Raw Materials

Introduction

Artificial graphite is manufactured from coke and binder.

Overview

Introduction

- Petrographic Atlas
- Naturally occurring raw materials are natural graphite and anthracite.

Coke is a solid high in content of the element carbon and structurally in the NON-GRAPHITIC STATE: It is produced by pyrolysis of organic material which has passed, at least in part, through a liquid or liquid-crystalline state during the CARBONIZATION process. COKE can contain mineral matter. Click here for coke grades. The production process of coke.

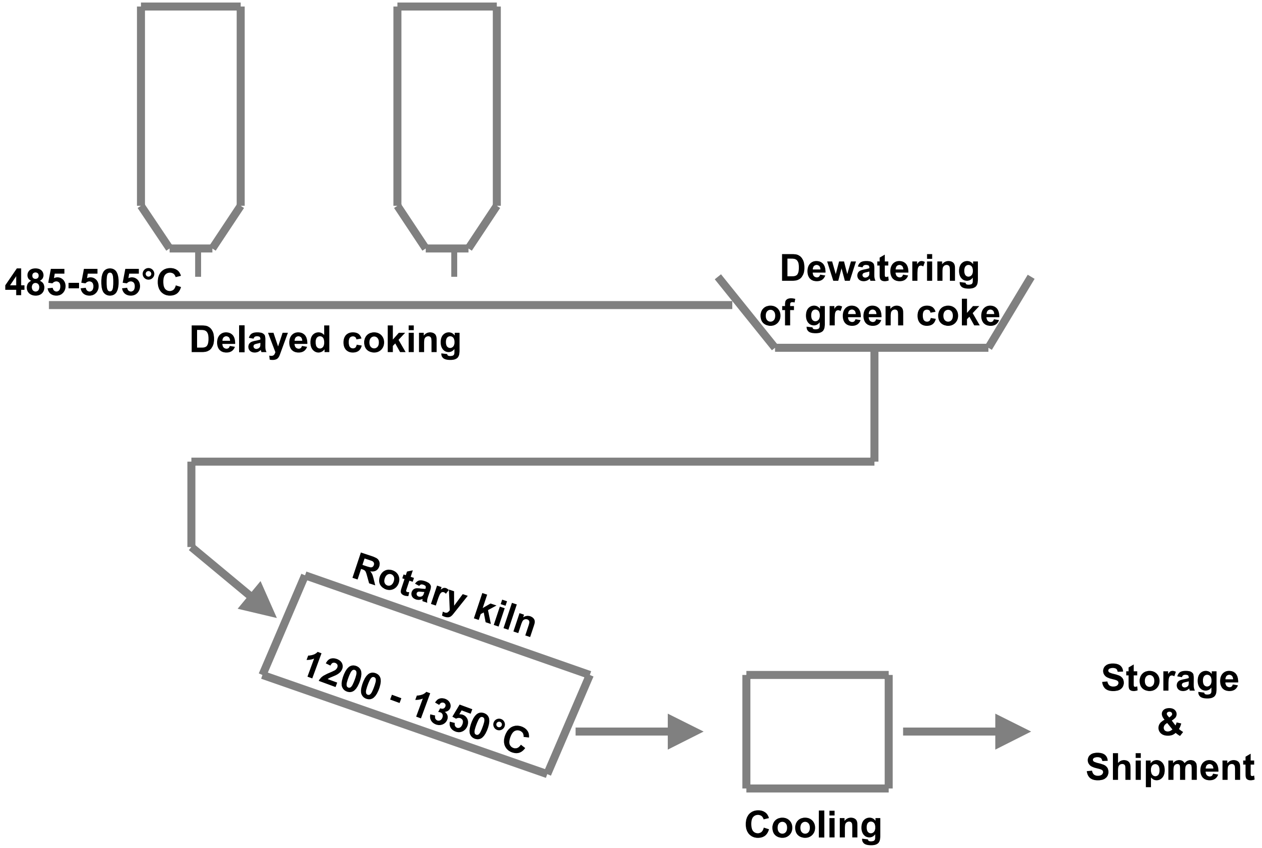
