

**ES- 33-2007**

**COAL TAR PITCH, HIGH TEMPERATURE**

CAS No: 65996-93-2

EINECS No: 266-028-2

**RISK REDUCTION STRATEGY**

**WORKERS**

*November 2007*

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## 1 Background

Coal tar pitch high temperature (CTP(ht)) is the solid fraction produced during the distillation of coal tars. Coal tars are condensation products obtained during the production of coke and/or natural gas through the destructive distillation of coal, called carbonisation or coking. The composition and properties of a coal tar (and coal tar pitch derived thereof) depend mainly on the temperature of carbonisation and, to a lesser extent, on the nature of the coal used as feedstock. High-temperature coal tars (CAS # 65996-89-6) is defined in EC as ‘the condensation product obtained by cooling, to approximately ambient temperature, of the gas evolved in the high temperature (greater than 700 °C (1292 °F)) destructive distillation of coal. A black viscous liquid denser than water. Composed primarily of a complex mixture of condensed ring aromatic hydrocarbons. May contain minor amounts of phenolic compounds and aromatic nitrogen bases’. The distillation of high-temperature coal tars results in tar oils (including naphthalene oil, creosote oil, anthracene oil, and creosote) and a solid fraction (coal tar pitch high temperature). When CTP(ht) is heated, Coal tar pitch volatiles (CTPV(ht)) are released. However, the term CTPV is not only used for volatiles released when coal tar pitch (CTP) is heated, but also for volatiles released when coal tar or its products are heated. Because of variation in source materials and manufacturing processes, including different temperatures and times of carbonization, no two coal tars or pitches are chemically identical. In general, however, approximately 80% of the total carbon present in coal tars exists in aromatic form. Volatile fumes, designated CTPV, are released when coal tar, CTP, or their products, are heated.

### CLASSIFICATION

#### Current classification (According to Annex I)

Classification :	Carc. Cat. 2
Symbol :	T
R-phrases :	45
S-phrases :	53-45
Notes :	H (pitch)

#### Proposed classification

Decisions by the Technical Committee on Classification and Labelling (TC-C&L) in October 2006 for physical and human health endpoints.

Classification :	Mut. Cat 2; Carc. Cat. 1; Repro. Cat. 2.
Symbol :	T; Xi
R-phrases :	41, 43, 45, 46, 60-61
S-phrases :	53 - 45

Notes : H (pitch)

### Occupational limit values

Occupational limit values for CTPV

Country/ organization	8-hr TWA  (in mg/m <sup>3</sup> )	Remarks	References
USA <ul style="list-style-type: none"> <li>■ ACGIH</li> <li>■ OSHA</li> <li>■ NIOSH</li> </ul>	0.2 0.2 0.1	As benzene soluble aerosol As benzene soluble aerosol As cyclohexane-soluble fraction  Classified as A1 carcinogen, i.e., confirmed human carcinogen: the compound is carcinogenic to humans based on the weight of evidence from epidemiological studies.	(ACGIH, 1999; ACGIH, 2002)  (ACGIH, 1999)  (ACGIH, 2002)
The Netherlands	-	Under consideration <sup>1</sup>	(Health Council 2006/01OSH)
UK	-	Listed among compounds which are currently on the work programme.	(HSE, 1999)
Germany	-	Listed as pyrolysis products from organic materials. They are classified among compounds which are capable of inducing malignant tumours as shown by experience with humans.  The TRK (Technical Guide Concentration) for BaP was 0.005 mg/m <sup>3</sup> for production, loading and unloading of pencil pitch, and in the area near the ovens in coking plants and 0.002 mg/m <sup>3</sup> for all other workplaces in Germany.	(DFG, 2001)
Sweden	not listed	The OEL for BaP is 0.002 mg/m <sup>3</sup> .	(NBOSH, 2002)

<sup>1</sup> The Health Council advises a value of 5,6 nanogr/m<sup>3</sup> (risk level of 10<sup>-6</sup>) for benzo(a)pyrene, with an upper limit of 560 nanogr/m<sup>3</sup> (risk level 10<sup>-4</sup>).

