
Carbon Black

Probst Nicolas

Industry
Technology
Properties
Applications

SOLHYCARB's DAY

CNRS-PROMES -1 MW Solar Furnace- Odeillo Font Romeu, Franc September 28, 2009

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

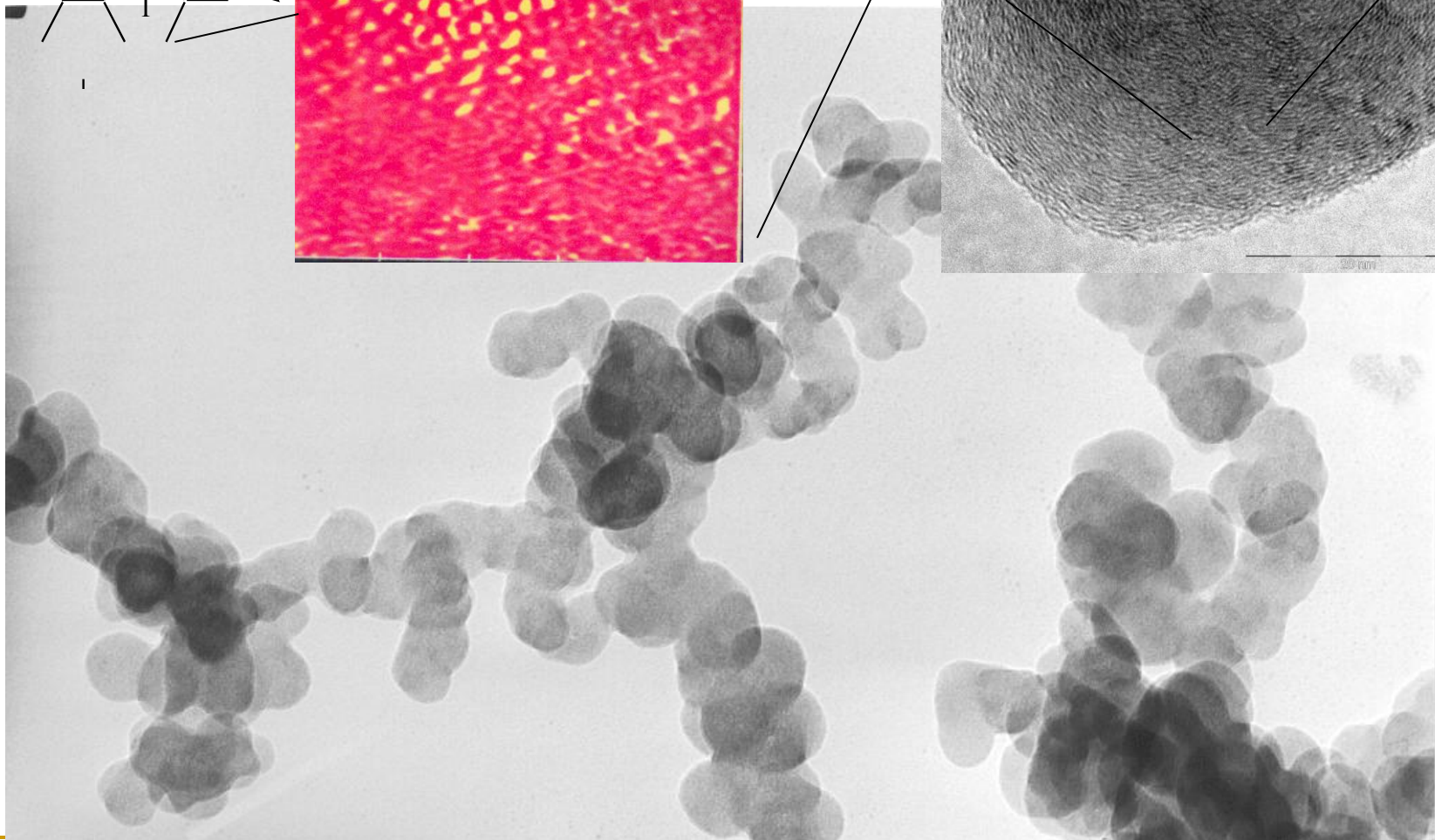
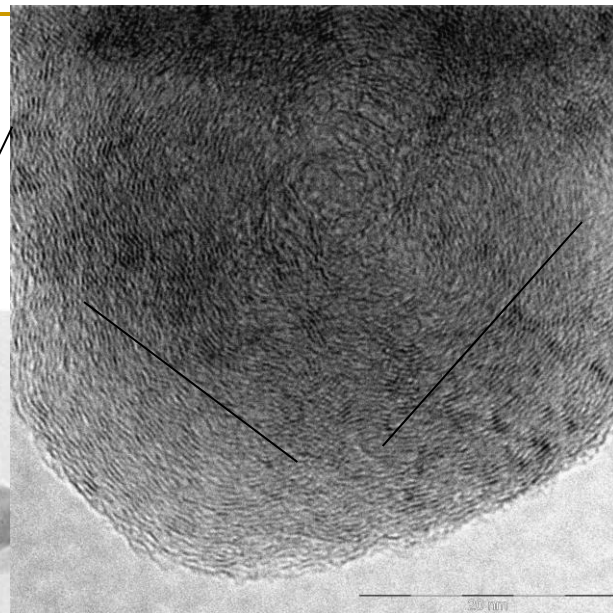
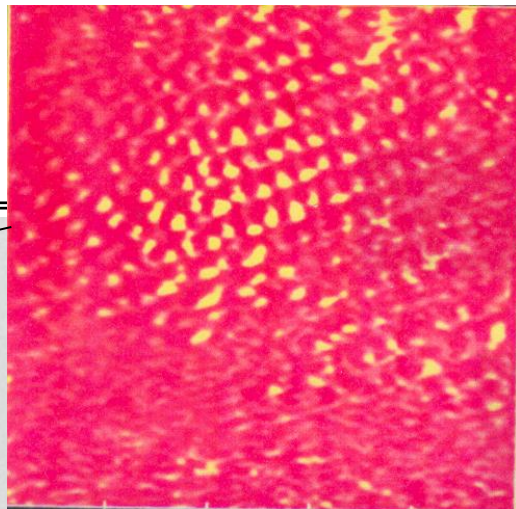
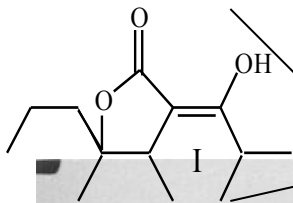
Carbon Black production[#]

