TI-2 Chemical Committee
Informative Report No. 9
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CARBON BLACK
AP-42 Section 5.3
Reference Number
3

Carbon Black

Informative Report No. 9 on the manufacture of carbon black is one of a series of survey reports prepared by APCA's TI-2 Chemical Committee on air pollution problems and control methods encountered in the chemical industry today.

Carbon black is ultrafine soot manufactured by the burning of hydrocarbons in a limited supply of air. This finely divided material (10 to 400 mμ in diam) is of industrial importance as a reinforcing agent for rubber and as a colorant for printing ink, paint, paper, and plastics.

Twenty years ago the mention of a carbon black plant evoked a vision of darkened plumes visible for miles, soot blanketed countrysides and blackened farm animals — mute evidence of stray carbon black that escaped with the vent gases. Carbon black plants polluted the atmosphere, the degree of pollution varying with the mode of production and separation of the black, and the geographic location of the plant. Those living in urban residential sites in the vicinity of manufacturing plants were grimly aware of the prevailing soot which was even more pronounced with a shift in wind. The plants then bore the stigma of dirt and their operating personnel singled out by their soiled work clothes and smudged faces. While this condition still exists at some isolated channel black plants, conditions have changed in most modern plants.

Most of the channel plants that formerly polluted the atmosphere with black smoke have been dismantled because of the rubber industry's shift to oil furnace black. Now 94% of the entire black production comes from furnace plants where the discharge of soot to the atmosphere can be controlled and prevented. There also has been an increasing awareness by the industry of the economic and public relation benefits resulting from the prevention of pollution. This has resulted in better designed plants, the use of more highly efficient separating systems, the application of stringent plant controls, and the maintenance of far better housekeeping. In modern furnace plants there is no need for stray black to pollute the air; plumes in the sky overhead can be colorless; verdure of the adjacent countryside can be retained and the plants can be unprecedently clean. Pressure will increase on those furnace plants which do not meet modern standards to comply and thus achieve pollution-free operations.

Informative Report No. 9 of the TI-2 Chemical Committee was first submitted to APCA's Steering Committee and Technical Council on November 22, 1966. It was processed in accordance with the 14 step procedure outlined in the March 1963 *Journal* and was finally approved by APCA's Board of Directors on November 7, 1967. In accordance with the objectives of the Association as they appear in Article XV, Section 4 of the By-Laws, each technical coordinating committee has the task of reviewing and amending its studies as often as necessary in the light of technological changes.

In accordance with procedures adopted by the APCA Technical Council and the Board of Directors, it is now published as representing "the best thinking of the Association."

Background Information on the Carbon Black Industry

Statistics

The U. S. carbon black industry is over 100 years old. In 1965, it produced 2.37 billion pounds of black (13.4 times as much as 40 years ago), valued at approximately 164 million dollars. The industry has expanded greatly in the past 50 years upon the discovery in 1913 of the ability of black to reinforce rubber. Previous use was only as a colorant but now 94% of the domestic shipments of black are used by the rubber industry and the remaining 6% by the printing ink, paint, paper, and plastics industries. Exports last year amounted to 9.7% of the total shipments.

Table I gives statistical background of the carbon black industry. This shows that channel black production is now at the same level as 40 years ago while furnace black production has increased 60-fold. Thermal black production tripled in the past 15 years.

Location of Plants

Manufacture of carbon black is carried on at 37 plants.[1] Their geographical distribution, the nearest residential areas, and population are listed in Table II. Residential areas may be very close to the plants or as far as 13 miles away, and the population may range from 537 to 76,000.[2] The total capacity of the plants is estimated at 2992 million pounds a year, comprising 154 million pounds channel black, 283, million pounds thermal black, 362 million pounds gas furnace black, and 2193 million pounds oil furnace black. In 1964, 52.4% of the black was produced in Texas and 32.6% in Louisiana.

Manufacturing Processes

Commercial processes of carbon black manufacture are in four categories and in the following order of importance:

1. Oil furnace process
2. Gas furnace process
3. Thermal (cyclic) process
4. Channel process

The fundamental steps in manufacture, regardless of the process used, are:

1. Production of black from feed stock
2. Separation of black from the gas stream
3. Final conversion of the black to a marketable product

In the channel and furnace process, the black is produced in burning the feed stock. In the thermal process, the feed stock is thermally decomposed into black and hydrogen. There is no burning.

In the channel process, the flames impinge on moving iron channels causing the black in the flames to be deposited on the channels. The black is scraped from the channels into hoppers and screw conveyed to a central point for finishing. In the other processes, the black is removed from the gas stream by separating systems compris-

Table I Statistical Background of the Carbon Black Industry[a]

Year	Production (millions of pounds)						
Year	Channel	%	Thermal	%	Furnace	%	Total
1965	149 555	6.31	274 429	11.60	1 942 768	82.09	2 366 752
1960	249 422	12.14	149 400	7.27	1 611 905	78.49	2 053 727
1955	359 487	20.61	136 907	7.85	1 247 118	71.52	1 743 512
1950	616 765	44.62	94 003	6.80	671 222	48.56	1 381 990
1945	538 539	51.16	—	—	514 259[b]	48.84	1 052 798
1940	491 765	86.45	—	—	77 027[b]	13.55	568 792
1935	316 284	89.66	—	—	36 465[b]	10.33	352 749
1930	350 300	92.18	—	—	29 700[b]	7.82	380 000
1925	143 700	81.00	—	—	33 700[b]	17.70	177 400

Year	Shipments (millions of pounds)				
Year	Domestic	%	Export	%	Total
1965[c]	2 336.8	90.30	250.8	9.70	2 587.6
1960	1 429.6	72.50	543.0	27.50	1 972.6
1955	1 373.8	75.15	454.2	24.85	1 828.0
1950	1 109.1	73.50	399.6	26.50	1 508.7
1945	846.2	63.31	173.8	17.04	1 020.0
1940	352.2	66.48	177.6	33.52	529.8
1935	245.4	63.31	142.2	36.69	387.6
1930	167.3	66.49	84.3	33.50	251.6
1925	132.4	75.40	43.2	24.60	175.6

Year	Applications of Domestic Shipments (thousands of pounds)				
Year	Rubber	Ink	Paint	Miscellaneous[d]	Total
1964	1 789 432	45 688	17 982	58 392[e]	1 911 494
1960	1 362 912	47 980	12 270	6 456	1 429 618
1955	1 286 861	55 313	13 061	17 942	1 373 777
1950	1 030 368	50 903	11 139	16 661	1 109 071
1945	804 386	22 824	7 421	11 631	846 262
1940	310 179	24 159	6 806	11 012	352 156
1935	213 708	15 177	6 550	9 916	245 351
1930	128 572	19 220	11 922	7 565	167 279
1925	86 329	22 389	11 757	11 973	132 448

Footnotes

- [a] Mineral Industry Surveys, U. S. Department of the Interior, Bureau of Mines, "Carbon Black."
- [b] Includes thermal production.
- [c] Estimated.
- [d] Plastics, food, etc.
- [e] Of this amount, 10 259 000 lb were shipped to the chemical and food industries; 12 281 000 lb to the plastics industry; 8 004 000 lb to the paper industry; and 27 848 000 lb were for other uses, e.g., cements, fertilizers, metals, shoes, and carburizing.

