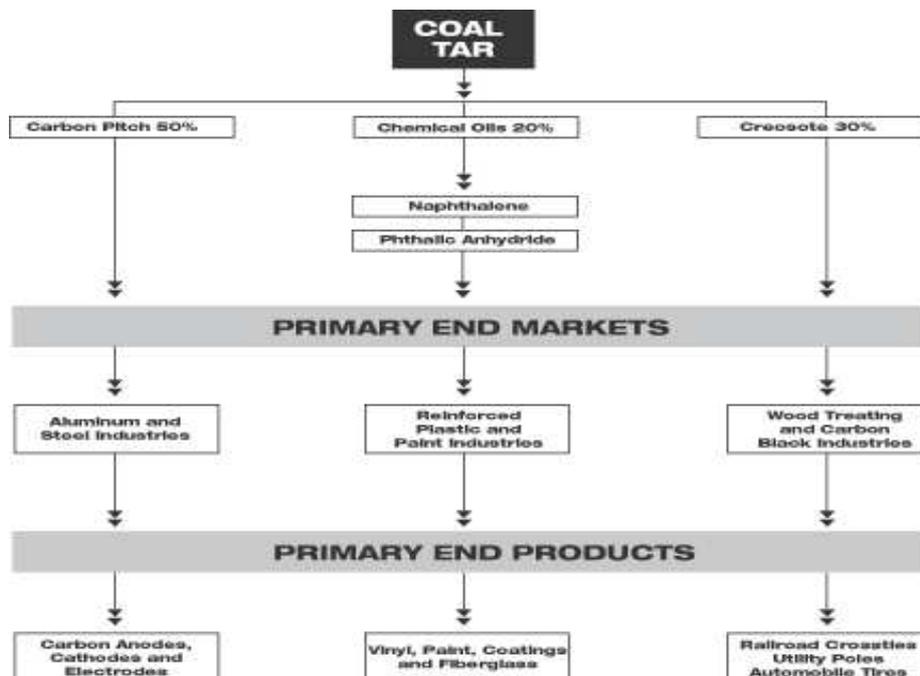


Figure 4: Primary end markets and end products for coal tar distillation products (Koppers, 2008)

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Coal tar pitch, high temperature (CTPHT) (CAS No 65996-93-2) is the residue from the distillation of high temperature coal tar (under vacuum in closed systems). It is a complex hydrocarbon mixture consisting of three- to seven-membered condensed ring aromatic hydrocarbons, high molecular weight compounds, heterocyclic compounds and benzocarbazoles (RAR, 2008a). CTPHT does not show a distinct melting or crystallisation point as it is composed of many different compounds which interact to form eutectic mixtures; rather, it is characterised by its softening point which can vary (from 30°C to 180°C), depending on the depth of distillation (KEMI, 1994; IUCLID, 2000).

In this regard, it is important to clarify that the terms ‘pitch’, ‘carbon pitch’ or ‘coal tar pitch’ are commonly used to refer to the residue left at the end of the distillation process. All the following synonyms can be found in literature: anode pitch, binder pitch, clay pigeon binder, electrode pitch, hard pitch, impregnating pitch, pitch, soft pitch, vacuum pitch (The Netherlands, 2008). In this case, the name - coal tar pitch, high temperature (CTPHT) - essentially reflects the fact that the residue or pitch is obtained from high temperature coking of coal tar. It, therefore, appears to be the case that CTP and CTPHT are (or have been) used rather interchangeably in the literature. This is further complicated by the fact that CTPHT is also known as (and has the following synonyms according to IUCLID (2000)) binder pitch, anode pitch or electrode pitch - although, technically, further processing (or coking) of CTP may be required to prepare these pitches. In this context, it is important to clarify that, for the purposes of this study, all information on CTP (except where explicitly stated) is assumed (and believed) to refer to CTPHT. Discussions with a coal tars manufacturer confirm that CTP and CTPHT indeed refer to the same substance.