Country/ organization	8-hr TWA  (in mg/m <sup>3</sup> )	Remarks	References
Denmark	0.2	As benzene-soluble fraction  Coal- and oil-derived substances, as well as coal tar products, including coal tar pitch distillates with boiling point > 200 °C are listed among substances which are considered to be carcinogenic.	(Arbejdstilsynet, 1996)
Norway	-	Reference is made to polycyclic aromatic hydrocarbons for which an exposure limit of 0.04 mg/m <sup>3</sup> has been established.	(Direktoratet for arbeidstilsynet, 1996)
European Union	not listed		(Hunter et al., 1997)

The U.S.A. uses, depending on the organization, an occupational exposure limit between 0.1 and 0.2 mg/m<sup>3</sup>. Except for Denmark no occupational exposure limit is set for CTP(ht). An occupational exposure limit is deducted from PAHs, BaP or other coal/oil-derived substances. The occupational exposure limit set by Denmark is within the range of that of the U.S.A. with 0.2 mg/m<sup>3</sup>.

## 2 The risk assessment results

### Production and use

Within the European Union, high temperature coal tar pitch is produced by ten companies at eleven sites in nine countries. The total European Union production capacity in 2004 was 1127,000 tonnes. The actual production output of coal tar pitch in that year was about 817,800 tonnes. Import from outside the EU was reported to be about 91,600 tonnes per year and export was about 355,600 tonnes per year. The total consumption of coal tar pitch in the EU from these figures is estimated to be about 554,000 tonnes per year.

Coal tar pitch is mainly used as a binding agent in the production of carbon electrodes, anodes and Söderberg electrodes for instance for the aluminium industry. It is also used as a binding agent for refractories, clay pigeons, active carbon, coal briquetting, road construction and roofing. Furthermore small quantities are used for heavy duty corrosion protection.

### **Use pattern for coal tar pitch. Sales in the EU in 2003.**

<b>Application</b>	<b>Industry category <sup>1)</sup></b>	<b>Use category <sup>2)</sup></b>	<b>Quantity (tonnes/year)</b>	<b>Percentage of total sales</b>
Anodes	8	2	322 500	71.3
Electrodes	8	2	81 400	18.0
Refractories	0	2	22 500	5.0
Road construction	16	2	800	0.2
Active carbon	0	2	7 900	1.7
Heavy duty corrosion protection	14	2/39	4 700	1.0
Roofing	16	2	3 200	0.7
Clay pigeons	0	2	5 800	1.3
Coal briquetting	9	2	3 700	0.9
Total			452 400	100

- 1) industrial category 0 is others, industrial category 8 metal extraction, refining and processing industry, industrial category 9 is mineral oil and fuel industry, industrial category 14 is paints, lacquers and varnishes industry, industrial category 16 is engineering industries: civil and mechanical
- 2) use category 2 is adhesives and binding agents and use category 39 is non-agricultural biocides

The exposure assessment will be focussed on the emission of PAHs on a local scale for production of coal tar pitch and the main applications, primarily because lower emissions for the other sources are expected<sup>2</sup>. Moreover, the amounts of coal tar pitch used for roofing and road paving decrease as it is replaced by petroleum pitch on account of the lower PAH content (worker hygiene). Some manufacturers claim to produce “environmentally” friendly clay pigeons by applying petroleum pitch in order to meet the EEC environmental protection directives, or apply no binder at all. The emission of PAHs at coke ovens are not considered because coal tar is produced at this process. Coal tar is used as a feedstock for the production of coal tar pitch and therefore the coke ovens are not part of the life cycle of coal tar pitch which actually starts the production stage of coal tar pitch.

With respect to the main applications of coal tar pitch, the following point sources will be considered:

- Anode production
- Aluminium production applying prebakes (with and without) anode baking.
- Aluminium production using Söderberg technology
- Graphite electrode production
- Production of steel, silicon, etc., applying electric arc furnaces with Söderberg electrodes.

The future consumption of pitches depends not only on human health risks and environmental hazards but also on economics due to progress of science and technology.

Since more than ten years a new technology has been developed at benchscale based on inert anodes to replace CTP(HT)-bound carbonated anodes but this technology is still immature and costly. Therefore, it can be expected that CTP(HT) will be used for more than decades in the primary aluminium smelters.

For refractories, the pitch industry now proposes pitches with a higher 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.

Most of the European countries have banned CTP(HT) in the road construction by law or agreement between trade unions and road building companies. In fact only very particular applications such as kerosene proof coatings for parking lots, airfields and taxi ways still use pitch as an emulsion. This market is decreasing and represents only 200 tonnes of pitch per year.

Pitch bound active carbons are more and more produced outside the EU and are anyway processed in closed vessels where the pitch is pyrolyzed to pure carbon with controlled emissions.

Roofing and corrosion protection with CTP(HT)-based products are declining dramatically and a phasing out of these artefacts is predicted in the next few years.

