CCSG

COAL CHEMICALS SECTOR GROUP

Input to the Public Consultation on ECHA's Draft recommendation for inclusion of CTPHT in REACH Annex XIV

Comments of the Cefic "Coal Chemicals Sector Group (CCSG)"

INTRODUCTION

This report is the response to the 6th public consultation of ECHA and the Member State Committee after proposing to prioritise Pitch, coal tar, high-temp. (CAS 65996-93-2), hereinafter referred to as CTPHT for inclusion in Annex XIV. This report is presented by the Cefic "Coal Chemicals Sector Group (CCSG)".

The Coal Chemicals Sector Group (CCSG) represents European producers of chemicals derived from coal tar (COT) distillation: RÜTGERS Group, Koppers Europe Group, Bilbaina de Alquitranes, Industrial Quimica del Nalón, DEZA, Tar Alliance AM, Daw Bytom.

The main product (approx. 50%) of the distillation of coal tar is the distillation residue CTPHT usually known as "coal tar pitch". The distillates are crude naphthalene and technical fractions (aromatic oils). The major single COT constituents are naphthalene (~10%), phenanthrene (~4.5%) and anthracene (~1.3%). Some constituents (e.g. naphthalene, anthracene, carbazole, phenol, cresols and xylenols) are commercially available.

The CTPHT was among the first substances included in REACH Candidate list on 13 January 2010. Early 2014 ECHA made a revised scoring assessment of CTPHT and concluded that the substance meet the requirements for the prioritisation for Annex XIV. On 1 September 2014 ECHA published the Draft Recommendation for inclusion of the substance in REACH Annex XIV and launched stakeholder consultations, running until 1 December 2014.

This report refers to the background document on CTPHT prepared by ECHA for the public consultation. In parallel there is a public consultation in response to the Commission's call for industry information on the economic impacts of the substances proposed for Annex XIV inclusion. The CCSG has also submitted a report to the Commission (via the ECHA website) on economic impacts.

The present report has the following sections:

1. Basics for a better understanding of CTPHT
2. Manufacture of CTPHT
3. CTPHT downstream use categories
4. CTPHT downstream user key industries
5. Complexity of stakeholder interaction

1. Basics for a better understanding of "Pitch, coal tar, high-temp. (CTPHT; CAS 65996-93-2)"

Mechanism of coke and graphite formation

Carbonaceous materials provide a unique set of properties. Worldwide natural resources of materials with low inorganic contaminants are not satisfying the demand of industry. Therefore industrial processes were developed to manufacture carbonaceous materials like graphite or tailor-made graphite precursors (coke). Carbonaceous materials with a graphitic structure provide for electrical conductivity, mechanical strength and a low thermal expansion. They can be used in the temperature range up to 3000°C and are chemically resistant to metals and slags formed when refining metal ores.

It is not common knowledge that Polycyclic Aromatic Hydrocarbons (PAHs) are building blocks to form graphitic structures. PAHs are planar molecules of a high thermal stability. PAHs polycondensate when heated under oxygen exclusion (pyrolysis, carbonisation, baking) whereas non-aromatic carbonaceous precursors like paraffin tend to decompose.

Fig. 1 provides a model for PAH arrangement capable to form a honeycomb structure (graphene sheet)[1]. In real production this transformation process is more complex and depends on raw material composition and processing conditions. Fig. 2 demonstrates the structural changes occurring with increasing processing temperature. Industrial processes usually stop at a temperature where the property profile of the carbonaceous structure allows a certain application. For graphite formation more than 2500°C are required.

In principle all carbonaceous solids can be converted into coke or graphite by pyrolysis. PAH formation is an unavoidable intermediate step of coke or graphite formation. The polycondensation/ decomposition ratio during pyrolysis determines the process yield and thus the suitability of a raw material.

The yield increases if the raw material had passed a high-temperature process thus already containing a significant PAH-level.

Raw material	Process temperature	coke yield (TGA 1000°C)
Bitumen (distillation)	350°C	17 %
Petroleum pitch (steam cracking)	800°C	34 %
Petroleum pitch (catalytic cracking)	750°C	38 %
Coal tar pitch (hard coal coking)	> 1000°C	42 %

[1] http://blogs.raincii.com/technical-excellence/rutgers-and-the-precursors-of-graphene-posted-by-winfried-boenigk/

<u>Fig. 1:</u> Model for graphene formation by PAH cross-linking

Fig. 2 Molecular re-arrangements when producing graphite[2]

Function of CTPHT

The predominant function of CTPHT is twofold. CTPHT is first used as a glue to bind solid particles and then cross-links the solid particles during pyrolysis.

