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# Comparison Between New Carbon Nanostructures Produced by Plasma with Industrial Carbon Black Grades

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**Abstract.** — Among the large number of processes parameters in Carbon Black (CB) manufacturing, temperature is certainly one of the most important. Whatever the process and the feedstock are, all the processes have in common a limited temperature, as a result of the feedstock energy content. In the first part of this paper, we establish relationships between temperature and texture of the blacks, based on the analysis of different CB grades. In a second step, we try to give explanations of some possible relationships between processes parameters and applicative properties of the blacks. Then, we present a new plasma technology for CB production from hydrocarbons cracking. The original technology will allow to investigate, at a pilot scale, a wide range of temperatures. Preliminary results obtained with the pilot are presented.

## Nomenclature

- $D$  : average particle diameter;
- $l_a$  : diameter of the coherent domain in  $(a, b)$  surface measured by TEM (002);
- $l_c$  : thickness of the coherent domain in the  $c$  direction measured by TEM (002),
- $L_1$  : diameter of the ideal layer measured by TEM (FR 002);
- $L_2$  : diameter of the continuous layer (TEM),
- $L_a$  : diameter of the coherent domain in  $(a, b)$  surface measured by X-ray diffraction,
- $L_c$  : diameter of the coherent domain in the  $c$  direction measured by X-ray diffraction.

## Introduction

The total world production of Carbon Black (CB) is about 6 million tons per year. Most of this production goes in the rubber industry (tires), other part is shared between inks, oil, metallurgy and electrochemistry (batteries, conductive plastics...).

Today, the main process being applied in CB manufacturing is the “furnace process” which is based on incomplete combustion of an hydrocarbon (heavy oil). This process is characterized

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by: poor carbon yields, low value and high pollution level of off-gases ( $\text{CO}_2$ ,  $\text{NO}_x$ , V.O.C.,  $\text{SO}_2$ ,... ). Moreover, a valuable commodity, the hydrogen, is lost. Among the other processes, the case of acetylene black process is very singular since pure acetylene is continuously introduced into a furnace where adiabatic decomposition occurs [1,2] as a consequence of the highly exothermic reaction:



Whatever the feedstock (decant oil, coal tar, ethylene tar or acetylene), for the furnace and the acetylene processes respectively, the reacting temperature is limited by the feedstock energy content. Most of the time, the maximum temperature in the cracking process varies in the range of 1200–1600 °C (furnace process) up to 2600 °C (acetylene process).

Several studies have been dedicated in the past to the idea of making simultaneously CB and  $\text{H}_2$  by cracking an endothermic hydrocarbon using an external energy supply [3–6] but all these studies have been carried out at laboratory scale (few kW). Now, because of new environmental concerns [7] and thanks to improvements in plasma technology, this idea is being given a new start, in particular, in Norway by Kværner Engineering a.s. [8] and in France [9].

In 1993, a new research program was initiated by École des Mines de Paris and CNRS in association with industrials (TIMCAL G+T, EDF and GDF). A new original plasma reactor using a 100–200 kW three phase-AC source was set-up [10,11]. This pilot, located at Odeillo-France is operating since March 1994.

The objectives of the research were:

- to demonstrate the feasibility of a new plasma process at a pilot scale;
- to investigate virgin domains to produce new grades of CB in the temperature range from 2,000 °C up to 10,000 °C;
- to improve the knowledge of relationships between temperature and CB grades;
- to set-up a new clean process in which hydrogen could be recovered.

In the first part of this paper, we will briefly present the state of the art related to the knowledge of CB morphology (texture and structure). From the comparison between furnace black and acetylene black, we will discuss the influence of processes parameters (mainly temperature) on the CB characteristics.

In the second part of this paper, we will try to develop some relationships between CB microtexture and their applicative properties.

The third part of this paper will be dedicated to the presentation of the new plasma technology and to the analysis of the first results.

Finally, conclusions and outlook of the program will be presented.

