Title: HIGH PURITY CARBON BLACK COMPOSITION IN THE FORM OF A POWDER OBTAINED BY PYROLYSIS OF A SOLID CARBONIZABLE MATERIAL, PROCESS THEREOF

Abstract: A high purity carbon black composition in the form of a powder, resulting from the pyrolysis of a solid carbonizable material comprising: more than 75 per cent of carbon black, less than 0.0002 per cent of arsenic, less than 2 per cent of chloride(s), less than 0.03 per cent of copper, less than 5 per cent of zinc, and impurities. The percentages are expressed in weight with respect to the total weight of the composition and the composition has a total hydrocarbon content lower than 0.5 per cent. Such a composition is obtainable by a pyrolysis process of a solid carbonizable material wherein a rotary reactor comprising wings attached to the internal surface of the cylindrical body in a line by line shifted pattern is used. The recovered composition is directly useful in the plastic and rubber product industry, and more particularly in the tire industry.
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
HIGH PURITY CARBON BLACK COMPOSITION IN THE FORM OF A POWDER OBTAINED BY PYROLYSIS OF A SOLID CARBONIZABLE MATERIAL, PROCESS THEREOF

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

The invention relates to a process for recovering high purity carbon black composition from a solid carbonizable material.

More particularly, the invention relates to a process whereby a carbon black composition with a high degree of purity is directly obtained in a powder form by pyrolysis of a solid carbonizable material in a rotary reactor of very original internal structure.

The recovered carbon black composition is preferably in a powder form and has very low contents of arsenic, chlorides, copper, zinc, residual hydrocarbons and other impurities.

2. BRIEF DESCRIPTION OF THE PRIOR ART

Traditionally, pyrolysis reaction of a solid carbonizable material is carried out in a static or in a rotary reactor as exemplified in CA-A-2,194,505 and CA-A-2,194,805, respectively.

The carbon black composition obtained with such reactors is in the form of agglomerates which have to be grinded to be of commercial interest.

Moreover, the recovered carbon black composition contains high contents of undesirable substances like arsenic, chlorides, copper, zinc, residual
hydrocarbons and other impurities, which limit the commercial use of the recovered carbon black, particularly in the field of plastics.

It is obvious that a separate and efficient recovery of parasitic materials would increase the profitability of a process for producing carbon black, since arsenic, cadmium, copper, zinc and residual hydrocarbons are valuable as such.

**OBJECT AND SUMMARY OF THE INVENTION**

A first object of the invention is a high purity carbon black composition in the form of a powder, which is characterized by a low content of arsenic, cadmium, copper and zinc and residual hydrocarbons.

The high purity carbon black composition is in the form of a powder comprising:

- more than 75 per cent, preferably more than 80 per cent of carbon black,
- less than 0.0002 per cent, preferably less than 0.0001 per cent of arsenic,
- less than 2 per cent, preferably less than 0.02 per cent of chloride(s),
- less than 0.03 per cent, preferably less than 0.004 per cent of copper,
- less than 5 per cent, preferably less than 4 per cent of zinc, and
- impurities.

The percentages are expressed in weight with respect to the total weight of the composition.

The composition has a hydrocarbon content lower than 0.5 per cent, preferably lower than 0.3 per cent.

Another object of the invention is to provide a pyrolysis process for directly recovering a high purity carbon black composition preferably in a powder form, from a solid carbonizable material.
According to the invention, the pyrolysis process for recovering a high purity carbon black composition by pyrolysis of a solid carbonizable material in a rotary reactor having a cylindrical body with an internal surface, side walls and axial shafts respectively projecting perpendicularly from the side walls, comprises the steps of:

a) introducing said solid carbonizable material into the rotary reactor;

b) creating a vacuum in the rotary reactor by means of a pumping system, so as to extract oxygen-containing gases present in the pyrolysis reactor;

c) stopping the pumping system when the subatmospheric pressure in the pyrolysis reactor is between 1 and 2.5 Psi;

d) heating the rotary reactor with a burning combustion gas and starting the rotation of the rotary reactor;

e) recovering during the rotation and heating of the rotary reactor pyrolysis gas from the reaction zone of the rotary reactor;

f) stopping the heating and the rotation of the rotary reactor when the total hydrocarbon content, present in the gases after condensation and separation of the oils, is decreased to a value ranging from 0 to 15%; and

g) recovering high purity carbon black composition.

The process is characterized in that the rotary reactor further comprises wings attached to the internal surface of the cylindrical body in a line by line shifted pattern.
This process is similar to the pyrolysis processes described in Canadian patents CA-A-2,194,505 and CA-A-2,194,805 or in Canadian patent application CA-A-2,232,015 except that the reactor which is used for carrying out the process is not a conventional static or rotary reactor but a rotary reactor having plurality of internal parallel networks of wings.