Liquid CTPHT is mixed with solid particles and coats these particles. The resulting viscous paste is pressed, vibrated or extruded into the shape (usually rectangular solids or cylinders) required for a specific use. The shaped bodies are pyrolysed (carbonised) in a furnace.

The initially thermoplastic CTPHT glue is now a solid with a low electrical resistivity, high mechanical strength and chemical resistance to slag or metal penetration. This explains why CTPHT is today state-of-the-art in many processes.

To conclude:

The pitch, coal tar, high-temp (CAS 65996-93-2)

is used as an intermediate and is transformed into

coke (coal tar), high-temp. pitch (CAS 140203-12-9).

[2] H. Marsh und J. Griffiths, „A high resolution electron microscopy study of graphitization of graphitizable carbon“, Extended Abstracts International Conference on Carbon, Toyohashi Japan, 81 (1982)

For 90% of the volume of coal tar pitch high temperature, this intermediate use is at the first industrial DU of the producer or, in some cases at the level of the second industrial DU, but not further down the supply chain. The remaining non-intermediate uses are very limited.

2. Manufacture of CTPHT (comment regarding CTPHT background document chapter 3)

CTPHT is manufactured from "Tar, coal, high-temp. (COT; CAS 65996-89-6)", a 3.5% co-product of the dry distillation of hard coal in a cokery. COT is collected at the cokery, shipped to tar distillation plants and converted into several new products (end of COT life).

Some COT is traded. About 50 kt/y are consumed as reducing agent in blast furnaces.

The production/use pattern for COT is as follows:

Year		2011	2012	2013
COT Production[3]	[kt]	1,506	1,455	1,443
COT Import[4]	[kt]	89	166	56
COT Export[5]	[kt]	23	- 21	- 7
COT other uses	[kt]	- 50	- 50	- 50
Total COT for distillation	[kt]	1,522	1,550	1,442

This is a significant reduction from 2007/2008 with a EU coal tar production level of 1,750 kt/y basicly due to a shift of steel industry capacity from Europe to Asia. CTPHT is the largest COT product (~50 %w/w). Today's EU COT availability allows the production of appr. 750 kt/y CTPHT. Additional CTPHT volumes are accessible by importing COT or CTPHT.

The 2009 Annex XV dossier reports a CTPHT production of 1,000 kt. The same market data source updated the 2013 CTPHT production volume to 806 kt[6]. Industry estimates a total annual CTPHT availability of 890 kt.

[3] 3.5% of metallurgical coke production
[4] EUROSTAT
[5] EUROSTAT
[6] International Tar Association, Istanbul Oct.15-17, 2014; Dr. Zygmunt Stompel "European Coal Tar Industry - 2014 Overview

Best estimate of today's annual EU28+EEA CTPHT consumption is 570 kt:

Year		2013
CTPHT Production	**[kt]**	**830**
CTPHT Import	[kt]	60
CTPHT Export	[kt	- 320
CTPHT Consumption	**[kt]**	**570**

The production volume is well below the volume of 1,000 -10,000 kt/y reported in the CTPHT background document chapter 2.2. One reason is that CTPHT suppliers report the sales volumes in their REACH registration and the downstream user co-registrants (acting as importer) report volumes for the same uses. The IUCLID reporting system is not preventing multiple counting of identical uses.

Currently there are nine plants producing CTPHT:

BE, CZ, DE, DK, ES (2 sites), GB (2 sites), and PL.

All other CTPHT registrants have registered for import purposes only.

<u>Fig. 3</u> EU28 CTPHT production sites (no site in NO, IS, LI)

3. CTPHT downstream use categories (comment regarding CTPHT background document chapter 2.2 and 3)

The main user of CTPHT based products are industries manufacturing aluminium, steel, ferroalloys and other metals. The main reason is the use of demanding process conditions in these industries excluding other materials for efficient processes. Some advantages of CTPHT have been described before.