## CB Structure and Texture – Influence of Processes Parameters

*Case of Furnace CB Grades.* — Three levels of arrangements are generally distinguished in the structure of “furnace” CB grades:

- 1) a *particle* is the smallest spherical material we can observe;
- 2) an *aggregate* is an assembly of several particles;
- 3) an *agglomerate* is an assembly of aggregates.

The particle is an amount of carbon atoms in a more or less organized form. Most of the bonds are of chemical nature ( $\text{sp}^2$  and  $\text{sp}^3$ ).

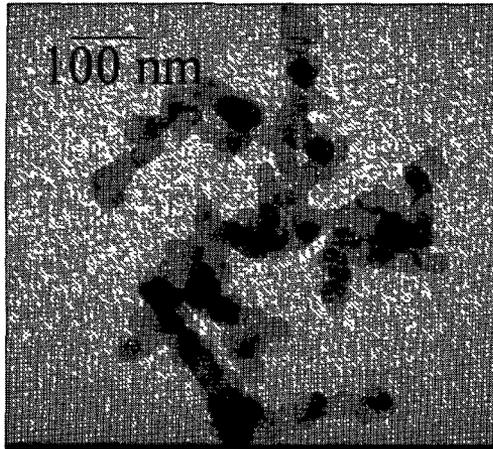


Fig. 1 — Electron micrography of a typical furnace black

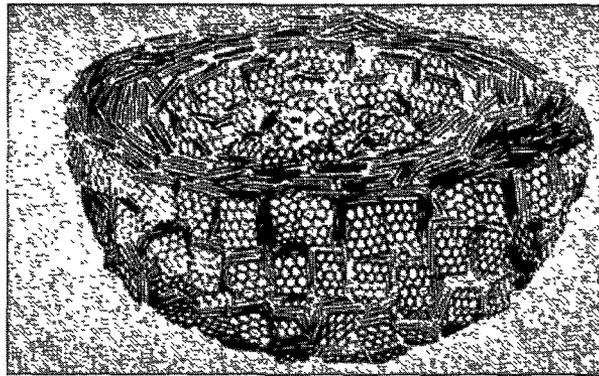


Fig. 2. — Model of a particle: Heindenreich, Hess and Ban (1968).

The aggregate is composed by particles bonded together with some chemical bonds and some physical attractions. The size and shape of an aggregate define the “structure” of the black.

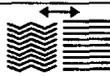
The agglomerate is a mixture of aggregates held together with only physical bonds. Thus, during energetic dispersion, like ultrasonic dispersion for sample examination or industrial mastication, agglomerates can be easily destroyed.

Coming back to the particle, it is now generally agreed that a particle is a spherical mass of carbon atoms more or less organized. Average diameters are in the range of 30–80 nm. The inside seems less organized than the surfaces which look like graphitic layers overlapping themselves as in Figure 2.

It is clear that the same form of organization exists in all “furnace” CB grades without significant differences. The particles are generally made of crystallites whose average dimensions (X-ray) are:  $L_a$ : 2.3–2.6 nm and  $L_c$ : 1.3–1.5 nm. These lengths correspond to three to four graphite layers (*c*-axis).

Among the set of parameters describing a CB grade and determining its applicative properties, specific area is certainly one of the most important.

Table I. — *Microtextural classification of acetylene black proposed in [12].*

TYPE	I	II	III	IV	V
crystallographic parameters relationships (TEM)	$l_a \approx l_c$ $L_1 = L_2$	$l_a = L_1 < l_c$ $L_1 = L_2$	$l_a < l_c < L_2$ up to $l_a \approx l_c \approx L_2$	$l_c \ll L_2$	$l_c \lll L_2$
stacking coherent domain					
LAYERS	 $N \approx 3$ $L_1 = L_2$ $= 0.8 \text{ nm}$	 $N \approx 4$ $L_1 < L_2$	 $N \approx 10$ $L_2 \approx 5 \text{ nm}$	 $N \approx 5/6$ $L_2 > 5 \text{ nm}$	 $N \approx 7/8$ $L_2 > 10 \text{ nm}$

