Feb. 14, 1961 I. WILLIAMS 2,971,822

PROCESS FOR PRODUCING CARBON BLACK

Filed Aug. 2, 1956

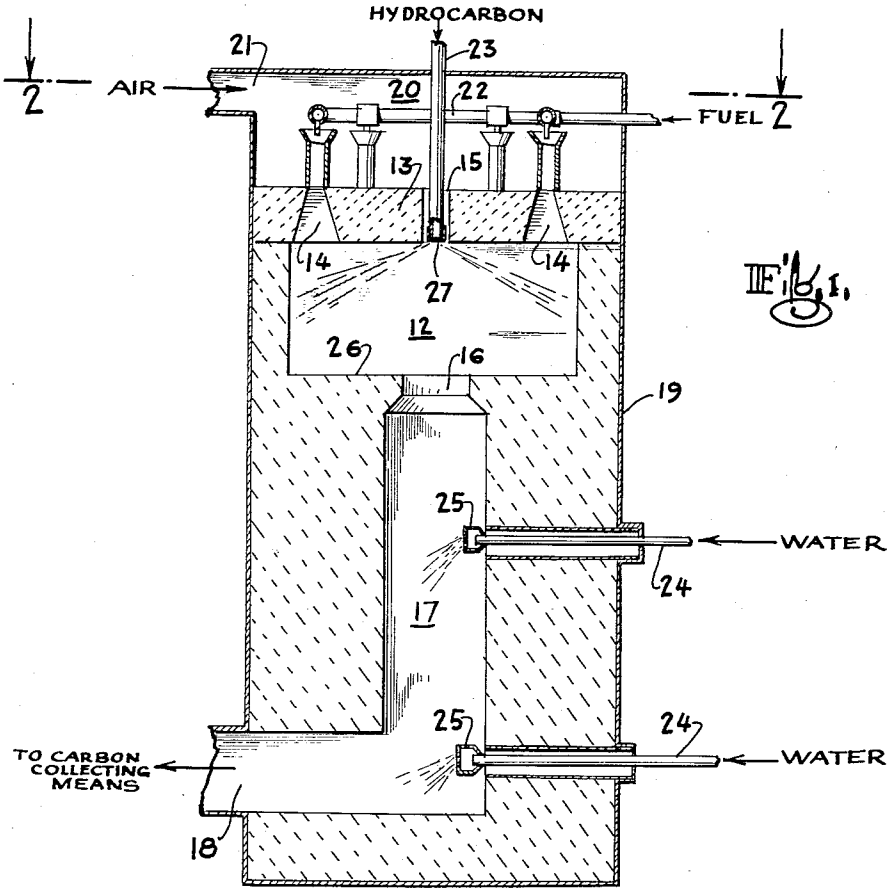


Fig. 1.

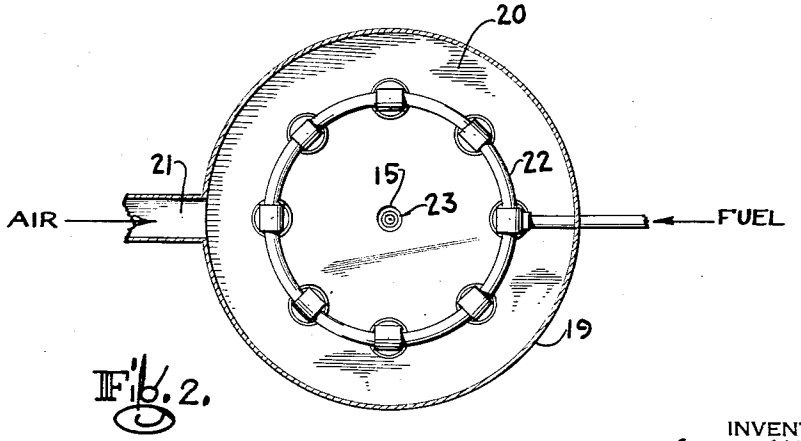


Fig. 2.

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PROCESS FOR PRODUCING CARBON BLACK

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7 Claims. (Cl. 23—209.4)

This invention relates to an improved process for making carbon black by the controlled thermal decomposition of hydrocarbons and to an improved furnace in which the process can be carried out.