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<sup>2</sup> At present information on the emission of PAHs from the use of coal tar pitch as binder for refractories is very limited. However, it can not be excluded that the PAH emission from the use of this application can be significant (comparable to the main applications, depending on the abatement techniques used)

The use of pitch bound coal briquettes is forbidden in some countries (Germany and Scandinavia). This market is also 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. Capacities of 2,000 ktonnes/year of briquettes existing in the early 80's in Europe are now decreased to 150 ktonnes/year, also using more environmental friendly binders like starch and molasses. Also here a full phasing out of the use of CTP(HT) can be expected in the next few years.

Clay pigeons manufacturers, claiming environmental protection, displaced carbopitch by petrochemical binders for more than 80% of their production and the former clay pigeons being exported outside the European Union.

In summary, the pitch market, decreasing in Europe for economical reasons, will remain only for electrodes, anodes and graphite artefacts.

With respect to the main applications of CTP(ht), the following scenario's are considered to be relevant for occupational exposure assessment.

#### Production and Use Scenarios

- Occupational Scenario 1: Production of CTP(ht) in coal tar distillation plants
- Occupational Scenario 2: Use as a binding agent for electrodes
- Sub-scenarios: (i) Use as a binding agent in electrodes in the aluminium industry
- (ii) Use as a binding agent in graphite electrode production and impregnation of electrodes
- Occupational Scenario 3: Use as a binding agent in the Asphalt industry
- Sub-scenarios: (i) Use as a binding agent in road construction
- (ii) Use as a binding agent in roofing and waterproofing
- Occupational Scenario 4: Use as a binding agent for refractories
- Occupational Scenario 5: Use as a binding agent for active carbon
- Occupational Scenario 6: Use in heavy duty corrosion protection
- Occupational Scenario 7: Use as a binding agent in coal briquetting
- Occupational Scenario 8: Use as a binding agent for clay pigeons

The database on possible health hazards induced by CTP(ht) is rather limited, implicating that a full risk assessment for all the required endpoints is not possible. There is, though, quite some information from epidemiological studies on workers in specific industrial processes where CTP(ht) is produced and/or used, that indicate that carcinogenicity is a striking hazard associated with CTP(ht). This is attributed to the presence of the PAHs in CTP(ht). Given the uncertainties with respect to the effects of other chemical constituents of CTP(ht) and related substances also exposed to, it is not completely sure that carcinogenicity is the only relevant effect of CTP(ht). However, as it is also noted that the carcinogenic potencies of these PAHs are quite high, limitation of the risks for cancer will automatically reduce the risk for any other possible effect, quite possibly even to zero. Therefore, in spite of the limited available



data on non-carcinogenic properties of CTP(ht), it is decided in the risk assessment report for CTP(ht) that further testing for some endpoints will be subordinated to conclusions on risks based on carcinogenic and mutagenic properties, using the best-studied PAH BaP as a guidance substance for exposure to CTP (ht) in various worker exposure scenarios, in line with the available meta-analyses on lung and bladder cancer where BaP was also used as exposure indicator. In addition, as these analyses has collected, analysed and summarised all available data on CTP(ht) exposures in a scientifically sound manner, it is considered to yield the best estimates.

### **Summary of the conclusions**

**Conclusion (i)** There is a need for further information and/or testing.

**Conclusion (ii)** There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

**Conclusion (iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

Conclusion (i) applies to skin irritation, systemic toxicity after repeated exposure, and effects on reproduction. The conclusion can be put 'on hold' and the necessity for further testing be revisited after a risk reduction strategy.

Conclusion (ii) applies to acute toxicity, skin sensitisation, eye irritation, and corrosivity.

Conclusion (iii) applies to mutagenicity, and carcinogenicity, effects that cannot be excluded for exposure (inhalation and dermal) arising from production and use as an intermediate.

It is noted that the excess lifetime risk under occupational conditions of exposure points to very low acceptable exposure levels with regard to carcinogenic effects, which implies a considerable reduction of the current limit values. It is expected that compliance to these low exposure levels will prevent effects other than carcinogenic effects to occur.

## 3

### Current risk reduction measures

**3.1** In all working processes an adequate level of containment is necessary, based on the workplace specific risk assessment evaluation according to Directive 89/391/EEC, 98/24/EEC and, especially, 2004/37/EC. The information in the risk assessment report should be an important input for the workplace specific risk assessment and evaluation.

**3.2** The Safety Data Sheet according to Directive 91/155/EEC should contain all relevant information from the risk assessment report.