CASE OF CONDUCTIVE BLACKS. — If we now consider the case of CB obtained at higher temperature, especially the case of acetylene black, Bourrat [12] showed that the structure of these *blacks* could obviously differ from the above description. In particular, it was shown that the distinction between particle and aggregate was not so clear. The author established a statistical microtextural classification of *blacks* based on TEM analysis of the aromatic layer, its diameter and spatial distribution. It involved the differentiation of five types of stacking order, related to short-distance order (microtextural scale). In addition to the measure of  $l_a$  and  $l_c$  parameters <sup>(1)</sup> which are defined as:

- $l_a$ : diameter of the coherent domain in  $(a, b)$  surface measured by TEM (002);
- $l_c$ : thickness of the coherent domain in the  $c$ -direction measured by TEM (002).

The author has introduced the following parameters

- $\gamma$ : geometric twisting angle of layers, measured by TEM;
- $L_1$ : diameter of the ideal layer measured by TEM (FR 002);
- $L_2$ : diameter of the continuous layer (distorted), measure by TEM.

A synthetic classification of such *blacks* into the five types is given in Table I. The majority of industrial acetylene black grades, used for conductive applications, were studied in [12]: Atochem (S70 and Y50A), Union Carbide (UCET), Piesteritz (P1042S), Shawinigan (Shawinigan 50%), Denka (Denka 50%) and Knapsack. In addition to these *blacks*, two other grades. Atochem (Y50 B) and Ensagri (Ensagri super S) were analyzed. The first one corresponds to a black obtained from a mixture of benzene and acetylene. Although the process related to the second one is confidential, it could result from an incomplete combustion of benzene and oxygen.

The Ensagri grade, probably obtained at the lowest temperature, belongs to the first category. The textural arrangement is common to a wide range of low temperature CB grades and is made of 3–4 carbon layers. The Y50 B grade, which corresponds to a mixture between benzene and acetylene belongs to type II and shows an increase in the aromatic layer. The Denka and Ucet grades, corresponding to acetylene black (types II and III) show an increase of the aromatic layer characterized by a huge lateral extension of the layers ( $L_2$ ) which may

<sup>(1)</sup>  $l_a$  and  $l_c$  differ from  $L_a$  and  $L_c$ , measured by X-ray

reach several tenths of nm. The last grade, S70, is the most organized. It corresponds to a mixture of acetylene and preheated air which gives a temperature greater than the acetylene cracking. It is characterized by an increase of  $L_2$ .

What is very interesting to notice is that, the higher the temperature and the residence time of the process are, the most important the atomic organization of the microtexture is. From type I to type V, the microtexture is characterized by an increase of the aromatic layer diameter and a decrease of the distortions.

### Relationship Between Texture and Applicative Properties

Studies carried out on the analysis of acetylene black microtexture are very interesting because they partially explain the properties of Acetylene Black in conductive applications.

Furthermore, applicative tests in batteries, show a clear correlation between the dimension of the layers in the ( $a$ ,  $b$ ) direction ( $L_2$ ) and the quality of *blacks* in dry cells (conductivity and internal resistance) which highly increases from type I to type V. However, the microtexture does not explain alone the conductive properties of acetylene black. Indeed it is known that the texture of aggregate plays also an important role.

Now, an important question that has remained open for a long time for CB researchers is – why acetylene black (which is exactly at the centre of the ASTM <sup>(2)</sup> diagram giving reinforcing properties of CB) have very poor reinforcing properties despite a specific area and an iodine number <sup>(3)</sup> similar to a typical furnace black?

For this case also, this important question may find an explanation from the microtexture analysis. If we assume that the “reactivity” of CB in elastomer is determined to a large extent by the number of crystallites located at the surface of the black, considering that:

- 1) the carbons inside the crystallite and the crystallites inside the particles have no reason to react with elastomer chains;
- 2) the carbons inside the surface layer are not as reactive as those at the crystallite rims or edges.