In my United States Patent No. 2,625,466, issued January 13, 1953, I have described a furnace for the production of carbon black composed of a combustion chamber having an inlet wall, a substantially flat exit end wall and side walls enclosing a combustion chamber relatively flat from inlet to outlet wall, a hydrocarbon injector tube in the center of the inlet end wall opening into the combustion chamber coaxially therewith and terminating in a nozzle producing a spray in the shape of a cone expanding at an angle of from about 20–30°, a series of burners opening into the inlet end of the combustion chamber at a plurality of positions around the combustion chamber adjacent the side walls and mounted perpendicularly for discharging in the direction of the exit end wall, an outlet orifice in the center of the exit end wall of an area equal to that of the base of the spray cone, and a reaction chamber in open communication with the combustion chamber through said outlet orifice.

In this prior furnace, carbon black is produced by a method involving injecting into the combustion chamber, at the plurality of positions around the combustion chamber adjacent the side walls, a combustible mixture of a hydrocarbon fuel and air, directing the mixture and the combustion gases formed from the burning mixture perpendicularly to the exit end wall such that they impinge on said wall in such manner as to cause the combustion gases to become violently turbulent and to flow to the center of the combustion chamber, thence to the outlet orifice, simultaneously injecting into the combustion chamber from the inlet or head end thereof an expanding cone of a substantially gaseous hydrocarbon, directing such cone of hydrocarbon axially of the combustion chamber into the turbulent mass of combustion gases toward and in large part through the outlet orifice into the reaction chamber where the carbon for the most part is formed.

Whereas this prior process and apparatus successfully produce carbon black, it is difficult to control the operations in such manner that carbon of uniform quality is invariably obtained. Accordingly, a primary object of the present invention is to provide a process and apparatus having all the advantages of the earlier invention but which is easily controlled to provide carbon of constant uniform quality. Another object is to produce carbon of fine particle size leading to superior performance in various commercial products using the same.

In relation to the furnace of said prior patent, the apparatus of the present invention includes a combustion chamber which is likewise relatively flat from inlet to outlet wall, having similar arrangements of the burners and hydrocarbon injector tube and an outlet orifice in the center of the exit wall. The new furnace differs in several primary respects including the conversion of the

combustion chamber into a combination combustion-reaction chamber, the carbon being produced for the most part or substantially wholly in this chamber, leaving at most only a small amount to be completed in the "reaction" chamber openly communicating with the outlet orifice, this said latter mentioned chamber now serving primarily as a quenching chamber.

These major differences include the following:

(1) A different spray nozzle, employed as the hydrocarbon injector tube extending through the inlet wall, is of a character which introduces the hydrocarbon in the shape of a substantially hollow wide angle cone spray or mist of very fine particle size.

(2) The central outlet orifice in the opposite end wall is of sufficiently small area in relation to said wall and to said cone of sprayed material that not only are the flame and combustion gases caused to impinge upon the exit wall for effecting violent turbulence in the chamber, but the sprayed hydrocarbon is caused to flow obliquely toward the side wall or walls of the chamber and into the turbulent mass rather than in the direction of the outlet orifice.

(3) The chamber connected to said outlet orifice, here serves almost entirely for cooling the reaction mass and is provided with a fluid spray arranged for rapidly accomplishing the quenching function.

For obtaining carbon of better or optimum quality or under more desirable or optimum conditions, the dimensions of the various parts of the furnace of the invention differ from those of the prior furnace, all as hereinafter disclosed.

In the drawing:

Fig. 1 is a vertical section through the center of the furnace, and

Fig. 2 is a horizontal section taken on line 2—2 of Fig. 1.

With reference to the drawing, there is illustrated a combustion-reaction chamber **12** of relatively shallow depth from the top or inlet end to the bottom or outlet end, this chamber preferably being of cylindrical shape having a depth from about ½ to about equal the diameter. The head or inlet end **13** is provided with a multiplicity of burners **14**, suitably eight, substantially at the extremities of the inlet end and mounted such that the flame produced travels along and adjacent to the side walls in a direction perpendicular to the exit wall. The inlet wall **13** is provided with an opening **15** directed axially of the reaction chamber.

The outlet or bottom end wall of the chamber contains a centrally located outlet orifice **16** which should be of from about 3 to 10% of the area of the end wall. This outlet orifice is in open communication with the cooling or quenching chamber **17** in turn discharging through the outlet tube **18** leading to a carbon collecting means (not shown). The heat-resistant, refractory walls of the furnace are covered with a steel jacket **19** which extends beyond the combustion reaction chamber **12** and forms a plenum chamber **20** into which air is introduced through the inlet conduit **21** from a fan (not shown). The plenum chamber **20** is designed to supply air at any pressure up to about 150 inches of water.