Overview

Raw Material for Carbon/Graphite Products

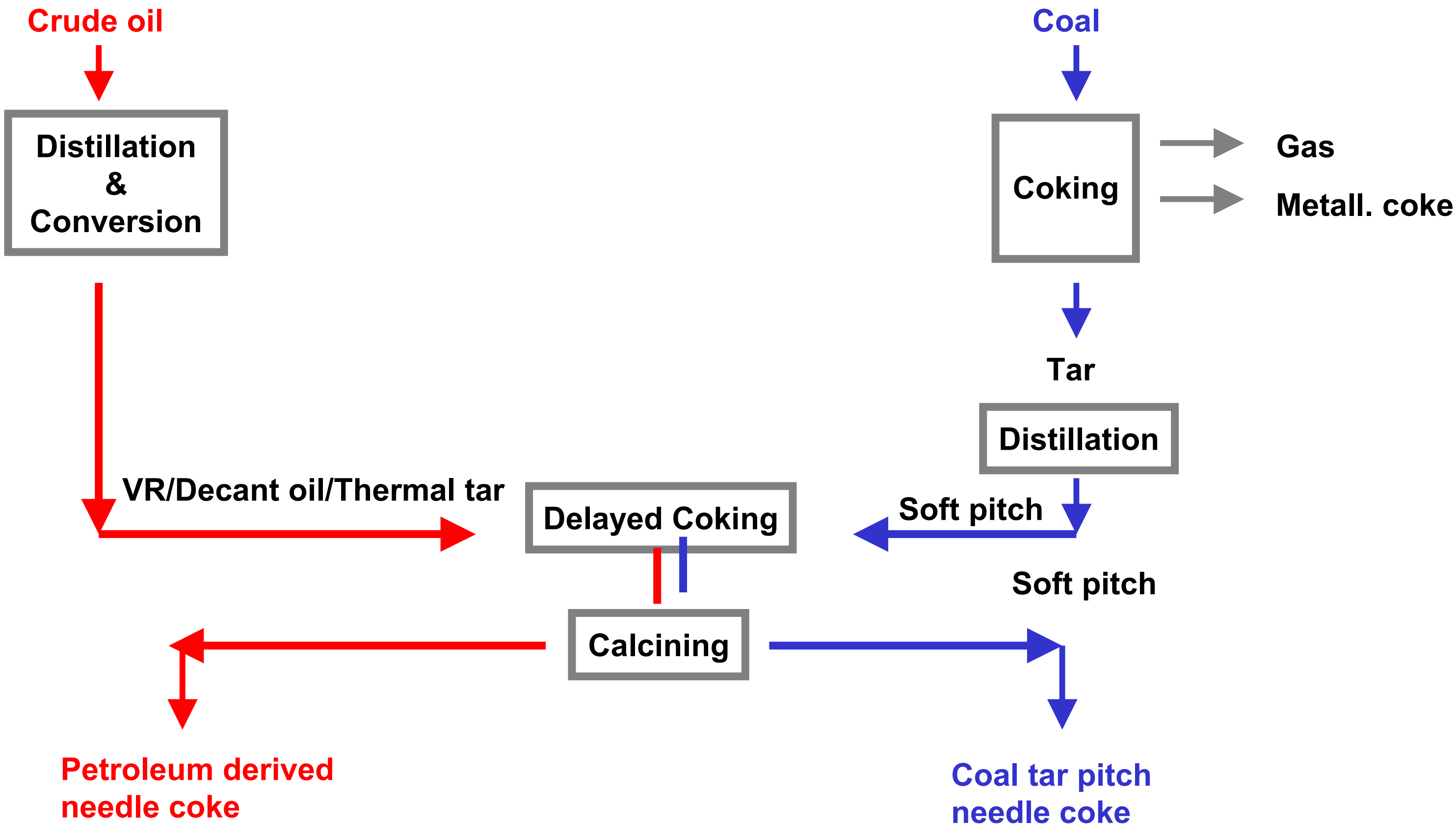
	GE/NIP	CARBON EL.	CATHODES	B.F. LININGS
Dry Raw Materials	Pet coke	ECA Anthr. Graphite (*) Pet coke	ECA Anthr. GCA Anthr. Graphite (*) Pet coke	ECA Anthr. GCA Anthr. Graphite (*) Pet coke
Binders	Pitch	Pitch	Pitch	Pitch

(*) various grades

Coke Production



Needle Coke Production



Coke grades

GRADE	COKING
Fluid Coke	Fluid Coking
Fuel Coke	Flexi Coking
Anode Coke	Delayed
Needle Coke	Coking

Cokes

Coke is a synthetic raw material used for producing carbon in combination with binding agents (or binders).

