June 10, 1952 W. C. EKHOLM 2,599,981

CARBON BLACK

Filed Dec. 22, 1949

FIG. 1

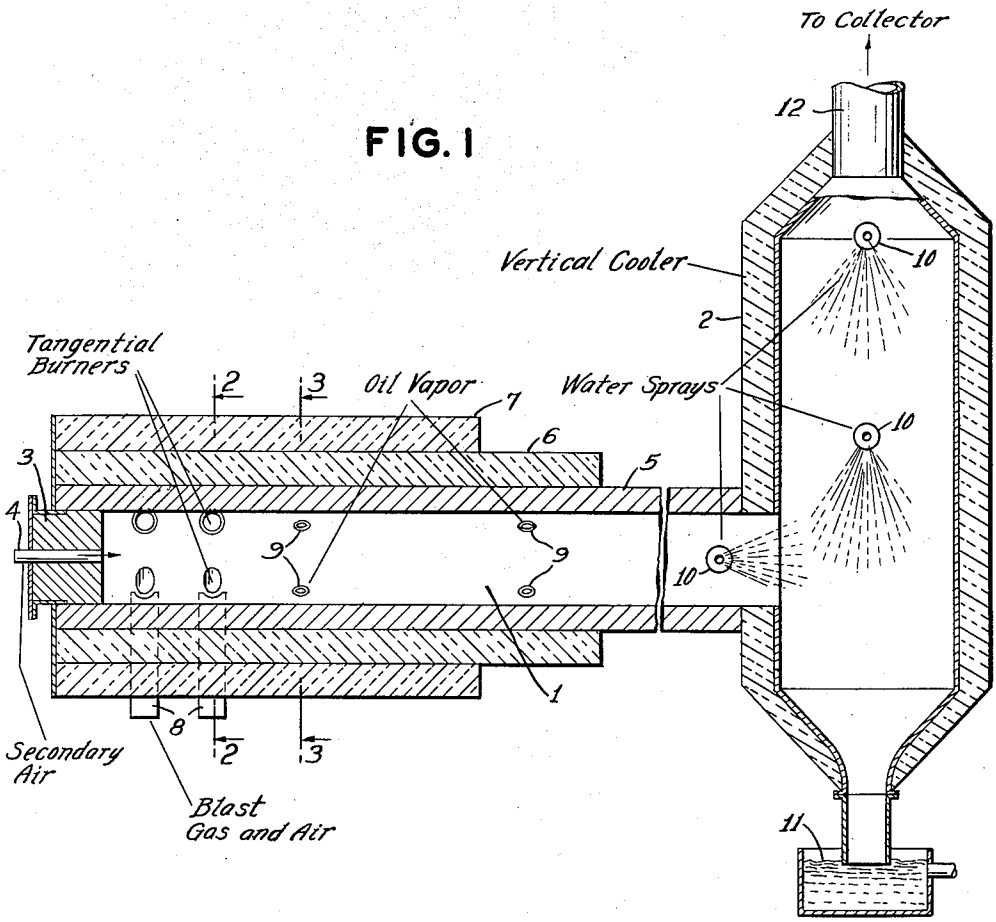


FIG. 2

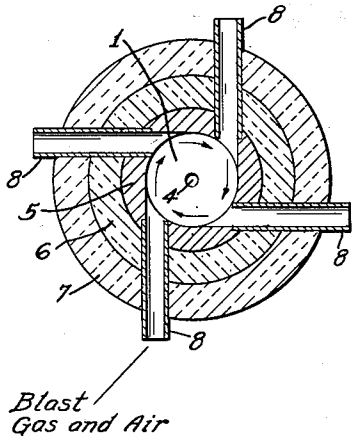
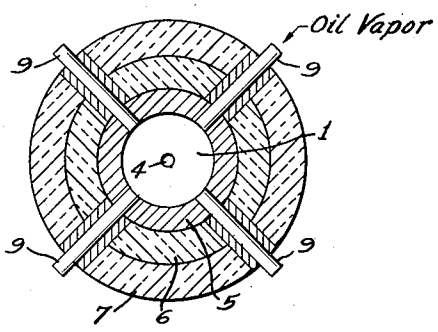


