CARBON BLACK

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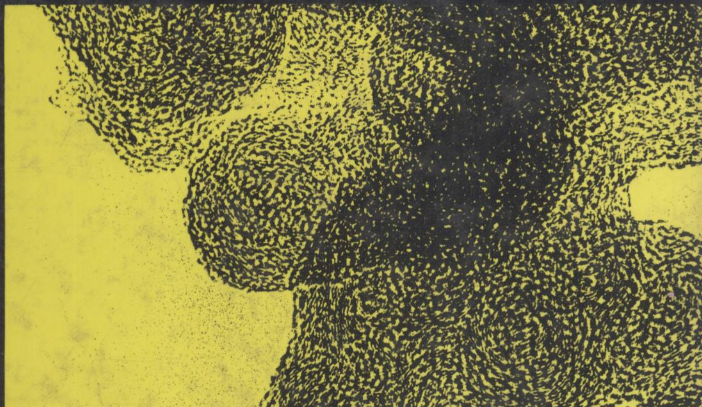

Physics, Chemistry, and Elastomer Reinforcement

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and Elastomer Reinforcement

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Carbon Black

Dedicated to all to whom black is beautiful

PREFACE

Carbon black is a truly remarkable material. Its manufacture is so simple that it was known and used as a colorant in antiquity. In recent years it was found to be a raw material of prime importance in the manufacture of rubber tires, without which automotive and air transportation as we know it would not be possible.

The chemistry and physics of this material formerly thought to be "inert" is far from being a dull subject. It has fascinated not only those engaged in the technology and application of carbon black, but it has also inspired a great many purely fundamental investigations in scientific laboratories of universities and research institutes all over the world.

It is, therefore, hardly surprising that the literature on carbon black and its application is extensive. It is found in rubber, paint, and printing ink trade journals, in general scientific and technical journals, and in periodicals covering such specialized subjects as colloid chemistry, rheology, polymer physics, etc., as well.

The objective of this book is to bring together, in one volume, the most important of the many widely-scattered contributions to the physics and chemistry of carbon black and its manufacture with a special view to its elastomer reinforcing characteristics. Obviously, this book is far from a complete review of the subject. It is, in many ways, a critical review in which we have not hesitated to accentuate investigations which are, in our view, important contributions. Moreover, being human and having spent the better part of a lifetime in carbon black research, we did not neglect to present our own investigations and our own views.

A number of scientists of our institute, specialists in their chosen fields, have made important contributions to this volume. We

gratefully acknowledge the substantial aid given to us by the following: Dr. J. Lahaye, in chapter 2, Dr. A. Sevenster, in chapter 3, Dr. P. Ehrburger, in chapters 3 and 4, Dr. J. Schultz, in chapter 4, and Dr. E. Papirer, in chapter 5.

Finally, we want to acknowledge the advice we received from several scientists, particularly Drs. E. M. Dannenberg and A.I. Medalia, Cabot Corporation, and we gratefully thank our many colleagues who provided us with original drawings and photomicrographs, especially Mr. P. A. Marsh, J. M. Huber Corporation.

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Chapter 1

MANUFACTURE OF CARBON BLACK

1.1. DEFINITIONS

Carbon black is formed by incomplete combustion of many organic substances: solid, liquid, or gaseous. Its production is so simple that it was known in antiquity. The Chinese and Hindus used carbon black as a colorant in inks in the third century A.D.

The generic term "carbon black" now refers to a group of industrial products consisting of furnace blacks, channel blacks, thermal blacks, and lamp blacks. They are materials composed essentially of elemental carbon in the form of near-spherical particles of colloidal sizes, coalesced mainly into particle aggregates obtained by partial combustion or thermal decomposition of hydrocarbons.

Furnace blacks are made in a furnace by partial combustion of hydrocarbons. Channel blacks are manufactured by impingement of natural gas flames on channel irons. Thermal blacks are produced by thermal decomposition of natural gas, while acetylene black, a special type of thermal black, is made by exothermic decomposition of acetylene. Lampblack is made by burning hydrocarbons in open, shallow pans.