There are different kinds of coke, e.g. **petroleum coke**, **pitch coke**, **metallurgical coke**, **carbon black**, **needle coke**.

For a summary of their characteristic date click here.

Characteristic data

	Petrol Coke	Pitch Coke	Metallurgical Coke
Density at 1300°C (g/m^3)	**2.11 - 2.14**	**2.07 – 2.11**	**Missing**
Ash (%)	**0.1 – 0.3**	**0.2 – 0.4**	**Missing**
Sulphur (%)	**0.2 – 1.8**	**0.2 – 0.6**	**Missing**
CTE (10^{-6}/K)	**4.5 – 10.5**	**8.0 – 10.5**	**Missing**

CTE: Coefficient of Thermal Expansion, determined from coke grain after heating to 2800°C

Standard Properties of coke

Coefficient of Thermal Expan-sion CTE:	**most important quality factor because the electrode CTE mostly influences material behavior**
Xylene Density:	**gives a rough idea about the coke quality but depends on calcining conditions (temperature)**
H-content:	**gives information on calcining temperature**
S-content:	**gives information on puffing (N-content in case of CTP cokes)**
VBD:	**gives information on the packing density**
Ash:	**gives information on the feed**
Graphitizability Index:	**calculated structural index from microscopy analysis, strongly correlated with CTE**

Different kind of cokes

Petroleum coke (picture)

Petroleum coke, as far as quantity is concerned, is the most important raw material, and it is formed in a wide range of structures - from highly anisotropic needle coke to nearly isotropic fluid coke. The highly anisotropic needle coke, due to its structure, is indispensable for the manufacture of high-performance electrodes used in electric arc furnaces, where a very high degree of electrical, mechanical and thermal load-bearing capacity is required. For fine-grained graphites, it plays a less significant role, since its highly ordered structure is destroyed by the crushing and milling operations which are used to obtain a powder with the required low grain size. Petroleum coke is almost exclusively produced by the delayed coking process, which is a mild slow carbonising procedure of crude oil distillation residues. Click here for the table comparing the characteristics of petrol, pitch and metallurgical coke.

Different kind of cokes

Green coke

When petroleum coke is produced by the delayed coking process which is a mild slow carbonising procedure of crude oil distillation residues, it is called green or raw coke. It still contains considerable amounts (approximately 5 to 12%) of aliphatic constituents, hydrogen and heteroelements; which, at elevated temperatures, are set free as volatile matter. This mass loss leads to high shrinkage of the coke and to the formation of pores and cracks, which generally rules out a direct processing of green coke to shaped artefacts. Therefore, they are mixed with either a coal tar pitch of relatively low viscosity or an anthracene-oil refluxed pitch or a crude tar. The green coke is calcined at 1200 to 1400°C mainly in rotating kilns or hearths. During this treatment the volatile constituents of the coke are reduced to less than 0.5%.

Different kind of cokes

Pitch coke

Pitch coke is manufactured from thermally treated coal tar pitch either by using the delayed coking process, or by means of conventional coking procedures. Its structure is less ordered than petroleum coke, but its strength and hardness are higher. Click here for the table comparing the characteristics of petrol, pitch and metallurgical coke.

Application of pitch

Characterization

Typical properties

Function of binder pitch

Function of Binder Pitch

1 – Plastifies the green mix, thus permitting the body to be shaped (by extrusion, moulding, vibration.....);

2 – Acts as a binder in the green body: glues the mix dry components;

3 – Acts as a binder in the baked artefact as “pitch coke” and connects the dry components definitively.

4 – The amounts of pitch required depends on the property of filler material and grain size.

Application of binder pitch

- Aluminium industry	- Prebaked anodes - Söderberg anodes - Ramming paste - Cathodes
- Electric Steel Industry	- Graphite electrodes
- Speciality Application	- Clay pigeons - Refractory bricks - Brushes - Specialy graphite - Carbon electrodes - Fibres - Carbon/carbon composites - Calcium carbide - Arc carbon (welding) - High temp. processing of metals, glass and ceramics - Mechan. graphite

Pitch Characterization

Pitch

- **homogeneous phase composed of several hundreds compounds (multi-ringed aromatics & heteroaromatics)**
  30 % can be identified only
- **Solid phase (quinoline insolubles, QI)**

- primary QI
  - **normal QI**: **soot**, **spherulitic carbon**
  - **pyrolytic carbon**
  - **pitch coke**
  - **carry-over**: **cenospheres**, **coke**, **coal**, **mineral matter**
- secondary QI
  - **carbonaceous mesophase**