The burners **14** are supplied with hydrocarbon fuel by means of pipe **22**. The hydrocarbon feed stock to be decomposed into carbon is introduced through conduit **23** extending through the opening **15** and terminating in the nozzle **27** of the character hereinafter described. The wall of the furnace adjacent the quenching chamber **17** is provided with one or more openings **24** near or adjacent the outlet orifice **16** through which pipes extend, terminating in spray heads **25**, adapted to spray cooling fluid into the flowing stream of reaction products passing through the chamber and to quench the same very rapidly.

The volume of the cooling chamber 17 is suitably from 10% to 50% of the volume of the combustion-reaction chamber and its shape, preferably cylindrical, is such that it permits rapid quenching of the carbon laden gases. A suitable size for the quenching chamber 17 is one having a cross-sectional area of about twice that of the outlet orifice communicating therewith from the combustion-reaction chamber. To obtain adequately quick cooling in this chamber, the first or top cooling spray nozzle 25 should be mounted only a short distance from the outlet orifice 16 and with this arrangement the initial quenching of the carbon laden gases is effected in about .005 to .01 second after leaving the combustion-reaction chamber.

In view of the higher velocity of chemical reaction involved in the process of the invention, the carbon-producing hydrocarbon is preferably one of considerable positive free energy. Normally liquid or oily hydrocarbons of substantial molecular weight can be used, those preferred being highly unsaturated or aromatic hydrocarbons. Saturated hydrocarbons of 9 or more carbon atoms can be successfully employed and those of a lesser number of carbon atoms are of relatively little value.

The amount of air introduced into the combustion chamber may be varied to a substantial extent and suitably can be from somewhat more air than that required for complete combustion of the fuel to an amount as high as half the theoretical quantity necessary to burn both the fuel and the carbon-producing hydrocarbon. The amount of air or oxygen employed may provide a considerable excess of free oxygen in the cooled gases, for the reaction is ordinarily accomplished so rapidly that complete combustion of the oxygen need not take place.

The combustion and carbon-producing are most effectively accomplished under one embodiment of the invention when the intake and discharging rates of the furnace are controlled in such manner as to provide a positive pressure in the combustion-reaction chamber, the preferred conditions being a pressure of at least 20 inches of water.

To accomplish required subdivision and directional flow of the hydrocarbon feed, the spray nozzle 27 in the injector tube may be provided with a perforated disk, and the thickness of the disk will provide the hollow cone spray and determine the angle of the cone, the widest angle being produced by a thin disk and the narrowest angle by a thicker disk. A conventional spray nozzle of a type providing a whirling mass of hydrocarbon just before it enters the opening in the flat disk can be successfully employed. In accomplishing the spraying operation, the disk should be such as to provide a cone-shaped spray of a minimum angle of about 50°, it being necessary, as stated, that the spray cone be substantially hollow. Cone sprays of angles up to 140° give carbons of increasingly fine particle size. Spray angles of substantially less than 50°, such as one of 40° or less, yield carbon of more than twice the particle sizes obtained with the use of angles between about 50° and 150°.

The location and positioning of the burners to provide a ring of flame and combustion gases adjacent to the side walls of the reaction chamber are of importance to the success of the furnace in causing the flame to impinge on the exit wall or ledge 26 of the combustion reaction chamber whereby the flame cannot be blown away from the burner when the furnace is operated at high velocities and a turbulent mass of hot gases is provided in the chamber.

The construction of the furnace as described above brings about an extremely rapid intermingling of the carbon-producing hydrocarbon with the hot combustion gases whereby most perfect and rapid vaporization of the hydrocarbon in mist form occurs and a higher dilution of the hydrocarbon with hot inert gases is obtained. The highly desirable ultimate result is that carbon particles of much finer grade can be and are obtained.

For producing the highly desirable or optimum results the conditions of operation must be carefully controlled.

In general the reaction must be carried out in a very short period of time. The space velocity through the furnace should be from 300 to 700 cu. feet per cu. foot per minute based on the volume of the gas measured under normal atmospheric conditions, and the gases should become heated in the range of 2200° to 2750° C. Under these conditions the residence time of the reactants in the reaction chamber is of the order of .013 to .03 second. The carbon-producing hydrocarbon is decomposed almost completely within the combustion reaction chamber and the carbon particles formed are of a smallness previously unattainable.