Table II Carbon Black Plants in the United States (1965)

State	Producer	Plant Location	County[a]	Nearest Residential Area[a]	Miles from Plant	Population[a]	Manufacturing Process	Production Capacity (millions of lb/yr)
Arkansas	Columbian	El Dorado	Union	El Dorado	0	25 292	Furnace	87
California	Continental	Rogas	Kern	Bakersfield	12	65 500	Furnace	50
	Shell	Shell Point	Contra Costa	Pittsburg	5	19 062	Thermal	18
	United	Fleta	Kern	Mojave	3	2 000	Furnace	64
Kansas	Columbian	Hickok	Grant	Ulysses	8	3 684	Furnace	58
Louisiana	Cabot	Cabot	St. Mary's	Centerville	10	537	Furnace and Thermal	299
	Cabot	Tate Cove	Evangeline	Ville Platte	7	7 512	Furnace	175
	Columbian	Carboco	Avoyelles	Cheneyville	1	1 037	Furnace	80
	Columbian	N. Bend	St. Mary's	Centerville	10	537	Furnace	120
	Continental	West Lake	Calcasieu	West Lake	0	3 311	Furnace	70
	Thermatomic	Sterlington	Ouachita	Sterlington	0	1 138	Thermal	145
	United	United	St. Mary's	Weeks	5	1 138	Furnace	200
New Mexico	Continental	Witco	Lea	Eunice	5	3 531	Furnace	25
	United	Johnson Siding	Lea	Eunice	10	3 531	Channel	30
Oklahoma	Continental	Ponca City	Kay	Ponca City	0	24 411	Furnace	85
Texas	Cabot	Skellytown	Carson	Borger	13	20 911	Channel and Furnace	28
	Cabot	Big Spring	Howard	Big Spring	0	31 230	Furnace	130
	Cabot	Pampa	Gray	Pampa	0	24 664	Furnace	55
	Columbian	Seagraves	Gaines	Seagraves	0	2 307	Channel and Furnace	115
	Columbian	Youens	Montgomery	Conroe	9	9 192	Furnace	121
	Continental	Sheerin	Moore	Sunray	7	1 967	Furnace	75
	Huber	Borger	Hutchinson	Borger	0	20 911	Channel and Furnace	91
	Huber	Eldon	Harris	Baytown	7	39 000	Furnace	156
	Phillips	Borger	Hutchinson	Borger	0	20 911	Furnace	290
	Phillips	Echo	Orange	Orange	5	25 605	Furnace	60
	Richardson	Sid Richardson	Ector	Odessa	9	76 000	Channel	60
	Richardson	Big Spring	Howard	Big Spring	0	31 230	Furnace	50
	United	Kosmos	Aransas Pass	Aransas Pass	1	6 956	Furnace	150
	United	Norrick	Wheeler	Shamrock	5	3 113	Furnace	105
								2 992

[a] Road Atlas, Rand McNally & Co., Chicago, Ill., 1965.

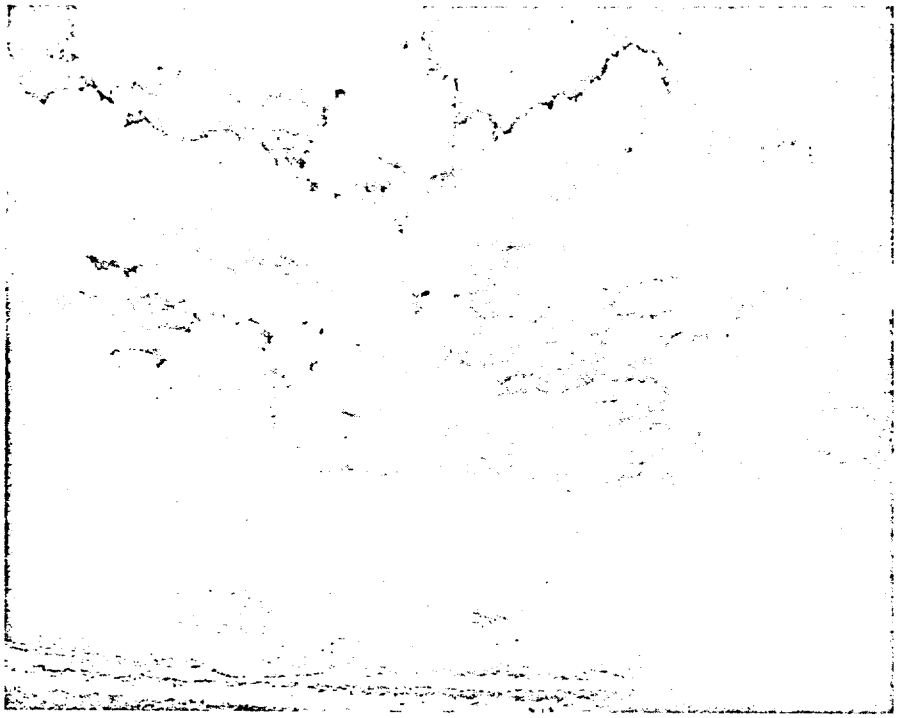

Fig. 1A. Channel black plant—ground view.

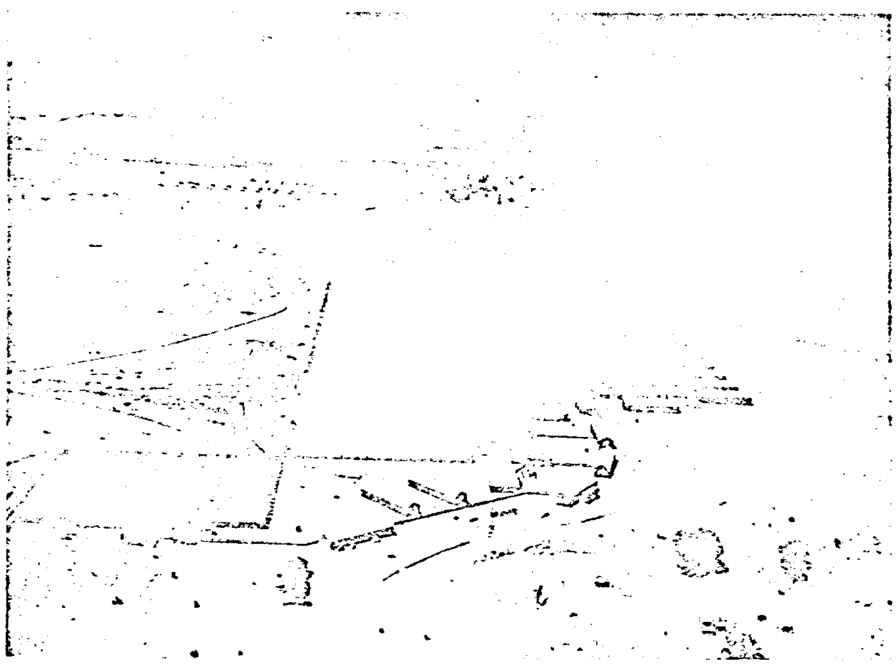

Fig. 1B. Channel black plant—aerial view.

ing electrical precipitators and/or cyclones and bag filters and the collected black is conveyed either pneumatically or by belt to a central point for finishing.

Channel plants are usually located in remote sparsely populated districts where gas is available and no other industrial outlet for this gas exists. The copious volumes of dense black smoke vented by channel plants (Fig. 1) pollute the atmosphere. No way has yet been developed to separate the escaping black from the vent gases at channel plants. The gases need first to be confined and any attempt to do so upsets burning conditions in the "hot houses" and drastically affects yield and quality of the black. The situation is entirely different in furnace and thermal plants. Improved plant designs and modern technology of black separation and recovery enable these plants to vent their off-gases virtually free from soot.[3] Consequently there is little particulate pollution at these plants (Fig. 2).

Feed Stocks for Carbon Black Manufacture

Natural Gas

Natural gas is used in all processes, except that in the oil furnace process, it solely provides a convenient source of heat to dissociate the oil. The natural gas used in 1964 amounted to 106,759 M cu ft, valued at 13.34¢ per M cu ft and yielded 4.38 lb black per M cu ft.[1] Table III contains an analysis of typical natural gas used.[3]

Table III Analysis of Natural Gas for Carbon Black Manufacture

Application		Channel Process (mol. %)	Gas-Furnace Process (mol. %)
Methane	C_1	83.74	87.70
Ethane	C_2	7.32	3.94
Propane	C_3	3.67	2.29
Iso-butane	C_4	0.30	0.41
N-butane	nC_4	1.08	0.76
Iso-pentane	iC_5	0.32	0.23
N-pentane	nC_5	0.27	0.22
Hexanes +	C_6	0.30	0.26
Helium		—	0.09
Carbon dioxide		0.86	0.04
Nitrogen		1.74	4.06
Oxygen		—	0.00
British thermal units		1161.75	1070.00
Specific Gravity		0.685	0.648

Until 20 years ago, carbon black was made solely from low priced natural gas. But with increase in gas price, limited availability because of increasing demands by pipelines, and the need of improved types of black for use in synthetic rubber, petroleum oil became the preferred feed stock for black manufacture.