Typical Properties of Pitch

	Binder Pitch	Impregnation Pitch
Softening point (M)°C	83 - 115	65 - 90
QI %	5 - 13	1 - 5
TI %	24 - 33	14 - 20
Coking value %	50 - 60	42 - 48
Viscosity (150°C) mPas	1206 - 4500	300 – 1200

Different kind of fillers

Carbon black (picture)

In contrast to the soot formed under normal combustion conditions, industrial carbon blacks, with maximum particle diameters of several nanometres, are produced on a large scale at considerably higher temperatures. They are practically free from physiologically hazardous polycyclic aromatic hydrocarbons (PAHs). These blacks have a very fine particle size, which makes them unsuitable for processing directly into solid shapes.Therefore, they are mixed with either a coal tar pitch of relatively low viscosity or an anthracene-oil refluxed pitch or a crude tar of high viscosity or a mixture of these substances to give a plastic material which is formed by tamping or extruding into bale or noodle-shaped bodies that can be processed more easily. These petroleum artefacts are baked and calcined at temperatures between 1200 and 1400°C. The material thus produced is called carbon black or lamp black coke and may be used the same way as petroleum, metallurgical, green, or pitch coke. This relatively expensive manufacture of a raw material is justified by some very special properties of the product obtained. The very low microcrystalline order of the carbon black is not significantly improved even by graphitisation. Especially the crystalline growth along the a-axis remains limited, so that the graphitised carbon black coke retains its microcrystallinity already set by the initial particle size of the carbon black. This results in a very consistent, relatively high electrical resistance, and high hardness compared with other graphite material. These properties make such raw material well suited for electric carbon brushes and for special mechanical applications. For data of the crystallite size L_a along the a-axis and of the average layer distance c/2 click table.

Different kind of cokes

Needle coke:

Needle coke is the commonly used term for a special type of coke with extremely high graphitizability resulting from a strong preferred parallel orientation of it's turbostratic layer structure and a particular physical shape of the grains.

Click here for the production process of needle coke.

Typical needle coke properties

Typical Needle Coke Properties

Property / *Coke grade*	*Base premium*	*Intermediate premium*	*Super Premium*
CTE 20-200°C µm/(K.m)	< 0,65	< 0,5	< 0,4
Xylene density g/cm³	2,11 - 2,12	2,12 - 2,13	2,13 - 2,15
H-content %	0,035 - 0,05	0,035 - 0,05	0,035 - 0,05
S-content %	< 0,60	< 0,55	< 0,50
Vibration density g/cm³	0,78 - 0,82	0,78 - 0,82	0,78 - 0,82

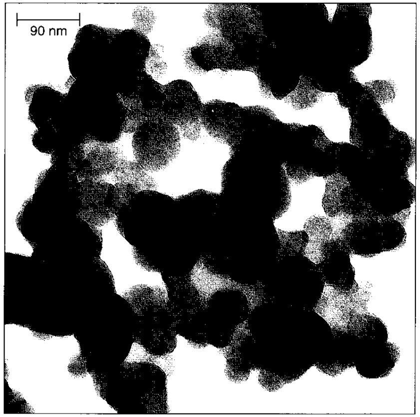
Tab. 1: Typical coke properties for graphite electrode production

