Carbon Black

Probst Nicolas

Industry
Technology
Properties
Applications
Carbon Black

- The first commercial nano-material
- An allotrope of carbon, mainly differing from graphite and so-called amorphous carbon by its physical arrangement
- Used since more than 5000 years in pigmentation
- Found its major development with automobile and more specifically the tyre industry as rubber reinforcing agent
- Is produced for more than 99% by partial combustion processes
- Is produced in millions of tons/a
<table>
<thead>
<tr>
<th></th>
<th>2007</th>
<th>2008</th>
<th>2009 f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Black Production</td>
<td>9979.5</td>
<td>9767.6</td>
<td>9068.3</td>
</tr>
<tr>
<td>North America</td>
<td>1857.4</td>
<td>1761.4</td>
<td>1583.2</td>
</tr>
<tr>
<td>Leading EU Countries*</td>
<td>1113.6</td>
<td>1048.0</td>
<td>808.4</td>
</tr>
<tr>
<td>Leading Asian Countries</td>
<td>4685.2</td>
<td>4675.1</td>
<td>4617.4</td>
</tr>
<tr>
<td>China</td>
<td>2300.0</td>
<td>2361.0</td>
<td>2473.3</td>
</tr>
<tr>
<td>India</td>
<td>557.0</td>
<td>567.6</td>
<td>587.7</td>
</tr>
<tr>
<td>Japan</td>
<td>830.2</td>
<td>814.5</td>
<td>724.0</td>
</tr>
<tr>
<td>Other Leading Asia**</td>
<td>998.0</td>
<td>931.9</td>
<td>832.4</td>
</tr>
<tr>
<td>Brazil</td>
<td>354.0</td>
<td>387.5</td>
<td>350.2</td>
</tr>
<tr>
<td>Egypt</td>
<td>210.0</td>
<td>225.6</td>
<td>191.3</td>
</tr>
<tr>
<td>Russia</td>
<td>664.0</td>
<td>618.0</td>
<td>553.8</td>
</tr>
<tr>
<td>All Other Countries</td>
<td>1095.3</td>
<td>1052.0</td>
<td>964.0</td>
</tr>
</tbody>
</table>

* France, Germany, Hungary, Italy, Netherlands, Spain
** Indonesia, South Korea, Thailand

# data forwarded by Notch Consulting
Conductive carbon black
Ensaco 250
Carbon Black Production Processes

Acetylene Black

\[ n \text{ C}_2\text{H}_2 \rightarrow n \text{ C} + \frac{n}{2} \text{ H}_2 \]
Carbon Black Production Processes

- **Partial Combustion Process**

  **Combustion**
  
  \[ C_nH_{2n+x} + (3n/2+x/4)O_2 \rightarrow nCO_2 + (n+x/2)H_2O + \text{Energy} \]

  **Cracking**
  
  \[ C_nH_{2n+x} + \text{Energy} \rightarrow C_nH_b + (n+x/2-b/2)H_2 \]

  **Synthesis**
  
  \[ C_nH_b \rightarrow n\text{C} + b/2H_2 \]

  \[ n \geq b \]
Carbon Black Production Processes

**Plasma Process**

**Cracking**

\[
C_nH_{2n+x} + \text{Electrical Energy} \rightarrow C_nH_b + (n+x/2 - b/2) H_2
\]

**Synthesis**

\[
C_nH_b \rightarrow n \text{C} + b/2 H_2
\]
Raw Materials for partial combustion process

Major criteria:
Global combustion enthalpy >> Global cracking energy

- Coal tar distillates
- Petroleum oils
  - Steam cracker oils:
    - Naphta
    - LPG
    - C4
  - Catcracker oils
- Mixed oils
Commerically known production processes

- lamp black process
- channel black process
- furnace black process
- Degussa gas black process
- acetylene black process
- thermal black process
- gasification black process
- MMM (Timcal) black process
Furnace black process