FIG. 3



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Patented June 10, 1952

2,599,981

UNITED STATES PATENT OFFICE

2,599,981

CARBON BLACK

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Application December 22, 1949, Serial No. 134,520

7 Claims. (Cl. 23—209.4)

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The present invention relates to the manufacture of carbon black and particularly to the process involving the thermal decomposition of a hydrocarbon by separately injecting it into a turbulent stream of hot furnace gases.

In the Wiegand and Braendle Patent No. 2,378,055 there is described an improved process of the type just noted in which a combustible mixture of a fluid hydrocarbon fuel and air is blasted into one end of an elongated, unobstructed chamber to form a turbulent stream of hot blast flame gases. This turbulent stream of blast flame gases courses through the furnace chamber and, at a point removed from the point of entry of the combustible mixture to the furnace chamber, the hydrocarbon to be decomposed is separately and forcefully injected into the turbulent stream of gases.

The present invention provides an improvement in the method of operation just noted and particularly an improved method of effecting the mixing of the hydrocarbon to be decomposed with the hot blast flame gases.

In operations such as specifically illustrated in the patent, the hydrocarbon to be decomposed is injected radially into the furnace chamber, advantageously as relatively small, high velocity streams positioned directly opposite one another. Difficulty has been experienced in this type of operation where the diameter of the furnace chamber has been too greatly increased. Rectangular furnace chambers have been extensively used in large commercial sized installations, but here, too, it has been found desirable to limit the width of the chamber to not in excess of about 2 feet, and preferably not greater than about 1 foot, in order to maintain a uniform pattern of the streams of hydrocarbon to be decomposed so as to get uniform mixing of the hydrocarbon with the blast flame gases.

One difficulty of the type noted which has been experienced is that of spacing the make gas tubes so as to prevent channelling of blast flame gases through the chamber in between the streams of the hydrocarbon to be decomposed. This difficulty has been minimized by close spacing of the make tubes. However, in commercial installations, this solution has introduced new problems. The increased number of tubes requires a complicated manifolding system which is serviced with great difficulty. Deposition of carbonaceous residues in the tubes, or in the manifold, tends to disrupt the distribution of make gas to the tubes and results in some tubes being overloaded, while others are underloaded.

The present invention provides an improved method of operation whereby much of the difficulty heretofore experienced in effecting rapid, uniform mixing of the hydrocarbon to be decomposed with the blast flame gases is avoided.

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I have found that these channels of inadequately mixed blast flame gases may be avoided and, at the same time, the number of make gas streams reduced by using a reaction chamber of circular section, injecting the combustible mixture into the reaction chamber as streams moving at high velocity in a substantially circumferential, or tangential, direction and separately, downstream from the point of injection of the combustible mixture, forcefully injecting the hydrocarbon to be decomposed into the chamber in a substantially radial direction.

By this method of operation, it appears that the blast flame gases tend to follow a more or less helical path through the chamber and, therefore, a path of much greater length, so that for a given time within a reaction chamber of a given length much higher blast gas velocities may be maintained than would be possible if the blast flame gases were passed axially through the chamber. Accordingly, the requirement of careful coordination between furnace diameter and mass velocities is materially relaxed and much greater leeway in the ratio of blast flame gases to hydrocarbons to be decomposed is permissible.

It appears, therefore, that an advantage of the tangential injection of the blast flame gases is that it permits much higher velocities of the blast flame gases than is practical where the blast flame gases flow substantially longitudinally through the chamber.

These higher blast flame velocities make it practical to increase the make gas injection velocities. By reason of the latter, the make gas injection tubes may be maintained at a lower temperature and a richer make gas may be used without encountering serious coking problems in the tubes. Further, by the use of higher make gas injection velocities, the number of make gas injection tubes may be reduced which further simplifies construction and maintenance problems.

