Status of Coal Tar Pitch, high temperature (CTPht) as an intermediate in the manufacture of carbon and graphite products

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Summary

Intermediate *means a substance that is manufactured for and consumed in or used for chemical processing in order to be transformed into another substance […].*

On-site isolated intermediate *means an intermediate not meeting the criteria of a non-isolated intermediate and where the manufacture of the intermediate and the synthesis of (an)other substance(s) from that intermediate take place on the same site, operated by one or more legal entities.*

Transported isolated intermediate *means an intermediate not meeting the criteria of a non-isolated intermediate and transported between or supplied to other sites. Ref. REACH Art 3.15(c)*

Intermediates are ***exempted*** *from authorisation. (ref REACH Art. 2(1c) and Art. 2(8b))*

During manufacturing of carbon & graphite products coal tar pitch, high temperature (CAS-No. 65996-93-2) as used in the carbon and graphite industry is transformed by a thermally induced chemical synthesis into coal tar pitch coke (CAS-No. 140203-12-9). Consequently, coal tar pitch is considered as an intermediate under the REACH legislation. This is valid regardless of this chemical synthesis taking place at the manufacturer site (on-site isolated intermediate) or at the end user site (transported isolated intermediate).

CTPht is also used with adequate fillers in ramming pastes, taphole clays, mouldables, groutes, collar pastes. These pastes are sold to the end-user without thermal treatment at the manufacturer site. All types of pastes (e.g. lining, collar, ramming) with a primary seal function may not be considered as intermediates acc. to REACH, Art. 3,15.

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Production Process of Carbon Materials and Graphite Materials

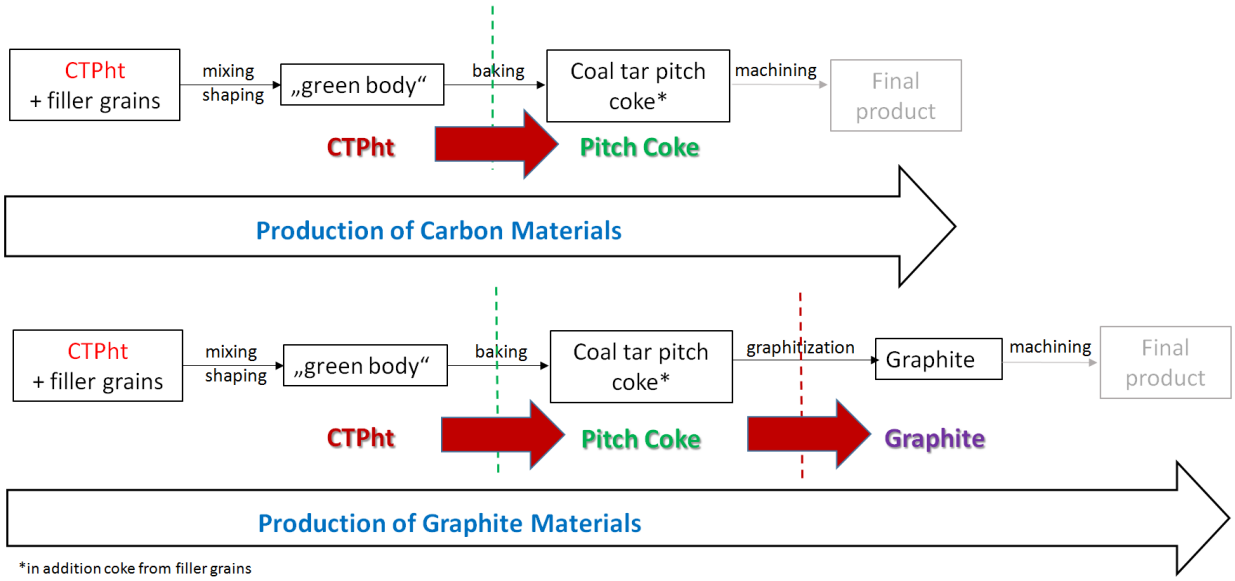


Fig.1: General Overview: Production of Carbon and Graphite Materials

Introduction

ECGA members use coal tar pitch, high temperature (CTPht; CAS-No. 65996-93-2) to manufacture coal tar pitch coke (CAS-No. 140203-12-9) during the production of polygranular carbon materials or synthetic graphite materials (Fig.1, 3).

