METHOD OF MAKING CARBON BLACK

A method of making tailored carbon black in a plasma process. A method of making tailored carbon black in a plasma process is described, including subjecting the carbon black particles during and/or after formation to functionalizing agents in a controlled manner so as to impart a degree and/or density of functionalization onto the carbon black particles so as to adapt the particles to a particular pre-intended application.
METHOD OF MAKING CARBON BLACK

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application No. 62/202,498, filed August 7, 2015, which application is incorporated by reference herein in its entirety.

TECHNICAL FIELD

[0002] The field of art to which this invention generally pertains is methods for making use of electrical energy to effect chemical changes.

BACKGROUND

[0003] There are many processes that can be used and have been used over the years to produce carbon black. The energy sources used to produce such carbon blacks over the years have, in large part, been closely connected to the raw materials used to convert hydrocarbon containing materials into carbon black. Residual refinery oils and natural gas have long been a resource for the production of carbon black. Energy sources have evolved over time in chemical processes such as carbon black production from simple flame, to oil furnace, to plasma, to name a few. As in all manufacturing, there is a constant search for more efficient and effective ways to produce such products. Varying flow rates and other conditions of energy sources, varying flow rates and other conditions of raw materials, increasing speed of production, increasing yields, reducing manufacturing equipment wear characteristics, etc. have all been, and continue to be, part of this search over the years.

[0004] The systems described herein meet the challenges described above, and additionally attain more efficient and effective manufacturing process.
BRIEF SUMMARY

[0005] A method of making carbon black in a plasma process is described, including subjecting the carbon black particles during and/or after formation to surface functionalizing agents in a controlled manner so as to impart a degree and/or density of functionalization onto the carbon black particles so as to adapt the particles to a particular pre-intended application.

[0006] Additional embodiments include: the method described above where the functional groups comprise oxygen containing functional groups; the method described above where the functional groups are introduced in the reactor, pelletizer, and/or dryer; the method described above where the functional groups comprise carboxylic acid and/or phenolic groups; the method described above where the density of the functionalization is up to about 30 micromol/m²; the method described above where the carbon black particles are subjected to the functionalizing agents at temperatures up to about 500° C; the method described above where the functionalizing agents contain one or more oxidizing agents; the method described above where the functionalizing agents contain one or more of \( \text{H}_2, \text{CO, CO}_2, \text{O}_2, \) water vapor, nitrogen, \( \text{N}_2\text{O, NO}_2, \) ozone, ammonia, amines, methyl amines, hydroxides, \( \text{H}_2\text{O}_2, \) acids, \( \text{HNO}_3, \) persulfates, hypohalites, halites, halates, perhalates, permanganates, carbonates, bleach, nitric acid, potassium permanganate, sulfuric acid, diazonium salts, diazonium salt of sulfanilic acid, nitrates, nitrate salts, organic nitrates, peroxides, and alkali metal super peroxides.; and the carbon black produced by the process described above.

DETAILED DESCRIPTION

[0007] The particulars shown herein are by way of example and for purposes of illustrative discussion of the various embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the
invention. In this regard, no attempt is made to show details of the invention in more
detail than is necessary for a fundamental understanding of the invention, the
description making apparent to those skilled in the art how the several forms of the
invention may be embodied in practice.

[0008] The present invention will now be described by reference to more detailed
embodiments. This invention may, however, be embodied in different forms and
should not be construed as limited to the embodiments set forth herein. Rather, these
embodiments are provided so that this disclosure will be thorough and complete, and
will fully convey the scope of the invention to those skilled in the art.

[0009] Unless otherwise defined, all technical and scientific terms used herein have
the same meaning as commonly understood by one of ordinary skill in the art to which
this invention belongs. The terminology used in the description of the invention herein
is for describing particular embodiments only and is not intended to be limiting of the
invention. As used in the description of the invention and the appended claims, the
singular forms "a," "an," and "the" are intended to include the plural forms as well,
unless the context clearly indicates otherwise. All publications, patent applications,
patents, and other references mentioned herein are expressly incorporated by reference
in their entirety.