Example 1

A vertical furnace such as shown in the drawing was used. It had a shallow combustion-reaction chamber 15 inches in depth and 32 inches in diameter. The outlet orifice from this chamber had a diameter of 7 inches and a length of 6 inches. The quenching chamber connected to this orifice was 12 inches in diameter and 40 inches long. The water spray in the quenching chamber was connected in at a level 18 inches below the exit or bottom surface of the combustion-reaction chamber.

For accomplishing the heating, the fuel used was natural gas of 1020 B.t.u. rating. This gas together with air was burned in eight inspirator type burners extending through the head of the combustion-reaction chamber. The hydrocarbon to be cracked was a viscous residue from the catalytic cracking of petroleum having an A.P.I. gravity of 2.6, a distillation range between 370° and 680° F. and an aniline number of 53. This oil was preheated to 625° F. and then forced at a pressure of about 150 pounds per square inch at a rate of 2.9 gallons per minute through the injector tube in the center of the inlet head of the furnace into and through one of several nozzles producing sprayed hydrocarbon in the form of a hollow cone of differing angles as indicated below, the spray nozzles projecting below the inner surface of the head about ½ inch.

One hundred ninety-seven cubic feet of gas and 2929 cubic feet of air per minute were supplied to the burners. One hundred twenty cubic feet of air per minute were introduced through the head around the hydrocarbon injector tube which was cooled by the air. All gases were measured at 30 inches of mercury pressure at a temperature of 60° F. These rates of gas and air introduction provided a space velocity of 570 cubic feet per cubic foot per minute for gas passage through the furnace. The temperature within the combustion-reaction chamber was approximately 2550 to 2750° F.

In carrying out the processes of the several tests disks of different thicknesses were employed to provide cones of the varied degrees of spread set forth in the following table. Samples of the carbons produced in the respective tests were collected and examined for particle size and tested for tinting strength in a newspaper ink composition. The results determined were as follows:

Test	Degrees spread of Cone	Lbs. Yield per Gal.	Ave. Dia. in Millimicrons	Tinting Strength, Percent of Channel Carbon
1	30	3.3	70	92
2	40	3.4	70	93
3	70	3.5	22	99
4	100	3.4	12	104
5	140	3.4	7	109

The carbons produced by tests 1 and 5 were also compared by testing them for reinforcing action in smoked sheet rubber compounds. It was found that 35 parts of the product of test 5 produced the degree of stiffness obtained only by the use of 50 parts of the product of test 1.

In another series of tests carried out in substantially

the same manner as those set forth above, it was determined that the average particle diameter of the carbon product was 75 millimicrons when the angle of the spray was 20 degrees; whereas a spray cone angle of 50 degrees reduced the average particle size to 28 millimicrons, and an angle of 60 degrees reduced it further to 25 millimicrons. A pronounced refinement of the size of the carbon particles is obtained when the cone or spray of the hydrocarbon mist is caused to expand on an angle of at least about 50°.

Example 2

The same furnace described in the above example was employed except that the gas burners there used were replaced with atomizing oil burners. The hydrocarbon fuel employed as well as the carbon-producing hydrocarbon used in this process had an A.P.I. gravity of 18 and an aromatic content of 47%. This oil was preheated to 450° F. before being introduced into the furnace, both that used for burning and that used for cracking. Air was introduced at the rate of 3030 cubic feet of air per minute and the oil was burned at the rate of one gallon per minute. Thirty cubic feet of air per minute were introduced around the hydrocarbon injector tube. The oil was introduced through the injector tube at the rate of 3 gallons per minute in the form of a hollow cone spray of a 140° angle. The temperature within the reaction chamber was approximately 2680° F.

The carbon was collected by passing the same through an electrical precipitator and cyclone collectors, and it had a bulk density of only about 0.3 pound per cubic foot, the diameter of the particles being about 6 millimicrons.

Example 3

A furnace similar to that used in Example 1 was employed. However, the outlet orifice from the combustion reaction chamber was only 5.6 inches in diameter and the quenching chamber was only 9 inches in diameter. Natural gas having a B.t.u. value of 1050 per cubic foot was introduced into the eight burners at a rate of 169 cubic feet per minute. Air was introduced through the burners at the rate of 2215 cubic feet per minute and into the opening surrounding the hydrocarbon injector tube at the rate of 98.5 cubic feet per minute. The cracking stock employed was a catalytic recycle oil obtained as a by-product from the manufacture of gasoline, having a distillation range of 370°–597° F., and 52% of the content was soluble in sulfuric acid. After being preheated to 600° F. the oil was injected through the hydrocarbon injector tube into the furnace at the rate of 3.5 gallons per minute in the form of a substantially hollow cone having a spray head or angle of 140°. The temperature within the reaction chamber was approximately 2710° F.