Products which contain polygranular carbon are for example cathodes, carbon electrodes (Soederberg electrodes), and furnace linings (Fig. 3). Products which contain synthetic graphite are for example graphite electrodes, specialty graphite, graphite cathodes and graphite linings (Fig. 4).

Carbon materials are manufactured in different steps. After forming a so-called *green body* from the filler grains and coal tar pitch, chemical reactions (polycondensation, polymerization) during baking transfer coal tar pitch into coal tar pitch coke. By an additional graphitization step (heat treatment > 2200 °C) carbon materials can be transformed into synthetic graphite (Fig. 2, 3, 4, 8).

Densification of carbon bodies by coal tar pitch impregnation and subsequent rebaking induces the same chemical reaction as during the first bake. The coal tar impregnation pitch is transferred into coal tar pitch coke (Fig. 5, 6, 7).

The geometrical shapes of these carbonaceous or graphite bodies do not allow their final application. Consequently, they must be considered mixtures or substances, respectively, until

they are machined to the final shape. This machining step transfers these bodies into articles (Fig 2, 3, 4, 8).

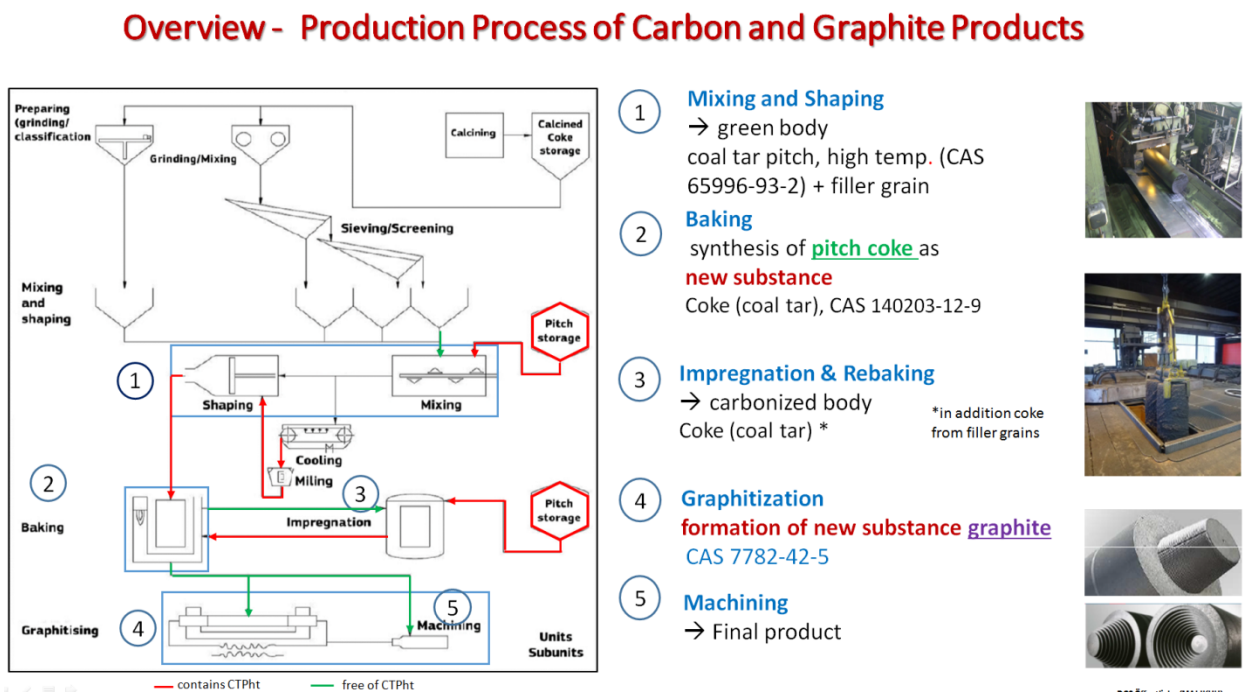


Fig. 2: Overview – Production Process of Carbon and Graphite Materials

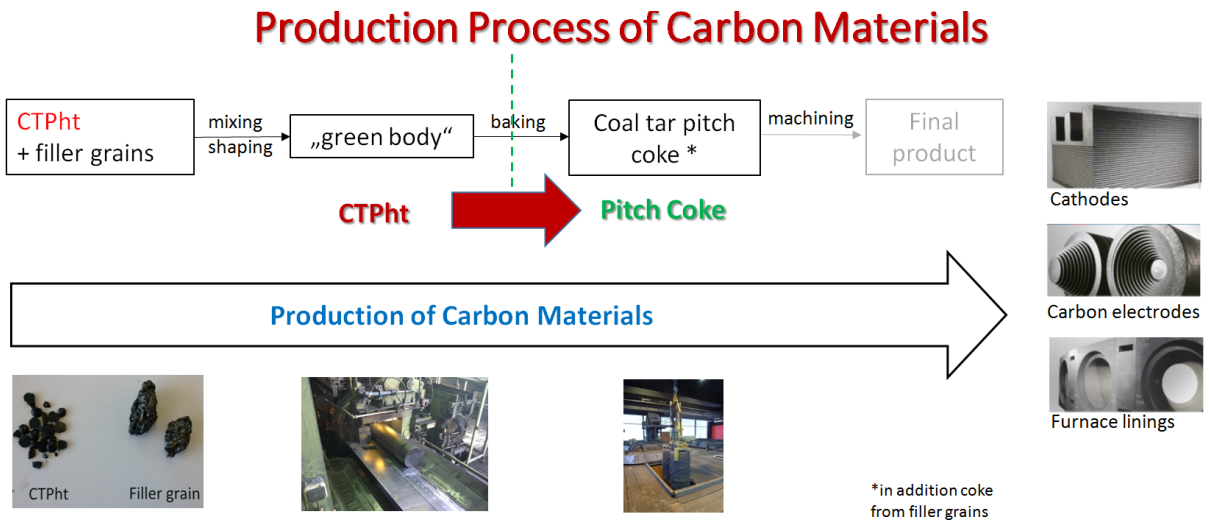


Fig. 3: Manufacturing process of Carbon Materials

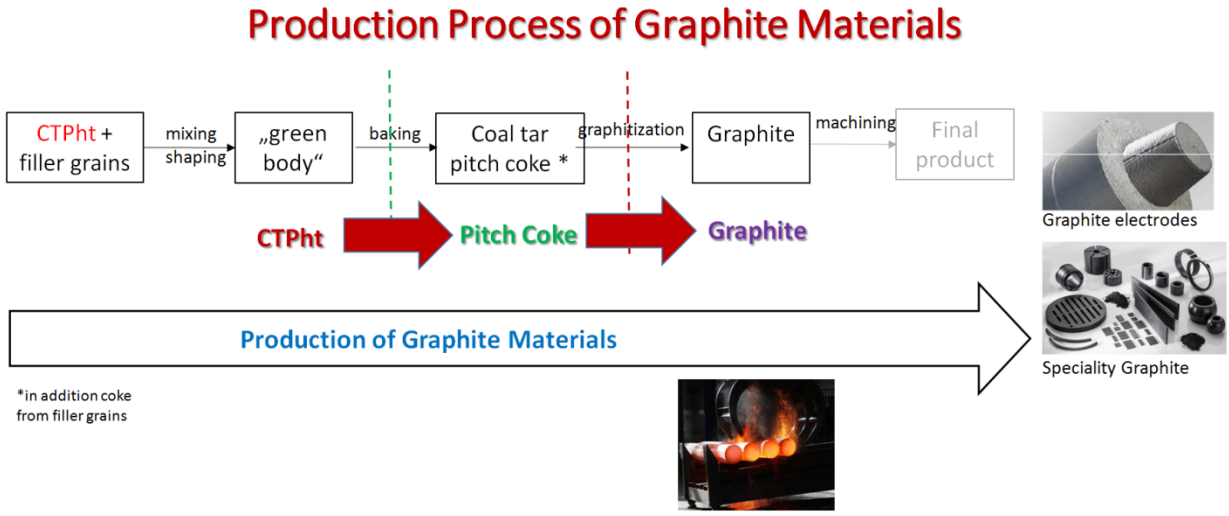


Fig. 4: Manufacturing process of Graphite Materials

Mixing and forming:

Due to the unmeltable nature of the filler grains (e.g. coke, graphite, anthracite), the manufacturing process of polygranular carbon materials entails several process steps. In a first step the “green body” is produced. The filler grains are incorporated homogeneously into the CTPht (pitch) (which serves as a meltable parent substance/precursor for the pitch coke) by the physically mixing the components at temperatures at which the pitch is liquefied. In a subsequent forming step (extrusion, moulding) an approximate geometry is shaped; typical shapes are

cylindrical or rectangular. During cooling to room temperature, the pitch solidifies, maintaining its chemical identity. The so called "green body" is still a mixture of substances (Fig. 2, 3, 4).

The green body at this stage still does not fulfill the criteria of an article in accordance with REACH, because its shape and intrinsic properties do not meet the requirements of the final product. These are first met after baking or graphitization, followed by machining.

CTPht is used with adequate fillers in ramming pastes, taphole clays, mouldables, groutes, collar pastes. These pastes are sold to the end users without thermal treatment at the manufacturer site.

CTPht is also used in Søderberg electrodes and briquettes. CTPht in these products is transformed in situ via the chemical synthesis polycondensation and polymerization (continuous self-baking) turning the electrode mass into Coal Tar Pitch coke (CAS-No. 140203-12-9) at the bottom tip of the electrode column, based on the heat supplied into the process. CTPht in such products can thus be considered being a transported isolated intermediate.

