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MANUFACTURE OF CARBON BLACK

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Fig. 1.

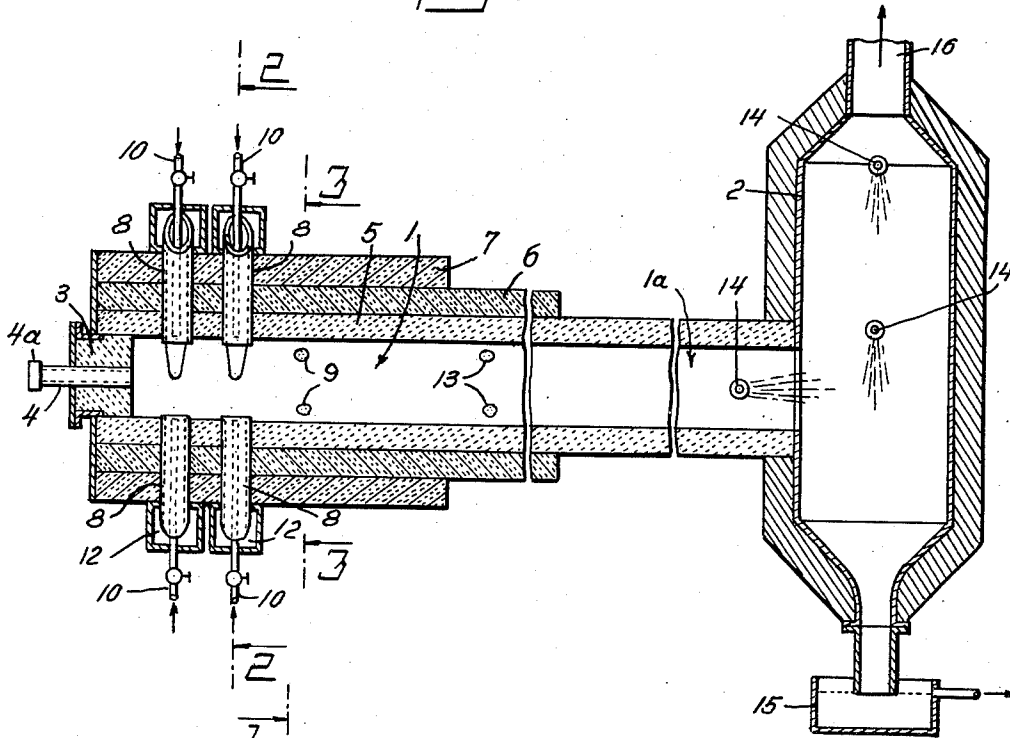


Fig. 2.

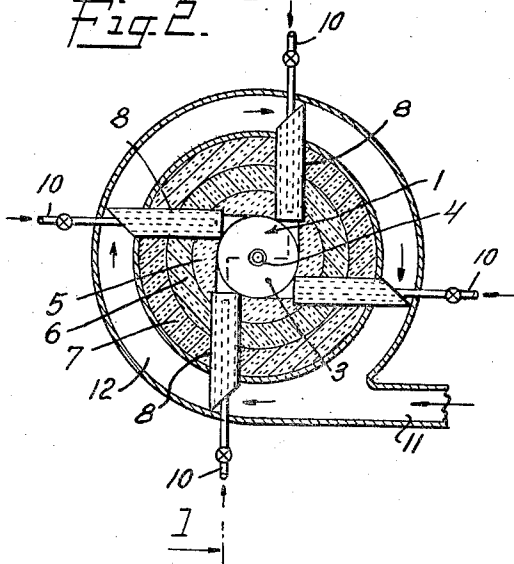
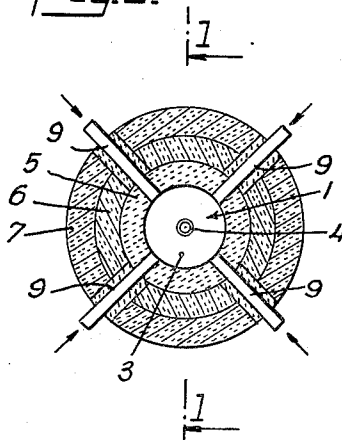


Fig. 3.



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MANUFACTURE OF CARBON BLACK

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4 Claims. (Cl. 23—209.4)

The present invention relates to the manufacture of furnace black and particularly to a process of the type involving the thermal decomposition of a hydrocarbon by rapidly and uniformly mixing it with a hot gaseous medium at a temperature well in excess of that at which the hydrocarbon is decomposed to furnace black.