The carbon-laden reaction gases were quenched to a temperature of 1200° F. by means of water sprayed downwardly in the quenching chamber at a point 30 inches from the outlet surface of the combustion-reaction chamber. In the lower part of the quenching chamber the gases were further quenched to a temperature of 425° F. after which the gases were passed through an electrical precipitator and cyclone collecting system. The collected carbon had a bulk density of about 0.3 pound per cubic foot, and the average diameter of the particles was about 6 millimicrons.

The carbon produced by the process of this example was compared with a standard I.S.A.F. carbon (produced in an intermediate super abrasion furnace) by compounding the respective carbons in rubber compositions of comparable constitution, the formulas being appropriately changed to compensate for the differences in the surface areas of the carbon and the amount used of the carbon produced by the present invention being only 70% of that employed in the formula containing the I.S.A.F. carbon.

	A	B
GRS Synthetic rubber	100	100
I.S.A.F. carbon	50	
Experimental carbon		35
Zinc oxide	5	5
Stearic acid	1.5	1.5
Sulfur	1.8	2.0
Mineral Oil	7.5	7.5
Santocure [1]	1.0	1.2

[1] Santocure is a reaction product of mercaptobenzothiazole and cyclohexylamine.

Each of these compounds was vulcanized at 300° F. for 60 minutes.

Compound	Lbs. Load at 300% Elongation	Lbs. Tensile	Durometer Hardness	Abrasion Loss, cc.
A	1,910	3,720	63	2.41
B	2,160	3,900	64	2.09

It should be understood that the present invention is not limited to the details of apparatus and operating conditions herein described but that it extends to all equivalents which will occur to those skilled in the art upon consideration of the terms and scope of the claims appended hereto.

I claim:

1. In a carbon-producing process employing a combustion chamber of shallow depth from end to end having in one end wall a centrally located hydrocarbon injector and burner means disposed around said chamber, said burner means being supplied with fuel and excess air and projecting flames and gases directly along the side wall of said chamber into impingement with its other end wall to maintain a turbulent mass of flames and gases around said chamber adjacent said other end wall, said other end wall having an outlet orifice substantially at its center, the steps which comprise introducing into said chamber through said injector a mist of a carbon-producing hydrocarbon oil of positive free energy in the form of a hollow cone expanding obliquely toward said side wall into said turbulent mass of flames and gases, the angle of said cone being at least 50°, decomposing said hydrocarbon oil predominantly within said chamber, flowing the resulting carbon and reaction gases through said outlet orifice, and quenching the outflow promptly after its emergence from said outlet orifice, whereby carbon of extremely fine particle size is obtained.

2. In a carbon-producing process employing a combustion chamber of shallow depth from end to end having in one end wall a centrally located hydrocarbon injector and burner means disposed around said chamber, said burner means being supplied with fuel and excess air and projecting flames and gases directly along the side wall of said chamber into impingement with its other end wall to maintain a turbulent mass of flames and gases around said chamber adjacent said other end wall, said other end wall having an outlet orifice substantially at its center, the steps which comprise introducing into said chamber through said injector a mist of a carbon-producing hydrocarbon oil of positive free energy in the form of a hollow cone expanding obliquely toward said side wall into said turbulent mass of flames and gases, the angle of said cone being between 50° and 150°, decomposing said hydrocarbon oil predominantly within said chamber, flowing the resulting carbon and reaction gases through said outlet orifice, and quenching the outflow promptly after its emergence from said outlet orifice, whereby carbon of extremely fine particle size is obtained.

3. In a carbon-producing process employing a combustion chamber of shallow depth from end to end having in one end wall a centrally located hydrocarbon injector and burner means disposed around said chamber, said burner means being supplied with fuel and excess air and

projecting flames and gases directly along the side wall of said chamber into impingement with its other end wall to maintain a turbulent mass of flames and gases around said chamber adjacent said other end wall, said other end wall having an outlet orifice substantially at its center, the steps which comprise introducing into said chamber through said injector a mist of a carbon-producing hydrocarbon oil of positive free energy in the form of a hollow cone expanding obliquely toward said side wall into said turbulent mass of flames and gases, the angle of said cone being at least 50°, decomposing said hydrocarbon oil predominantly within said chamber within a period of from .013 to .03 second, flowing the resulting carbon and reaction gases through said outlet orifice, and quenching the outflow promptly after its emergence from said outlet orifice, whereby carbon of extremely fine particle size is obtained.