[0010] Unless otherwise indicated, all numbers expressing quantities of ingredients,
reaction conditions, and so forth used in the specification and claims are to be
understood as being modified in all instances by the term "about." Accordingly, unless
indicated to the contrary, the numerical parameters set forth in the following
specification and attached claims are approximations that may vary depending upon
the desired properties sought to be obtained by the present invention. At the very least,
and not as an attempt to limit the application of the doctrine of equivalents to the
scope of the claims, each numerical parameter should be construed in light of the
number of significant digits and ordinary rounding approaches.

[0011] Notwithstanding that the numerical ranges and parameters setting forth the
broad scope of the invention are approximations, the numerical values set forth in the
specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. Every numerical range given throughout this specification will include every narrower numerical range that falls within such broader numerical range, as if such narrower numerical ranges were all expressly written herein.

[0012] Additional advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

[0013] Carbon blacks (CB) made with a particular surface chemistry can impart improved performance in rubber, composite, and other applications. Typically carbon black produced by plasma and other high temperature processes have performed poorly in rubber compounds in the past. However, when surface functionality can be controlled, carbon blacks with superior performance properties when compared to traditionally produced plasma blacks can be produced, e.g., even out performing some typical oil based furnace blacks.

[0014] The performance can be improved, for example, through the creation of oxygen functional groups at the carbon surface. In the typical furnace process, functional groups can inherently exist at the surface, for example, due to the existence of a time-temperature profile that can be characterized as having the CB in contact with tail gas composed of water, hydrogen, carbon monoxide, carbon dioxide and various other gases. These gases can be in intimate contact with the CB while the CB is still at high temperature (e.g., about 600 °C) which can enable the formation of surface functional groups. Due to the lack of oxygen groups in the tail gas in a typical plasma process, surface functional groups will typically not form, and the material can have what is known as "dead surface". This dead surface can be characterized as not
having a substantial amount of water uptake when exposed to a range of relative humidity (RH) conditions (for example, from about 0 % to about 80% RH).

[0015] Controlled oxidation can place specific groups at the surface. For instance, the surface of furnace black might be comprised of 60:40 (mole equivalents) phenolicxarboxylic acid groups whereas with a controlled surface the ration could be comprised of 10:90 phenolicxarboxylic acid groups. The carboxylic acid groups will typically be more reactive to rubber or SBR (styrene butadiene rubber) and more likely to form what is known as "bound rubber". A larger amount of bound rubber could result in lower vibration, hysteresis, treadwear, and/or higher reinforcement, in addition to other possible benefits such as increased vehicle miles per gallon (mpg).

[0016] What is disclosed herein, is the control of the surface chemistry of the CB by improving such things as the reactor mixing, pelletizer additives and oxidation of the surface in the dryer through the introduction of air or other oxidizers to contact the product at temperature. Adding oxidizers to the reactor gasses could produce similar improvements and represent a part of what is described herein. Modification of the surface chemistry by changing the mixing so that the same surface area product forms at a different temperature; modifying the surface chemistry of the product by the use of additives to the pelletizer; modifying the surface chemistry of the product by the use of changing the gas phase chemistry in the dryer, and modifying the surface chemistry by changing the gas phase chemistry in the reactor and/or heat exchanger and/or degas vessel, are all included herein.

[0017] Due to the combination of time-temperature profile and the atmosphere at such a time-temperature reaction, oxygen groups typically form at the surface of carbon black when made utilizing the traditional furnace process. The typical atmosphere or tail gas of a furnace reactor that burns oil and possesses a water quench can comprise the following components (according to Donnet's Carbon Black, t2nd Edition, pub. by Marcel Dekker, 1993, the disclosure of which is herein incorporated by reference (at page 46)).
Table 1

<table>
<thead>
<tr>
<th>Tail Gas Component</th>
<th>Volume Percent</th>
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<tr>
<td>(\text{N}_2)</td>
<td>61-67</td>
</tr>
<tr>
<td>(\text{CO}_2)</td>
<td>3.5</td>
</tr>
<tr>
<td>(\text{CO}_2)</td>
<td>11-15</td>
</tr>
<tr>
<td>(\text{H}_2)</td>
<td>12-24</td>
</tr>
<tr>
<td>(\text{CH}_4)</td>
<td>0.02-0.5</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_4)</td>
<td>0.02-0.5</td>
</tr>
</tbody>
</table>