Then we can give an approximation of the surface density of crystallites for several CB grades. For this purpose, we will define two parameters  $SDC_1$  and  $SDC_2$ . The first one,  $SDC_1$ , is defined as the ratio of the number of crystallites at the surface of a particle over the particle volume. The assumptions made are: a perfect spherical particle and a crystallite diameter evaluated from X-ray measurements ( $L_a$ ):

$$SDC_1 = \frac{\pi D^2}{\frac{L_a^2}{\pi D^3}} = \frac{6}{DL_a^2} \quad [L^{-3}].$$

The second one,  $SDC_2$ , is defined as the ratio of the specific area (BET) over the area of a crystallite. As before, the crystallite diameter is evaluated from X-ray measurements ( $L_a$ ):

$$SDC_2 = \frac{\text{Specific Area}}{L_a^2} \quad [M^{-1}].$$

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<sup>(2)</sup> Diagram gives reinforcing properties of carbon blacks of a function of specific area (BET) and iodine number.

<sup>(3)</sup> The iodine number is the result of a normalized applicative test giving the absorption potential of a black

Table II. — *Characteristics of some industrial carbon black.*

		Specific Area BET ( $\text{m}^2 \text{g}^{-1}$ )	Average $L_c$ (nm)	Average $L_a$ (nm)	D: Average particle diameter (nm)	$\text{SDC}_1$ ( $\times 10^2$ ) ( $\text{nm}^{-3}$ )	$\text{SDC}_2$ ( $\times 10^{-19}$ ) ( $\text{g}^{-1}$ )
CH	Channel	110	1.3	2.3	28	4.050	2.0793
F1	Furnace	74	1.4	2.4	29	3.591	1.2847
F2	Furnace	23	1.5	2.6	80	1.109	0.3402
TH	Thermal	13	1.7	2.8	215	0.3559	0.1658
A1	Acetylene	73	2.7	4.8	40	0.5208	0.3168
A2	Acetylene	120	2.7	10	25	0.24	0.12

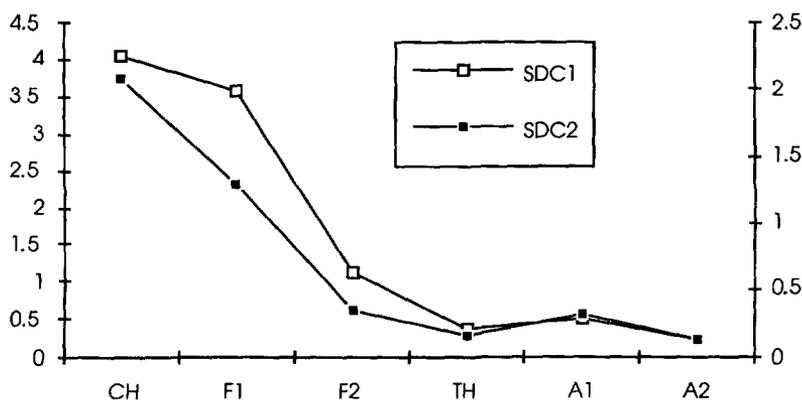


Fig. 3 — Surface density of crystallites for industrial CB grades

These two parameters are not independent since the ratio  $\text{SDC}_1$  over  $\text{SDC}_2$  is linked to the particle density. Indeed, the dimension of this ratio is  $[\text{ML}^{-3}]$ .

In the following table (Tab. II), we give the above parameters for 5 industrial CB grades, classified with decreasing of reinforcing properties <sup>(4)</sup> and increasing of conductive properties.

- 1 Channel, CH, former Spheron 6;
- 2 Furnace, F1, former Vulcan 3 and F2, former Sterling S;
- 1 Thermal, TH, former Sterling FT;
- 1 Acetylene, A1, Shawaningan and A2 Atochem S70

It is then particularly interesting to notice with this example that, whatever the parameter is, it fits very well with both the reinforcing properties and the conductive properties of the black one can experimentally observe.