Petroleum Oil

Liquid hydrocarbons (selected fractions from petroleum, or coal tar) are used only in furnace black manufacture. Table IV contains the analysis of several typical feed stocks.[4] 334,874 thousand gallons of oil valued at 6.79¢ per gallon were used to produce 87.5% of the 2.25 billion pounds of black made in 1964. The average yield was 4.65 lb per gallon of oil.[1] The main petroleum stocks used are: (1) cracked fuel oil from thermal cracking of cycle stocks or the vacuum flash distillate from such cracked fuel oil; (2) thermal or catalytic cycle stocks; and (3) aromatic extracts from catalytic cycle stocks. The best raw material especially suited for the production of modern high structure carbon blacks is highly aromatic, low in sulfur, high molecular weight resins and asphaltenes, substantially free of suspended ash, carbon, and water.[5,6]

Grades and Prices of Carbon Black

More than 135 grades of carbon black are currently marketed to meet a wide range of industry specifications.[7] Price is affected by the rigidity and number of specifications imposed on the product. A range of prices by use is shown with the higher prices being charged for more specialized products which are more expensive to produce.

End Use	Price, $ Per Pound
Rubber reinforcing	0.055 - 0.105
Printing ink	0.0575 - 0.23
Paint	0.0575 - 1.83

Shipments

The very nature of carbon black, its fluffiness, lightness, and tendency to dust, imposes more than usual care in the packaging, shipping, and handling of the black to avoid pollution. For many years, black was packed only in paper sacks (3-ply Kraft) in 12.5, 25, or 50 lb. Sometimes special grade blacks (such as color) are overslipped in polyethylene bags to minimize moisture absorption. The introduction of pelleted black about 35 years ago, thus converting the finely divided powdered material into a free-flowing and relatively dust-free material, made possible the shipment of black in bulk. Bulk black is a full 1/2¢ a pound cheaper than bag material and handling costs are much less than bag black. Furthermore, operations are cleaner, since handling systems are enclosed, and product contamination is eliminated. Bag black takes up considerable space. From 50 to 75% of the shipments of black in 1965 by major producers were in bulk. Thirty per cent of the black is currently marketed in 50 lb paper sacks. Black is now being shipped either in paper sacks, sealdbins (collapsible rubber containers), metal tote bins, or in bulk in closed hopper cars. Ninety per cent of the bulk black is shipped in hopper cars. Export shipments of black are in sacks.

Methods of Manufacture

Channel Process

Natural gas is burned with a continuous small wide thin luminous fan-shaped flame, Fig. 3, from small slotted (0.021 - .056 in.) steatite or lava tips. Insufficient air for complete combustion is supplied to the gas, and black is formed in the gas flames and deposited by impingement upon the flat under-surface of moving channels. It is removed and falls into fixed collecting hoppers as the channels slowly reciprocate continuously past a series of stationary scraper blades. The black is transported with a screw conveyor system, mikropulverized, pelleted (if black in dust-free form is required), packed in bags or stored in bulk (if pelleted).

A schematic flow diagram of the channel process is shown in Fig. 4.[9] A typical channel plant may cover many acres and may be composed of several hundred steel buildings (called "burner houses" or "hot houses") housing some 2000 to 4000 flames and the appropriate number of channel irons, upon

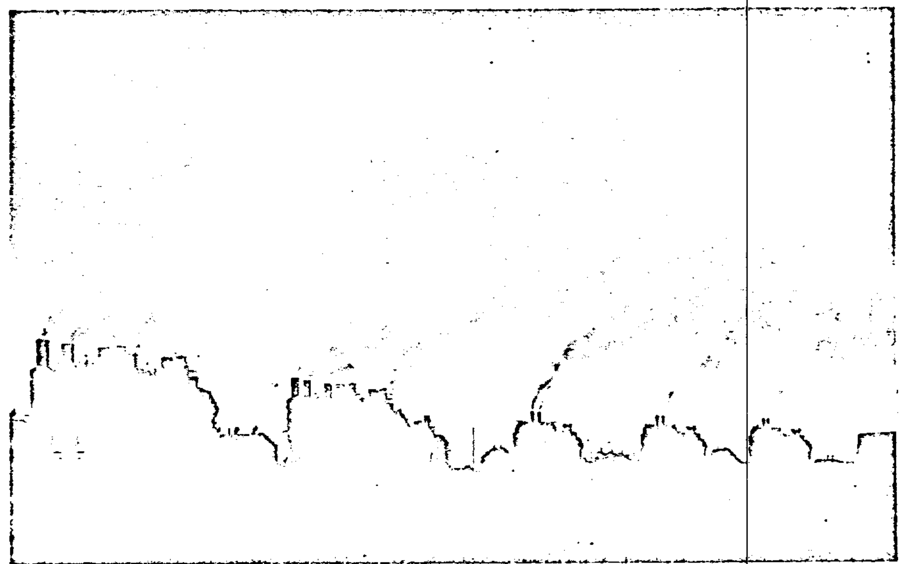

Fig. 2A. Old type furnace black plant.

Fig. 2B. Modern furnace black plant.

Table IV Analysis of Feed Stocks for Furnace Black Manufacture

Feed Stock	1	2	3	4	5
Density (lb/gal)	8.843	8.796	9.307	9.012	8.254
Molecular weight	270	275	265	240	500
Bureau of Mines					
Correlation Index	117	116	144	123	73
Empirical yield (lb/gal)	3.53	3.49	4.20	3.84	2.15
% Carbon	90.63	90.07	90.37	88.99	88.24
% Hydrogen	8.27	8.30	7.11	7.48	10.48
% Sulfur	1.11	1.20	1.77	2.73	0.49
API gravity @ 60°F	1.5	2.7	−4.8	0.8	7.6
Viscosity @ 180°F	71.8	196.0	202.0	55.5	55.0
Pour point (°F)	35	53	55	3	83
Flash point (°F)	210	335	260	145	160
Distillation range					
first drop	308	465	382	398	350
50%	807	802	767	731	725
Last drop	995	993	928	880	920
Aromatics (% by weight)	72	78.7	85.9	77	65

Feed stocks 1 - are used for oil furnace black manufacture and feed stock 5 for gas enrichment in manufacturing gas furnace black.

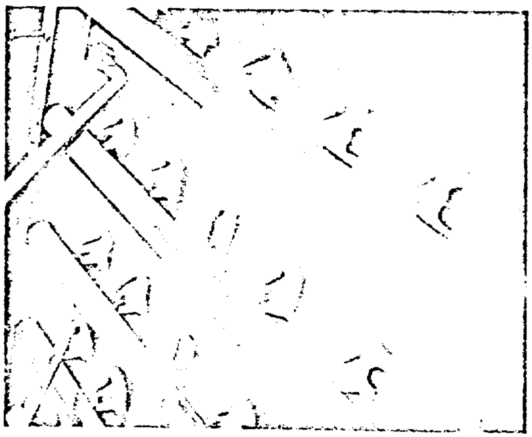

Fig. 3. Flames in channel black plant.

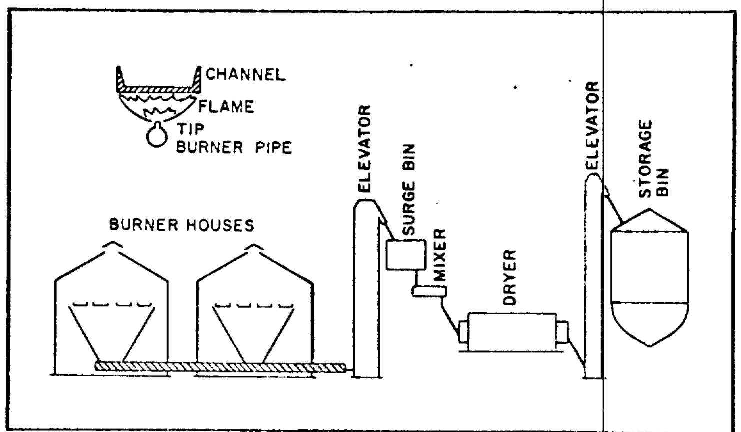

Fig. 4. Flow diagram of channel process.

which the flames impinge and deposit carbon black. Each burner house is approximately 150 ft long, 10 to 14 ft wide, and about 10 ft high.

Gas rates are on the order of 45 to 80 cu ft per 24-hr day per burner tip and may range from 150 000 to as high as 260000 cu ft of gas for 24-hr day per hot house.