Low oxygen, low density, short residence time, high temperature

Origin Degussa

Probst Nicolas
Carbon black formation

- Nucleation: molecule → particle
  - Particle growth
- Aggregation of particles to multi-centre larger spherical particles
  - Multi-centre-particle growth
- Aggregation into small aggregates combining a few particles
  - Aggregate growth
- Agglomeration to form larger entities by Vander Waals forces
Basic characteristics

- **Morphology**
  Characteristics linked to the form and size of the carbon black primary particles and their arrangements:
  - particle:
    - TEM – image analysis
    - Calculation: \[ \text{diameter} = \frac{6000}{S.p} \]
    - average size
    - size distribution
  - aggregate:
    - average aggregate size
    - aggregate size distribution
  - agglomerates
    - stability

- **Specific surface area**
  - Nitrogen surface area: ASTM D6556:
    - Total (BET)
    - External STSA
  - CTAB surface area: ASTM D3765
  - Iodine Number: ASTM D1510
Basic characteristics (continued)

- Morphology (continued)
  Characteristics linked to the form and size of the carbon black primary particles and their arrangements:
  - OAN (oil absorption number): ASTM 2414
  - COAN (crushed oil absorption number): ASTM 3493
  - Void Volume ASTM 6086
  - Stokes diameter: Disc centrifuge Photosedimentometry

- Shape: TEM ASTM 3849
Basic characteristics (continued)

- **Texture**
  - We can distinguish between internal and external texture
    - **external:**
      - Porosity:
        - Most common: NSA – CTAB
        - Nitrogen adsorption
        - Mercury porosimetry
      - Graphiticity: Scanning tunneling microscopy
    - **internal:**
      - Graphiticity: X Ray diffraction
      - $L_c, L_a, c/2$

- **Tint strength: ASTM D3265**
  - $Tint (\% \text{ rel. IRB3}) = 56 + 1.06 \times CTAB - 0.00275(CTAB)^2 - 0.26COAN - 0.2(N2SA-CTAB)$
Mercury porosimetry: Ensaco 250
Basic characteristics (continued)

- **Surface chemistry**

  Under the term surface chemistry many different parameters are considered, some of them give a global appreciation, others describe very specific characteristics.
  - pH: ASTM D1512
  - surface energy: IGC (inverse gas chromatography) at finite dilution
  - energetic sites: IGC at infinite dilution
  - chemical surface groups

- **Electrical surface charges** constitute a global assessment of surface chemistry
Characterization of the Surface Heterogeneity by Static Gas Adsorption

Attribution of energy sites I-IV to surface microstructures

A. Schröder, Thesis, 2000
Impurities can be considered as another characteristic of specialty carbon blacks. The presence of:

- Water : ASTM D1509
- Sulfur : ASTM D1619
- Volatiles
- poly-aromatic hydrocarbons:
  - Toluene discoloration : ASTM D1618
  - Solvent extract : ASTM D4527
  - Carcinogenic components
- metal traces
- sieve residue : ASTM D1514
- ash : ASTM D1506
Interrelationship of major carbon black parameters
### Table 11. Oil Rate, Reaction Temperature, and Primary Particle Size

<table>
<thead>
<tr>
<th>Oil rate, kg/h</th>
<th>Reaction temperature, °C&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Primary particle size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>4060</td>
<td>1450</td>
<td>44</td>
</tr>
<tr>
<td>3660</td>
<td>1500</td>
<td>35</td>
</tr>
<tr>
<td>3170</td>
<td>1570</td>
<td>26</td>
</tr>
<tr>
<td>3060</td>
<td>1580</td>
<td>24</td>
</tr>
<tr>
<td>2740</td>
<td>1630</td>
<td>21</td>
</tr>
<tr>
<td>2370</td>
<td>1680</td>
<td>19</td>
</tr>
</tbody>
</table>

<sup>a</sup>Temperature of the reactor wall.