A still further advantage of the tangential injection of the blast flame is that thereby the blast flame in the region of its initial development, is in closer contact with the furnace walls than where longitudinal blast flame injection is employed. The advantages of surface combustion are, in part at least, attained and the permissible range of ratios of air to natural gas in the combustible mixture is materially broadened.

The improved process is applicable to operations in which natural gas, or other normally gaseous hydrocarbons, is decomposed to form the carbon black. It is, however, especially advantageous in operations adapted to form the carbon black by decomposing a higher molecular weight hydrocarbon, for instance, a petroleum distillate. A particularly desirable heavier hydrocarbon is a

distillate of the type resulting from the cracking of petroleum and comprising around 20–60%, usually in the range of 30–50% by weight of aromatic constituents, as determined by the test method D–875–46T of the American Society for Testing Materials. It should most suitably have an aniline cloud point as determined by the method prescribed by the said society and designated D–611–46T, within the range of 10° to 125° F. Its end point should not exceed 725° F. and preferably should be somewhat lower.

These higher molecular weight hydrocarbons appear to be more readily thermally decomposed than is natural gas, for example, and should be mixed uniformly with the blast flame gases proportionately more rapidly. It is desirable, therefore, to accelerate in some way the mixing of the hydrocarbon with the blast gases. This is accomplished in accordance with the present invention by intensifying the blast gas velocity and turbulence by blasting the combustible mixture into the furnace tangentially, or substantially so, and separately injecting the hydrocarbon to be decomposed substantially radially into the resulting swirling mass of blast flame gases advantageously at a point near the perimeter of the whirling gas stream, i. e., adjacent the furnace wall, thus insuring the desired rapid and uniform mixing of the heavier hydrocarbon with the blast flame gases.

In order further to expedite the complete dispersion of the heavier hydrocarbon in the blast flame gases, I have found it especially advantageous to dilute the vaporized heavier hydrocarbon by mixing steam, air, or other diluent, therewith, advantageously in proportions within the range of 1 to 2 volumes of steam for each volume of oil vapor. Mixing of steam with the hydrocarbon to be decomposed has been found particularly beneficial in carrying out the present process, especially where it is desired to produce carbon black of the type used in the compounding of rubber of the tire tread type.

According to a preferred aspect of my invention, a petroleum distillate of the aromatic type just described is vaporized and the vapors mixed with steam in proportions within the range of about 1 to 2 volumes of steam per volume of hydrocarbon vapors (each measured at 60° F. and 760 millimeters of mercury) and this mixture is separately and forcefully injected directly into the rapidly swirling flame gases in a substantially radial direction, with respect to the swirling motion of the blast flame gases, and is thereby substantially instantaneously dispersed in those blast flame gases and further diluted and thereby heated to the decomposition temperature of the hydrocarbon.

Instead of using steam along as a diluent for the heavier hydrocarbon, natural gas may be used, either together with steam, or alone, as a diluent for the heavier hydrocarbon. Or, in place of the steam, a substantially inert gas, such as carbon dioxide, or nitrogen, may be employed. The use of air as a diluent has also been found advantageous in certain types of operation.

The invention will be further described and illustrated by reference to the accompanying drawings which show conventionally and somewhat diagrammatically apparatus found particularly useful in carrying out the process and of which:

Figure 1 is a longitudinal, sectional view in elevation of a reaction chamber, together with accessories including adjacent cooling equipment;

Figure 2 is a transverse, sectional view of the reaction chamber along the line 2—2 of Figure 1; and

Figure 3 is a transverse sectional view of the reaction chamber along the lines 3—3 of Figure 1.

In the apparatus shown, the reference numeral 1 indicates a cylindrical, elongated reaction and cooling chamber opening at one end into a vertical cooler 2. At the lefthand end, the reaction chamber is closed by the end block 3, and extending axially through this block is a conduit 4 adapted to the introduction of secondary air into the furnace chamber, as desired.