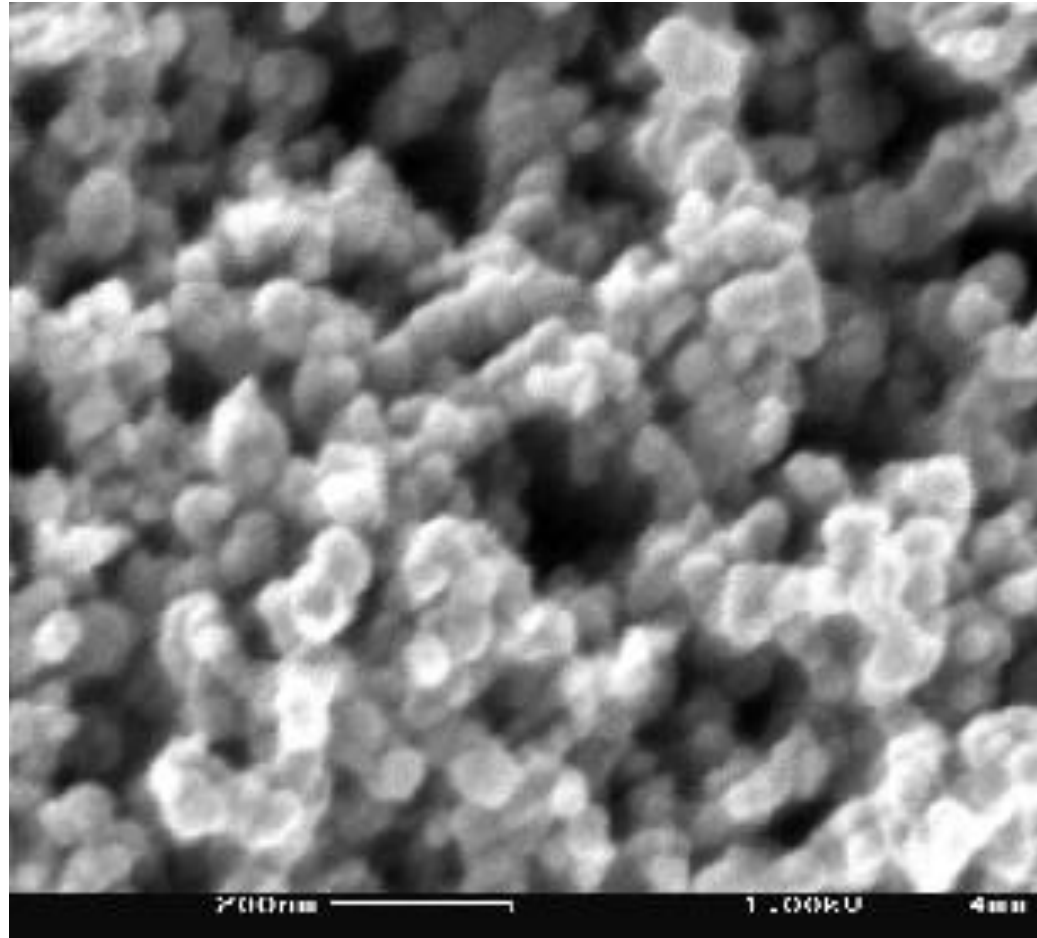
	2007	2008	2009 f
Carbon Black Production	9979.5	9767.6	9068.3
North America	1857.4	1761.4	1583.2
Leading EU Countries*	1113.6	1048.0	808.4
Leading Asian Countries	4685.2	4675.1	4617.4
China	2300.0	2361.0	2473.3
India	557.0	567.6	587.7
Japan	830.2	814.5	724.0
Other Leading Asia**	998.0	931.9	832.4
Brazil	354.0	387.5	350.2
Egypt	210.0	225.6	191.3
Russia	664.0	618.0	553.8
All Other Countries	1095.3	1052.0	964.0

* France, Germany, Hungary, Italy, Netherlands, Spain

** Indonesia, South Korea, Thailand

[#] data forwarded by Notch Consulting

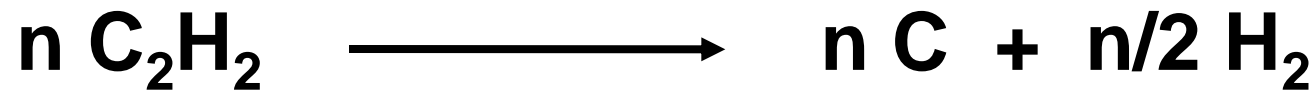




Conductive carbon black Ensaco 250

Carbon Black Production Processes

⇒ Acetylene Black



Carbon Black Production Processes

✧ Partial Combustion Process

Combustion

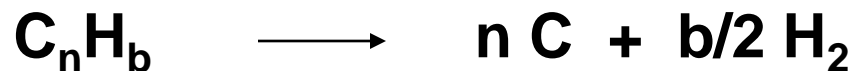


Cracking



$$n \geq b$$

Synthesis



Carbon Black Production Processes

❖ Plasma Process

Cracking



$$n \geq b$$

Synthesis



Raw Materials for partial combustion process

Major criteria:

Global combustion enthalpy \gg Global cracking energy

- Coal tar distillates
- Petroleum oils
 - Steam cracker oils:
 - Naphta
 - LPG
 - C4
 - Catcracker oils
- Mixed oils