Air is supplied through openings at the base of each building and the spent gases and products of combustion pass out of the hot house through openings and stacks in the roof. Combustion is controlled by natural draft openings in the top and bottom of each house. Draft control is visual and dependent upon the skill of the operators. A large excess of air holds the temperature of the house below 1000°F. However, this large excess of air does not completely burn the natural gas because the combustion time from the gas tip to the channel is very short and mixing of air and gas in this interval does not occur.[10]

Screw conveyors pick the black up from the various houses and convey it to the processing area where an air separator removes particles of grit (hard calcined carbon). The fluffy black is then further processed through a high-speed hammer mill (mikropulverizer) to break up lumps that form in the conveyors, and also to render any remaining grit particles extremely fine. It also pulverizes oversize product pellets that recycle from downstream screening. The black then passes to the pelletizing step and subsequent packaging.

Since the density of carbon black as manufactured is 1 to 5 pounds per cubic foot and is much too light to ship economically, it is the usual practice to agitate the loose black to increase its bulk density to 10 to 18 pounds per cubic foot. Agitation is usually accomplished by placing the black in a tank and subjecting it to the beating action of rods attached to a rotating shaft. The beating action drives the carbon particles closer together and simultaneously drives out a portion of the entrained gases, thus increasing the density. It is also possible to densify carbon black by other means, such as compression (a practice long abandoned) and pelletization. When the desired density has been reached, the carbon black is drawn from the agitator tank by vertical screw conveyors which press the carbon black downward into shipping bags.

When burning natural gas alone in the channel process and with the aid of flame shields and air guiding devices within the hot house, the maximum yield of black obtainable is about 2.5 pounds per thousand cubic feet of gas burned. In view of the rapidly increasing cost of natural gas, it has become highly desirable, for economic reasons, to enrich the gas with oil.[11] It has been found that incremental yields from various cracked recycle and cracked distillate oils average about 2.5 pounds of black per gallon. For enrichment, any liquid hydrocarbon can be used having a distillation end point of below about 950°F.[12,13]

Channel black production in 1965 amounted to 149,555,000 lb, equivalent to only 6.31% of the total produced.[1] It was made in five plants, one of which is located in New Mexico and the other four in Texas.

Thermal Process

Thermal blacks are produced by the thermal decomposition of natural gas in the absence of air or flame.[14] In order to create sufficient heat to carry on this cracking, which is an endothermic reaction, part of the gaseous hydrocarbon being used must be burned with air to heat the system to cracking temperature. Theoretically, from every thousand cubic feet of methane thus treated, 31.82 lb of carbon are formed as well as 2000 cu ft of hydrogen. The carbon is present in the ratio of approximately 31 lb to 11 lb of hydrogen.[15] While the yield is considerably improved over the channel process (up to 16 lb per 1000 cu ft), the serious limitation is coarser particles which neither have the reinforcing properties nor the color of channel black.[16]

The thermal process, Fig. 5, comprises[17]: (1) the cracking units, (termed generators) consisting of checkerwork furnaces; (2) coolers; (3) carbon collectors; and (4) packing. The furnaces are 12 to 14 ft in diameter and 25 to 35 ft high,[18] and consist of a riveted steel shell, insulated and lined with refractory brick and filled with checker brick similar to a blast furnace stove.

Thermal black production differs from other carbon black operations in that it is cyclic rather than continuous.[19] The process is intermittent, the checkerwork

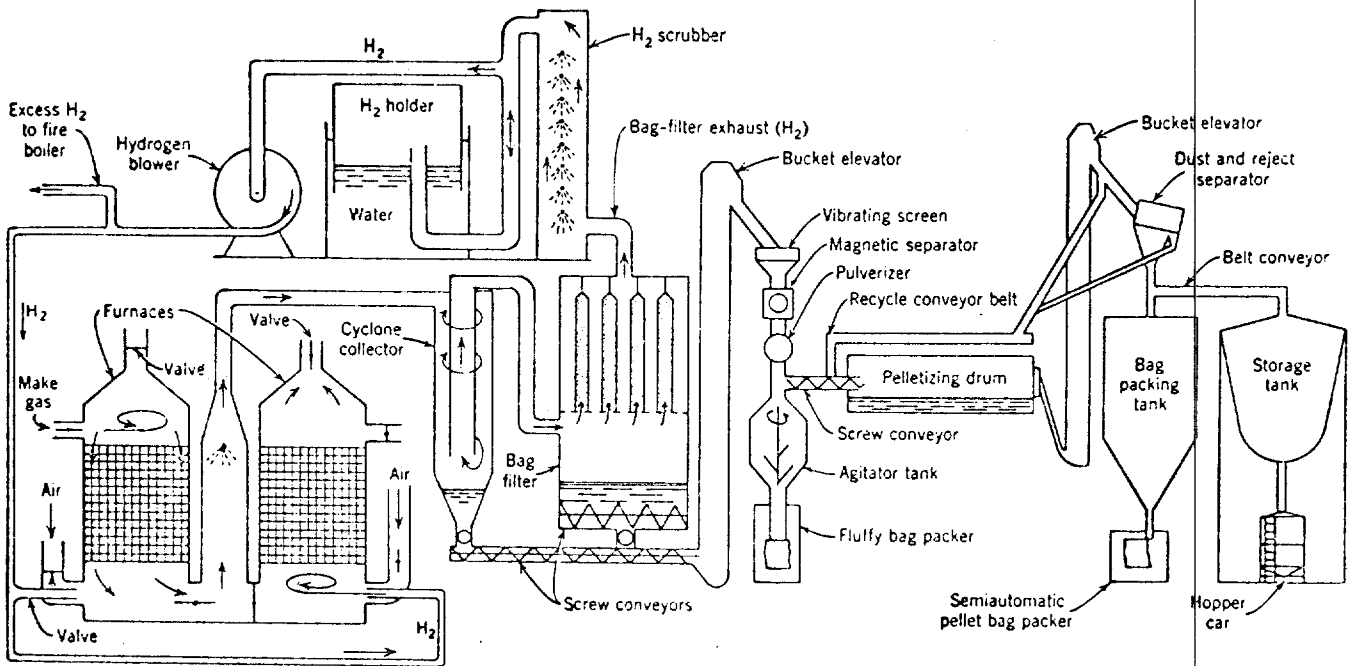

Fig. 5. Flow diagram of thermal process—Cabot's plant at Franklin, La. (Courtesy of Cabot Corp.)

being first heated to 2400 to 2800°F[10] by the complete combustion of a blast of natural gas and air introduced at the bottom. When the bricks are brought up to the required temperature, the stack (vent to the atmosphere) is closed and natural gas is admitted from the top of the furnace for the decomposing part of the cycle. Thermal black is produced as the heat from the brickwork decomposes the gas into a smoke of thermal carbon plus quantities of hydrogen.[20] When the bricks become cool, the natural gas flow is shut off and the remaining carbon smoke is flushed out into the cyclone separators. The complete cycle for a single generator requires approximately ten minutes. Of this time about half is required for heat-up and half for the cracking process.[19]

The effluent gas from the generator, which is on the production cycle, consisting of about 90% hydrogen, 6% methane, and a remaining complex mixture of higher hydrocarbons, carries the suspended black.[21] The smoke from the furnace is passed countercurrently through a watersprayed cooling tower to cool the smoke sufficiently to about 125°C. This temperature allows it to be safely filtered through the cloth bags in the collectors and yet not wet either the bags or the carbon. Recovery is about 40 to 50% of the carbon in the fuels. The unrecovered carbon is lost as hydrocarbon in the effluent gas and a portion adheres to the surface of the generator checker brick and is burned off on each heat cycle. The hydrogen-rich gas from the bag filter is cooled, dehumidified, compressed, and used as fuel for reheating the generators. Since more hydrogen is produced than is required for reheating, the excess is usually employed to fire boilers, thus providing the steam and electric power necessary to operate the plant.[21]

The collected black is transported by screw conveyors to the processing area where it is passed through a magnetic separator, screen, and hammer mill. It may then be packed through an auger packer as fluffy black in 25 or 50 pound paper bags, or passed through pelletizing equipment which transforms the fluffy black into a free-flowing product. As such, it may be packed into paper bags through semiautomatic valve packing machinery or loaded directly into bulk hopper cars. Table V, is a typical chemical analysis of the natural gas used:[17]

Distinct advantages lie in the use of natural gas, since it is both clean and easy to handle and since the discharge to the atmosphere is well filtered. The net result is that the outskirts of the latest thermal black plant (Fig. 6) are not soot covered and particulate pollution from the plant is very low.[19]