**A4 ANNEX 4. USES OF CTPHT DESCRIBED USING THE USE DESCRIPTOR SYSTEM SET OUT IN THE GUIDANCE ON INFORMATION REQUIREMENTS AND CHEMICAL SAFETY ASSESSMENT, CHAPTER R.12**

<b>End use description</b>	<b>Sector of Use (SU)</b>	<b>NACE<sup>1</sup></b>	<b>Type of Preparation Product Category (PC)</b>	<b>Process Category (PROC)</b>	<b>Article Category (AC)</b>	<b>TARIC Code<sup>2</sup></b>	<b>Consumer exposure</b>	<b>Quantities used</b>
Binding agent in the production of:  (a) Prebaked electrodes	SU3 - Industrial manufacturing (all)	C20.5.9 - Manufacture of other chemical products n.e.c.	PCxyz - Other products (UCN Code B20300 - Other binding agents)	PROC5 - Mixing or blending in batch processes for formulation of preparations and articles (multistage and/or significant contact). Industrial setting	Not applicable	Not applicable	No	400
(b) Graphite electrodes	SU3 - Industrial manufacturing (all)	C20.5.9 - Manufacture of other chemical products n.e.c.	PCxyz - Other products (UCN Code B20300 - Other binding agents)	PROC5 - Mixing or blending in batch processes for formulation of preparations and articles (multistage and/or significant contact). Industrial setting	Not applicable	Not applicable	No	200
(c) Søderberg electrodes	SU3 - Industrial manufacturing (all)	C20.5.9 - Manufacture of other chemical products n.e.c.	PCxyz - Other products (UCN Code B20300 - Other binding agents)	PROC5 - Mixing or blending in batch processes for formulation of preparations and articles (multistage and/or significant contact). Industrial setting	Not applicable	Not applicable	No	50

End use description	Sector of Use (SU)	NACE <sup>1</sup>	Type of Preparation Product Category (PC)	Process Category (PROC)	Article Category (AC)	TARIC Code <sup>2</sup>	Consumer exposure	Quantities used
Binding agent in the production of other refractory agents	SU3 - Industrial manufacturing (all)	C23.2.0 - Manufacture of refractory products	PCxyz - Other products (UCN Code B20300 - Other binding agents)	PROC5 - Mixing or blending in batch processes for formulation of preparations and articles (multistage and/or significant contact). Industrial setting	Not applicable	Not applicable	No	37.5
Production of Active Carbon (Carbon Fibres)	SU10 - Chemical formulation and/or repackaging	C20.6.0 - Manufacture of man-made fibres	PC2 - Adsorbens	PROC2 - Use in closed, continuous process with occasional controlled exposure (e.g. sampling); industrial setting;	C20 - Other		No	12.8
Paints and coatings	SU10 - Chemical formulation and/or repackaging	C20.3.0 - Manufacture of paints, varnishes and similar coatings	PC1 - Adhesives, Sealants  PC9 - Coatings and paints, fillers, putties, thinners	PROC5 - Mixing or blending in batch processes for formulation of preparations and articles (multistage and/or significant contact); industrial setting	Not applicable	Not applicable	Unlikely, as mainly used in specialist applications	7.5
Binding agent for coal briquettes	SU3 - Industrial manufacturing (all)	C19.1.0 - Manufacture of coke oven products	PC13 - Fuels	PROC5 - Mixing or blending in batch processes for formulation of preparations and articles (multistage and/or significant contact); industrial setting	Not applicable	Not applicable	No, as CTPHT is totally volatilised in the production process	6.8
Binding agent for clay targets	SU18 - Manufacture of furniture	C32.3.0 - Manufacture of sports goods	PCxyz - Other products (UCN Code B20300 - Other binding agents)	PROC14 - Production of preparations or articles by tableting, compression, extrusion, pelettisation; industrial setting	Not applicable	Not applicable	Yes	6.0