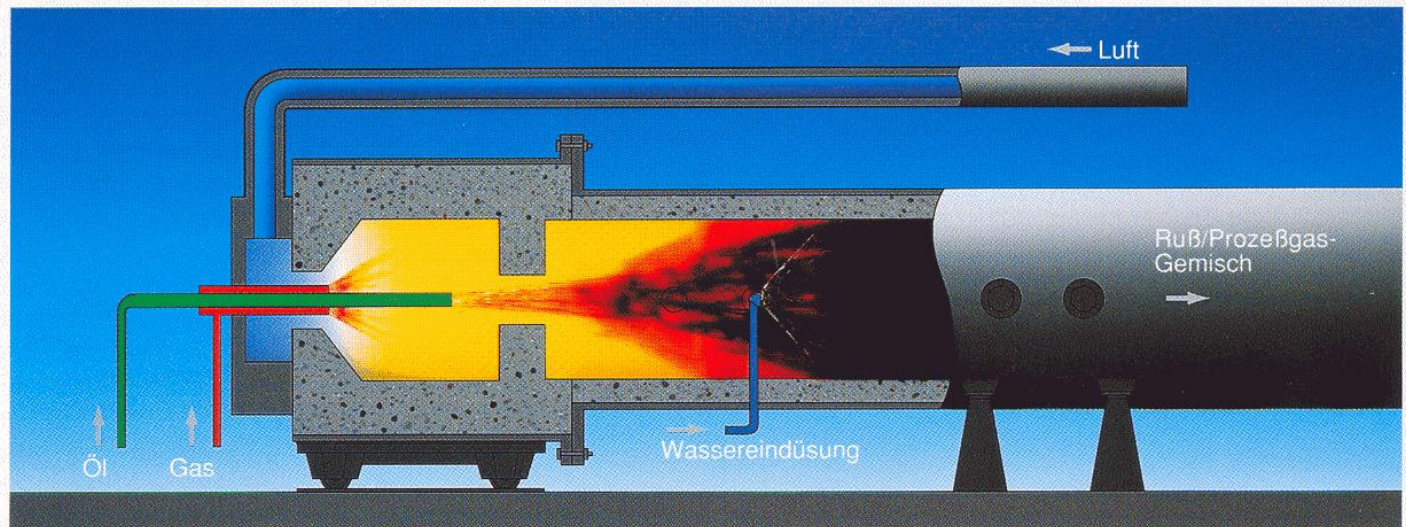
Commercially known production processes

- **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**

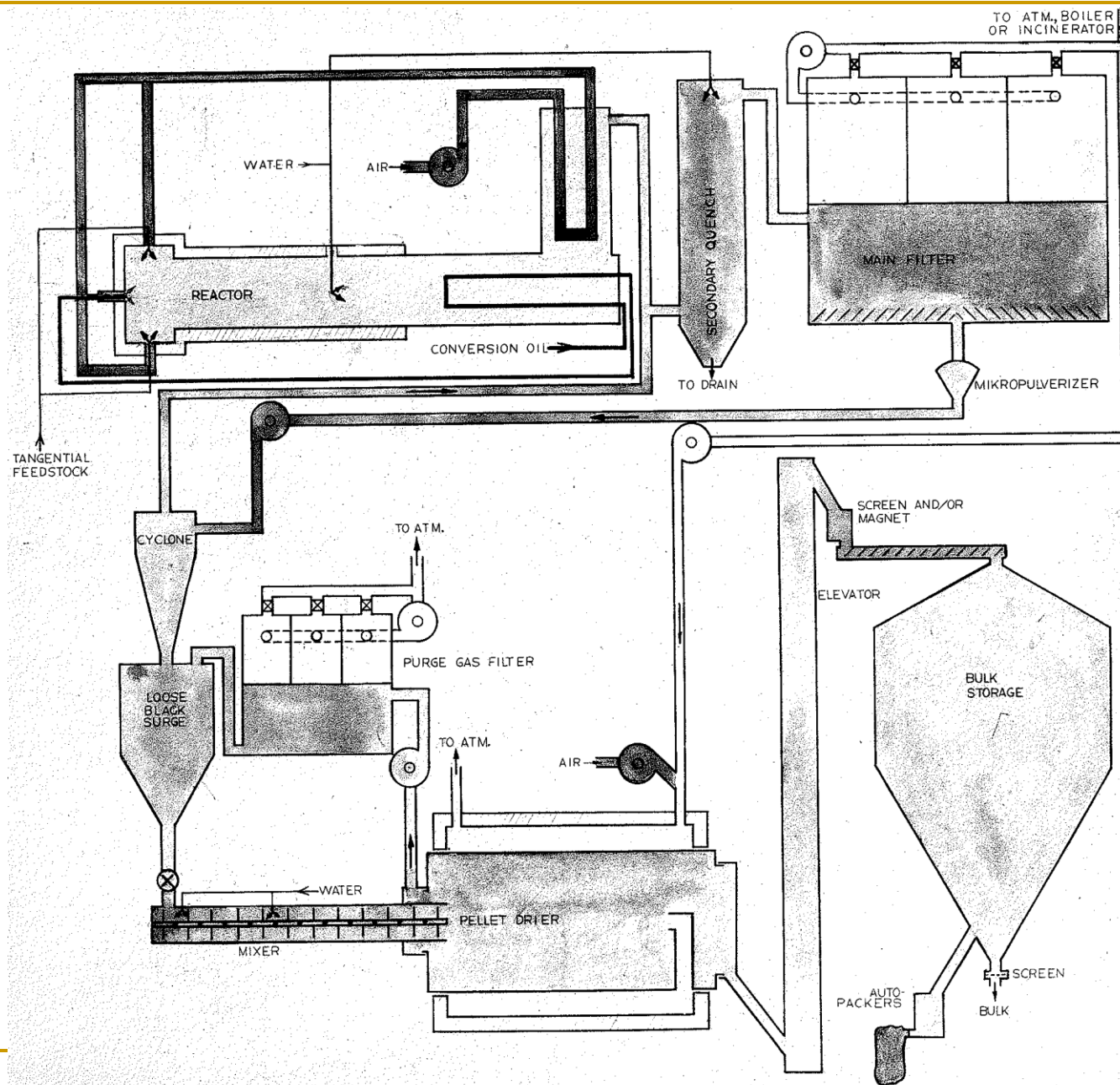
Furnace black process

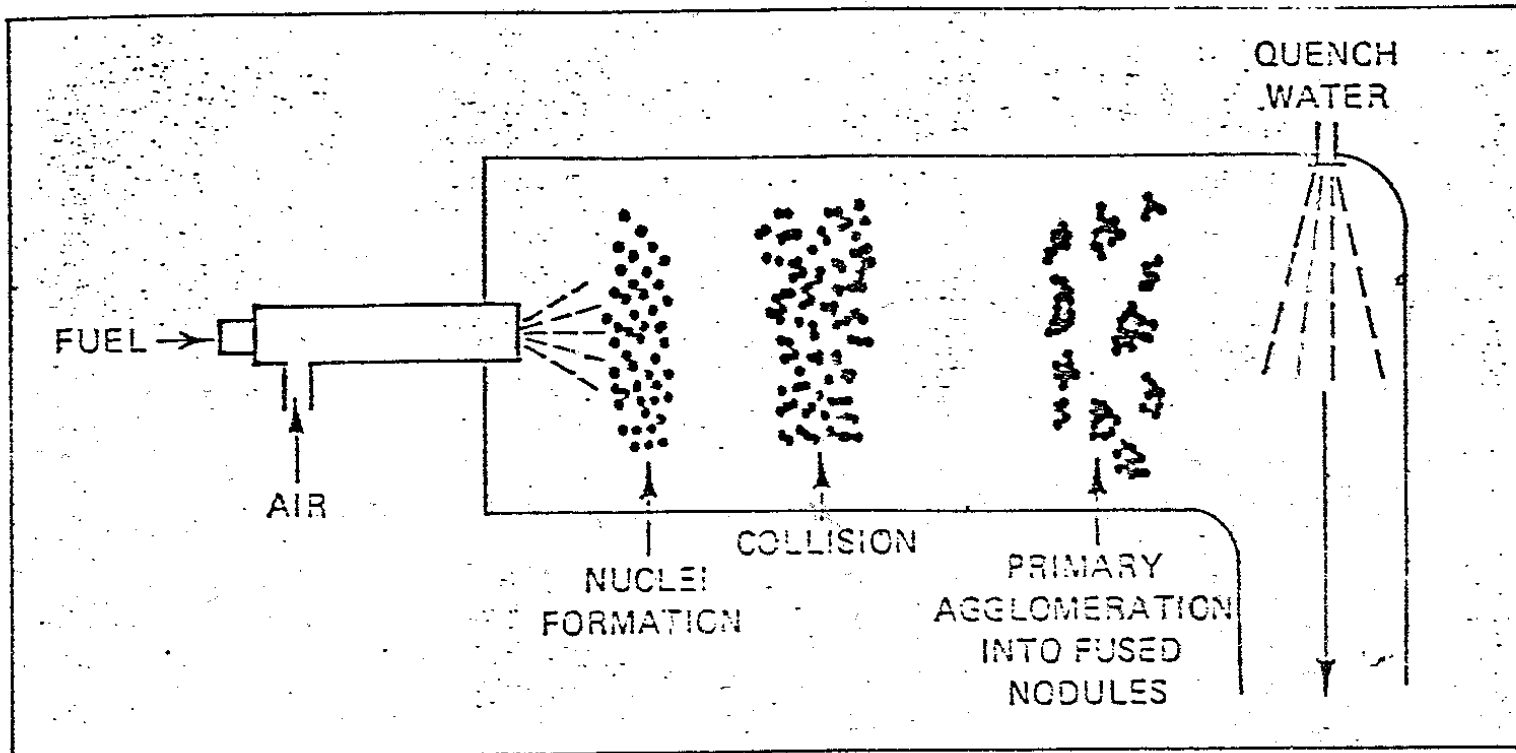
Low oxygen, low density, short residence time, high temperature

Abb. 2:
Schema eines
Furnaceruß-Reaktors



Origin Degussa





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: $\text{diameter} = 6000/S.p$