In operations of this general type, it has previously been proposed to blast 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 chamber wall and to burn the combustible mixture as it enters the chamber to form a swirling cyclone of blast flame gases passing longitudinally through the chamber, and to inject the hydrocarbon to be decomposed, herein designated hydrocarbon make, into this swirling body of hot blast flame gases in a substantially radial direction so that the hydrocarbon is rapidly mixed with the blast flame gases and decomposed by heat absorbed therefrom. A process of this type is described and claimed in application Serial No. 134,520, filed December 22, 1949.

For smooth operation of the tangential blast burners in a process of the type just noted, it has been found that the combustible mixture should contain a proportion of oxygen such as to result in an oxidizing blast flame. Where smaller proportions of oxygen or air are used, one is apt to experience flare-backs into the burner ports, unless the hydrocarbon injection nozzles of the blast burners are advanced to a position where they are subject to rapid deterioration by radiant heat from the furnace chamber.

The oxidizing character of the blast flame gases in the mixing and carbon forming zones has been found materially to influence the surface characteristics of the resultant furnace black. The differences between carbon blacks with respect to surface characteristics have been attributed to differences in the amounts of oxygen, hydrogen, or other gases, chemically combined with or otherwise attached to the surfaces of the carbon particles. Where an oxidizing blast flame is used in the process just described there is a tendency to activate the surfaces of the carbon particles formed and this materially influences the behavior of the resultant furnace black, especially when used in rubber compounding. Activation of the black generally retards the rate of cure, lowers the rebound, increases hysteresis losses and reduces resistance to blow-out of the resultant rubber compound.

This influence of the oxidizing blast on the surface characteristics of the resultant furnace blacks has been observed, regardless of whether the hydrocarbon make is natural gas, a petroleum distillate, or a heavy residue type of hydrocarbon, but is especially noticeable when a heavy residue is used and appears to increase with the aromaticity of the make. Though the embodiment of those characteristics in a furnace black is, for some purposes, highly desirable, it is sometimes undesirable, depending upon the intended use of the carbon black.

For some years, furnace carbons have been made by decomposing natural gas, or the like. More recently, the use of normally liquid hydrocarbons for this purpose has become increasingly important due to the growing demand for natural gas for other purposes. In operations of the type described, the hydrocarbon make may be either a gaseous hydrocarbon, natural gas, for instance, or a normally liquid hydrocarbon distillate, or even heavy, tar-like petroleum residues, such as result from the thermal cracking of cycle stock from a catalytic cracking process, the latter usually being highly aromatic.

The use of such heavier, normally liquid hydrocarbons has several economic advantages. Through their use, the yield of carbon black from apparatus of a given size may be substantially increased and further, the heavy residues, particularly, are presently available at relatively low cost.

However, furnace blacks produced from these normally liquid hydrocarbons, usually possess certain peculiar characteristics, different from those produced from natural gas and, similarly, the furnace blacks produced from the heavy petroleum residues, especially highly aromatic residues, are usually characteristically different from those produced from hydrocarbon distillates or residues of lower aromaticity or from normally gaseous hydrocarbons.

I have discovered that the normal characteristics, especially the surface characteristics, of the furnace carbons produced as just described, may be materially altered by separately introducing a hydrocarbon, herein referred to as auxiliary make, into the swirling suspension of carbon black, while the latter is passing through a zone of the reaction chamber just downstream from the carbon forming zone and while the suspension is still at a reactive temperature of the suspended carbon black and above the decomposition temperature of the auxiliary make, so as to rapidly and uniformly mix the auxiliary make with the furnace black suspension.

Where the primary hydrocarbon make is natural gas, or the like, I have found that the surface activity of the resultant furnace black may be materially altered without materially changing the other characteristics of the furnace carbon by introducing a similar hydrocarbon as the auxiliary make.

Where the primary hydrocarbon make is a normally liquid hydrocarbon, the auxiliary make is, with advantage, a gaseous hydrocarbon, such as natural gas, or a normally liquid hydrocarbon of lower molecular weight and lower aromaticity than the primary make. By this means, not only the surface characteristics, but also other characteristics of the resultant carbon black, are materially changed, the resultant carbon black assuming more nearly the characteristics peculiar to furnace blacks made from the gas, or such lighter oils, without material loss of the economic advantages derived from the use of these heavier oils as the principal hydrocarbon make.

Predicated upon this discovery, my invention, in its broader aspect, comprises the step of rapidly and uniformly mixing an auxiliary hydrocarbon make with the carbon black suspension while at a reactive temperature of the suspended carbon and at a temperature above the decomposition temperature of the auxiliary make. More advantageously, the auxiliary make so introduced is of a molecular weight and aromaticity at least as low as, and preferably somewhat lower than, that of the hydrocarbon from which the carbon black suspension was formed, i. e., the principal make, and is introduced as a gas or vapor.