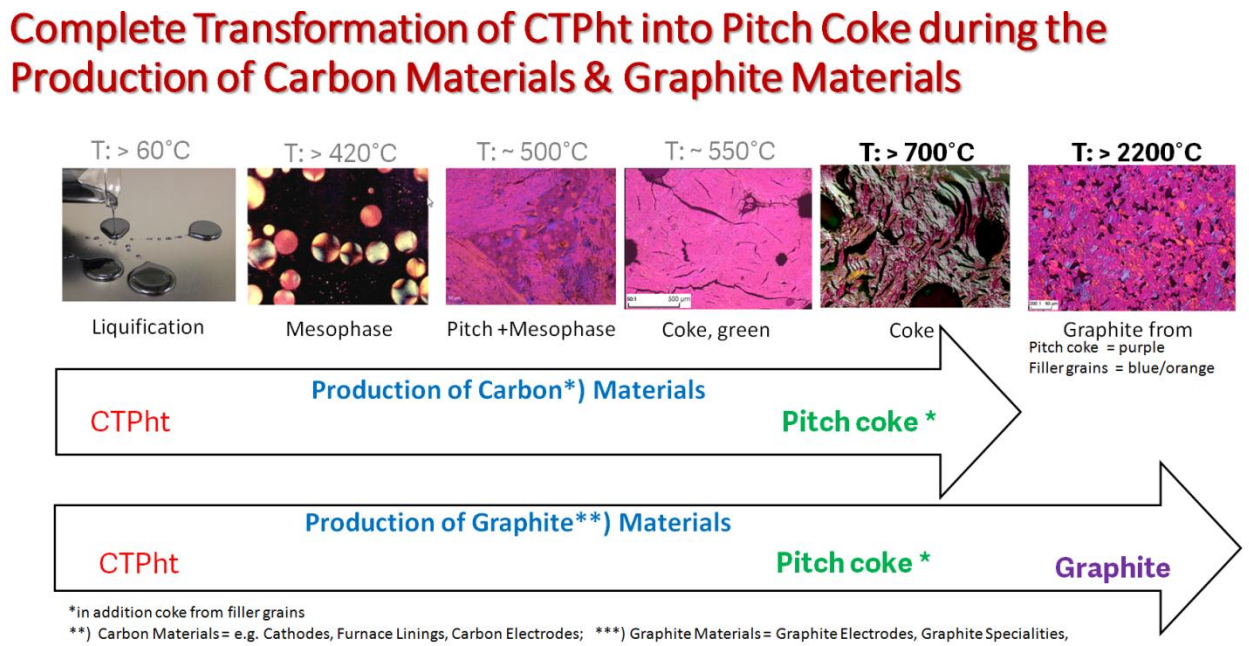


Fig. 5: Transformation of CTPht into coal tar pitch coke

Baking (carbonization, pyrolysis):

The synthesis of the coal tar pitch coke matrix (also called "carbonised mixture") is achieved by exposing the "green body" to minimum temperatures of around 550 °C, (see also Fig. 6, TGA-DTGA-Analysis). The substance CTPht serves as the meltable parent substance (precursor) for the final product, i.e. coal tar pitch coke (CAS-No. 140203-12-9), resulting from its chemical reaction (synthesis). The manufactured coal tar pitch coke is formed via complex chemical

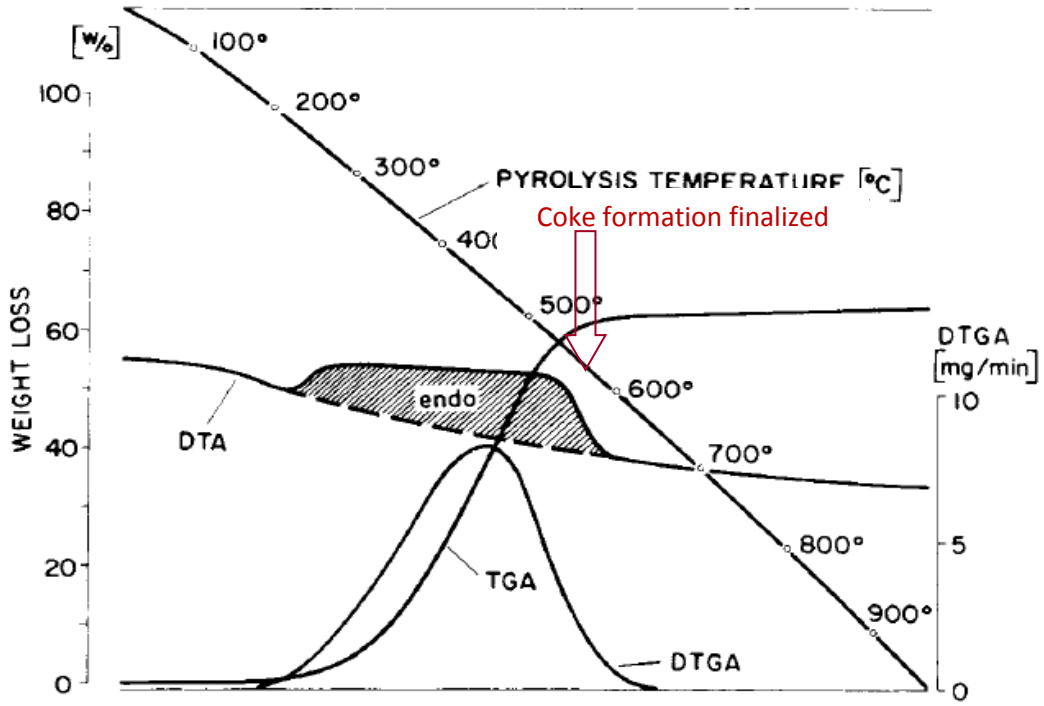
reactions (polycondensation and polymerization)[1] primarily in the liquid crystalline state (mesophase). This is a crucial condition for the subsequent manufacturing of synthetic graphite. The chemical reactions start at temperatures > 420 °C under the release of gaseous (e.g. hydrogen, benzene, carbon monoxide) and condensable products (e.g. polycyclic hydrocarbons). During liquid-phase pyrolysis of the coal tar pitch optically anisotropic spherulites (mesophase) are formed (Fig. 5). The spherulites are nematic liquid crystals composed of large lamellar aromatic molecules which touch each other and finally coalesce. These characteristic morphological features in the liquid phase are the results of multiple pyrolytic reactions that cause hardening to a semi-coke and ultimately coal tar pitch coke. The transformation into pitch coke is considered complete after achieving temperatures ~ 550 °C (Fig. 5, 6) based on customer requirements of the carbonaceous body such as thermal and electrical conductivity and oxidation resistance, as well as mechanical characteristics such as hardness, the elasticity module and strength.