A preferred embodiment of the invention will now be described with reference to the appending drawings. It should be noted that the appending drawings illustrate only one embodiment of this invention and are therefore not to be considered as limiting the scope of the present invention which may form the subject of other effective embodiments.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 is a side view of a rotary reactor (1) according to the invention for the pyrolysis of tires. This reactor (1) has a cylindrical body (4) and side walls (5, 5') also known as shells. The cylindrical wall (4) of the reactor (1) bears on its internal side a plurality of wings (3) which are disposed in a line by line shifted pattern. The wings (3) are attached on the internal side of the wall (4) of the cylindrical reactor (1). Axial shafts (2, 2') are attached respectively perpendicularly to the shells (5, 5').

Figure 2 is a cross sectional view taken along line II-II', of the cylindrical pyrolysis reactor (1) shown in Figure 1. Wings (3) with a parallelepiped like shape are disposed uniformly as a network on a circle on the internal surface of the wall (4) of the reactor (1).

Figure 3 is a cross sectional view taken along line III-III' of the cylindrical pyrolysis reactor (1) shown in Figure 1. The wings (3) are disposed uniformly on a circle on the internal surface of the wall (4) whose circle is parallel to the circle defined in the sectional view according to II-II'. The wings (3) of the circle defined in the
cross sectional view taken along line III-III' are parallel and offset when compared with the wings (3) of the nearest circle which is represented in Figure 2.

Further features of the invention and more particularly the features of the high purity carbon black obtained by the process according to the invention are illustrated in Figures 4 to 13.

Figure 4 is a grain size analysis of a fine sample of a carbon black powder (CBp) according to the invention obtained by using a disk centrifugation particle sizing (DCP), a) is a cumulative curve and b) is a weight fraction distribution.

Figure 5 is a grain size analysis of a CBp coarse sample CBp according to the invention obtained by using a disk centrifuge particle sizing (DCP), a) is a cumulative curve and b) is a weight fraction distribution.

Figure 6 is a diffractogram of CPp fine fraction of the heat treatment at 1000°C.

Figure 7 is a comparison of diffractograms of a non heated CBp fine fraction (68% amorphous) with the same sample heat treated for 1 and 4 hours at 1000°C in a covered crucible.

Figure 8 is the comparison of two diffractograms of CBp fine and coarse fraction.

Figure 9 represents diffractograms for a CBp coarse fraction with and without background and noise correction.

Figure 10 is the diffractogram of white crystals formed in and on the crucible after heat treatment.

Figure 11 is the spectral analysis from an energy dispersive system of a scanning Electron Microscope.
Figure 12 illustrates an equipment for the pyrolysis of tires according to the patent application CA-A-2,232,015.

Figure 13 illustrates an equipment for the pyrolysis of tires according to the invention which is similar to the equipment described in Figure 12 except that a rotary reactor, as illustrated on Figures 1 to 3, is used instead of the traditional rotary reactor illustrated on Figure 12.

**DETAILED DESCRIPTION OF THE INVENTION**

The process for recovering a high purity carbon black composition by pyrolysis of a solid carbonizable material according to the invention is characterized in that the rotary reactor thereby used comprises wings attached to the internal surface of the cylindrical body in a line by line shifted pattern.

The wings of the rotary reactor are attached to the internal surface of the wall in parallel networks. The wings of every pair of adjacent networks are offset.

These networks of wings prevent agglomeration of the recovered carbon black and simultaneously improve the separation of carbon black from metals.

The rotary reactor according to the invention is cylindrical in shape with an internal radius preferably ranging between 0.90 and 1.5 meters. More particularly, this radius is more preferably equal to about 1.20 meters.

The side walls of the rotary reactor are in form of disks which are parallel to the pattern of wings.

The internal length of the cylindrical body preferably ranges between 5 and 9.5 meters. Preferably, the internal length is equal to about 6 meters.

The wings may have different forms but preferably have a parallelepiped like shape.
According to a preferred embodiment of the invention, the wings have a parallelepiped like shape slightly modified with a concave surface in contact with the internal surface of the cylindrical body of the rotary reactor.

According to a further preferred embodiment of the invention, the wings are disposed on parallel circles on the internal surface of the cylindrical body of the rotary reactor.

The pyrolysis reactor is preferably heated and rotated for 2.5 to 4 hours, and more preferably for about 2 hours.

The length of a wing preferably ranges between 1/6 and 1/3 the size of the internal radius of the cylindrical body of the rotary reactor, and is preferably about 1/4 of the size of the internal radius of the reactor. As an example, the length of a wing is comprised between 15 and 50 cm.