Different kind of cokes

- Picture of petroleum coke

Different kind of fillers

- Picture of carbon black



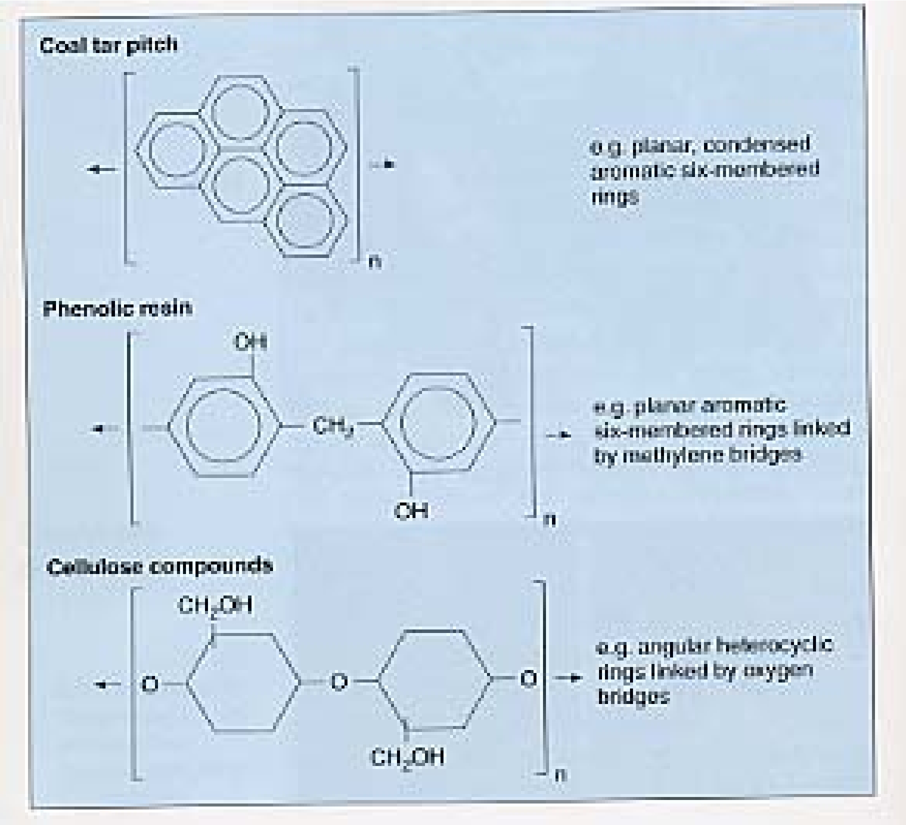
Characteristic data of raw materials

	Graphitized carbon black coke	Graphitized petroleum coke	Natural graphite
L_a (nm)	5-15	> 40	100 – 100.000
C/2 (nm)	0.350 +/- 0.005	< 0.340	<0.336

Binders

Binding agents are used to agglomerate the solid particles to each other. Their high wetting ability thus transforms the mix into a plastic state for subsequent molding or extrusion. In addition, binders must produce a high coking residue in order to produce the necessary strength of the carbon artefacts. The structure of the binder coke formed plays a marked role for many technical applications, as its graphitizability depends largely on the binder coke structure. In addition to the solid phase, the binder also influences conductivity, strength, density and sliding properties of the artefacts. Thermoplastic substances, especially some resin systems, yield only a relatively low coking residue, and they are not suited for the manufacture of all products which require a carbonising or graphitising step. Consequently the binders tend to dominate the properties of the final product as it is consisting up to 70% by weight of the binding agent. Organic binding agents are: **pitch**, **phenolic resins**, **cellulose compounds**. Click here to view their chemical structure. The yield of the coking residue may be increased by condensation processes, either by thermal condensation up to 300°C or above or by chemically adding sulphur, chlorine or nitrogen compounds, also at elevated temperatures. This increased coke yield is coupled with a higher isotropy of the binder coke structure depending on the nature and amount of the condensating agents. For a number of special carbon grades, synthetic resins with a high coke yield may be used as binders. These are almost exclusively thermally setting, duroplastic resins on the base of phenol formaldehyde, furan and furfuryl alcohol.

Chemical structure



Binders

Pitch

Pitch is an organic compound and has a distinct aromatic structure. Due to its high proportion of substituted and condensed benzene rings, it already has the distinctly preformed hexagonal lattice structure of graphite, thus facilitating the formation of well-ordered graphitic domains during graphitisation. Pitch proves to be the most advantageous binder. It is the distillation residue of coal tar; and according to the desired application purpose, it is produced from selected or thermally processed raw tars. Since it is a solid at room temperature, it is usually characterised by its softening point and coking residue and selected according to its application.

Chemical structure of pitch

Binders

Phenolic resins

Upon thermal curing, phenolic resins form an amorphous three-dimensional network structure, which is interconnected by oxygen and/or aliphatic methylene bridges. Therefore the formation of a graphitic layer lattice is considerably impeded so that the graphitizability of a phenol based resin coke is markedly less in comparison to a pitch coke although the pure phenol itself has an aromatic configuration.

Chemical structure of phenolic resins

Binders

Cellulose compounds

Cellulose compounds are systems without aromatic structures at all and yield a binder coke residue, which is practically impossible to graphitise.

Chemical structure of cellulose compounds

Binders

Furan or furfurylalcohol resins

Furan or furfurylalcohol resins do not have an aromatic structure nor a six-member ring configuration. They are thus practically impossible to graphitise.