End use description	Sector of Use (SU)	NACE <sup>1</sup>	Type of Preparation Product Category (PC)	Process Category (PROC)	Article Category (AC)	TARIC Code <sup>2</sup>	Consumer exposure	Quantities used
Impregnating, coating, and adhesive material used for roofing	SU19 - Building and construction work	F43.9.1 - Roofing activities	PC10 - Building and construction preparations not covered elsewhere	PROCxyz - Open processing and transfer operations at elevated temperature	C18.2 - Building material for outdoor use	Not applicable	Possible short exposure (1 day) at very low frequency (10 yrs)	5.3
Binding agent for road construction	SU19 - Building and construction work	F42.1.1 - Construction of roads and motorways	PC10 - Building and construction preparations not covered elsewhere	PROCxyz - Open processing and transfer operations at elevated temperature	C18.2 - Road surface material	Not applicable		1.5
Medicinal Products	SU10 - Chemical formulation and/or repackaging	C21.1.0 - Manufacture of basic pharmaceutical products	PC29 - Pharmaceuticals	PROC3 - Use in batch and other processes (synthesis) where opportunity for exposure arises; industrial setting	Not applicable	Not applicable	Yes	

Notes:

1. NACE codes are used as additional descriptors to SU.
2. TARIC codes are used as additional descriptors to AC.

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## A5 ANNEX 5. FURTHER INFORMATION ON ALTERNATIVES

### A5.1 Review of efforts towards developing alternatives to CTPHT-based electrodes

Information obtained from a literature review indicates that recent research work has examined the development of alternative binders from various sources of pitches, namely,

- *petroleum pitch*, which is a residue produced from heat-treatment and distillation of petroleum fractions;
- *coal-extracted pitch*, a product of the pre-hydrogenation of coal followed by extraction using a dipolar solvent; and
- *gasification pitch*, which are distilled by-product tars produced from the coal gasification process.

Each of these alternative pitches was mixed with a standard coal tar pitch at various mixtures and laboratory-scale test anodes were formed and studied. The results of this study (PSU, nd) show that the petroleum pitch offers a potential to be used as additives to the standard coal tar pitches for use as binders in aluminium anode production, while the addition of coal-extracted pitch and gasification pitch give comparable anode properties when the ratio of standard coal tar pitch and alternative pitch is greater than 50:50. PSU (nd) note that further work needed to be conducted to study the causes of improvement of adding alternative pitches to better understand the roles of the binders from various types of pitches.

Another major manufacturer of coal tar pitch is also involved in strategies towards developing petroleum-enhanced coal tar pitches. This company notes that, with the exception of a few instances, the aluminium industry's experience with 100% petroleum pitch has been less than desirable with uneconomical carbon consumption and poor performance experienced.

During the development of coal tar/petroleum pitch products, the aim has been to combine the positive characteristics of both the coal tar and petroleum components to produce a quality product with equal or improved properties. In 1994, this company began testing of the coal tar/petroleum pitch product on a commercial scale. Results of early testing indicated that acceptable performance was obtained with some small performance disadvantages, especially with respect to air reactivity. Since the development of the first product, efforts to improve these slightly deficient performance characteristics have resulted in a product with improved performance. This company indicates that the use of petroleum-enhanced coal tar pitch is the preferred long-term solution to coal tar because:

- 1) it is the most economical alternative;
- 2) the performance has been proven over three years of commercial use;
- 3) the required petroleum material is readily available and the supply has potential to grow with demand; and
- 4) a product of consistent quality is provided (Koppers, 1998).