Thermal blacks are the coarsest of the commercial carbon blacks with medium thermal black ranging between 400 and 500 mμ in diam and the fine thermal grade averaging 150 to 120 mμ.[21] The fine grade is made by a process[22,23] essentially the same as the medium grade; the difference being that in making the fine grade, a portion of the resultant gas is recirculated, and acts as a diluent for the natural gas being decomposed, thereby allowing the particles of carbon to be formed in a more dilute atmosphere. The dilution principle is so effective it reduces the average particle size of the fine grade to about one-fifth that of the coarse grade.[17]

Furnace Process

The furnace process now dominates in carbon black manufacture and like the channel process, it also involves incomplete combustion of hydrocarbons. But, unlike the channel process with its backbone of thousands of small flames and miles of channel collecting surfaces, the furnace process employs a single huge flame confined in a refractory lined furnace and using a large volume of hydrocarbons and air. The fundamental equipment of the furnace process is also entirely different from that serving the channel process. Flexibility in furnace design and in effecting partial combustion has resulted in various

Table V Typical Chemical Analysis of Natural Gas Used in Manufacturing of Carbon Black

	Volume Natural Gas (%)	Volume Resultant Gas (%)
Carbon Dioxide	0.4	0.9
Illuminants	0.7	1.3
Hydrogen		85.4
Carbon Monoxide		1.1
Methane	93.8	5.0
Nitrogen	5.1	6.3

furnace processes. There are two categories of furnace black processes, depending upon whether natural gas or oil is employed as the feed stock. Differently designed furnaces (referred to as converters or reactors) convert the hydrocarbon into carbon black and the resulting blacks are referred to as gas furnace blacks and oil furnace blacks.

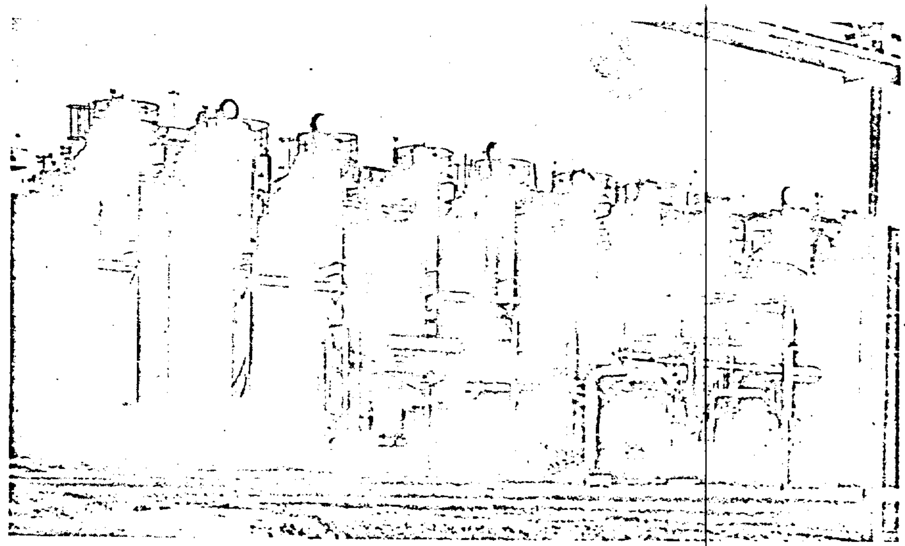

Fig. 6. Modern thermal black plant at Franklin, La. (Courtesy of Cabot Corp.)

Gas Furnace Process

Figure 7 shows a schematic flow diagram. A typical furnace or reactor used in this process is that of Hanson and Skoog (Fig. 8).[24,25] It is refractory lined and is designed with special inlets or ports for natural gas and for air. An annular mixing orifice formed of refractory material is located within the converter. The flue from each furnace meets in a manifold leading to the unit cooler and collecting system. Operating steps of the gas furnace process are as follows:

1. In the Hanson-Skoog furnace, the process utilizes a turbulent mixture of air and natural gas in such proportions that a partial combustion of the natural gas is effected. Hydrocarbon gas at the rate of 560 cu ft/min and a limited supply of air (2520 cu ft/min—a ratio of 4.5:1) are fed continuously into the furnace. The volume, velocity, and direction of the air and gas are so adjusted and correlated that a partial combustion reaction occurs in a vigorous luminous swirling mass of flame which moves through the furnace at a relatively high velocity. Temperatures of 2200° to 2600°F result. The unburned hydrocarbon gas is dissociated with the production of carbon black, gaseous products, and water vapor.

2. The temperature within the furnace is controlled by the air-gas ratio, flow, turbulency, and extent of combustion permitted. Also the extent of combustion permitted regulates the temperature of the reaction and the type and yield of carbon black which is produced. Too low a temperature or insufficient air induces cracking and polymerization and creates a black with high benzene extractable matter.

3. The flue gases, largely carbon monoxide, hydrogen, nitrogen, and water vapor, carry the hot carbon from the furnace through a long horizontal brick-lined flue some three feet in diameter, to a cooling tower where water sprays reduce the temperature from about 1800 to 500°F. Agglomeration of the fine black particles occurs either in an electrostatic field provided by an electrical precipitator or by centrifugal force in cyclone collectors. When the electrical precipitator is used about 30%, depending on the grade of black produced, is shaken off the electrodes into the collecting hopper attached to the bottom of the precipitators and the remainder of the flocculated black is caught, to a very large extent, in the cyclone collectors which follow the precipitator and which are generally supplemented by appropriate bag filters to remove last traces of black. The permanent gases including the carbon monoxide and condensable vapors (steam) are discharged through the stack of the final collector direct to the atmosphere. The black is carried to the finishing area by screw or pneumatic conveyors.

The Carbon Black Industry in the U. S. does not find incineration of the effluent economical at present to destroy the carbon monoxide. Two plants in the U. K. are currently required to oxidize the effluent. Current studies on CO pollution of the atmosphere may indicate the need for incineration at U. S. plants in the future, and regulatory agencies may be requesting such additional steps in the near future. Most plants do not use sour natural gas as a feed stock, but if they should, the effluent would also contain ppm quantities of H_2S and free sulfur.

Blacks produced by the gas furnace process have a particle size intermediate between channel black and thermal black and are used primarly in tire carcasses and mechanical rubber goods For the larger particle size furnace black, the yield may be 25 to 30%, and for the smaller particle size black, only 10 to 15%. The efficiency of the gas furnace process thus depends upon the quality of black produced.

It is now common practice to enrich the natural gas with petroleum oil in order to obtain a greater throughput of carbon black through the gas furnace plant. A typical rate of enrichment is in the order of 5.65 gallons oil per 1000 cu ft of gas.

Oil Furnace Process

The oil furnace process is similar to the gas furnace process except that the raw material used is oil instead of natural gas and the furnace design is also different. Each producer has developed and patented furnace designs. The design of the furnaces and burners constitutes an important part of carbon black technology. A flow diagram of the oil furnace process used at a large modernized plant is shown in Fig. 9.

The heart of the plant is the reactor. The refractory lined steel furnaces vary from 10 to 30 ft in length and 6 to 30 in. in internal diameter, depending upon the grade of black to be produced. Oil, which is conditioned by preheating to 550 to 700°F, is introduced into the combustion zone of the reactor along with air and gas and burned to provide the heat necessary to crack the oil.

Typical oil, air, and gas rates used in the manufacture of the four principal grades of oil furnace blacks are shown in Table VI. The aromatic feed stock is sprayed into the combustion mass where a portion of it burns with the excess air. Air and gas are kept at a constant weight and the weight of oil is varied to maintain a furnace temperature of about 2500°F. The oil is cracked to carbon and hydrogen with side reactions producing carbon dioxide, carbon monoxide, and water. Trace amounts of acetylene and methane are also present.