 - average size
 - size distribution
- **Specific surface area**
 - Nitrogen surface area: ASTM D6556:
 - Total (BET)
 - External STSA
 - CTAB surface area: ASTM D3765
 - Iodine Number: ASTM D1510
- **aggregate:**
 - average aggregate size
 - aggregate size distribution
- **agglomerates**
 - stability

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

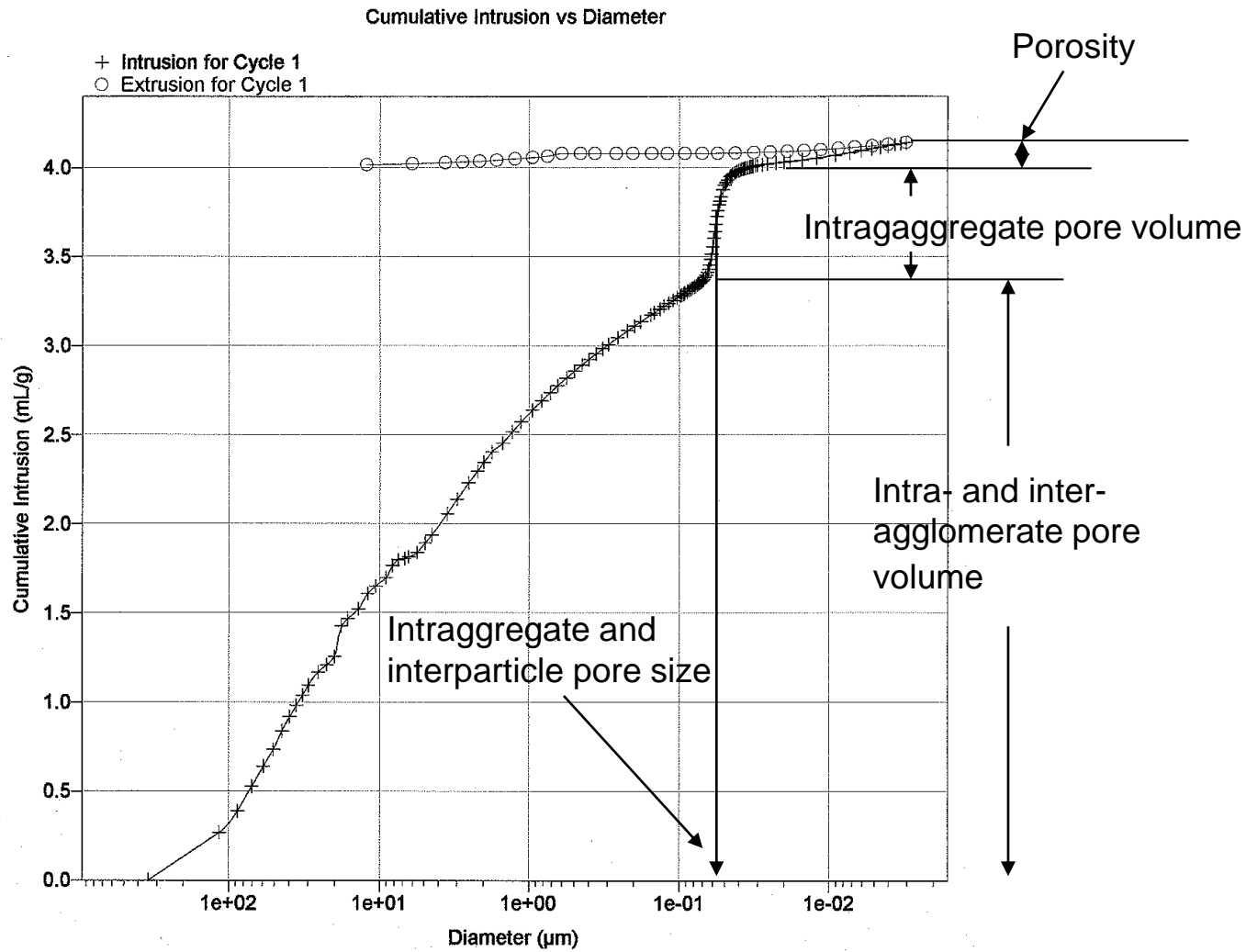
□ internal:

■ Graphiticity : X Ray diffraction

- Lc, La, c/2

■ Tint strength : ASTM D3265

- $\text{Tint (\% rel. IRB3)} = 56 + 1.06 \cdot \text{CTAB} - 0.00275(\text{CTAB})^2 - 0.26 \cdot \text{COAN} - 0.2 \cdot (\text{N2SA} - \text{CTAB})$



Mercury porosimetry: Ensaco 250

Basic characteristics (continued)

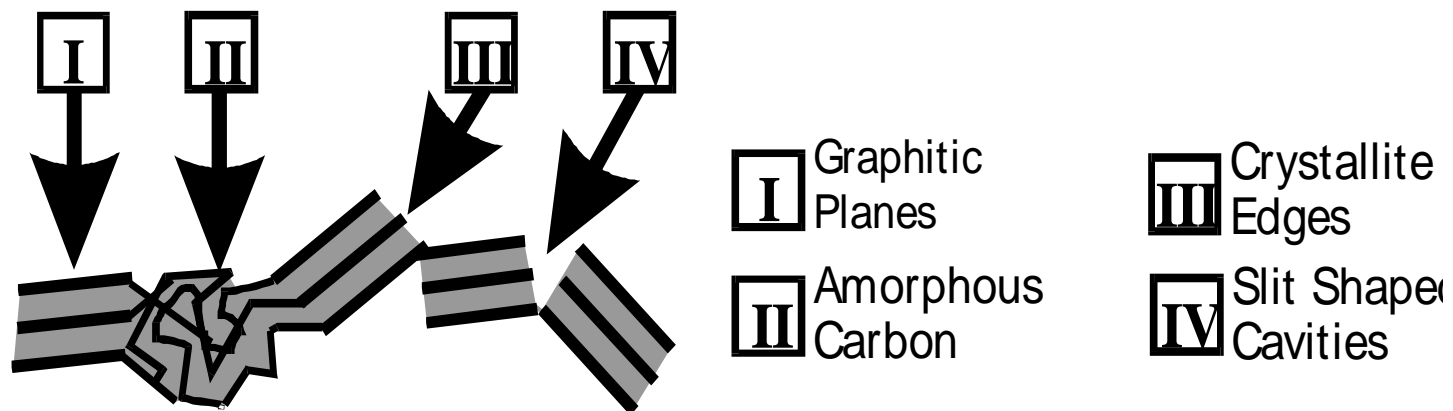
■ Surface chemistry

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

Basic characteristics (continued)