CTPHT is either used as such or mixed with other coal tar fractions to meet the technical specification for a specific use.

3a. Intermediate and non-intermediate uses

i) Intermediate uses:

1. In almost all cases of downstream use, either the first or the second downstream user transforms CTPHT (via carbonisation in a furnace at a temperature above 700°C) into another substance, pitch coke, correctly named "Coke (coal tar), high-temp. pitch (CAS 140203-12-9)". Pitch coke is exempt from REACH registration and authorisation under Annex V[7].

   The volume of CTPHT that is an intermediate used for the synthesis of pitch coke in the EU is approximate 89% (510 kT).

   Note that not all uses are handled as an intermediate under Strictly Controlled Conditions (SCC) which means that the registration dossier carries a full registration despite CTPHT acting as an intermediate.

   Pitch coke is a vital product and is used by the Aluminium and other metals smelters industries. Pitch coke- cross-linking petroleum coke grains- has the essential property required for example in an aluminium smelter: it conducts electricity and this is fundamental for the electrolysis process that produces aluminium from cryolite. CTPHT does not conduct electricity and cannot be used in a smelter process.

2. Intermediate in the manufacture of carbon black:
   For a volume of CTPHT (40 kT), use is as an intermediate for the production under SCC of carbon black (CAS 1333-86-4).

[7] ECHA Guidance for Annex V Exemptions from the obligation to register, Version 1.1 Nov 2012, p.43

3. Intermediate in the manufacture of other substances:
   CTPHT is also used as an intermediate in the manufacture of a range of other substances, again each with their own CAS number, for example (Coke (coal) semi (CAS 68409-95-0), Coke (coal tar), high-temp. pitch (CAS 140203-12-9) and Pitch, coal tar, high-temp., heat-treated (CAS 121575-60-8))

ii) Exempt uses

CTPHT is used in low volumes (1 kt) as a fuel, exempt from authorisation under article 56(4)(d).

iii) Non-intermediate uses:

1. Clay targets for (moving) target shooting:
CTPHT is mixed with solids and directly incorporated into articles. The volumes involved are 15 kt.

2. Airport runways and heavy-duty corrosion protection (professional use)
CTPHT is mixed with other coal tar substances and with solids for use in the repair of airport runways and for corrosion protection . Volumes are approx. 2 kt.

3b. Detailed list of uses and volumes

The CTPHT downstream uses and related volumes can be categorized as follows:

End of CTPHT life before use: at DU 1 level, the CTPHT is transformed to another substance.

USE 1. INTERMEDIATE USE: CTPHT is mixed with solids, shaped and carbonised to form pitch coke (CAS 140203-12-9) [**360 kT**]. The products that result include:

a. Binder for prebake anodes for the aluminium industry

b. Binder for cathodes for the aluminium industry

c. Binder for graphite electrodes for the steel industry

d. Binder for prebake electrodes for the metallurgical processes, CaC_2

e. Binder or coating agent for carbon/graphite specialities

f. Binder for activated carbon production

g. Binder for carbonised refractory products

USE 2: INTERMEDIATE USE: CTPHT fills pores of prebaked products and is carbonised to form pitch coke (CAS 140203-12-9) [**40 kT**]. The products that results include

a. Impregnating agent for graphite electrodes

b. Impregnating agent for graphite electrode connectors (nipples)

End of CTPHT life during use: at DU 1 level the CTPHT is mixed and shaped (e.g. to form anodes); the shaped bodies still containing CTPHT are then shipped to DU2. At DU 2 level (e.g. aluminium smelters) there are 2 steps: (i) the shaped bodies are carbonised to form pitch coke containing articles (ii) the carbonised pitch coke products are used in the aluminium production process.