The reactor converts approximately 55% of the feed's carbon content to carbon black. The remainder passes through the process in the form of gaseous combustion products. Process variables that are adjusted to produce a

Table VII Composition of Gaseous Components of Exhaust After Carbon Black Has Been Removed

	Semi-reinforcing Furnace Grade (Large Particle Size Black) % (dry basis)	Intermediate Super Abrasion Furnace Grade (Small Particle Size Black) % (dry basis)
Carbon dioxide	*ca.* 5	4.3
Carbon monoxide	*ca.* 5	11.8
Hydrogen	17 - 18	13.9
Methane	*ca.* 1	0.76
Acetylene	*ca.* 1	0.31
Nitrogen	Balance	Balance
Hydrogen sulfide (ppm)	300 - 400	300 - 400
Sulfur (ppm)	200 - 400	200 - 400

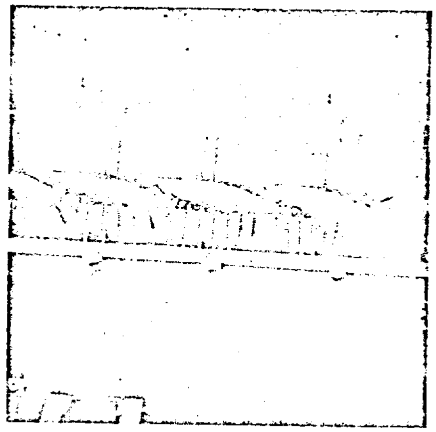

Fig. 10A. Pin shaft in drums for pelleting carbon black by wet process.

Fig. 10B. Drums for pelleting carbon black by wet process.

reported in the effluent by Russian investigators. The comments under Gas Furnace Process regarding incineration of the effluent also applies to the oil furnace process. Incineration of the sulfur compounds will produce SO_2 and SO_3 which in certain areas may also be found to be objectionable. Water vapor constitutes 40 to 45% by volume on wet basis. With the modern separating and collecting equipment in use, the separation of the carbon black from the gas stream is highly effective, for no black is visible in the vented off-gases.

The second stage is for the purpose of transferring the separated black to a convenient location where it can be more readily converted to a marketable product. Accordingly, the separated black is now pneumatically conveyed to the finishing area. The conveyor stream containing 200 to 250 gr/cu ft is passed to the so-called secondary collection system, which consists of a cyclone and a bag filter. The secondary cyclone separator has a 54 in. diam and is 10 to 12 ft high. The secondary filter is designed to operate at about 4 cu ft/min/ft^2 of cloth area. As these gases are low in temperature, synthetic fabrics instead of glass can be used for the bags.

Conversion of Carbon Black to a Marketable Product

In the finishing area, the black is first passed through a hammer mill (mikropulverizer) to break up lumps formed in the conveyors. The bulk density of the black from the hammer mill is 5 to 12 lb/cu ft, depending on the grade of black produced. In this form, it is fluffy, quite dusty, and not marketable. The black is accordingly converted into pellets or beads to a bulk density of about 20 to 35 lb/cu ft, depending upon the grade of black produced. In this form, it is dust-free and of sufficiently high density to warrant shipment.

Pelleting may be accomplished by either a dry or wet procedure. If the former is used, the fluffy black is conveyed to large closed horizontal rotating steel drums where the agitation results in a steady increase in bulk density and final conversion of the black into free-flowing pellets. In the wet procedure, the pulverized material is mixed with approximately one part of water to two parts of black in a mixer, comprising a horizontal housing containing a revolving axial shaft on which pins are mounted (Fig. 10). Agitation by the pins causes the mixture to form nearly spherical particles, measuring $^1/_{16}$ to $^1/_8$ in in diam. These pellets are then conveyed to driers for the removal of the water. Drying temperature is 375 to 450°F, depending on the product load. The discharged pellets are ready for screening, storage, and bagging. Oversize product pellets from downstream screening are recycled to the hammer mill for repulverization.

Separation and Collection Equipment

The types of equipment commonly used for effectively separating and collecting finely divided black from a gas stream are agglomerators, electrostatic precipitators, cyclone separators, scrubbers, and bag filters. When combinations of these are connected in series with each other and a bag filter constitutes the final separation step in the system, then better than 99% recovery of the black from the combustion gases can be obtained and the fume from the stack will be colorless

In old plants, the black laden gases are first cooled to about 450 to 550°F, and then passed through a dry electrostatic precipitator which agglomerates the black. The increased diameter and density of the agglomerated black allows it to be removed from the gas stream by passing through several cyclone separators. Together these have a recovery efficiency of 85 to 90%, leaving about 10% of the initial carbon to be removed before the off-gases are vented to the atmosphere. This is accomplished either by a bag filter to give 99% recovery or a wet scrubber system with 97 to 98% collection overall. The system may comprise water scrubbing and wet electrostatic precipitation or washing in a slot scrubber followed by a wet cyclone scrubber. In order to recover the black, the slurry is circulated back to the reactors where it is used for quench. The black is thus re-entrained in the smoke and recovered.

The electrostatic precipitator functions well in agglomerating furnace blacks. However, it is a high first-cost apparatus and suffers somewhat from lack of flexibility when switching from one grade of furnace black to another and/or to different flow rates. It must be shut down for frequent cleaning of the electrical system and is sensitive to electric surges due to lightning storms or other causes. Power consumption for energizing the electrodes and for pumping gas through the precipitator is low. Cost of the cyclones used in conjunction with electrostatic precipitators is relatively low compared with the cost of the precipitator and auxiliaries.[23]

The electrostatic precipitator is rapidly disappearing from use in the carbon black industry. Even at some older plants they are no longer in operation, being shut off to save operating and maintenance expenses. They are

Table VIII Typical Efficiency of Various Separating & Collecting Equipment for a Carbon Black Stream Containing 14 gr/cu ft.

Type	Per Cent Recovery	Discharge Concentration (gr/cu ft)
Electrostatic Precipitator	20	11
Cyclone Separator	50	7
Scrubber	75 - 85	2 - 4
Bag Filter	99.9+	0.01

not energized and no carbon black is removed from them. The current trend is to do without electrostatic precipitators when building new furnace black plants. Rather the trend is to mechanical agglomeration placed ahead of bag filters. At the time when the older plants were built, filters had not yet been suitably designed and the use of cyclones by themselves was inadequate.

Because of the increasing difficulty of collecting finer particle size blacks due to the low total black concentration in the gases, and the great increase in construction and equipment costs, the carbon black industry turned to agglomeration apparatus of lower first cost and of equivalent or superior performance compared with the electrostatic precipitator. Accordingly, in more plants, the black laden gases, likewise cooled to about 550°F, enter a series of large diameter cyclones (usually four) which separate about 70% of the carbon. The gases with the remaining black may be cooled further to about 360°F. They then pass to a bag filter which separates the remaining black from the combustion gases for an over-all recovery of 99+%.

At lately built plants, cyclones (as well as electrical precipitators) have been dispensed with and the design for carbon black separation calls for a system with an agglomerating device[29] and a single bag filter connected in series. The agglomerating device performs no separation, but its peculiar construction is well suited for rapid agglomeration of all the very fine particles of black entrained in the combustion gases. It transforms them with centrifugal force into larger agglomerated particles which can then easily be separated from the gas stream in a bag filter.

Sonic agglomeration of carbon black[28] utilizing high-frequency sound waves to separate carbon black from the gas stream has been tried at one gas furnace black plant[16] in place of electrostatic precipitation. The results proved unsuccessful.[30]

The typical efficiency of various separating and collecting equipment for a carbon black stream containing 14 gr/cu ft is given in Table VIII.

Electrostatic Precipitator

A typical dry electrostatic precipitator used in carbon black plants has a rated capacity of 50,000 cu ft of gas/min. It has 20 sets of curtain rods consisting of 0.375 in rods mounted vertically in a frame of 1.5 in. pipe, with the high tension wires between the sets of rods. The precipitator contains two sets of electrodes. Between these electrodes a unidirectional potential difference of about 70,000 volts is maintained. The electrical discharge ionizes the gas passing through the field. The ultimate result is that particles of black that have a negative charge and those that acquire a negative charge by attachment of negative gas ions are drawn towards the positive collecting electrode. A precipitator will create about 10^8 to 10^9 ions/cm^3 indicating the particles are fully charged in 0.1 sec or less.[31]

The curtain rods (collecting electrodes) are periodically rapped[32] pneumatically by plate rappers in order to dislodge the black as it collects. A mechanical rapper is used on the high tension wires. The black drops into a hopper from which it is continuously removed.

Predicting the performance of an electrostatic precipitator will depend to a large extent on factors, such as gas flow, particle size distribution, and black loading.[31]

Scrubbers

Wet scrubbers, despite their high recovery efficiency, have very limited use in the United States for separating carbon black from a gas stream. Neither are wet electrostatic precipitators currently in use by the carbon black industry in this country.