Another paper (Koppers, nd) describes further efforts to develop coal tar/petroleum pitches. The product development effort took a dual product path with one product targeted for prebaked anode and graphite electrode binder applications. This product eventually contained approximately 15% of the petroleum component and 85% of the coal tar component and was designed to perform in a similar fashion to the traditional coal tar binder pitch. The product was designated Type A pitch. The second product was developed specifically to reduce polynuclear aromatic (PNA) emissions

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from Söderberg plants and was designated Type B pitch. Type B pitch is produced by a patented process which results in a binder pitch which contains 40 % less PNA's than a typical coal tar pitch. Type B pitch is composed of approximately 40% of the petroleum component and 60% of the coal tar component. Type A pitch is now a proven commercial product with over five years of commercial use. At the time, Type B pitch did not have the extent of commercial use as Type A pitch; however, it produces significantly lower BaP emissions. With the likelihood of increasing environmental pressures for the reduction of emissions, Type B pitch may be the most economical alternative. Development efforts will continue to develop new and improved coal tar/petroleum pitch products (Koppers, nd). Fischer (nd), however, notes that for coal tar pitch/petroleum pitch blends, process adaptation during paste production is required in order to obtain a good anode quality.

A paper presented at the 1997 TMS Annual Meeting (Marzin *et al*, 1997) suggests that a petroleum pitch, specially developed for aluminium anodes was produced, at commercial scale, as a real alternative to coal tar pitch. Using a highly aromatic refinery stream and well designed process conditions, the paper indicates that it is possible to produce the right chemical composition needed for a high quality binder material for anodes. Through a Dynamic Process Optimization study, the paste formulation and parameters were adjusted to produce full size anodes with 100% petroleum pitch. The performance of baked anodes was similar to coal tar pitch anodes, with the advantage of a much lower content of PAHs (Marzin *et al*, 1997). EAA (2009), however, notes that the use of petroleum pitch lowers the emissions of high molecular weight PAH components, but not the low molecular components and does not lead to lower emissions of other volatile compounds.

Finally, the use of wood char as an alternative to coal tar pitch in carbon anodes is also being explored by researchers through the Light Metals Flagship (Australia) (CSIRO, nd). Biomass is an attractive alternative because it is renewable and has a low sulphur and ash content. Using biomass for anodes production would also make the process greenhouse neutral – carbon dioxide liberated in the production process is absorbed by the successive growing of trees. However, the low density of wood char means additional processing is required to produce aluminium anodes.

Researchers are thus blending charcoal with biopitch to make a coke-like material in an effort to overcome this issue. Characterising various charcoals and their properties is an important part of the project. This knowledge will help researchers develop bioanodes that perform the same function as traditional anodes. Early research suggests anode production from softwoods and hardwoods will require different process methods because of their unique cellular structures (CSIRO, nd).

## **A5.2 Uses of organic binders in refractories applications**

The discussion below focuses on the two main types of organic binders - pitches and resins - which have verifiable use experience in refractories.

With regard to pitches, it should be noted that these can be derived from either coal or petroleum. However, Schacht (2004) indicates that both types of pitches have fallen out of favour due to their carcinogenic properties and PAH contents. However, he notes that coal tar pitches contain around 6% by weight of quinoline insolubles (small, solid, organic particles), while petroleum pitches do not have these insolubles. For this reason, petroleum pitch is also used for impregnating previously shaped refractories and enhancing slag resistance (as it does not contain quinoline insolubles that can block pores in the refractory body and limit the pitch penetration (Schacht, 2004)). This is consistent with information by Ewais (2004) which confirms that the physical properties of the

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pitch influence processing behaviour; conversely, the choice of the binder is also determined by the particular processes in use.

The RAR (2008) also notes that the pitch industry is proposing to use pitches with a higher softening point resulting in a lower BaP content of 300 ppm compared to current levels in pitches ranging up to 20,000 ppm. This appears to be consistent with the fact that, although hard coal pitch has the best performance/cost ratio of all coking binders, due to stricter environmental protection legislation, standard coal tar pitches seems to have been almost completely substituted by petroleum pitches or pitches from a special high temperature vacuum treatment of coal tar pitch (Routschka, 2007). This indeed results in a reduction in the level of PAHs to as low as a tenth of the level found in bricks bonded with coal tar pitch (Routschka, 2007).