In addition to these components, water vapor is typically present at about 35% - 45%. Elevated temperatures in air can cause the surface oxidation of carbon black where the temperatures can be as low as about 250 °C - 400 °C. (Carbon Black, Donnet, p.47). For the plasma black process with hydrogen quench, ideally there is zero oxygen present. This means that there will typically be no surface oxygen functional groups in the final product. There are many applications that benefit from having these oxygen function groups at the surface. In this way, the furnace black process can appear to have some advantage over a plasma black process. However, because the functional groups at the surface of a furnace black are there by happenstance, this material may not be fully optimized for any particular application. However, as described herein, with the plasma black process the option exits to fine tune the surface chemistry of the black to the exact parameters of the desired application. For the operators of the furnace black process to take advantage of this process, they would have to either surface modify the current non-ideal particles or heat treat (to the point of full oxygen removal) to start with a non-oxygenated surface and then treat with reactive moieties to obtain the more optimized surface.

EXAMPLE 1

The following equilibrium is established (in the furnace black process), wherein the rate constant increases with increasing temperature. The pressure of the environment is also important. In a vacuum or atmosphere where continuous gas flow over the surface is present, the right-hand side of equation 1 will be heavily favored.
For a pressurized system the left hand side of equation 1 will be favored. CO and CO₂ are released from the surface at lower temperatures (about 250 °C - 400 °C) and hydrogen is released at higher temperatures (about 800 °C and greater) where graphitization is taking place.

\[
\text{HO-CB-CO}_2\text{H} \rightleftharpoons \text{CB} + \text{CO: (g)} + \text{CO (g)} + \text{H}_2(\text{g})
\]

Equation 1. Equilibrium equation for formation of surface groups on CB.

[0020] Again, if there is a flowing stream of inert gas or vacuum present, then the right hand side of equation 1 is favored and this can result in some amount of mass loss. Under pressure and in the correct atmosphere, the left hand side of equation 1 will be favored. Preferably the pressurization of the vessel would involve raising the vessel to greater than atmospheric pressure but typically less than 10 bar.

[0021] The mixture of functional groups at the CB surface from the furnace process is simply the product as it is made. In that regard it is truly an uncontrolled, unoptimized product. The tailoring of the groups is just simple not easily doable with the furnace process. With the process described herein, it is possible to tailor the surface of the CB to the specific application. It is further possible to tailor the performance of the CB within the application. For example, if carboxylic acid groups increase the bound rubber content in SBR polymer composites, then the ability to control the surface characteristics of the CB could allow for the tuning of the amount of bound rubber and thus fine tune or reduce the amount of road noise, vibration, or even improve the in mpg of the tire based upon this improved quality.

[0022] In the above example, the functional surface groups at the CB surface could be 50/50 carboxylic acid and phenolic as made similar to what is produced in a conventional furnace process, while the process described herein could allow for tailoring of the surface functional groups at 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, or 10:90, for example. This does not exclude the possibility of even much more detailed tuning of the surface groups. Some, or even most, of these types
of composites would not be accessible through furnace black, gas black, lamp black, thermal black, etc. technology. A more detailed surface composition could comprise epoxy, quinone, carboxylic acid, phenol, ether, anhydride, carbonyl, lactone, among other reactive groups at for instance a ratio of 5:5:35: 30:10: 5:5:5, for example.

[0023] In addition to controlling the ratio of the surface composition, there is the additional dimension of the amount or density of surface functional groups on the CB. For instance the amount of functional groups on a typical furnace black could be one micromol/meter (m)². While this has been used in the tire industry in the past, this is simply the amount that is obtained in a typically furnace black process. Through tuning the chemistry, pressure and temperature of the process described herein, a range of densities, for example, anywhere from 0 to 30 micromol/m² can be obtained. This fine tuning capability can allow for the direct control of the interfacial surface energy between the rubber and particle and also allows for optimal bonding between these materials. It can similarly tailor surface chemistry for superior performance in other applications, reducing viscosity build in inks, improving dispersability in paints, superior color development in masterbatches, and perhaps improved conductivity in plastics through superior dispersion. In each application, the chemistry can be tailored not just to an application, but to each compound or vehicle (liquid system) used within an application.