Cyclone Separators

Two main types of cyclone separators are utilized in carbon black collection: (1) medium efficiency or high throughput cyclones. They are generally of fairly large diameter and are used singly; (2) modern high efficiency, high-velocity cyclones usually nested in groups of 2, 4, 8, or more. Primary cyclones are of various sizes. A typical cyclone used (old design) is 11 ft in diam and 35 ft high. The cyclone based on the new design (high efficiency) is 6 ft in diam and 15 ft high. Secondary cyclones are only 54 in. in diam and 10 to 12 ft high. Cyclones have an agglomerating effect on the black due to the centrifugal motion created within the equipment.

Bag Filters

In bag filters, the black laden gas stream enters the open bags at the bottom and passes through the cloth, depositing solids on the cloth, and the clean gas discharges to atmosphere. The bags are cleaned by reversing the flow of the gas and repressuring. The temperatures involved rule out the use of cheap reliable filter media, such as cotton, wool, and "orlon." The maximum working temperature of these materials is about 275°F. These filters faced considerable corrosion problem until bags of woven glass fabric made from staple yarn were introduced. Filtration can thus be carried out at temperatures up to 550°F. However, the brittle fibers cannot stand up to the constant, or the intermittent shaking required to free the black collected on the cloth and the cloth wears out quickly. To solve this problem, cloth manufacturers coat the fibers with resins and silicone oils to help fibers slip over each other more easily. Typical bag filter material used by one major black producer consists of glass fiber, graphite silicone coated, and sewn with Teflon thread. The bags are 5.5 in. in diam in 124 and 137 in. lengths, and also 11 in. in diam, 30 ft 5 in. long.

Filter bag life varies greatly depending on several factors, such as gas-to-cloth ratio (or how heavily the cloth is loaded), the grade of black being produced, and the type of cloth used. Typical bag life is about 12 months. During this period the bag is on stream continuously, except during the cleaning cycle, which ranges from 15 to 40 sec every 15 min average. The cleaning is accomplished either by mechanical shaking, sonic cleaning or reverse flow cleaning and shaking. On-stream time for most filters will approach or exceed 95% of a year.

The filter is not shut down for inspection. When a bag fails it will tint the filter's effluent; in other words bag leakage is detected by a dirty stack. This leakage is then traced to a specific compartment or group of bags which are then isolated—sometimes kept out of service and sometimes replaced immediately. The entire filter is not usually shut down for cloth replacement. The compartments may be rebagged without interrupting the operation of the rest of the filter. However in some cases, it may be necessary to cut back on plant output; the production being reduced by turning off the oil to one furnace.

Primary bag filters take care of reactor off-gas with the entrained black; sec-

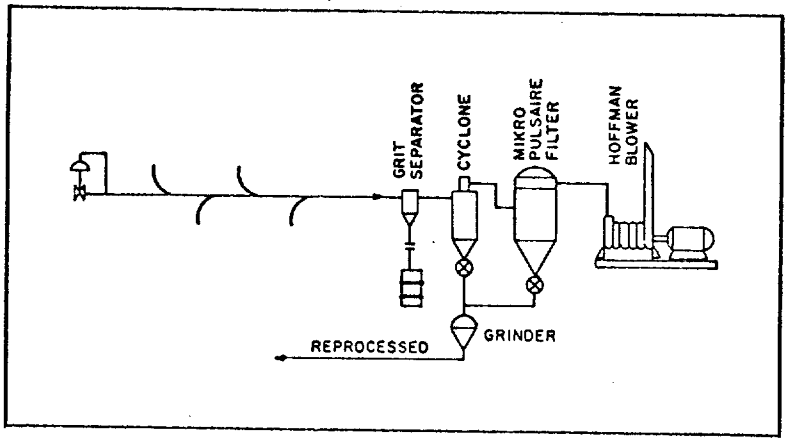

Fig. 11. Vacuum cleanup system in modern furnace black plant.

ondary bag filters handle the returns from the pneumatic system. Primary bag filters have from 6 to 18 compartments each, about 9 ft by 11 ft by 15 ft high, and are capable of handling from 5000 to 6000 cfm gas at approximately 400°F. Secondary bag filters normally have fewer compartments and handle much smaller volumes of gas (*ca.* 900 to 1000 cfm per compartment).

In carbon black manufacture, bag filters are eliminating the need of electrostatic precipitators, scrubber units, and even cyclone separators. A bag filter is a high maintenance item. However, its collection efficiency, when compared to that of the precipitator *in carbon black manufacture,* induces producers to use cyclones and filters; an agglomerating device and filters; precipitators, cyclones and filters (as in the case of older plants) or precipitators, cyclones, and wet scrubbers - *but not* precipitators and/or cyclones alone.

Operations within a Carbon Black Plant which Give Rise to Air Pollution

Loose carbon black, being fluffy and very light, readily dusts on handling and dissipates in the atmosphere. In the production, collection, and handling, every effort is made at the plant to contain the black and prevent any loss in the interest of ecomony as well as in the interest of avoiding pollution. The efforts pay off in efficiency of plant operations, worker morale, community relations, and adherance to applicable laws. The following operations, when they are not properly controlled, are sources where stray black tends to originate and pollute the atmosphere. The listing of these sources does not indicate approval of the pollution but rather serves as a check list for improving operating methods in these areas.

Spillages of the fluffy black before pelleting is the greatest source of pollution.

When pellets cease to form in the dry pelleting process the drum has to be emptied and reloaded with fresh loose black, be reseeded, and pelleting resumed. The emptying of the drum will naturally result in black spillage.

The cleaning of clogged screens, located either at the top of the storage tank into which the finished black is screened or at the pelleting section where oversized pellets are screened out, also causes black to be discharged in the atmosphere.

Whenever samples of black are drawn from the production line, or at the mixers in the pelletizing section, or at the driers, or at the packers some spillage of black invariably occurs and some of it dusts into the atmosphere.

Whenever a production line is plugged the remedial measures are either to pound the line or use a vibrator. If this proves ineffective high-pressure air is used to dislodge the black and perforce into the atmosphere.

Carbon black is so finely divided that whenever a leak develops in plant equipment, such as in the conveyor system, or in the bins, or at the bagging equipment, black will seep out and dust into the atmosphere.

Equipment in plants, particularly those located in the Gulf Coast area, tend to corrode more rapidly due to the salty air and corrosive effect of wet black. Leaks in the conveying system, caused by atmospheric corrosion, can cause the black to escape and dust in the atmosphere.

The erosive character of black causes conveying equipment to wear out more rapidly and sometimes leads to the formation of holes through which the black dissipates to the atmosphere.

Black will also seep from portions of the conveying equipment which may not be completely dust tight due to defective seals or worn sprockets in the screw conveyor, or from defective buckets in the elevator and dust in the air.

The atmosphere is polluted by black spilled from open or torn bags, from bags that have inadvertently been chafed and broken during stacking in the warehouse, or from spilled black during loading or unloading in box cars or trucks.

Some loss of black to the atmosphere occasionally occurs in the hand pulling (packing) of bag black or the bulk loading of hopper cars. However, where vacuum packing of bags is used the packing system is hermetically sealed; there is no waste of black and consequently no pollution. Some black escapes into the air when, in the loading of hopper cars, the flexible loading pipe is shifted from one compartment to another even though the valve in the pipe may shut off the flow of the black. There is also dusting of black in loading a sealdbin at the time when the loading pipe is inserted in the top of the sealdbin.

The cleaning of equipment in process of being repaired will release black to the atmosphere. This is minimized by use of portable vacuum devices to clean the equipment immediately after opening for repair.

Fire in bag black may burn away the paper and the black will spill and dust in the atmosphere; in the event of a fire in a bag filter the rotary valve at the base has to be opened and the burning, as well as the contaminated black, must be removed. Air pollution will result.

Wastage of black occurs during the cleaning and sweeping of the bottom of hopper cars.

Less than 100% efficiency of a collecting system will result in the venting of black with the off-gases into the atmosphere.

Winds will help to accelerate the dissipation of loose black into the atmosphere, especially where plants are located in the open spaces.