The invention has been found to be of particular utility in operations of the type just described in which the principal hydrocarbon make is radially injected into

the furnace chamber, either in the form of a gas, or vapor, or a liquid spray, and rapidly and uniformly mixed with the hot oxidizing blast flame gases, and provides an improved method whereby the normal characteristics of the furnace carbon may be materially changed at will.

Like the principal hydrocarbon make, the auxiliary make is injected directly into the swirling mass of hot gases and is practically instantaneously uniformly mixed therewith.

While I cannot state with certainty the exact function of this auxiliary hydrocarbon, it is my present belief, substantiated by extensive investigation, that the auxiliary hydrocarbon is decomposed to form a thin film of carbon of a different character on the surfaces of the carbon nuclei already formed from the principal hydrocarbon make. It appears that the subsequently formed film of carbon on the carbon black particles masks the highly active surface, for instance, of the initially formed carbon black particles to a greater or less extent. Whatever the true explanation, I have found that the resultant carbon black possesses many of the desirable characteristics of a carbon black produced solely from the auxiliary make, even though the principal hydrocarbon make may be a heavy residue oil.

By regulating the proportion of the auxiliary make, relative to the primary make, the surface activity of the resultant carbon black may be varied over a considerable range. The auxiliary hydrocarbon thus added should not exceed 25% by weight of the principal hydrocarbon make and should usually be substantially less than 25%. Proportions as low as 1% of the principal hydrocarbon make, and at times even somewhat less than 1%, will generally be found to influence the surface characteristics of the resultant carbon.

The invention will be further described and illustrated as to the presently preferred modification thereof with reference to the following drawings, of which

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

Figure 2 is a transverse section of the reaction chamber and blast burners along the line 2—2 of Figure 1; and

Figure 3 is a transverse section of the reaction chamber along the line 3—3 of Figure 1 showing more clearly the arrangement of the hydrocarbon make injection ports and tubes.

In the apparatus shown, the numeral 1 indicates a cylindrical reaction chamber one end of which opens into the vertical cooler 2 through the preliminary cooling duct 1a. At its left-hand end the reaction chamber is closed by a block of refractory material 3 provided with an axially positioned pipe 4 through which the blast burners may be ignited, and which, in operation, is normally closed by the cap 4a.

The chamber 1 is delineated by cylindrical side wall 5 of highly refractory material which, in turn, is covered by layers 6 and 7 of heat insulating material. Extending through the layers of heat insulating material and the furnace side wall, substantially perpendicular to the longitudinal axis of the chamber, are four blast burner ports 8, each entering the furnace chamber in a circumferential or tangential direction, as more clearly shown in Figure 2 of the drawings.

The apparatus shown is provided with two identical sets of these blast burner ports positioned at different distances from the block 3. In operation, one or both sets of ports may be used as desired, or one or more burners of the separate sets may be used.

Further downstream, the furnace chamber is provided with a set of four radially directed hydrocarbon make injection tubes 9, spaced 90° apart and extending through the layers of insulating material and the furnace side wall, as more clearly shown in Figure 3 of the drawings. These make injection tubes are provided for in-

jecting into the furnace chamber the principal hydrocarbon make in gaseous or vapor form. Where the hydrocarbon make is injected into the chamber in liquid form, suitable atomizing or spray nozzles will be substituted for the open-ended make gas injection tubes, specifically shown.

In operation, a fluid hydrocarbon fuel is supplied to the blast burners through valved tubes 10 projecting axially through the respective burner ports and terminating short of the inner wall of the furnace chamber. Air for combustion is forced by any suitable means through the conduit 11 and introduced tangentially into the annular duct 12, as more clearly shown in Figure 2 of the drawings, each set of blast burners being equipped with a separate air duct. The outer ends of the burner ports 3 open into the air duct 12 and advantageously are cut at an angle, as shown in the drawings, so as to utilize the whirling motion of the air in the duct to facilitate the directing of the air through the respective ports.

By the burner arrangement shown, a combustible mixture of the air supplied through conduit 11 and hydrocarbon fuel supplied through the tubes 10 is tangentially injected at high velocity into the furnace chamber to form a swirling cyclone of blast flame gases passing longitudinally through the chamber. The principal hydrocarbon make is radially injected into this swirling body of hot gases through the make injection tubes 9 and is substantially instantaneously uniformly mixed therewith, and is decomposed by heat absorbed therethrough to form carbon black particles in suspension in the furnace gases.