The thickness of a wing is preferably comprised between 0.3 and 1.3 cm and preferably it is about 1 cm.

The height of a wing is preferably comprised between 5 and 10 cm. Preferably it is about 7 cm.

The distance between two next to next networks of wings is preferably between 15 and 45 cm, and preferably it is about 30 cm.

The rotary reactor moves at a rotating speed which preferably ranges between 5 and 15 rpm and it is preferably about 10 rpm.

According to a preferred embodiment of the invention, the pyrolysis reactor is heated and rotated for 1.5 to 4 hours and more preferentially for about 2 hours.

In order to improve heat transfer, the wings are positioned in such a way as to be parallel to the end walls of the reactors.
According to a preferred embodiment of the invention, the solid carbonizable material which is introduced in step a) in said rotary reactor is selected from the group consisting of wood chips, shavings, sawdust and similar wood particles, car fluff, plastics, soils contaminated with hydrocarbons, coal, coal residues and tires.

According to a most preferred embodiment, the solid carbonizable material consists of tires.

The recovered high purity carbon black composition is preferably in a powder form. For commercial reasons, the recovered powder is divided in two fractions: a fine and a course fraction which do not need further grinding.

The chloride(s) present in the composition according to the invention is (are) selected from the group consisting of sodium chloride, potassium chloride, magnesium chloride and calcium chloride.

According to a preferred embodiment, only traces of calcium chloride are present in the compositions of the invention.

The high purity carbon black composition recovered by the process of the invention is in the form of a powder made of granules of a size ranging from 0.1 to 30 micrometers.

Due to their powder form, the high purity carbon black compositions recovered by the process of the invention are directly useful in the plastic and rubber product industry, and more particularly in the tire industry.

The following specific examples intended to illustrate the present invention, but the scope of the invention is not to be considered to be limited thereby.
COMPARATIVE EXAMPLE 1

A recovery plant as shown in Figure 12 with a static reactor (1) was used to selectively recover gases produced in a pyrolysis reactor of the type used in a batch type process as described in the Canadian patent CA-A-2,287,047.

The pressure within the reaction zone was generally maintained at ambient pressure with a negative pressure continuously applied to the gas-vapor outlet conduit to remove the gas-vapor stream from the reaction zone.

First, 6,363 kg of used car tires in a shredded form were introduced in the static reactor (1) having a volume of 30 m³.

Then, a vacuum was created in the static reactor (1') by means of a pumping system, so as to extract oxygen-containing gases present in said reactor. The pumping system was stopped when the pressure in the pyrolysis reaction reached 1.5 Psi.

The pyrolysis reactor was heated at a temperature of 475°C with a burning gas with 1800 btus and the reactor rotated at a rotating speed of 9 rpm.

Then, the residual gases going through the condenser (2) had a THC which was equal to 0% at the beginning of the reaction and which progressively increased up to 100% after 4 hours. At this time the residual gases were sent to the gas storage tank (8). After 2.45 hours, when a THC value of 59% was reached, the recovered gases were sent to the flare (9) and the heating and rotation of the reactor was stopped at a THC value of 15%.

After 4.3 hours, the exothermic phase of the pyrolysis was completed.

Then 3,690 kg of carbon black in the form of briquettes were recovered. The THC of the recovered briquettes was of 1.2%. The briquettes contain 10% weight percent of residual metallic filaments.
The weight of the briquettes ranged from 50 to 150 g.

The composition of the briquettes as reported in Table V was of:

- 16.1 per cent of carbon black,
- 0.000171 per cent of arsenic,
- 0.0221 per cent of chloride(s),
- 4.85 per cent of zinc, and
- traces of impurities.

The overall productivity of the pyrolysis was of 32 per cent for carbon black and of 47 per cent of pyro-oil.

**COMPARATIVE EXAMPLE 2**

A recovery plant according to the invention as shown in Figure 13 with a 30 m³ rotary reactor (1') of the type illustrated on Figure 1 was used to selectively recover gases produced during the pyrolysis reaction.

The rotary reactor had a cylindrical body with an internal length of 609.6 cm, an internal radius of 121.92 cm and the wings attached to the internal surface of the cylindrical body were in a line by line shifted pattern.

The wings had a slightly modified parallelepiped like shape with a concave surface in contact with the internal surface of the cylindrical body of the reactor.

The wings had a length of 10 cm, and a thickness of 0.8 cm, and a height of 7 cm.

The distance between two next to next parallel networks of wings was of 30 cm.

First, 6,420 kg of used car tires in a shredded form were introduced in the rotary reactor (1') having a volume of 30 m³.
Then, a vacuum was created in the rotary reactor by means of a pumping system, so as to extract oxygen-containing gases present in the rotary reactor. The pumping system was stopped when the pressure in the pyrolysis reaction reached 1.5 Psi.