Resins were originally derived from coal, but presently most resins come from petroleum sources. Both Schacht (2004) and Ewais (2004) indicate that due to the potential health (and environmental) hazards in the handling of pitches, resins and polymers have become favoured alternatives. Phenolic resins do not contain carcinogenic substances in comparison with the pitches.

Two major thermosetting phenolic resins are used in the refractories industry: novolacs and resoles. Novolacs require the addition of a hexamethylene tetramine catalyst for polymerisation during coking, while resoles contain a built in catalyst (Schacht, 2004). Compared with pitches, mild elevated temperatures are required during the production process (based on a cold mixing method) which results in energy savings. Phenolic resins (both novolacs and resoles) are also preferred because they are thermosetting and can be pyrolysed during coking to achieve a high carbon yield. Other advantages are that: (a) the products can be processed in uncured conditions; (b) the products have no plastic phase when heated up (in contrast to tar-pitch binders); and (c) the carbon content can be increased to augment resistance to abrasion and slag attack (Ewais, 2004).

Phenolic resins, however, have some drawbacks (Ewais, 2004; Schacht, 2004):

- phenolic resins generate gases such as ethylene, phenol, cresol and xylenol when carbonised in temperature ranges of 350 - 650°C causing air pollution and odour;
- the structure of the phenolic resin used as binder is dense and, as such, is liable to destruction due to the evolution of decomposition gas on heating;
- the carbon produced from phenolic resin is a glassy carbon, inferior in resistance to spalling (breaking off of some fragments); and
- care needs to be taken regarding curing of the resin as some resins tend to harden in a comparatively short time reducing the time the mix can be retained before it must be shaped into bricks or other desired shapes. Care also need to be paid to the wettability of graphite by resins, as some chemicals used in graphite beneficiation process can impact on this feature.

### **A5.3 Alternatives to roofing applications of CTPHT**

Examples of alternative roofing systems include:

- **EPDM membrane:** a single-ply synthetic rubber roofing membrane which has good weatherability and is impermeable to water so can be used in all climate zones. It seems to

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require little maintenance once installed and so has a low lifetime cost. According to its material safety data sheet, a potential hazard associated with its use appears to be the potential for toxic fumes to be given off if it is burnt;

- ***Thermoplastic polyolefin***: a new single-ply product which has an expanding market due to its ease of installation, reflective and energy-saving qualities and durability. As with EPDM, a potential hazard appears to relate to toxic gases if the material is burnt;
- ***Modified bitumen roofing***: this involves reinforcing materials coated with bitumen and the addition of polymers to the bitumen to achieve improved characteristics. There is usually a mechanically attached base sheet. The hazards associated with modified bitumen relate to skin contact with hot product (leading to burns) and inhalation of fumes (leading to respiratory tract irritation, nausea and unconsciousness). As the fumes are flammable, work should be done in a well-ventilated area;
- ***Liquid-applied monolithic roof system***: this is made of high-tech polymeric resins such as urethanes, or bitumens which have been modified with polymers such as SEBS. The roofing material is applied as a liquid using brushes or rollers, and cures quickly to form a tough, rubber-like membrane with no seams. Liquid coatings have few hazards because they are installed cold. Bitumen was the first form of liquid waterproofing and has been used for thousands of years. Benefits of new liquid roofing systems include (a) seamless membranes with no joins even on complex roofs; (b) ease of installation; (c) their cost effectiveness; (d) membranes can be applied on top of existing roofs; (e) they can cope with a range of temperatures; (f) they can be walked on; and (g) a lifespan in excess of 25 years;
- ***Built-up asphalt roofs***: these are similar to coal tar roofs but use asphalt and gravel instead of coal tar bitumen; and
- ***Metal sheeting*** e.g. lead, copper and slate or clay tile.