The chamber 1 is formed by the cylindrical wall 5 of highly refractory material which, in turn, is covered externally by layers 6 and 7 of heat insulating material.

Extending through the layers of heat insulating material and the furnace wall and substantially normal to the longitudinal axis of the chamber, there are four blast burner ports 8, each entering the furnace chamber in a circumferential direction, as more clearly shown in Figure 2 of the drawings. The apparatus shown is provided with two substantially identical sets of these blast burner ports positioned at different distances from the end block 3.

Further downstream, the furnace chamber is provided with a set of four radially extending tubes 9 spaced 90° apart and extending through the layers of insulating material and the furnace wall as more clearly shown in Figure 3 of the drawings. These tubes are provided for the injection into the furnace chamber of the hydrocarbon to be decomposed and will normally be positioned with their inner ends flush with the inner walls of the furnace chamber. Still further downstream, the furnace is provided with a second set of hydrocarbon injection tubes 9 substantially identical with that just described.

These hydrocarbon injection tubes should be fabricated from highly refractory material, for instance, Carbofrax, Alundum, or the like. The burner ports 8 should be fabricated of or lined with a similar refractory material.

Spaced along the vertical cooler 2 are water sprays 10 for assisting in cooling the hot effluent furnace gases. Similar sprays may be positioned in the downstream portion of chamber 1 adjacent the vertical cooler.

In operation, a combustible mixture of a fluid hydrocarbon fuel and air is blasted at high velocity through the circumferential blast burner ports 8, is ignited and burned within the chamber to form a hot, highly turbulent mass of blast flame gases rapidly swirling through the furnace chamber in a more or less helical path. This combustible mixture may be injected into a zone of the chamber more or less removed from the end block 3 by selection of one or the other of the sets of blast burner ports. The hydrocarbon to be decomposed is injected into the chamber through the radial tubes 9 and, as previously described, is extremely rapidly and uniformly mixed with the swirling stream of blast flame gases, and is heated thereby and decomposed to form carbon black in suspension in the furnace gases. As the suspension continues through the downstream end of the chamber and through the vertical cooler, it is cooled by contact with the water sprays 10. Any unvaporized water from these sprays, together with any carbon knocked out of the suspension, passes downwardly through the

vertical cooler into the sump 11 and cooled suspension passes from the upper end of the vertical cooler through conduit 12 to conventional separating and collecting apparatus, as well understood in the art.

The number and diameter of the circumferential blast burner ports have not been found to be critical so long as they have the capacity for filling the furnace chamber with the violently turbulent blast flame gases. With a furnace chamber approximating 1 foot in diameter, I have found that a ring of four blast ports, each 2 inches I. D. and positioned 3 to 6 inches from the inner face of the end block 4 to be adequate for this purpose.

Similarly, the number and size of the hydrocarbon injection tubes are subject to some variation. Four Carbofrax tubes, ½ inch I. D., positioned as shown in the drawings and located 1 to 4 feet downstream from the blast burner ports have been found highly satisfactory.

In using higher molecular weight hydrocarbons, such as herein described, I have found that the period of time during which the hydrocarbon and decomposition products thereof should remain in the reaction chamber at reaction temperatures, in order to result in a carbon black having certain desirable rubber compounding characteristics, is less than the so-called "contact time" where natural gas is used as the "make." This contact time, i. e., the period of time between injection of the hydrocarbon and the quenching of the product to below the reaction temperature, may be varied by providing a number of spray heads along the downstream portion of chamber 1 and selecting the proper spray, or sprays, so as to cool the suspension at the proper time to below the reactive temperature.

It will be understood, of course, that the contact time is arrived at by calculation and cannot otherwise be more positively determined in the absence of more precise information as to the exact path of the gases through the chamber. Contact time so calculated has been found to be a rather dependable guide in practical operation.

In general, contact time at temperatures above 2,000° F. should not exceed 0.5 second. Satisfactory operation has been obtained with contact time within the range of 0.02 to 0.3 second. In these operations, water spray was used to quench the suspension. It will be understood, however, that waste gases from the process, natural gas or any convenient fluid of relatively low oxidizing potential may be used to effect cooling of the suspension.