[0024] Because the traditional furnace process doesn't allow for the control of these parameters, it could be advantageous to take a furnace black and treat the surface in the same fashion as the plasma blacks made by a typical plasma process, or any of the above techniques. Increasing the density of functional groups and changing the ratio of the groups present (through increasing the density) can improve the performance of traditional furnace and other process blacks. In this regard the furnace black can be better tuned for the final application.
EXAMPLE 2

[0025] Three exemplary methods which can be used to treat the CB surfaces as described herein, can include, for example, the use of: 1-high temperatures and weak reagents; 2-low temperatures and strong reagents; 3-high temperatures and strong reagents. For the first situation, the CB can be preheated and then doused with gas and steam. The CB could be at room temperature or up to 400 °C. when doused with reagent gases. A list of less reactive gases is given below: H₂, CO, CO₂, O₂, water vapor. Nitrogen can also be present simply to control the amount of dousing. More reactive gases are listed below: N₂O, NO₂, ozone, ammonia, methyl amines, other general amines.

[0026] More reactive ingredients for the functionalization of the surface can include peroxides such as H₂O₂, acids such as HNO₃, persulfates, hypohalites, halites, halates, or perhalates, permanganates, bleach, which is a hypohalite, is a low-cost example of one of these reagents. Combinations of these reagents can yield especially strong reaction conditions, for example, nitric acid in combination with hydrogen peroxide or potassium permanganate with sulfuric acid.

[0027] Included in the stronger reagents family are any diazonium salt-based methods. For instance, it may be advantageous to react the diazonium salt of sulfanilic acid with the CB surface in order to obtain sulfonate functionality. One skilled in this art could see how this general diazonium based strategy could be used to corporate a wide variety of functional groups at the surface. One advantage over the furnace black process is that the surface tuned by the methods described herein could have only the desired functionality and would not possess the inherent byproducts of the furnace process (e.g., random, uncontrolled deposition of oxygen groups at the surface).

EXAMPLE 3

[0028] Any combination of the above could be used to design the optimum particle surface. One of the methods to treat the surface could be to treat in a pressurized vessel to optimize the results based on equation 1. Another method could be to add the
reagents to the pelletizer and then dry at moderate temperatures (about 150 °C -250 °C). The latter method would be more amenable to stronger reagents listed above. However, small amounts of strong reagents in a pressurized vessel might also be employed. Optionally, the hydrogen from the degas step can be partially removed and the hydrogen in the pores remain. To this partially degassed CB, air can be added in such a way as to avoid explosive combinations of hydrogen and oxygen. Upon diffusion of oxygen into the pores of the CB and while the temperature is being elevated, the reaction of H₂ and O₂ can be facilitated in such a way as to provide localized heat to the CB surface. This could further enable reaction to take place to form oxygenated surface functional groups.

EXAMPLE 4

[0029] For even greater control of the reaction at the surface, it might be desirable to douse the reactor, allow for diffusion of gaseous molecules/reagents and then raise the temperature or add a catalyst. The diffusion could be aided through the pressurization of the system. An example could be the following: 1-degas H₂ out of the system utilizing N₂; 2-replace N₂ with 50/50 CO/H₂O; 3-system is inherently at about 250 °C; 4-allow for diffusion to occur at pressure (up to 10 min.); 5-ramp temperature to about 500 °C. If heat transfer from pressurized reactor walls is slow, then alternative designs can be considered that would minimize the amount of space between reactor walls and the center of the CB mass. Another alternative in the case of slow diffusion of heat is to add a substance (reactive A) that will absorb to the surface of the CB followed by a second step of adding reactive B that will react exothermically with reactant A to provide a temperature activated surface and the final reactant. An example of this could be H₂ and O₂ to form H₂O at between about 400 °C and 500 °C. H₂O would then proceed to react with the CB surface and provide oxygen functionality, or an intermediate between elemental hydrogen plus oxygen and the resulting water can react, e.g., an OH radical.
The water spreading pressure (WSP) referred to below is taken from US patent 8,501,148, the disclosure of which is herein incorporated by reference. Briefly, the mass increase is measured in a controlled atmosphere where the relative humidity is increased slowly over time. The increase is from 0 to 80% relative humidity and the WSP ($\pi^e$) is determined as the following equation:

$$\pi^e = \frac{RT}{A} \int_0^{P_0} H_2O \ (\text{moles/g}) \ dP$$

Where $R$ is the gas constant, $T$ is the temperature, $A$ is the N$_2$ surface area (SA) - (ASTM D6556) of the sample and $H_2O$ is the amount of water adsorbed to the carbon surface at the various RH's. $P$ is the partial pressure of water in the atmosphere and $P_0$ is the saturation pressure and $g$ is gram. The equilibrium adsorption is measured at various discrete RH's and then the area under the curve is measured to yield the WSP value. Samples are measured at 25°C using the 3Flex system from Micromeritics. The region being integrated is from 0 to saturation pressure. The $d$ has it's normal indication of integrating at whatever incremental unit is after the $d$, i.e., integrating at changing natural log of pressure.