■ Impurities

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

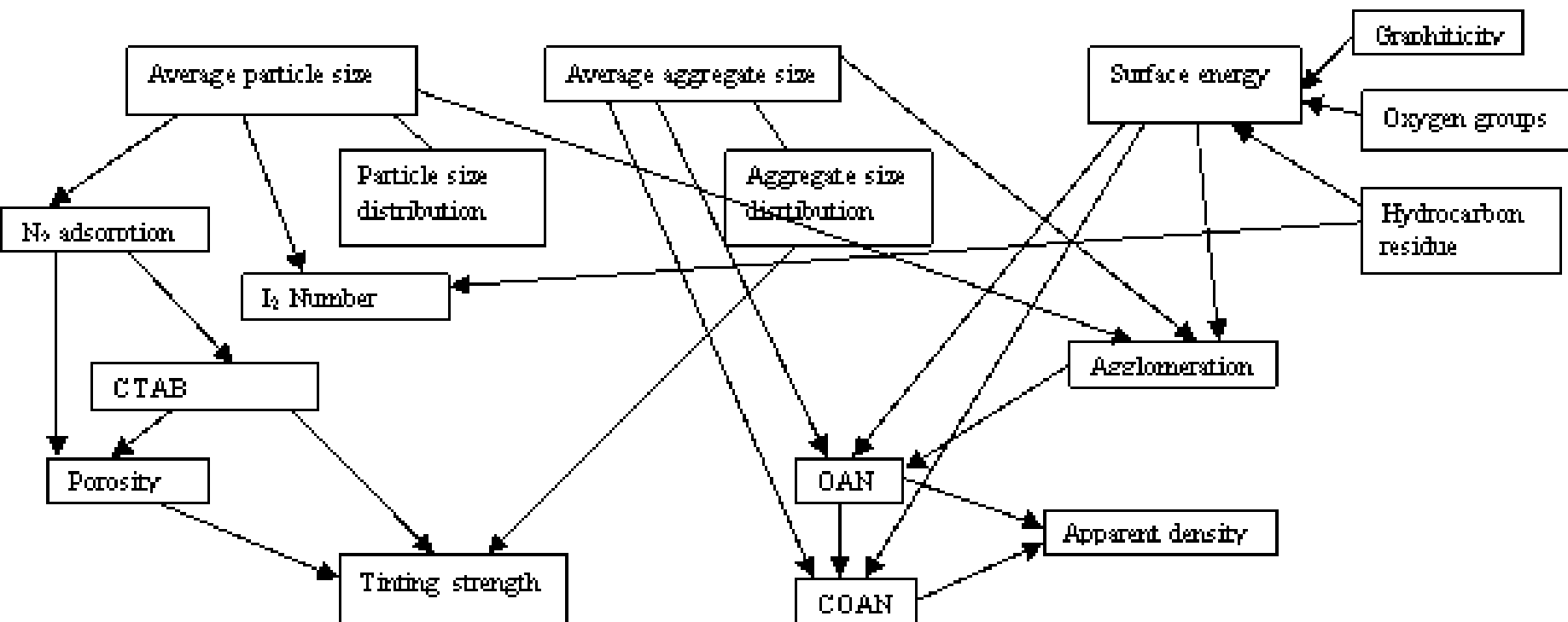


Table 11. Oil Rate, Reaction Temperature, and Primary Particle Size

Oil rate, kg/h	Reaction temperature, °C ^a	Primary particle size, nm
4060	1450	44
3660	1500	35
3170	1570	26
3060	1580	24
2740	1630	21
2370	1680	19

^a *Temperature of the reactor wall.*

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

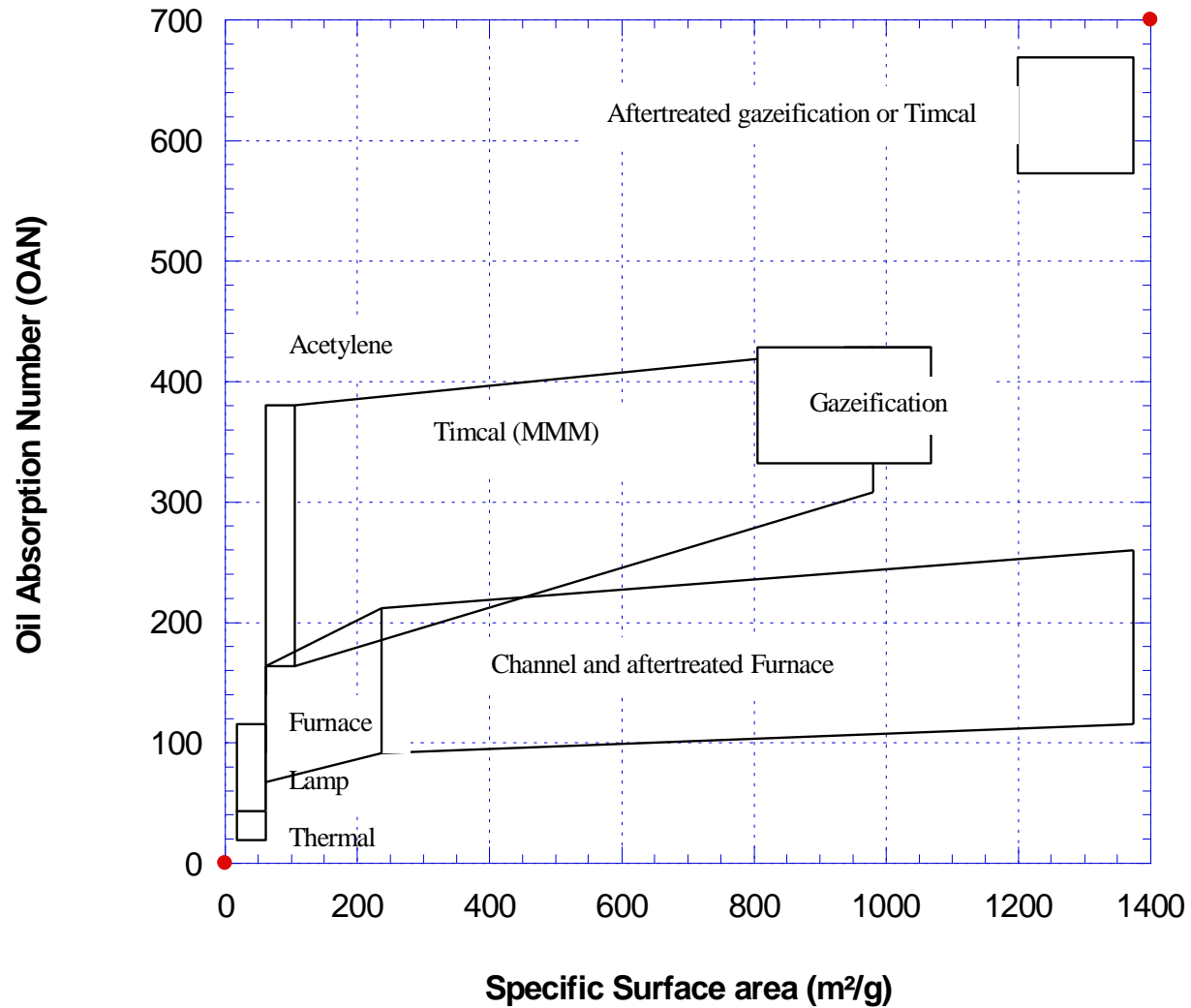
Table 10. Range of Variation of Furnace Black Properties

Properties	Variation	Properties	Variation
N ₂ surface area, m ² /g	15 - 450	Blackness, My	210 - 270
Iodine adsorption, mg/g	15 - 450	Tinting strength	60 - 130
CTAB, m ² /g	15 - 350	Volatiles, %	0.5 - 6
Mean particle size, nm	10 - 80	Toluene extract, %	max.0.5
DBP, ml/100g	40 - 200	pH ^a	6 - 10