The blast port velocities at which the combustible mixture enters the furnace chamber is of primary importance. Velocities within the range of approxmiately 60 feet per second to 180 feet per second have been successfully employed. However, port velocities of about 80 feet per second have been found highly satisfactory in commercial operations.

In the apparatus shown in the drawing, the burner ports are shown to lie in a plane perpendicular to the longitudinal axis of the chamber. It will be understood, however, that these ports may be directed somewhat downstream without departing from the spirit of this invention, provided the entering combustion mixture is injected into the furnace chamber in a direction substantially circumferential with respect to the chamber.

Likewise, the hydrocarbon injection tubes may be inclined somewhat from the transverse plane of the furnace chamber so long as they are directed substantially at the longitudinal axis of the chamber.

In the usual operation of my process, the tube 4 for injection of secondary air is not employed. However, operating conditions within the furnace may at times be more satisfactorily controlled by injecting a relatively small proportion of the air requirement into the chamber axially through conduit 4.

The process will be further illustrated by the following specific examples:

Example I

The invention has been utilized in a furnace constructed as shown in the drawing, and comprising a cylindrical reaction chamber 12 inches I. D. and 7½ feet long, discharging into a vertical spray cooler and having a set of four blast burner ports 2 inches I. D. positioned 6 inches downstream from the inlet end of the furnace and a second identical set of blast burner ports located 9 inches downstream from the first. A ring of four hydrocarbon injection tubes ½ inch I. D. was positioned 1 foot downstream from the second set of blast burner ports and a further identical ring of hydrocarbon injection tubes was positioned 3 feet 6 inches downstream from the second set of burner ports. In this operation, the blast air and blast gas was distributed uniformly to two side burners of the first set and the top and bottom burners of the second set and was supplied at a total rate of 37,000 C. F. H. of blast air and 3060 C. F. H. of blast gas, the ratio of blast air to blast gas being 12.2. Secondary air was supplied through the conduit 4 at the rate of 2800 C. F. H. Highly aromatic oil was supplied in vapor form at the rate of 40 gallons per hour and diluted by mixing with steam at the rate of 860 C. F. H. and injected into the furnace through the first set of tubes 9. In this operation, the yield was 2.4 pounds per gallon of oil.

The blast gas, i. e., fuel gas, used was natural gas of 960 B. t. u. The furnace temperature at a point about 2 feet downstream from the end block was 2,620° F. The hydrocarbon oil to be decomposed had the following properties:

ASTM distillation—	
IBP	362
10%	420
50%	472
90%	550
E. P.	620
Recovery	98
Residue	1.5
API gravity	23.3
Aniline cloud point °F.	38
Per cent olefins	22.1
Per cent aromatics	55.9

In substantially identical apparatus, the process was carried on under the conditions and with the results set forth in the following tabulation, the temperatures T–1, T–2, T–3, and T–4, being taken at the points approximately 1 foot, 2 feet 6 inches, 4 feet 6 inches, and 6 feet, respectively, from the inner face of the end block. In each of these runs, the hydrocarbon to be decomposed was injected through the tubes of the first set only and evenly distributed, the number of tubes of the set used in each instance being as indicated in the tabulation.