Carbon particles constituting the nuclei of the resultant carbon black product are formed in that zone of the furnace chamber just downstream from the hydrocarbon injection tubes 9 and the auxiliary hydrocarbon make is injected, at a zone still further downstream, into the resultant suspension through the auxiliary hydrocarbon injection tubes 13 which, with advantage, are arranged substantially the same as the tubes 9 of Figure 3 of the drawings.

The optimum position of the injection tubes 13 with respect to tubes 9 will depend somewhat upon other operating conditions, including the characteristic of the principal make injected through tubes 9, with respect to its decomposition rate, the temperature of the hot gases and the rate of flow of the gases through the furnace chamber but, in any event, they should be positioned at a zone of the chamber wherein the hot furnace black suspension is at a temperature sufficiently high to effect the decomposition of the auxiliary hydrocarbon. The auxiliary hydrocarbon is thus decomposed by heat absorbed from the hot suspension and, as previously noted, this decomposition appears to result in the forming of a thin film of a carbon of somewhat different characteristics over the surfaces of the preformed carbon black particles.

The resultant suspension of carbon black in the furnace gases passes from the furnace chamber through the preliminary cooling conduit 1a and upwardly through the vertical cooler 2 wherein the suspension is cooled by contact with water sprays 14. Any unvaporized water from these sprays, together with any carbon knocked out of suspension, passes downwardly from the vertical cooler into the sump 15 and the cooled suspension passes through the upper end of the vertical cooler through conduit 16 to conventional separating and collecting apparatus, as well understood in the art.

My improved process and the advantages derived therefrom will be further illustrated by the following specific examples:

Example I

This operation was carried out in apparatus such as specifically shown in the drawing, the inside diameter of the reaction chamber being 12 inches. The principal hydrocarbon make was a petroleum distillate and was

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sprayed into the furnace chamber by means of spray nozzles at the point indicated in the drawing by the reference numeral 9, using steam to atomize the oil. The operating conditions, yields, and characteristics of the resultant furnace black are set forth in the following tabulation. For comparative purposes, no auxiliary make was used in run No. 1. In runs Nos. 2, 3 and 4, natural gas was injected as the auxiliary make through 4½ inch tubes positioned as shown in the drawings, 2½ feet downstream from the principal make injection and in the amounts indicated.

Run No.	1	2	3	4
Air, Cu. ft./per hr.	47,000	47,000	47,000	47,000
Blast Ratio	12.5	12.5	12.5	12.5
Principal make, gals. per hr.	45.3	42.5	40.8	41.9
Auxiliary make, cu. ft./per hr.	0	1,400	1,480	1,620
Yield, lbs. per gal. of oil	2.58	2.19	2.43	2.65
Characteristics:				
Color ABC	136	120	123	127
Oil Absorption, gals./per 100 lbs.	15.2	15.1	15.1	15.0
Modulus 400% elongation—				
15 mins. cure	2,400	2,845	2,850	2,700
45 mins. cure	3,085	3,395	3,570	3,400
Tensile strength—				
15 mins. cure	4,000	4,500	4,175	4,300
45 mins. cure	4,150	4,200	4,000	4,300
Firestone blow-out test, minutes	19½	29¾	36	31¾

Color and oil absorption values given above were determined by standard test methods under comparable conditions. The modulus, tensile strength and blow-out values given are for standard tire tread compounds in which the respective carbon blacks were used, the values having been determined by standard test methods and under comparable conditions. The Firestone blow-out tests were made by placing a block of rubber, compounded with the particular carbon black being tested and measuring 1 inch by 1 inch by 1½ inch, between parallel metal plates, the lower of which was adapted to be oscillated and the upper plate weighted. The figures given represent the time in minutes required under oscillating conditions for the rubber test piece to deteriorate to an extent to permit the upper plate to drop to ¾ inch from the lower plate.

From the above tabulation, it will be observed that, by injection of the auxiliary gas, as herein described, the ABC color number of the black is materially reduced, while the modulus and tensile characteristics at the shorter curing time are substantially increased, indicating a more rapid curing rate. The time required to effect deterioration of the rubber sample containing such blacks under conditions of the Firestone blow-out test is shown to be greatly increased.

Example II

Similar tests were made on the same apparatus used in Example I, the principal make being a highly aromatic distillate oil and the auxiliary make being natural gas, except in run No. 5 where auxiliary make was omitted for comparative purposes. The auxiliary make was injected as described in Example I.