Another method to obtain information as to the functionality at the surface is to perform titrations as documented by Boehm (Boehm, HP "Some Aspects of Surface Chemistry of Carbon Blacks and Other Carbons." Carbon 1994, page 759), the disclosure of which is incorporated herein by reference. WSP is a good parameter to measure general hydrophilicity of CB, however WSP does not provide for the ratio of functional groups at the surface as can be measured through typical TPD, XPS, or other typical titration methods (Boehm).

The process described herein is an in situ (in reactor) method of tuning the surface chemistry of CB to form ideal particles for the intended application. The method itself can also be employed outside of the reactor, however, optimal efficiencies, e.g., such as cost savings, can be obtained within the reactor. Dimensions such as WSP and density of groups at the surface are controlled. The ratios of the functional groups and the WSP tunability are of particular importance as this will
enable performance in key applications such as the tire and rubber industry, among others. The implications are across all market segments which can be a crucial dimension in application performance.

[0033] Thus, the scope of the invention shall include all modifications and variations that may fall within the scope of the attached claims. Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.
What is claimed is:

1. A method of making carbon black in a plasma process comprising, subjecting the carbon black particles during and/or after formation to surface functionalizing agents in a controlled manner so as to impart a degree and/or density of functionalization onto the carbon black particles so as to adapt the particles to a particular pre-intended application.

2. The method of claim 1, wherein the functional groups comprise oxygen containing functional groups.

3. The method of claim 1, wherein the functional groups are introduced in the reactor, pelletizer, and/or dryer.

4. The method of claim 1, wherein the functional groups comprise carboxylic acid and/or phenolic groups.

5. The method of claim 1, wherein the density of the functionalization is up to about 30 micromol/m²

6. The method of claim 1, wherein the carbon black particles are subjected to the functionalizing agents at temperatures up to about 500° C.

7. The method of claim 1, wherein the functionalizing agents contain one or more oxidizing agents.

8. The method of claim 1, wherein the functionalizing agents contain one or more of \( \text{H}_2, \text{CO}, \text{CO}_2, \text{O}_2, \) water vapor, nitrogen, \( \text{N}_2\text{O}, \text{NO}_2, \) ozone, ammonia, amines, methyl amines, \( \text{H}_2\text{O}_2, \) acids, \( \text{HNO}_3, \) persulfates, hypohalites, halites, halates, perhalates, permanganates, carbonates, bleach, nitric acid, potassium permanganate, sulfuric acid, diazonium salts, diazonium salt of sulphanilic acid, nitrates, nitrate salts, organic nitrates, peroxides, and alkali metal super peroxides.

9. The carbon black produced by the process of claim 1.
### INTERNATIONAL SEARCH REPORT

**International application No.**

PCT/US2016/045793

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#### A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

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#### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

USPC - 106/472; 423/415.1; 423/449.1; IPC(8) - C01B 31/02; C09C 1/48; C09C 1/56; CPC - C01B 31/02; C08K 3/04; C09C 1/485; C09C 1/56; C09C 1/565; C09D 11/324 (keyword delimited)

Electronic data base consulted during the international search (name of data base and where practicable, search terms used)

Orbit, Google Patents, Google

Search terms used: carbon black, plasma, functionalize, agent, modified, density, loading, degree, micromol, phenolic, carboxylic

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#### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category</th>
<th>Citation of document, With indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>Y</td>
<td>US 6,197,274 B1 (MAHMOUD et al) 06 March 2001 (06.03.2001) entire document</td>
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Further documents are listed in the continuation of Box C.

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**Date of the actual completion of the international search**

19 September 2016

**Date of mailing of the international search report**

18 OCT 2016

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**Name and mailing address of the ISA/PTO Office**

Attn: ISA/US, Commissioner for Patents

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**Authorized officer**

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Form PCT/ISA/210 (second sheet) (January 2015)