Example	II	III	IV	V	VI	VII
Number of Tubes	4	4	2	3	4	4
Total Blast Air—C. F. H.	45,000	45,200	40,000	50,000	50,000	50,000
Secondary Air—C. F. H.	none	none	none	none	none	none
Total Blast Gas—C. F. H.	3,600	3,760	3,080	3,840	3,750	3,850
Blast Ratio—Air: Gas	12.5	12.0	13.0	13.0	13.7	13.0
Oil—Gal./Hr.	39	47.5	37	40	40	55
Steam—Lbs./Hr.	37	45	40.5	40.5	40.5	37
Steam—Per Cent of Oil Vapor	125	125	169	150	150	100
Blast Port Velocity—ft./sec. at 60° F.	77.3	77.9	68.6	85.7	85.6	85.8
Make Stream Velocity—ft./sec. at 60° F.	71.5	87.3	140	96.4	72.3	84.7
Make Stream Velocity—ft./sec. at 600° F.	146	178	284	195	146	172
Temperatures ° F.:						
T-1	2,705	2,615	2,620	2,670	2,640	2,440
T-2	2,715	2,680	2,660	2,680	2,670	2,520
T-3	2,680	2,645	2,690	2,580	2,780	2,570
T-4			2,620	2,550	2,730	2,540
Contact time to spray—seconds	.0418	.0420	.295	.238	.232	.249
Yield—Lbs./Gal. of Oil	2.8	2.6	2.0	2.3	2.0	2.53
Rubber Properties:						
Cure Time—minutes	40	40	40	40	40	40
Modulus at 300% elongation	1,610	1,740	1,400	1,320	1,285	1,790
Tensile Strength	4,050	3,950	3,900	3,925	3,925	3,775
Elongation	620	590	680	680	710	560
Hardness	62	62	59	60	60	62
Electrical Resistivity, Log R	2.9	3.9	2.7	2.4	2.2	3.2
Rebound (Optimum Cure)	59.0	59.0	61.0	57.4	57.9	60.5

The rubber properties given in the foregoing tabulation are those obtained by compounding the respective blacks with "low temperature polymer" synthetic rubber by the formula indicated below and vulcanizing the rubber composition as indicated.

LTP	100.000
Black	50.000
Zinc oxide	3.5
Paraflux	4.0
Circosol (2XH)	4.0
Stearic acid	2.0
Santocure	1.125
Sulphur	2.0

As illustrative of aromatic hydrocarbon distillates which have been used with outstanding advantages, there may be noted two types of oils, the characteristics of which are set forth in the following tabulation.

Sample	#1	#2
Gravity (A.P.I.)	24.5	24.7
Aniline Cloud Point—°F.	60.1	108
Distillation		
IBP—°F.	348	480
10% Point	406	508
50% Point	463	530
90% Point	537	568
End Point	622	588
Recovery, percent	98.5	99.0
Residue, percent	1.4	0.8
Loss, percent	0.1	0.2
ASTM D875-46T-Test		
Percent Naphthenes and Paraffins	32.32	40.40
Percent Aromatics	46.97	40.71
Percent Olefins	20.71	18.89

A distillate, such as sample 1, was used in the foregoing Examples IV, V, and VI and a distillate, such as sample 2, was used in Examples II, III, and VII.

Depending somewhat upon the desired characteristics of the carbon black product, the relative proportions of the blast air, the hydrocarbon fuel, the separately injected hydrocarbon and the secondary air used may be varied somewhat as illustrated by the foregoing examples. It will be understood, of course, that in all instances, the proportion of oxygen supplied will be substantially less than that required for the combustion of the fuel gas and the separately injected hydrocarbon. The invention contemplates operations in which the proportion of air and gas in the combustible mixture tangentially injected into the chamber, are such as to produce either an oxidizing, a neutral, or a reducing blast flame. The proportions of blast flame gases to the separately injected hydrocarbon, or mixture of hydrocarbon, steam, and the like, may likewise be varied somewhat. The proportion should, of course, in each instance be such that, upon mixing, the temperature of the resultant mixture will be at least sufficiently high to effect the thermal decomposition of the hydrocarbon to carbon black. Where the operation is such as to produce an oxidizing blast flame, some additional heat may be generated upon mixing with the separately injected hydrocarbon by the combustion of a portion thereof.

It is particularly desirable that the distance between the blast flame injection point and the make gas injection point be so correlated with the flight angle of the spiralling gas stream, that the respective make gas jets are directly in the path of a fully-developed stream of the blast gases and that there be little or no overlapping of the make gas streams. This tends to reduce uneven concentrations of the make gas in the spiralling gas stream.