The pyrolysis reactor was heated at a temperature of 500°C with a 1475 btus burning gas and rotated at a rotating speed of 9 rpm.

Then, the residual gases going through the condenser (2) had a THC which was equal to 0% at the beginning of the reaction and which progressively increased up to 100% after 4 hours. At this time the residual gases were sent to the gas storage tank (8). After 2.45 hours, when a THC value of 60% was reached, the recovered gases were sent to the flare (9) and the heating of the reactor stopped.

After 3.3 hours, the exothermic phase of the pyrolysis was completed.

After 4 hours, the reaction of pyrolysis was completed. 3,054 kg of carbon black in the form of a fine powder of the type N600 was recovered. The THC of the recovered carbon black was of 0.4%. The powder did not contain any metallic filaments and was divided for commercial reasons in two fractions thereinafter called “fine K-01-01” and “coarse K-01-02”. The fine K-01-01 and the coarse K-01-02 fractions were isolated from the carbon black composition recovered in Comparative Example 2, by using a cyclone and a dust collector.

The chemical analysis of the fine and of the coarse fractions K-01-01 and K-01-02 is illustrated in following Table I. The granules of said powder have a size ranging from 0.5 to 25 units. The residual metallic filaments were recovered separately.

The composition of the carbon black powder is reported in Table IV.

The overall productivity of the pyrolysis was of 37 per cent for carbon black and of 47 per cent for the pyro-oil.
Further physical properties of the thereby recovered carbon black powder and of the recovered oils are presented hereinafter.
CHEMICAL ANALYSIS OF A FINE AND COARSE GRAIN CBp SAMPLE FROM PYROLYSIS ACCORDING TO THE INVENTION AND A COMPARISON WITH A COMMERCIAL CB

TABLE I

<table>
<thead>
<tr>
<th>Elements</th>
<th>DL ppm</th>
<th>Carbon Black commercial</th>
<th>Fine K-01-01 ppm</th>
<th>Coarse K-01-02 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>2</td>
<td>sldd</td>
<td>1.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Al</td>
<td>100</td>
<td>sldd</td>
<td>11,000</td>
<td>10,100</td>
</tr>
<tr>
<td>C tot.</td>
<td>100</td>
<td>991,000</td>
<td>795,000</td>
<td>798,000</td>
</tr>
<tr>
<td>Cl₂</td>
<td>100</td>
<td>2,000</td>
<td>18,300</td>
<td>9,400</td>
</tr>
<tr>
<td>Ca</td>
<td>100</td>
<td>sldd</td>
<td>4,200</td>
<td>8,300</td>
</tr>
<tr>
<td>Cd</td>
<td>1</td>
<td>sldd</td>
<td>1.9</td>
<td>1.0</td>
</tr>
<tr>
<td>Cr</td>
<td>1</td>
<td>5,850</td>
<td>28</td>
<td>18</td>
</tr>
<tr>
<td>Co</td>
<td>100</td>
<td>sldd</td>
<td>290</td>
<td>290</td>
</tr>
<tr>
<td>Cu</td>
<td>1</td>
<td>sldd</td>
<td>360</td>
<td>250</td>
</tr>
<tr>
<td>K</td>
<td>100</td>
<td>sldd</td>
<td>1,700</td>
<td>1,700</td>
</tr>
<tr>
<td>F</td>
<td>500</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Fe</td>
<td>100</td>
<td>sldd</td>
<td>15,400</td>
<td>22,500</td>
</tr>
<tr>
<td>Hg</td>
<td>10</td>
<td>10 ppb</td>
<td>28</td>
<td>31</td>
</tr>
<tr>
<td>Mg</td>
<td>100</td>
<td>sldd</td>
<td>1,500</td>
<td>2,000</td>
</tr>
<tr>
<td>Mn</td>
<td>2</td>
<td>sldd</td>
<td>290</td>
<td>425</td>
</tr>
<tr>
<td>Mo</td>
<td>1</td>
<td>sldd</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Na</td>
<td>100</td>
<td>sldd</td>
<td>1,300</td>
<td>1,300</td>
</tr>
<tr>
<td>Ni</td>
<td>10</td>
<td>sldd</td>
<td>17</td>
<td>20</td>
</tr>
<tr>
<td>P</td>
<td>100</td>
<td>sldd</td>
<td>445</td>
<td>400</td>
</tr>
<tr>
<td>Pb</td>
<td>2</td>
<td>1.53</td>
<td>105</td>
<td>71</td>
</tr>
<tr>
<td>S tot.</td>
<td>1,000</td>
<td>5,800</td>
<td>30,700</td>
<td>28,100</td>
</tr>
<tr>
<td>Si</td>
<td>100</td>
<td>sldd</td>
<td>18,600</td>
<td>28,000</td>
</tr>
<tr>
<td>Se</td>
<td>0.1</td>
<td>n.d.</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Ti</td>
<td>100</td>
<td>sldd</td>
<td>12,100</td>
<td>820</td>
</tr>
<tr>
<td>Zn</td>
<td>0.5</td>
<td>sldd</td>
<td>48,000</td>
<td>43,400</td>
</tr>
</tbody>
</table>