Run No.	5	6	7
Air, Cu. ft./per hr.	47,000	60,000	47,000
Blast ratio	12.5	12.1	12.5
Principal make, gals./per hr.	42.2	43.1	41.7
Auxiliary make, cu. ft./per hr.	0	1,420	1,400
Yield, lbs. per gal. of oil	2.34	3.52	2.99
Characteristics:			
Color ABC	116	121	125
Oil Absorption, gals./per 100 lbs.	15.5	16.0	16.0
Modulus, 300% elongation	1,400	1,575	1,550
Tensile strength	3,675	3,650	3,750
Log R electrical resistivity	3.5	5.2	4.2

The test methods were the same in each instance.

Example III

In a somewhat similar operation in which the principal hydrocarbon make was a mixture of 75% pressure tar

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and 25% aromatic distillate, the ABC color number, oil absorption, modulus of elasticity, tensile strength, and log R electrical resistivity were all increased with a substantial increase in yield by the use of natural gas as the auxiliary make as herein described, the auxiliary make being supplied at the rate of 1,850 cubic feet per hour and the principal make being supplied at the rate of 35.6 gallons per hour.

Similar results have been obtained where the primary make is a heavy aromatic pressure tar, undiluted by distillate oil and the auxiliary make is natural gas, or a distillate oil of lower aromaticity than the pressure tar.

As previously noted, it is usually desirable to so proportion the hydrocarbon fuel and air in the combustible mixture as to produce an oxidizing blast flame. The invention is of particular utility as applied to an operation in which the blast flame gases are of an oxidizing character. It will be understood, however, that the invention in its broader aspect is not so restricted but contemplates the injection of the auxiliary hydrocarbon make of the type described into any hot turbulent gaseous suspension of preformed carbon particles under conditions such that the auxiliary hydrocarbon is rapidly, uniformly mixed with the hot suspension and decomposed by the heat absorbed therefrom to alter the characteristics of the initially formed carbon black.

The invention is especially applicable to operations carried out in a cylindrical reaction chamber into which the combustible mixture is tangentially injected and is burned to form a swirling cyclone of hot blast flame gases, as more particularly described herein. However, the invention also contemplates operations in which the combustible mixture is longitudinally directed into the chamber and burned therein to form a highly turbulent stream of gases, for instance, as more fully described in the copending application, Serial No. 16,585, filed March 23, 1948. In the latter type of operation, the furnace chamber need not be cylindrical but with advantage is of rectangular cross-section.

I claim:

1. In the process of producing carbon black by which a combustible mixture of a fluid hydrocarbon fuel and an oxygen-containing gas is blasted into one end of an elongated cylindrical reaction chamber in a direction substantially tangential to the chamber and burned therein to form a turbulent swirling body of oxidizing blast flame gases passing longitudinally through the chamber at a temperature in excess of that at which hydrocarbons are decomposed to form carbon black and a normally liquid hydrocarbon to be decomposed is separately injected into the swirling gases at a point downstream from the entry of said gases to the chamber and is decomposed by heat absorbed from the hot gases to form carbon particles in suspension, the step of separately mixing a normally gaseous hydrocarbon with the turbulent suspension while the latter is at a temperature in excess of that at which the gaseous hydrocarbon is decomposed to form carbon black, the proportion of gaseous hydrocarbon thus mixed with the suspension not exceeding 25% by weight of the initially injected hydrocarbon to be decomposed.

2. In the process of producing carbon black by the decomposition of hydrocarbons by which the hydrocarbons to be decomposed are mixed with a stream of hot gases flowing through an elongated reaction chamber at a temperature in excess of that at which the hydrocarbons are decomposed to carbon black and the hydrocarbons are decomposed in a zone of carbon black formation by heat absorbed from the hot gases to form carbon black in suspension therein and the suspension of the carbon black thus formed in the hot gases is continued through the chamber and is finally cooled and the carbon black separated therefrom, the step of rapidly and uniformly mixing with a turbulent stream of said carbon black suspension, while the latter is passing through a zone of the reaction chamber downstream from the carbon-forming

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zone, a normally gaseous auxiliary hydrocarbon of an average molecular weight lower than that of the hydrocarbons to be decomposed first injected into the stream of hot gases, while the suspension is at a temperature in excess of that at which the auxiliary hydrocarbon is decomposed to carbon black and in proportions such that the temperature of the mixture is not thereby reduced below the decomposition temperature of the auxiliary hydrocarbon.

3. The process in claim 2 in which the hot gases are composed of oxidizing blast flame gases.

4. The process of claim 1 in which the normally liquid hydrocarbon is a highly aromatic petroleum residue oil

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and the auxiliary gaseous hydrocarbon consists principally of methane.

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