Heavy oils and fences are not normally used to contain or hide spills. Dust stabilizers, such as heavy oil, have limited effect mainly because loose black from re-occurring spills blows more readily on the previously oil hardened surface. There are instances where location of a plant in a heavily wooded area has helped to prevent the spread of black spillage from maintenance operations.

In channel black plants, methods have not been developed to recover the black from the vent gases due to the extremely high flue product volume. Attempts to handle the smoke to effect 100% separation of the black upsets the draft in the burner houses and steadiness of the flames; as a result, the yields decrease and quality of the black is altered.

It should be noted that, where little has been done to alleviate sootfall at channel black plants other than to shut them down, considerable success has been achieved in cleaning up conditions at oil furnace black plants. Carbon black producers have long been anxious to eradicate their image as air polluters and they have constantly been installing necessary measures to halt such pollution.

Key design features include proofing all black handling equipment for sift tight operation, a plant-wide vacuum system (Fig. 11) to pick up all spills and, cleaning hopper cars and scaldbins. When an occasional spill does occur every effort should be made to pick up the black. Stray black picked up by the vacuum is disposed of by complete combustion to CO_2 or by reprocessing. Black handling equipment should be under slight negative pressure to retain the black in case of ruptures and the collecting system should be under a small positive pressure to keep air from entering and forming a combustible mixture with the furnace gas stream. Automatic controls of temperatures, feed rates, and off-gas rates have stopped mishaps that frequently occur during startup or shutdown of a reactor. Proper controls and operation can permit a furnace black plant to operate in well populated and even residential areas.

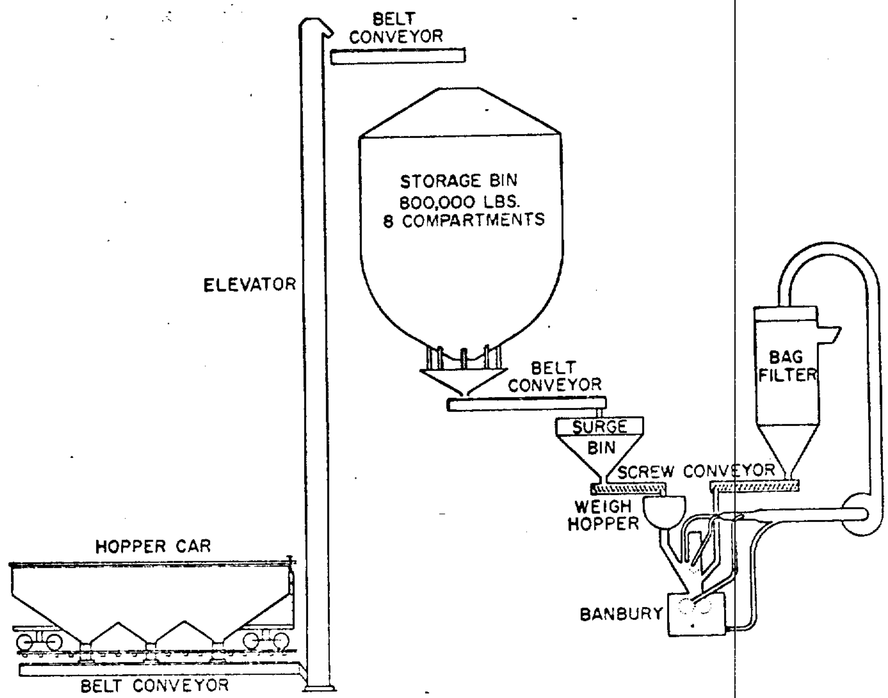

Fig. 12. Flow diagram of handling of carbon black in a tire factory.

Consumers' Handling of Carbon Black

In view of the sooty character of carbon black and its dusting tendency, consumer handling systems must also be carefully designed. Shown in Fig. 12 is a flow diagram of the handling of black in a tire plant from the unloading of hopper cars to the trapping of the dust created during the mixing of the black in the Banbury mixer. In detail, the black flows out of the hopper car into an enclosed pit and from there it is conveyed by means of a bucket elevator to the plant roof where it is transferred to a conveyor belt leading to a storage tank and from there it is transferred to a surge bin and weigh hopper feeding the Banbury. Dust is drawn from the mouth of the Banbury (at the door) and from the top of the Banbury (on each side of the ram) as well as from dust glands (each side) and from the cavity below the Banbury gate and is blown into the inlet Plenum of an Air Filter. (Blower delivers 10,000 cu ft/min at 10 in. static pressure.) The dust enters Orlon bag filters and most of the black precipitates to the conical hopper at the lower end of each bag. The very fine dust, which is held against the inside of each bag filter by the velocity of the air, is dislodged by jets of air from a secondary source. The black in the bottom of the hopper is returned to the Banbury by means of screw conveyor.

Shown in Fig. 13 is a flow diagram of the handling of black at a synthetic rubber plant at Baytown, Texas. This plant uses over 40 million pounds black a year in the preparation of black-rubber masterbatches. Styrene-butadiene rubber is masterbatched in the latex state with carbon black and the resultant mixture is coagulated; the rubber formed is dried and baled.[33] In detail, the black is received in hopper cars and in scaldbins. The black is discharged into an underground screw conveyor system, thence on to a belt that leads to a bucket elevator, and to a surge hopper. The whole system is completely enclosed and there is no loss of black. Dust seals are provided at each end of each elevator shaft. A slight negative pressure is maintained throughout the dry-black handling system. From there the pelleted black is fed to a mikropulverizer and ground at the rate of 8000 lb an hour, as it has to be in fine loose fluffy form in order to facilitate its dispersion. The pulverized black pours into a premix tank where the black is mixed with water and caustic to produce a

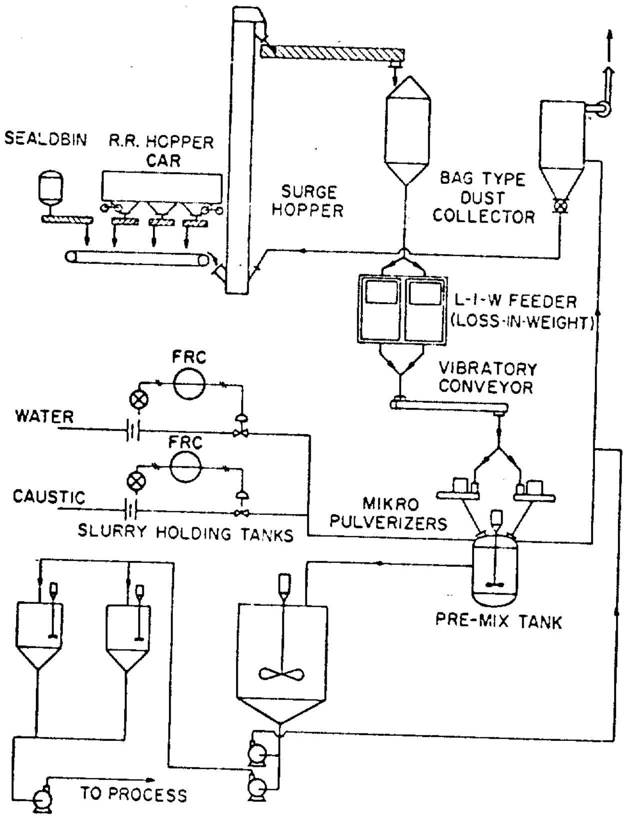

Fig. 13. Flow diagram of handling of carbon black in the preparation of carbon black slurry at United Carbon Co.'s synthetic rubber plant, Baytown, Texas.

7% slurry. (The caustic induces better wetting.) The wetted black is moved from the premix tank into separate tanks for improved blending and adjustment of flow. A bag type dust collector is placed in the system to handle whatever dust is generated at the mikropulverizers. The slurry is subsequently added to the latex, the mixture is coagulated, dried, and baled.

Acknowledgment

Grateful appreciation is expressed to the following collaborators without whose help this paper could not have been prepared for publication: R. A. Anderson, R. J. Barrus, H. S. Bowen, J. R. Boyle, Dr. P. M. Colling, F. T. Drape, M. J. Graham, James A. Guthrie, E. W. Howard, J. E. Kile, A. V. Krone, Hugh Langsford, C.M. McKay, R. H. Reynolds, Dr. N. L. Smith, M. A. Watring, W. E. Way, D. Whittle, P. Wilhelm, and D. C. Williams.

The author is also grateful to the Management of United Carbon Co. for permission to offer this paper for publication.

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