4. In a carbon-producing process employing a combustion chamber of shallow depth from end to end having in one end wall a centrally located hydrocarbon injector and burner means disposed around said chamber, said burner means being supplied with fuel and excess air and projecting flames and gases directly along the side wall of said chamber into impingement with its other end wall to maintain a turbulent mass of flames and gases around said chamber adjacent said other end wall, said other end wall having an outlet orifice substantially at its center, the steps which comprise introducing into said chamber through said injector a mist of a carbon-producing hydrocarbon oil of positive free energy in the form of a hollow cone expanding obliquely toward said side wall into said turbulent mass of flames and gases, the angle of said cone being at least 50° decomposing said hydrocarbon oil predominantly within said chamber, flowing the resulting carbon and reaction gases through said outlet orifice, said oil, fuel and air being introduced at rates which maintain the outflow from said chamber at a space velocity of 300 to 700 cubic feet per cubic foot per minute, and quenching the outflow promptly after its emergence from said outlet orifice, whereby carbon of extremely fine particle size is obtained.

5. In a carbon-producing process employing a combustion chamber of shallow depth from end to end having in one end wall a centrally located hydrocarbon injector and burner means disposed around said chamber, said burner means being supplied with fuel and excess air and projecting flames and gases directly along the side wall of said chamber into impingement with its other end wall to maintain a turbulent mass of flames and gases around said chamber adjacent said other end wall, said other end wall having an outlet orifice substantially at its center, the steps which comprise introducing into said chamber through said injector a mist of a carbon-producing hydrocarbon oil of positive free energy in the form of a hollow cone expanding obliquely toward said side wall into said turbulent mass of flames and gases, the angle of said cone being at least 50° decomposing said hydrocarbon oil predominantly within said chamber within a period of from .013 to .03 second, flowing the resulting carbon and reaction gases through said outlet orifice, and quenching the outflow within a period of from .005 to .01 second after its emergence from said outlet orifice, whereby carbon of extremely fine particle size is obtained.

6. In a carbon-producing process employing a combustion chamber of shallow depth from end to end having in one end wall a centrally located hydrocarbon injector and burner means disposed around said chamber, said burner means being supplied with fuel and excess air and projecting flames and gases directly along the side wall of said chamber into impingement with its other end wall to maintain a turbulent mass of flames and gases around said chamber adjacent said other end wall, said other end wall having an outlet orifice substantially at its center, the steps which comprise introducing into said chamber through said injector a mist of a carbon-producing hydrocarbon oil of positive free energy in the form of a hollow cone expanding obliquely toward said side wall into said turbulent mass of flames and gases, the angle of said cone being between 50° and 150°, decomposing said hydrocarbon oil predominantly within said chamber, so proportioning said air to said fuel and said oil that substantially all of said fuel and up to one-half of said oil is consumed, flowing the resulting carbon and reaction gases through said outlet orifice, and quenching the outflow promptly after its emergence from said outlet orifice, whereby carbon of extremely fine particle size is obtained.

7. In a carbon-producing process employing a combustion chamber of shallow depth from end to end having in one end wall a centrally located hydrocarbon injector and burner means disposed around said chamber, said burner means being supplied with fuel and excess air and projecting flames and gases directly along the side wall of said chamber into impingement with its other end wall to maintain a turbulent mass of flames and gases around said chamber adjacent said other end wall, said other end wall having an outlet orifice substantially at its center, the steps which comprise introducing into said chamber through said injector a mist of a carbon-producing hydrocarbon oil of positive free energy in the form of a hollow cone expanding obliquely toward said side wall into said turbulent mass of flames and gases, the angle of said cone being between 50° and 150°, decomposing said hydrocarbon oil predominantly within said chamber within a period of from .013 to .03 second, flowing the resulting carbon and reaction gases through said outlet orifice, said oil, fuel and air being introduced at rates which maintain the outflow from said chamber at a space velocity of 300 to 700 cubic feet per cubic foot per minute and which maintain a positive pressure equivalent to at least 20 inches of water in said chamber, and quenching the outflow within a period of from .005 to .01 second after its emergence from said outlet orifice, whereby carbon of extremely fine particle size is obtained.

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