^a *After-treated blacks: 2-6.*

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

Carbon Black Production Processes



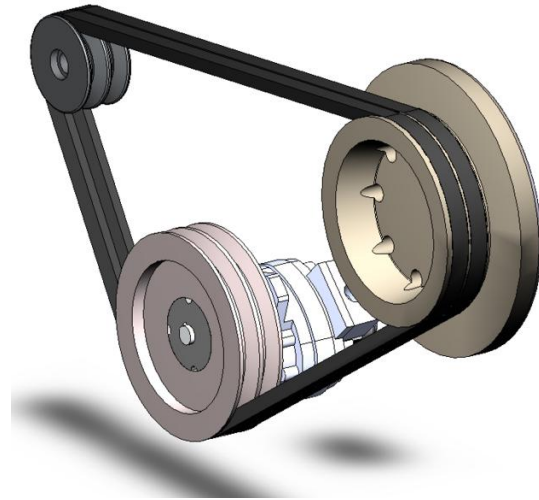
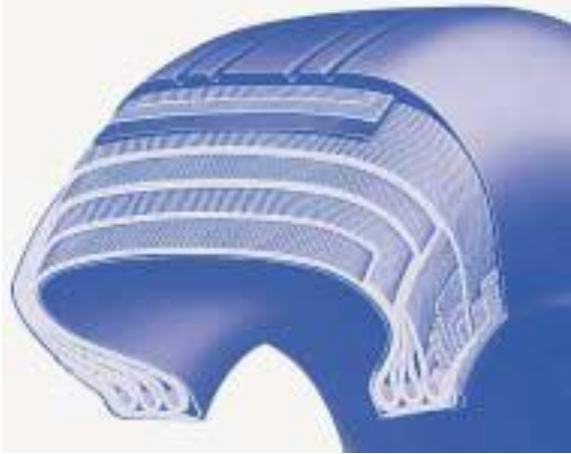
Functionalities of carbon blacks

- **Reinforcement**
- **Pigmentation**
- **Protection: UV, IR, Heat**
- **Rheology control**
- **Electrical conductivity**
- **Thermal conductivity**
- **Reduction agent**

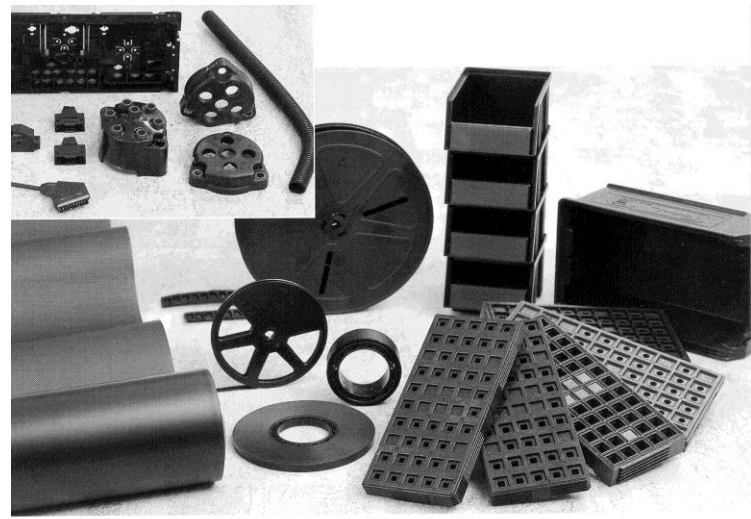
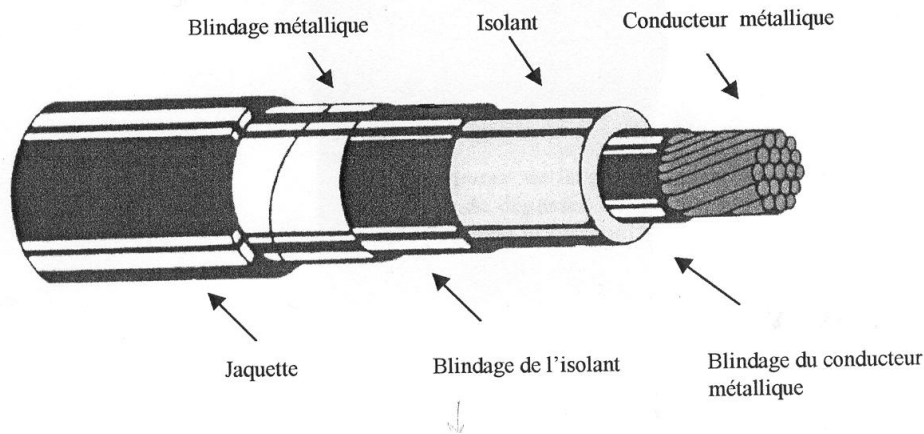
Property	Surface area	Structure (OAN)	Surface oxidation	Graphiticity
Reinforcement	↑	↑	↓	↓
Viscosity	↑	↑	↓	↓
Dispersion	↓	↑	↑	
Wetting	↓	↑	↑	
Jetness	↑	↓	↑	
Flow	↓	↓	↑	
Electrical conductivity	↓	↑	↓	
Thermal conductivity		↑	↓	↑