n.d.: Not determined
DL: Detection limit
sldd: Under the limit of detection
K-01-01 and K-01-02 are granules of carbon black recovered from a pyrolysis carried out according to the present invention.

CONDUCTIVITY OF A SLURRY MADE FROM CBp

The conductivity measurements were made using 5 g of solid in 200 ml of water and the slurry was agitated. The first measurement was made on a concentrate of long fibers and agglomerates of chars while the second reading was made on the coarse fraction (K-01-02) without any treatment of the solid. The values are given on the following table and are compared with tap and distilled water.

<table>
<thead>
<tr>
<th>Conductivity $\mu$S/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrate of fibers of K-01-02</td>
</tr>
<tr>
<td>K-01-02</td>
</tr>
<tr>
<td>Tap water</td>
</tr>
<tr>
<td>Distilled water</td>
</tr>
</tbody>
</table>

ASH DETERMINATION

The amount of ash was determined using 10 g of solid heated at 1100°C with oxygen until a stabilization of the sample weight was obtained.

The results are as follow:

| Fine sample | K-01-01 | 17.8% |
| Coarse sample | K-01-02 | 21.0% |

These values are as high as it should be expected from a carbon black obtained in this fashion compared to CB commercial with an ash value of less than 1%. 
STANDARD LIxivIATION TEST

The TCLP of the EPA was made on both coarse and fine samples without any prior treatment.

<table>
<thead>
<tr>
<th>Method</th>
<th>Fine K-01-01 mg/L</th>
<th>Coarse K-01-02 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>AAS &lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Cu</td>
<td>AAS &lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Ni</td>
<td>AAS &lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Cr</td>
<td>AAS &lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Zn</td>
<td>AAS 164</td>
<td>130</td>
</tr>
<tr>
<td>Cd</td>
<td>AAS &lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Se</td>
<td>AAS &lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Hg</td>
<td>AAS &lt;0.01</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

PARTICLE SIZE ANALYSIS

Each sample was prepared by adding 12 mg of the powder to 6 ml of 25% EtOH with 0.04% Triton x-100 in DI water. The samples were then probe sonicated for 2 min. At 1 second bursts followed by a low power sonic bath for 3 min. The measurements were made using a DCP disc centrifuge. The results are given on Figure 1 for both fine and coarse samples. A mean distribution curve is given with the corresponding cumulative curve. Contrary to what was expected, the results indicate that the finer material was found with the coarser fraction. This can be explained by the fact that the extremely fine fraction is more strongly adsorbed at the surface of the fibers and the agglomerated chars. The procedure outlined above permitted to liberate this finer portion and as a result the coarse fraction
displayed a finer mode. In reality, both samples were small in the pigment range but were still much larger than the commercial carbon black which is in the nanometer range.

As a potential filler the CBp need to be made of a fine particle size distribution. This is an important property for the filler its resultant strength and other physical characteristics.

**MODAL ABUNDANCE OF COMPOUNDS FORMING THE ASH USING X-RAY DIFFRACTION (AS REPORTED IN TABLE IV)**

Diffraction patterns were obtained with a Siemens D 500 step scanner using a cobalt tube and a silicon detector.