In a preferred method of operation, vaporized fuel oil, such as No. 2 cycle oil from a catalytic cracking operation, is vaporized and diluted with steam, usually in the ratio of 100 to 200 per cent, and normally 125 to 150 per cent, by volume, assuming 16 cubic feet of vapors per gallon of the oil. The injected steam appears to have several desirable effects. In the first place, the presence of steam appears materially to reduce the tendency for carbon deposits to form on the heater wall and within the make gas injection tubes and lines leading thereto. Secondly, the steam appears to act as an inert diluent. By regulating the proportion of steam, the fineness of the resultant carbon particles may, to some extent, be controlled. A third advantage derived from the use of steam is that it provides means for controlling the trajectory of the make gas streams, i. e., the extent of penetration into the layer of spiralling blast flame gases, while maintaining the desired ratio of air to oil.

While the invention is particularly applicable to operations in which the hydrocarbon to be decomposed is an oil, i. e., normally liquid hydrocarbon, the invention, in its broader aspect, is independent of the particular hydrocarbon decomposed. The hydrocarbon may be either liquid or gaseous, but the presently preferred hydro-

carbon is the petroleum distillate of the type elsewhere herein described in detail.

By modifying operating conditions, the characteristics of the resultant carbon black may be varied over a range extending, for instance, from a normal HMF carbon having a surface area of five acres per pound, to a furnace black having a surface area in excess of eleven acres per pound. As normally produced, these blacks, when compounded with an elastomer, produced stocks of very high modulus and unusually high wear resistance. The resultant black, then, as normally produced, is characterized by a very fine particle size with high modulus, or stiffness characteristics.

The invention, in its broader aspect, is independent of contact time. However, in normal operation, a value of about 0.06 second has been found adequate for complete reaction, where normally liquid hydrocarbon is used as the primary make, and further time does not appear to be necessary.

I claim:

1. The process for producing carbon black comprising in combination the following steps, blasting into one end of an elongated cylindrical reaction chamber a combustible mixture of a fluid hydrocarbon fuel and air in a direction substantially tangential to the inner wall of the chamber, burning the combustible mixture within the chamber to form a swirling stream of blast flame gases passing through the furnace chamber at a temperature in excess of that at which hydrocarbons are decomposed to form carbon black, separately and forcefully injecting into the swirling gases, at a point downstream from the point of entry of the combustible mixture to the chamber and in a zone near the periphery of the swirling gas stream and in a substantially radial direction, a stream of hydrocarbons, and thereby immediately subjecting the said stream of hydrocarbons as it enters the furnace chamber to the impact and shearing forces of the swirling gas stream, whereby the hydrocarbons thereof are rapidly mixed with the blast flame gases and decomposed by heat absorbed therefrom to form carbon black in suspension in the furnace gases, cooling the suspension, and separating and recovering the carbon black therefrom.

2. The process of claim 1 in which the combustible mixture is blasted into the chamber at a velocity within the range of 60 feet to 180 feet per second.

3. The process of claim 1 in which the combustible mixture is blasted into the chamber at a velocity of about 80 feet per second.

4. The process of claim 1 in which the radially injected hydrocarbon is a normally liquid hydrocarbon and is injected into the chamber in a vaporized state in admixture with steam.

5. The process of claim 4 in which the steam and hydrocarbon vapors are used in proportions of 1 to 2 parts of steam for each part of hydrocarbon vapors by volume.

6. The process of claim 4 in which the injected hydrocarbon is a petroleum distillate composed of aromatic hydrocarbons to the extent of at least 50% by weight.

7. The process of claim 4 in which the injected hydrocarbon has an end point not less than 725° F. and an aniline cloud point within the temperature range of 10° to 125° C.

WESLEY C. EKHOLM.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,163,630	Reed	June 27, 1939
2,375,795	Krejci	May 15, 1945
2,378,055	Wiegand et al.	June 12, 1945
2,440,424	Wiegand et al.	Apr. 27, 1948