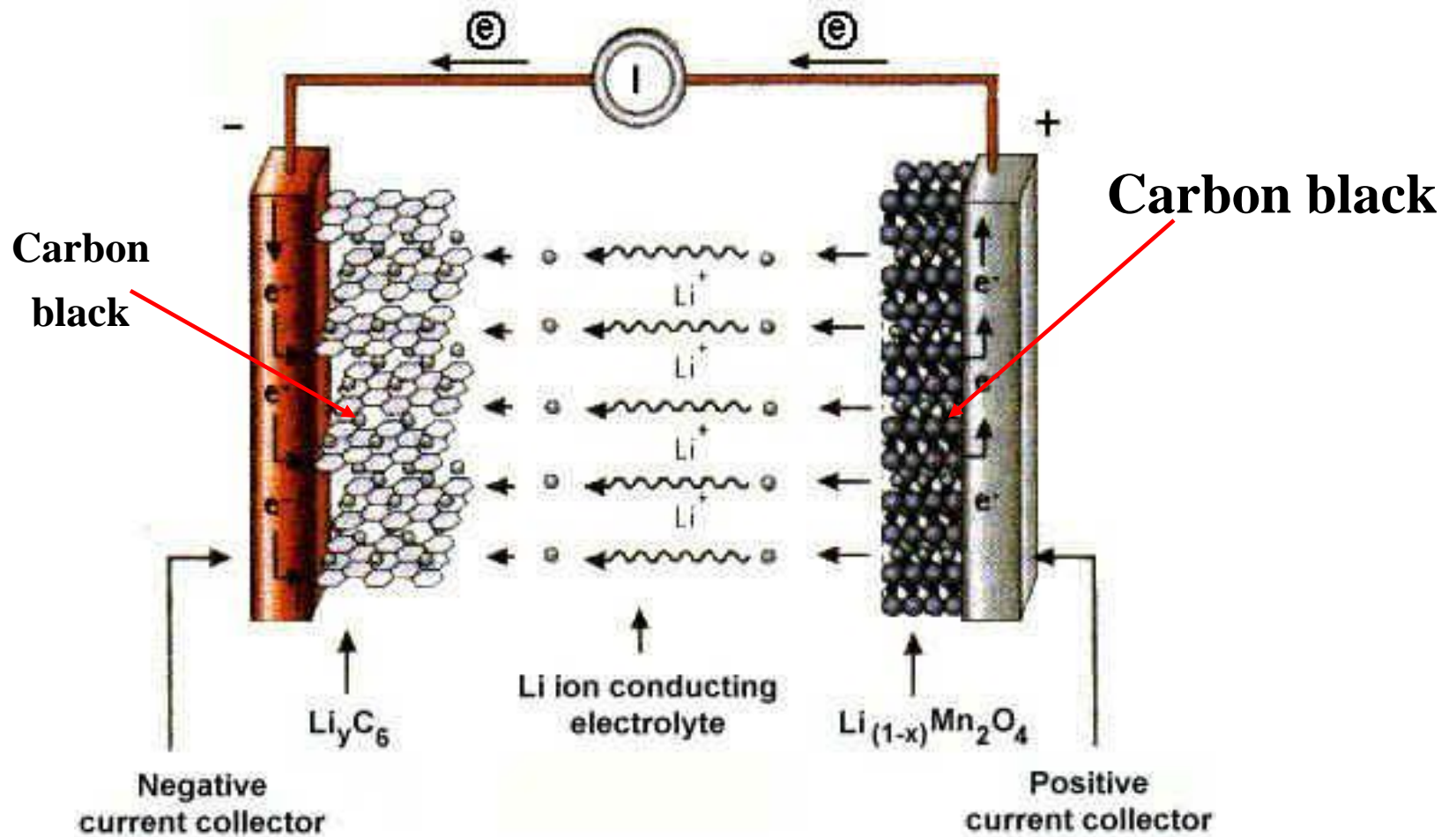
Application Domains

- Rubber
- Plastics
- Inks and paints
- High Voltage Cable
- Energy storage:
 - Li-ion batteries
 - Supra-capacitors



Câble d'énergie de moyenne tension

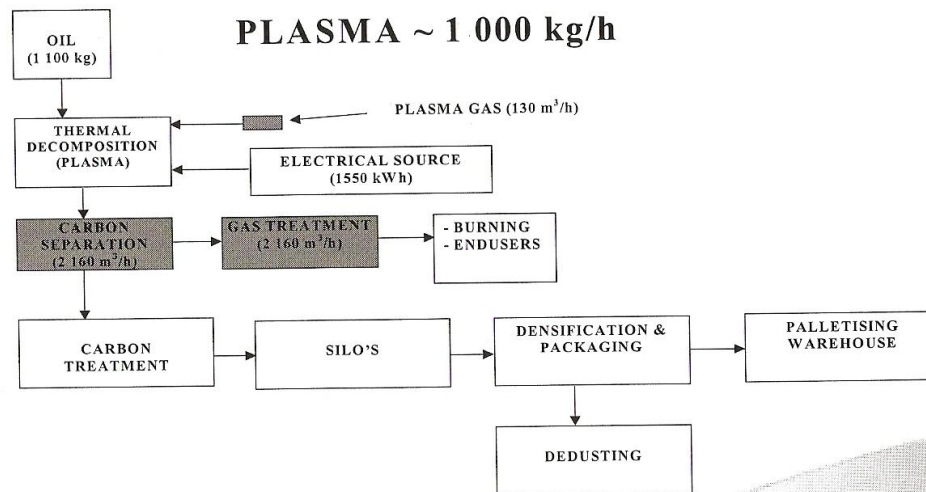
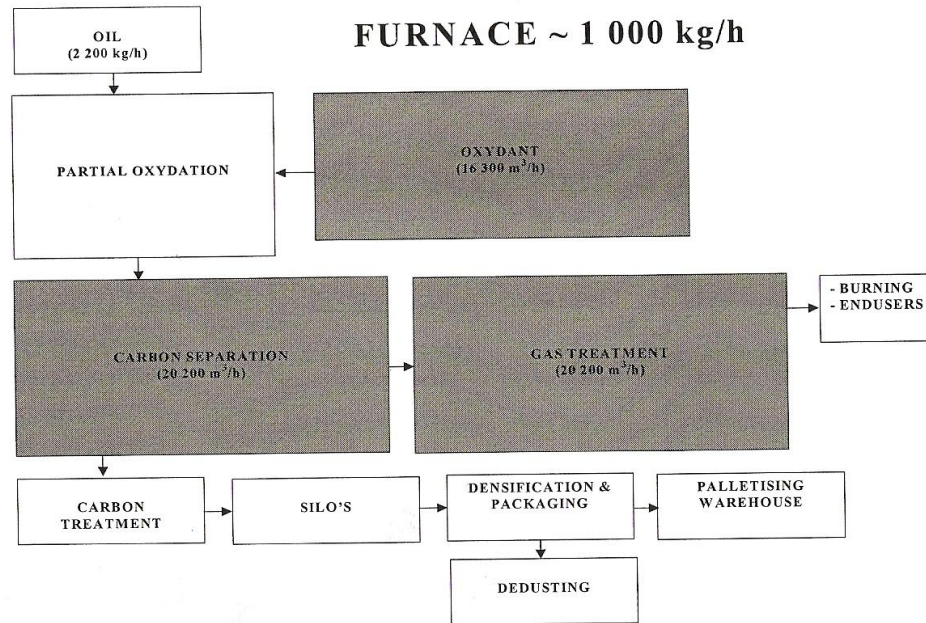




Li-ion Battery

Carbon Black Technology

Energy Consumption and CO₂ 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

■ 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**

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

~ 0.1 % of world CO₂ emission

Conclusion

- **Carbon black production via partial combustion has an important impact on:**
 - Fossil fuel consumption
 - Environment via CO₂ emission
- **Carbon black production via Solar Process :**
 - Would have an important contribution to the reduction of world CO₂ 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