The following table summarizes the results obtained from raw powders and samples heat treated to 1,000°C for 1 and 4 hours.
<table>
<thead>
<tr>
<th>Compounds or mineral equivalent</th>
<th>Fine K-01-01 no-heat %</th>
<th>Coarse K-01-02 no-heat %</th>
<th>Fine 1 hr 1,000°C K-01-01T</th>
<th>Coarse 1 hr 1,000°C K-01-02T</th>
<th>Fine 4 hrs 1,000°C K-01-01T4</th>
<th>Coarse 4 hrs 1,000°C K-01-02T4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>68.9</td>
<td>68</td>
<td>amor.</td>
<td>62</td>
<td>75</td>
<td>amor.</td>
</tr>
<tr>
<td>TiO₂</td>
<td>6.4</td>
<td>5.4</td>
<td>Zn,FeO₄</td>
<td>5.4</td>
<td>2.6</td>
<td>gahnite</td>
</tr>
<tr>
<td>ZnO</td>
<td>18.3</td>
<td>n.d.</td>
<td>ZnO₂</td>
<td>2.5</td>
<td>1.3</td>
<td>ZnO₂</td>
</tr>
<tr>
<td>TiO₂ anatase rutile</td>
<td>5.1</td>
<td>0.2</td>
<td>TiO₂ rutile</td>
<td>1.7</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>ZnS Sphalerite</td>
<td>16.0</td>
<td>15.1</td>
<td>ZnS Sphalerite</td>
<td>0.1</td>
<td>0.2</td>
<td>maghemite</td>
</tr>
<tr>
<td>Wurtzite</td>
<td>4.1</td>
<td>1.6</td>
<td>hematite</td>
<td>0.5</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>C graphite</td>
<td>1.1</td>
<td>1.6</td>
<td>C cristallin</td>
<td>1.1</td>
<td>7.9</td>
<td>C cristallin</td>
</tr>
<tr>
<td>C₄SO₃</td>
<td>0.4</td>
<td>0.2</td>
<td>n.d. SiC</td>
<td>n.d. SiC</td>
<td>n.d. SiC</td>
<td>n.d. SiC</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2.7</td>
<td>5.2</td>
<td>SiO₂ Quartz et cristobalite</td>
<td>2.3</td>
<td>11.1</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Quartz or cristobalite</td>
<td></td>
<td></td>
<td>Quartz or cristobalite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeS pyrrhotite</td>
<td>0.54</td>
<td>1.1</td>
<td>FeS</td>
<td>2.0</td>
<td>1.2</td>
<td>FeS</td>
</tr>
<tr>
<td>Clays</td>
<td>2.0</td>
<td>1.6</td>
<td>clays</td>
<td>n.d. micas</td>
<td>n.d. enstatite</td>
<td>5.4</td>
</tr>
<tr>
<td>CaCO₃ calcite</td>
<td>2.0</td>
<td>1.8</td>
<td>CaCO₃ calcite</td>
<td>n.d.</td>
<td>n.d.</td>
<td>feldspar</td>
</tr>
<tr>
<td>gukileite titanate of Mg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The heat treatment in a muffle furnace with a static air condition showed that the carbon chars still contained hydrocarbons. The zinc can be volatilized from the char and will crystallize immediately in the form of zinc oxide that forms a ring of white needles around the crucible.

5 HYDROGEN PEROXIDE WASHING

An attempt was made to use hydrogen peroxide to remove the zinc sulfide and in the process this reaction was accompanied with reduction in other metals. In other words an hydrogen peroxide treatment can remove a substantial part of the fibers by flotation, oxidized the zinc sulfide and other sulfides which goes into solution.

10 It was also noticed that this type of washing oxidized the remaining hydrocarbons and washed the fibers clean to the point that the white color was quite contrasting on a black background. The final product was different in appearance (black lustre and texture). The specific surface measurement were found to have increase from a value of approximately 20 m²/g to more than 80 m²/g. In a way, this material showed a slight display of being activated.

15 ATTEMPTS TO CLEAN THE CARBON SAMPLES

SCREENING

At first a simple screening technique was used to eliminate the fibers and the char agglomerates. This procedure was a success and a large concentrate of fibers was extracted as long as the screening was not done too violently to brake the fragile fibers.

MAGNETIC SEPARATION

With a strong magnet it is also possible to extract iron particles and other ferromagnetic compounds.
SURFACTANT WASHING

It is well known that this type of samples are difficult to wet, various types of surfactants can be used to wet, disperse and separate the initial bulk sample into fractions of cleaner materials. This is illustrated by the photos of Figure 3, from top to bottom we seen an agglomeration of fibers with char particles, followed with a concentrate of chars with fewer fibers and finally a fine grain illustrated by the top photo material that appears to be much cleaner. A chemical spectrum analysis still displays the same metals as contaminants, in all probability the amount of contaminants have been reduced to a certain extent but not to the level of a commercial carbon black.

From the preliminary test that was conducted on carbon black samples from a vacuum pyrolysis process, one may conclude that the material can be cleaned in several ways which will improve its chemical composition and other physical characteristics.

The extent the black char can be cleaned is function of the application and the cost to attain the desired purity. A chemical purity that will match the commercial carbon black is out of reach but intermediate products and purity are possible.

In addition to the conventional carbon black application, it could become a good candidate for activated carbon if steam or carbon dioxide is used. In addition using carbon dioxide the Boudoir reaction is possible which can produce a boudoir black used in organic colorants.