The shape, surface and design of the resulting so called "carbonised mixture" is of no relevance, as the "carbonised mixture" does not fulfill any other function besides use for further processing. The coal tar pitch coke body cannot be used without further processing and the shape of the block is a result of technical requirements. Consequently, the transformation product, coal tar pitch coke is a substance under REACH and not an article.

In the case of Soederberg electrodes (including cylinders, briquettes and blocks) that are transported to the end users, CTPht in such products can thus be addressed as isolated transported intermediate. At the end user sites, the electrode mass is baked into a solid body when reaching the hot zone (350 – 550 °C). As a result, CTPht is transformed into the new substance, i.e. coal tar pitch coke.

Coke (CAS-No. 140203-12-9) is exempted from registration in accordance with REACH, Annex V[2].

[1] The chemistry of the pyrolitic conversion of organic compounds to carbon; E. Fitzer, K. Mueller, W. Schaefer; page 237ff.
[2] ECHA guidance for Annex V: https://echa.europa.eu/documents/10162/13632/annex_v_en.pdf



(Ref.: Footnote 1; page 265)
Fig. 6: TGA for the pyrolises of coal tar pitch, softening point 55°C

TGA= Thermal Gravimetric Analysis
DTGA= Derivative Gravimetric Analysis
DTA = Differential Thermal Analysis

In materials science, thermoanalysis is a renowned method for the detection and quantification of chemical reactions and phase transition in solids. Figure 1 displays the Differential Thermoanalysis (DTA) and Thermogravimetric Analysis (TGA) of coal tar pitch as a function of temperature. The figure clearly illustrates an endothermic pyrolysis reaction at a temperature range between 250 and 600 °C. The strong DTGA signal proves the formation of a new substance, i.e. coal tar pitch coke. The absence of further DTA signals shows that this coal tar pitch coke phase is stable and does not undergo further phase transitions or reactions up to a temperature of 1000 °C.

This conclusion is further substantiated by electron microscopic examinations (see fig. 5) revealing corresponding morphological changes during the transformation of coal tar pitch into coal tar pitch coke.

Production Process Carbon & Graphite Materials - Impregnation

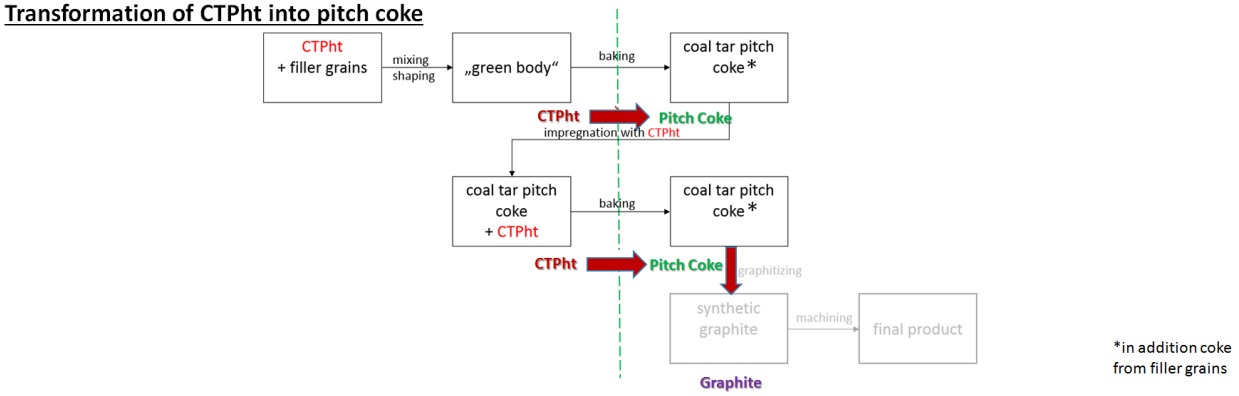


Fig. 7: Production process - Impregnation

Impregnation:

It is state of the art in particular for the production of graphite electrodes and graphite connecting pins to densify these baked materials by subsequent impregnation with coal tar pitch and rebaking. The aim of this process is to improve the mechanical properties according to customer requirements.

Liquid CTPht at temperatures > 150 °C is infiltrated under vacuum into the carbonized material followed by carbonization (T: > 550 °C) (Fig. 7).

The impregnation agent CTPht is completely transformed by the chemical reactions of polycondensation and polymerization into coal tar pitch coke, which is already described in previous section “Baking”.

The fact that the intermediate CTPht is used for (repeated) impregnation and baking steps does not have an influence on the purpose of the overall process (manufacture of a subsequent substance which then is used to produce other substances or specific products).

Production of Graphite Materials - Graphitization

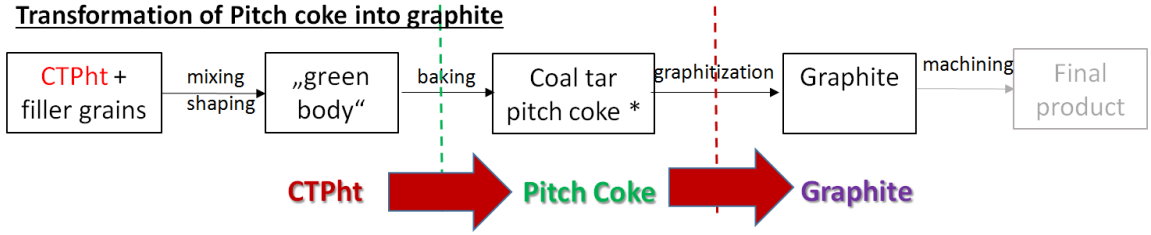


Fig. 8: Production Process - Graphitization

Graphitizing:

During the graphitization of baked carbon materials the coal tar pitch coke is transformed into graphite in a solid state reaction. This solid state reaction at temperatures above 2200 °C requires the liquid state pyrolysis during the baking process, providing the necessary pre-arrangement of the aromatic sheet structure (Fig. 8).

The resulting carbon materials are annealed at temperatures > 2200 °C at which the carbon atoms build a hexagonal graphite layer structure (CAS-No. 7782-42-5).
The structure of the carbon changes during graphitization as the temperature increases. The size and degree of perfection of the individual graphite crystallites increases and the purity of the material continues to improve, as virtually all impurities evaporate. Thermal and electrical conductivity and oxidation resistance are simultaneously improved during the graphitization process. Mechanical characteristics such as hardness, the elasticity module and strength, on the other hand, deteriorate. The increase in crystalline structure is also demonstrated in the increase in density and the reduction in the thermal coefficient of expansion.

Coke (coal tar), high temp. pitch (CAS-No. 140203-12-9) is completely transformed into the substance graphite (CAS-No. 7782-42-5) via solid state transformation.

Conclusion

According to the relevant sections of the REACH regulation[3], Art. 3(15), Art. 2(1c), Art. 2(8b) and the corresponding ECHA guidance documents[4] [5], the substance **CTPht is an intermediate under REACH**, both on-site isolated intermediates and transported isolated intermediates, when used in the process of “coal tar pitch coke synthesis” and therefore exempted from authorisation obligations.

[3] REACH regulation: http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:02006R1907-20140822

[4] ECHA – Guidance on intermediates: https://echa.europa.eu/documents/10162/13632/intermediates_en.pdf

[5] ECHA – Guidance on articles: http://echa.europa.eu/documents/10162/13632/articles_en.pdf