If these results could be generalized to other carbon black industrial grades, the indice numbers defined in this study,  $\text{SDC}_1$  and  $\text{SDC}_2$  should appear as being a simple and efficient way of characterizing carbon black.

<sup>(4)</sup> Reinforcing properties are evaluated from normalized specific experiments

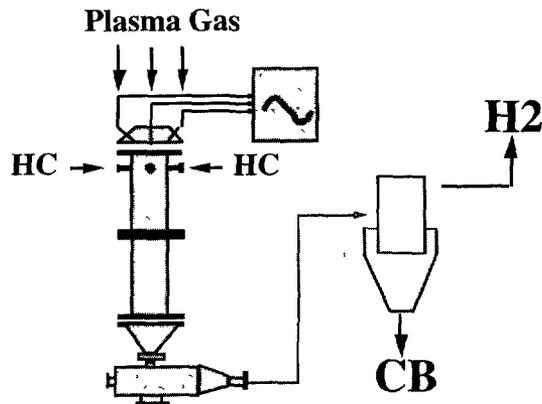


Fig. 4. — Scheme of the reactor.



Fig. 5 — View of the upper part of the reactor.

### Presentation of the New Plasma Technology

The reactor has been set-up at a pilot scale. It is mainly composed of (Fig. 4):

- a 100 kW 3-phase A.C. source with graphite electrodes, located at the top of the reactor,
- a high temperature reactive zone where the hydrocarbon (HC) is introduced;
- an insulated reacting chamber, 2 meter high,
- a tail filter where CB and H<sub>2</sub> are separated and collected (bag filter).

All kind of plasma gas can be used. The technology was patented BF n°9301554 dated 5/02/93. PCT extension is running.

While most of the large scale industrial plasma processes use DC plasma, the main characteristics and specificity of the process under development is related to the 3-phase AC source which has some similarities with electrometallurgy technologies.

In opposition to DC torches which are characterized by the very high speed of the output plasma gas flow — which could even be supersonic — this technology is adapted to processes

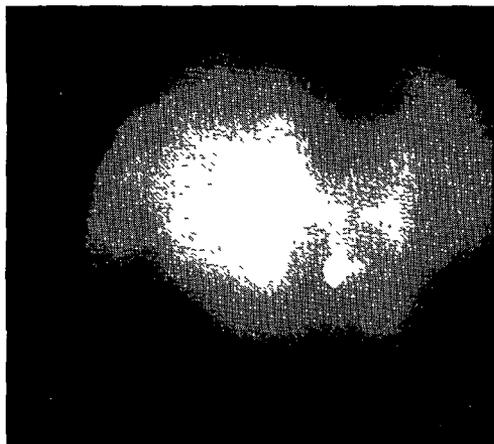


Fig. 6. — Internal view of the reactor

in which large high temperature volumes and long residence times are needed. The principle of the 3-phase AC plasma source is the following:

Three elementary torches with graphite electrodes are located at  $120^\circ$  at the top of the reactor. The plasma gas is admitted in an annular space between the electrodes and the nozzles. Each of the three electrodes acts successively as an anode and as a cathode. The arc is rotating at the current frequency (50 Hz). Because of the huge viscosity of the plasma (similar to that of a liquid) and due to the high chaos created along the discharge path between the active electrodes (two or three), the succession of arcs impulses the surrounding gases and creates a large turbulent volume downstream the tips of the electrodes. Electrode erosion is compensated by an automatic forward movement.

The temperature reached in the active volume of the reactor varies depends on operating conditions (mainly: electric power, nature of the plasma gas, flow rate...).

Heat and mass transfer into the reactor have been studied thanks to a MFD (Magneto Fluid Dynamic) model. The model developed gave temperature and velocity fields into the reactor. Results of the modelling have been in full agreement with experimental measurements obtained by calorimetry heat balance of the reactor, emission spectroscopy and by optical pyrometry.

In the arc zone, the temperature is about 5,000 K in the case of a nitrogen plasma while temperatures greater than 10,000 K were observed in the case of an argon plasma. Wall temperatures measured by optic pyrometry in the upper part of the reactor led to temperatures around 2,300 K.