An improved starting CBp would require a higher temperature of pyrolysis coupled to a longer residence time. Then the material could be cleaned through an air fractionation of the fibers and chars followed with an appropriate treatment depending on the application that is looked at.
The carbon black obtained was also analysed for impurities with the following results: arsenic 1.71 mg/kg; cadmium 4.60 mg/kg; chlorides 2210 mg/kg; chrome 9.50 mg/kg; copper 410 mg/kg; petroleum hydrocarbons 720 mg/kg; mercury less than 0.05 mg/kg; nickel 11.5 mg/kg; lad 144 mg/kg; sulphur 4.05 mg/kg and zinc 48,500 mg/kg. When burnt at 800°C, there was a carbon black loss of 83.9% of the carbon black sample.

**TABLE V**

<table>
<thead>
<tr>
<th></th>
<th>mg/kg</th>
<th>ppm</th>
<th>Briquettes</th>
<th>ppm</th>
<th>Hebco</th>
<th>02</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>1.71</td>
<td>1.71</td>
<td>0.000171</td>
<td>1.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cadmium</td>
<td>4.60</td>
<td>4.60</td>
<td>0.00046</td>
<td>1.9</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Chlorides</td>
<td>2,210</td>
<td>2,210</td>
<td>0.0221</td>
<td>18,300</td>
<td>9,400</td>
<td></td>
</tr>
<tr>
<td>Chrome</td>
<td>9.50</td>
<td>9.50</td>
<td>0.00095</td>
<td>28</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>410</td>
<td>410</td>
<td>0.041</td>
<td>360</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mercury</td>
<td>-0.05</td>
<td>-0.05</td>
<td>0.000005</td>
<td>28</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>11.5</td>
<td>11.5</td>
<td>0.00115</td>
<td>17</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Lad</td>
<td>114</td>
<td>114</td>
<td>0.0114</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphur</td>
<td>4.05</td>
<td>4.05</td>
<td>0.000405</td>
<td>48,000</td>
<td>4,340</td>
<td></td>
</tr>
</tbody>
</table>

The high purity carbon black according to the invention is not in form of briquettes or agglomerates and is free of metallic fibers.

It is in a powder form made of granules of a size ranging from 1 to 30 micrometers.

This new quality of recovered carbon black is comparable for its physical properties to the ranges N500 and N600 of the virgin carbon black available from the chemical industry.
CLAIMS

1. A high purity carbon black composition in the form of a powder, resulting from the pyrolysis of a solid carbonizable material comprising:

   - more than 75 per cent of carbon black,
   - less than 0.0002 per cent of arsenic,
   - less than 2 per cent of chloride(s),
   - less than 0.03 per cent of copper,
   - less than 5 per cent of zinc, and
   - impurities;

the percentages being expressed in weight with respect to the total weight of the composition,

said composition having a total hydrocarbon content lower than 0.5 per cent.

2. High purity carbon black composition according to claim 1, characterized in that said composition contains more than 80 weight per cent of carbon black.

3. High purity carbon black composition according to claim 1 or 2, characterized in that said composition contains less than 0.0001 weight per cent of arsenic.

4. High purity carbon black composition according to any one of claims 1 to 3, characterized in that said composition contains less than 0.02 weight per cent of chloride(s).

5. High purity carbon black composition according to any one of claims 1 to 4, characterized in that said composition contains less than 0.004 weight per cent of copper.
6. High purity carbon black composition according to any one of claims 1 to 5, characterized in that said composition contains less than 4 weight per cent of zinc.

7. High purity carbon black composition according to any one of claims 1 to 6, characterized in that the chloride(s) is (are) selected from the group consisting of sodium chloride, potassium chloride, magnesium chloride and calcium chloride.

8. High purity carbon black composition according to any one of claims 1 to 7, characterized in that the total hydrocarbon content is lower than 0.3 per cent.

9. High purity carbon black composition according to any one of claims 1 to 8, characterized in that said composition contains traces of calcium chloride.

10. High purity carbon black composition according to any one of claims 1 to 9, characterized in that said composition is in the form of a powder made of granules of a size ranging between 7 and 30 micrometers.

11. High purity carbon black composition according to claim 10, characterized in that the size of said granules ranges between 3 and 25 micrometers.

12. High purity carbon black composition according to any one of claims 1 to 11, characterized in that the solid carbonizable material consists of wood chips, shavings, sawdust and similar wood particles, car fluff, plastics, soils contaminated with hydrocarbons, coal, coal residues and tires.

13. High purity carbon black composition according to claim 12, characterized in that the solid carbonizable material consists of tires.