**3.3** Relevant OELs has been set in the past on the present product or can be deduced from limit values on PAHs, BaP or like products. However, some of these values are repealed in the mean time. At present there is no EU standard that is applicable to the present product.

## 4

### Possible further risk reduction measures

#### 4.1 Classification

The risk assessment report concludes to the necessity of a new, more severe classification. This proposal is subject to a separate EU decision scheme and cannot be evaluated here further. However, this proposal to establish a new, more severe EU harmonised classification is sustained. As a result, more restrictions in use and a heavier containment regime might be necessary as a consequence of the new classification.

**Conclusion:** a new, more severe EU harmonised classification is sustained, but cannot be evaluated here.

#### 4.2 Use restrictions

The risk assessment report has indicated a possible wide spread and open use of the present substance. A use restriction for a substance with the hazard characterisation of the present product is then to be considered in addition to the results from a new, more severe classification (see paragraph 4.1).

As a result of recent developments however, the use is or will soon be restricted to electrode production and use. This use is in well defined industrial locations.

Furthermore, the composition of the present product is being very much ameliorated with regard to carcinogenic compounds (substitution principle in the context of Directive 2004/37/EC).

The possibility of containment is high in the industrial premises concerned (no open use).

In conclusion, there is not enough reason for EU harmonised use restrictions, especially when the recommendations under paragraphs 4.1 and 4.3 are followed.

**Conclusion:** there is not enough reason for additional EU harmonised use restrictions.

#### 4.3 Occupational exposure limit

A European OEL is lacking. The establishment of a European OEL should be considered for substances with a use on many locations and in most EU countries, and with considerable risks. These requisites seem to be fulfilled.

The present substance is used in the metal producing industry. Furthermore, there are special production locations for the electrodes used in the metal producing industry. In most EU countries there are metal producing industries.

The present legal interventions within the EU differ considerably. It is desirable that more EU harmonisation is reached, especially on substances as the present one with considerable risks and use in most EU countries, under sometimes very different regimes.

Benzo(a)pyrene is used in the risk assessment report as the risk assessment marker chemical, and is probably a very good marker chemical to set the EU OEL.

**Conclusion:** there is a need for establishing a European OEL, probably on the marker chemical benzo(a)pyrene.

## **5 Assessment of further possible further risk reduction measures**

### **5.1 EU OEL**

#### *Effectiveness*

A European OEL for the present substance or the marker chemical benzo(a)pyrene will be an effective means to prevent health effects from worker exposure. Directives 98/24/EEC and 2004/37/EC prescribe that every Member State set a national OEL taking into account the EU OEL. Furthermore, the workplace specific risk assessment evaluation according to Directive 89/391/EEC, 98/24/EEC and, especially, 2004/37/EC by the employer must take into consideration (*inter alia*) this national OEL. Thereafter, the employer must take risk reduction measures to the effect that the health risk as identified in the workplace specific risk assessment will be eliminated or minimised.

Therefore, the EU OEL will have a direct impact on the workplace specific risk assessment and, moreover, on the resulting workplace specific risk reduction measures that eliminate or minimise possible health effects of worker exposure to the present substance.

#### *Practicability*

It is practical to eliminate or minimise possible health effects of worker exposure to the present substance by setting a EU OEL, probably for the marker chemical benzo(a)pyrene. In every Member State there will be, as a result of the EU OEL, a clear standard for accepted worker exposure to the present substance. This clear standard will be used by every employer to design his workplace, and by the enforcement authorities to assess the effectiveness of the workplace specific risk reduction measures. It is practical to have only one clear standard both for all workplaces and enforcement actions.

#### *Economical impact*

The employer has several options for workplace design based on the OEL. These options comprise, after first consideration of replacement: organisation of workplace and the system of work, protection equipment, number of workers exposed and duration and height of exposure. The employer may choose the appropriate measures with report to his specific conditions and possibilities. Therefore, the economic impact of a EU OEL will be acceptable as the resulting risk reduction measures can be tailored to each enterprise specific situation.

#### *Monitorability*

It is technical possible to monitor an OEL for benzo(a)pyrene. Monitoring is enforceable by the Member State authorities (normally the Labour Inspectorates).

## **6 Draft conclusions and recommendations**

The legislation for workers' protection currently into force at Community level is generally considered to give an adequate framework to limit the risks of coal tar pitch, high temperature to the extent needed and shall apply. There is no need for additional risk reduction measures in the context of the Existing Substances Regulation. However, based on the results of the risk assessment report, it is recommended within the framework of the legislation on worker protection

- to establish at Community level an occupational exposure limit, probably for the marker chemical benzo(a)pyrene.