USE 3: INTERMEDIATE USE: CTPHT is mixed with solids, shaped and shipped to DU 2; the CTPHT is then carbonised into pitch coke before being used in the production process of DU2 [**70 kT**].
The products produced by DU1 include:

a. Binder for Søderberg electrodes (aluminium, ferroalloys and other metallurgical processes)

b. Collar paste for prebake anodes for the aluminium industry

c. Binder for shaped refractories for the steel industry, alloys

d. Impregnating agent for refractories

USE 4: INTERMEDIATE USE: CTPHT in mixture with other coal tar fractions is mixed with solids, shaped then shipped to DU 2; the CTPHT is then carbonised into pitch coke before being used in the production process of DU2 [3 kT].
The products produced by DU1 include:

a. Binder for cathode ramming paste (maintenance of Al electrolysis cells) and furnace lining paste (metallurgical processes)

b. Binder for tap hole paste and runner mix (blast furnace iron production)

USE 5: INTERMEDIATE/EXEMPT USE: CTPHT in mixture with other coal tar fractions is oxidised [**40 kT**]

a. Use as raw material for "Carbon black (CAS 1333-86-4)" production (under strictly controlled conditions) – INTERMEDIATE

b. Use as fuel (energy recovery) – FUEL IS EXEMPT (Art. 56(4)(d))

USE 6: INTERMEDIATE USE: CTPHT is transformed in the manufacture of other substances without adding solids [**40 kT**]

Use as an intermediate in the production of other substances, e.g. Coke (coal) semi (CAS 68409-95-0), Coke (coal tar), high-temp. pitch (CAS 140203-12-9) and Pitch, coal tar, high-temp., heat-treated (CAS 121575-60-8. CAS 140203-12-9 (Pitch coke) is e.g. used for nuclear graphite applications, and CAS 68409-95-0 (semicoke) is used for the production of carbon ceramics.

Note: As mentioned previously, because not all these intermediate uses are under strictly controlled conditions as defined by the ECHA guidance, they are not registered as intermediates. However, as intermediates they fall outside the scope of authorisation as mentioned in Chapter 2.2 of the CTPHT background document (exemption under REACH Art. 2 8(b)). Note also that the end-of-life of CTPHT is under industrial control and that there is therefore no risk of exposure to CTPHT for the general population.

End of CTPHT life not achieved during use; here CTPHT is incorporated into articles or mixtures.

USE 7: NON-INTERMEDIATE USE: CTPHT is mixed with solids and shaped **[15 kT];** the article that results is clay targets.

Binder for clay targets (Leisure use organised by professionals)

USE 8: NON-INTERMEDIATE USE: CTPHT in mixture with other coal tar fractions is mixed with solids. **[2 kT]** The products that result include:

a. Binder for airport driveway repair work (technical reason: kerosene resistance)

b. Heavy corrosion protection for e.g. coating of pipelines and nuclear waste containers (professional use).

4. CTPHT Downstream use key industries

As the safe use of CTPHT requires substantial industrial infrastructure the number of sites is limited. Aluminium industry is by far consuming the largest CTPHT volume (60-70%). Electrolysis cells at aluminium smelter site consist of cathodes (put in place only once in a cell life) and consumable anodes.

Aluminium smelter in EU27+EEA[8] : 26 plants thereof 18 plants are manufacturing anodes:

Anode plants (Al): 14 (on smelter site; prebake technology)

1 stand-alone anode plant

3 (on smelter site; Søderberg technology)

⇨ 9 smelter rely on anode purchase only

The cathodes required for smelters are not produced in anode plants as they are passing a graphitization process not available in anode plants. They are purchased from carbon/graphite industry. The largest volume product of carbon/graphite industry is graphite electrodes for furnaces recycling steel scrap (EAF) thus related to steel industry. This demonstrates the dependency of industries. It is more efficient to use the existing infrastructure of a given plant for the manufacture of several CTPHT based products (cathodes and graphite electrodes in this case) requiring the same production process.

For more details we refer to submissions by the industries concerned.

[8] DHI/Arcadis Report for European Aluminium Association, "Risk Management Option Analysis "Pitch, coal tar, high-temp", March 2014

5. Complexity of stakeholder interactions (response to Background Document chapter 4)

The communication through the supply chain proofs to be difficult. The focus of each sector is different and it is extremely difficult to get the industries aligned in a project. This experience was gained when working on the Chemical Safety Reports for REACH registration. The confidentiality of some information requires using consultants for the exchange of information in the supply chain. Additional efforts to correct and refine the information and the conclusions are needed as the consultants usually understand the REACH process but not the supply chain and uses of a product.

Organisation of compliance with competition law requires much time which is in contrast to the more optimistic view of the Background Document Chapter 4. This means that CTPHT producers anticipate that authorisation dossier preparation will need more time than foreseen by ECHA.

CCSG Members are open to provide additional information clarifying questions.