Origin: Kühner and Voll; Carbon black 2nd Edition, J.B. Donnet
Table 10. Range of Variation of Furnace Black Properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>Variation</th>
<th>Properties</th>
<th>Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2 ) surface area, ( m^2/g )</td>
<td>15 - 450</td>
<td>Blackness, ( \text{My} )</td>
<td>210 - 270</td>
</tr>
<tr>
<td>Iodine adsorption, ( mg/g )</td>
<td>15 - 450</td>
<td>Tinting strength</td>
<td>60 - 130</td>
</tr>
<tr>
<td>CTAB, ( m^2/g )</td>
<td>15 - 350</td>
<td>Volatiles, ( % )</td>
<td>0.5 - 6</td>
</tr>
<tr>
<td>Mean particle size, ( nm )</td>
<td>10 - 80</td>
<td>Toluene extract, ( % )</td>
<td>max.0.5</td>
</tr>
<tr>
<td>DBP, ml/100g</td>
<td>40 - 200</td>
<td>( \text{pH}^a )</td>
<td>6 - 10</td>
</tr>
</tbody>
</table>

\(^a\) After-treated blacks: 2-6.

Origin: Kühner and Voll; Carbon black 2nd Edition, J.B. Donnet
Carbon Black Production Processes

- Aftertreated gazeification or Timcal
- Acetylene
- Timcal (MMM)
- Gazeification
- Channel and aftertreated Furnace
- Furnace
- Lamp
- Thermal

Oil Absorption Number (OAN)

Specific Surface area (m²/g)
Functionalities of carbon blacks

- Reinforcement
- Pigmentation
- Protection: UV, IR, Heat
- Rheology control
- Electrical conductivity
- Thermal conductivity
- Reduction agent
<table>
<thead>
<tr>
<th>Property</th>
<th>Surface area</th>
<th>Structure (OAN)</th>
<th>Surface oxidation</th>
<th>Graphiticity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reinforcement</td>
<td>↑</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>Viscosity</td>
<td>↑</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>Dispersion</td>
<td>↓</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Wetting</td>
<td>↓</td>
<td>↑</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Jetness</td>
<td>↑</td>
<td>↓</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Flow</td>
<td>↓</td>
<td>↓</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>↓</td>
<td>↑</td>
<td>↓</td>
<td>↑</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>↑</td>
<td>↑</td>
<td>↓</td>
<td>↑</td>
</tr>
</tbody>
</table>
Application Domains

- Rubber
- Plastics
- Inks and paints
- High Voltage Cable
- Energy storage:
  - Li-ion batteries
  - Supra-capacitors
Câble d'énergie de moyenne tension

- Blindage métallique
- Isolant
- Conducteur métallique

- Jaquette
- Blindage de l'isolant
- Blindage du conducteur métallique
Li-ion Battery

Carbon black

Negative current collector

Li$_y$C$_6$

Li ion conducting electrolyte

Li$_{(1-x)}$Mn$_2$O$_4$

Positive current collector

Carbon black
Carbon Black Technology
Energy Consumption and CO$_2$ Emission
Fossil fuel consumption
Furnace Process

- To produce 1 MT Carbon Black
  - 2 MT of Hydrocarbon are needed
    - Highly aromatic oil
  - Electrical Energy

- 3.6 MT of CO₂ are produced

10 Mio MT of carbon Black generate 36 Mio MT of CO₂

~ 0.1 % of world CO₂ emission

Solar or Plasma Process

- To produce 1 MT of Carbon Black
  - 1 MT of Hydrocarbon is needed
    - Any hydrocarbon
    - Vegetable oil
  - Electrical or solar energy

- No or no direct CO₂ Emission
Conclusion

- Carbon black production via partial combustion has an important impact on:
  - Fossil fuel consumption
  - Environment via CO$_2$ emission

- Carbon black production via Solar Process:
  - Would have an important contribution to the reduction of world CO$_2$ emission
  - Would reduce fossil fuel consumption by 50 %
  - Would allow the use of any hydrocarbon and even vegetable oils

- A major effort will be required to allow the fine tuning of carbon black parameters in a Solar Process, comparable to the furnace process
Thank You for your attention