14. Process for recovering high purity carbon black composition by pyrolysis of a solid carbonizable material in a rotary reactor having a cylindrical body with an internal surface, side walls and axial shafts respectively projecting perpendicularly from the side walls,
said process comprising the steps of:

a) introducing the said solid carbonizable material into said rotary reactor;

b) creating a vacuum in the rotary reactor by means of a pumping system, so as to extract oxygen-containing gases present in said pyrolysis reactor;

c) stopping the pumping system when the subatmospheric pressure in the pyrolysis reactor is between 1 and 2.5 Psi;

d) heating the rotary reactor with a burning combustion gas and starting the rotation of said rotary reactor;

e) recovering during the rotation and heating of the rotary reactor pyrolysis gas from the reaction zone of the rotary reactor;

f) stopping the heating and the rotation of the rotary reactor when the rate of total hydrocarbon content, present in the gases after condensation and separation of the oils, is decreased to a value ranging from 0 to 15%; and

g) recovering high purity carbon black composition;

said process being characterized in that the rotary reactor further comprised wings attached to the internal surface of the cylindrical body in a line by line shifted pattern.

15. Process according to claim 14, characterized in that the side walls are in form of disks which are parallel to the pattern of wings.

16. Process according to claims 14 or 15, characterized in that the cylindrical body has an internal radius ranging from 0.90 to 1.5 meter.
17. Process according to claim 16, characterized in that the internal radius is equal to about 1.20 meters.

18. Process according to any one of claims 14 to 17, characterized in that the cylindrical body has an internal length ranging from 5 to 9.5 meters.

19. Process according to claim 18, characterized in that the internal length of the cylindrical body is equal to about 6 meters.

20. Process according to any one of claims 14 to 19 characterized in that the wings have a parallelepiped like shape.

21. Process according to any one of claims 14 to 20, characterized in that the wings have a parallelepiped like shape slightly modified with a concave surface in contact with the internal surface of the cylindrical body.

22. Process according to any one of claims 14 to 21, characterized in that the wings are disposed on parallel circles on the internal surface of the cylindrical body of the rotary reactor.

23. Process according to any one of claims 16 to 22, characterized in that a wing has a length comprised between 1/6 and 1/3 of the size of the internal radius of the cylindrical body of the rotary reactor.

24. Process according to claim 23, characterized in that a wing has a length which is about 1/4 of the size of the internal radius of the cylindrical body of the rotary reactor.

25. Process according to any one of claims 16 to 24, characterized in that the length of a wing is comprised between 15 and 50 cm.

26. Process according to any one of claims 16 to 25, characterized in that a wing has a thickness comprised between 0.3 and 1.3 cm.
27. Process according to claim 26 characterized in that the thickness of a wing is about 1 cm.

28. Process according to any one of claims 16 to 27, characterized in that a wing has a height comprised between 5 and 10 cm.

29. Process according to claim 28 characterized in that the height of a wing is about 7 cm.

30. Process according to any one of claims 16 to 29, characterized in that the distance between two next to next parallel networks of wings is comprised between 15 to 45 cm.

31. Process according to claim 30, characterized in that the distance between two next to next parallel networks of wings is about 30 cm.

32. Process according to any one of claims 16 to 31, characterized in that the rotary reactor moves at a rotating speed comprised between 5 and 15 rpm.

33. Process according to claims 32, characterized in that the rotating speed is about 10 rpm.

34. Process according to any one of claims 14 to 33, characterized in that the reactor is heated and rotated for 1.5 to 4 hours.

35. Process according to claim 34 characterized in that the pyrolysis reactor is heated and rotated for about 2 hours.

36. Process according to any one of claims 14 to 35, characterized in that the solid carbonizable material consists of wood chips, shavings, sawdust and similar wood particles, car fluff, plastics, soils contaminated with hydrocarbons, coal, coal residues and tires.
37. Process according to claim 36, characterized in that the solid carbonizable material consists of tires.

38. High purity carbon black composition as obtained by a process according to anyone of claims 14 to 37.

39. High purity carbon black composition according to anyone of claims 1 to 13, for use in the plastic and rubber industry.

40. High purity carbon black composition as obtained by a process according to anyone of claims 14 to 37, for use in the plastic and rubber industry.
C:\D5000\DATA\X0101T_RAW X0101T 1000C 1H (CT: 3.0s, SS:0.010dg, WL: 1.7890Ao)
36-1451 ZnO Zincite, syn(WL: 1.7890Ao)
23-1123 FeS Iron Sulfide, syn(WL: 1.7890Ao)
22-1012 ZnFe2O4 Franklineite, syn(WL: 1.7890Ao)
34-0180 TiO2 Rutile, syn(WL: 1.7890Ao)
25-0284 C Graphite, syn(WL: 1.7890Ao)
33-1161 SiO2 Quartz, syn(WL: 1.7890Ao)
36-1450 ZnS Wurtzite-2H, syn(WL: 1.7890Ao)
21-1272 TiO2 Anatase, syn(WL: 1.7890Ao)

FIG. 6