### Product Characteristics

First cracking experiments were carried out using light hydrocarbons, mainly natural gas and ethylene. A large number of processes parameters like: input electric power, nature of the plasma gas, injection conditions (position in the reactor, flow rate, output velocity,...) were investigated. It is particularly interesting to notice that, despite the large number of processes

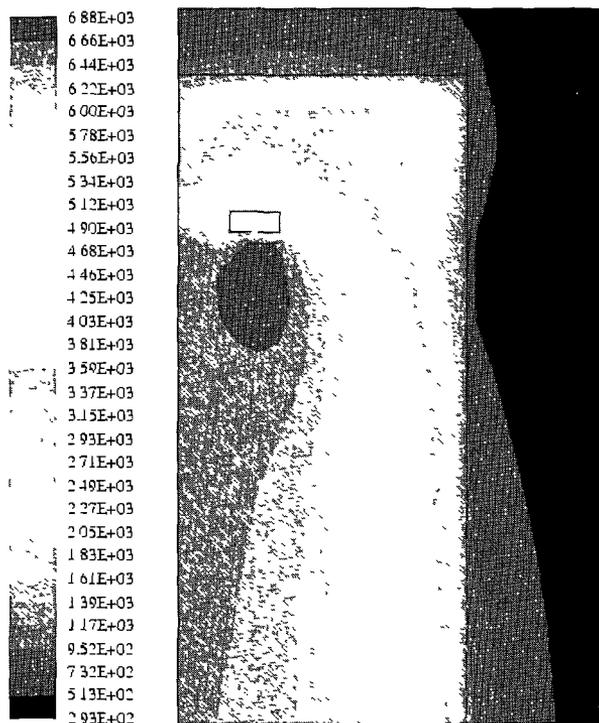


Fig 7. — Temperature field of the upper part of the reactor (2D axial symmetry) in the case of a nitrogen plasma gas in the absence of hydrocarbon injection (modelling results with a laminar model).

parameters, three main families of Carbon Black were observed:

The first family is related to the products obtained by injecting the hydrocarbon into the arc zone. These products correspond to a highly organized (turbostratic arrangement) carbon black ( $d_{002} = 0.342$  nm). They are made of thin ramified aggregates, similar to acetylene black. Micrographies show that the texture is characterized by a concentric organization. In contrary to the case of furnace black where aggregates are made of a set of spherical particles, the particles are flat, sometimes hollow and resembling to crinkled paper material (Fig. 8)

The diameter of the continuous aromatic layer,  $L_2$ , is highly greater than 10 nm. This confirms that the higher the temperature and the residence time of the process are, the most important the atomic organization of the microtexture is.

Table III gives a comparison between such a Plasma Black (PB), industrial CB grades F1 (furnace), acetylene black A1 and an Asheson graphite which average particle size is 50  $\mu\text{m}$ .

As expected, all the analysis confirmed that the products were close to acetylene black, in the domain “between” acetylene black and graphite, due to the high temperature. The two other families of products were both obtained by injecting the hydrocarbon downstream the arc zone. In that case, isolated particles having no “long distance” structure were always obtained.

Family 2 is not the most interesting one since it is related to isolated “amorphous” spherical particles ( $0.36 > d_{002} > 0.35$  nm) with a structure corresponding to a “low temperature” carbon black. They very likely correspond to a growth in a low temperature region of the reactor ( $T < 1600$  °C).

Table III. — Comparison between furnace black, acetylene black, graphite and a typical plasma black (PB).

	$L_c$ (nm)	$c/2$ (nm)	BET ( $\text{m}^2 \text{g}^{-1}$ )	$\text{SDC}_1$ ( $\times 10^2$ ) (nm) $^{-3}$	$L_2$ (nm)
F1 (Furnace)	1.4	0.3622	74	3.591	0.8
A1 (Shawaningan)	2.9	0.3526	73	0.5208	5
Graphite (50 $\mu\text{m}$ )	> 10	0.3355	10	$\approx 10$	$\gg 1000$
PB	5.7	0.342	40	0.15	$\gg 10$



Fig. 8 — TEM Micrography of a plasma black corresponding to family 1 (Bourrat [13]).

*Family 3* is more interesting. Indeed, the particles are highly crystallized ( $0.342 > d_{002} > 0.338$  nm) and show a clear polygonal shape. In opposition with structures corresponding to family 1 which have a 2D turbostratic organization, the particles are partially graphitized and bring up a 3D organization. It is highly possible that these particles correspond to amorphous particles initially belonging to family 2 which have been recirculating in the arc zone (Fig 9).

Every sample were analysed by Soxhlet extraction in order to detect the possible presence of “light” Fullerenes (C60 and C70). Despite the fact that some large hollow particles belonging to the first family look like “giant Fullerenes” (Fig. 10), all the analysis were negative. The main explanation could be the presence of hydrogen.

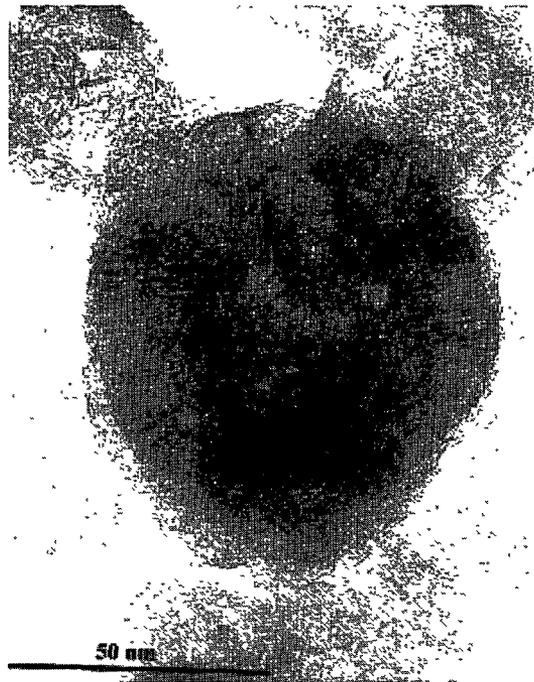


Fig 9. — T E.M Micrography of a plasma black corresponding to family 3 (Bourrat [13])

### Conclusion and Outlook of the Research

Due to their own nature, the traditional methods of producing carbon black appear to be confined within a temperature contained between 1200 °C and 1600 °C or, in the case of acetylene, within a small domain centred around 2500 °C.

Thanks to the use of an external energy supply, the new AC three phase plasma reactor opens the way to the decomposition of hydrocarbons under temperature conditions remaining unexplored up to now. Results obtained by the use of natural gas and ethylene, led to the production of original blacks.

A first family of products was made by injecting the hydrocarbon in a very hot region, in the arc zone. The products obtained in these conditions were very close to acetylene black, in the domain between acetylene black and graphite. These *blacks* let predict interesting properties for conductive applications (batteries, conductive plastics, ..).

On the other hand, injecting the hydrocarbon downstream the arc zone led to the production of original and unexpected products characterized by a low “long distance” organization and an unusual high level of graphitisation. Potential applications of such products have still to be investigated since they are very different from all industrial carbon black grades.

It is highly possible that the two families are the results of very different growth processes. In the first case, the growth process should not be very different from the acetylene black one (decomposition of acetylene into aromatic hydrocarbons and polycondensation of aromatic hydrocarbons) while, in the second case, a two step process is highly possible (growth of carbon particles in a low temperature region then thermal treatment by recirculating in a very hot region).



Fig. 10 — T E.M Micrography of a hollow plasma black particle corresponding to family 1 (Bourrat [13]).

Future works will focus on

- accurate investigation of the plasma black properties;
- qualitative and quantitative improvement of the process. In particular, optimization of the mixing between the plasma flow and the hydrocarbon;
- improvement in the knowledge of relationship between the processes parameters and the carbon black properties.

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