1.2. THE FURNACE PROCESS

The furnace process is commercially by far the most important process. The older gas furnace process, introduced in 1922 by the General Atlas Company, U.S.A. [1], is used for the production of blacks of larger particle sizes, of diameters above about 50 nm (nanometer, 10^{-9} m). Manufacture of smaller particle size furnace blacks is carried out in the oil furnace process, which was developed in 1942 by J. C. Krejci [2] and which permits the production of most furnace blacks.

In the gas furnace process [3] a diffusion flame is created by burning part of the gas with added air. The rest of the gas is thermally decomposed in the flame, forming the desired carbon black. The gas used is natural gas, consisting predominantly of methane. The quality and yield of the product are determined by the temperature of the flames, 1260 to 1420°C (2300 to 2600°F) regulated by the ratio of gas and air, usually about 1:5, and by conditions of turbulence of the gas mixture. The firebrick-lined, insulated furnaces are either rectangular, usually of dimensions of the order of 1.20 x 3.00 m diameter and 4.30 m length (4 ft x 10 ft x 14 ft) or cylindrical, frequently with a diameter of 1.50 m (5 ft) and a length of 9.80 m (32 ft). Each furnace contains generally six burners through which the air-gas mixture is passed into the flame. Figure 1.1 shows a schematic representation of the gas furnace process [4].

Separation of the black from the flue gases and pelletization of the black is identical to methods used in the oil furnace process, as described later. Yields are of the order of 25 to 40% for the larger particle size blacks, such as SRF (semireinforcing furnace)(8 to 12 lb/1000 ft^3 or 120 to 190 g/m^3 of gas) and may drop to 20% for FF (fine furnace) types of black. In the oil furnace process [4-8]

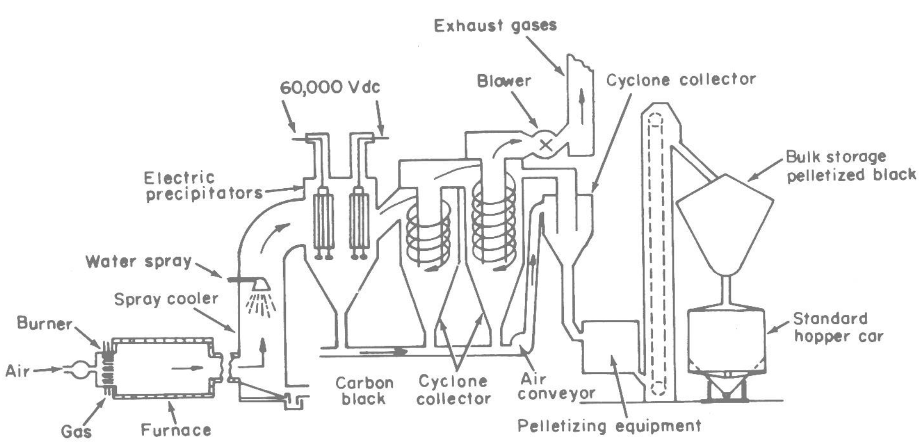

FIG. 1.1. Gas furnace process, flow diagram.

liquid fuel is injected into the flame to produce carbon black. The flame itself is generally produced from natural gas, but occasionally from liquid fuels. The process is operated in units consisting of a burner section, a furnace section, a quench section, and a collection system. Horizontal as well as vertical furnaces are in use, either rectangular or cylindrical, lined with firebrick and insulated. A schematic representation of the oil furnace process is given in Figure 1.2, while an aerial view of a carbon black plant with gas and oil furnace units is given in Figure 1.3.

An often-used horizontal cylindrical furnace has an inner diameter of about 1 m (3 ft 4 in.) and a length of about 10 m (33 ft). It is lined with a special mullite containing 90 to 99% alumina, backed with a high-temperature castible refractory and insulated. Fuel is admitted into the burner section, together with air and, frequently, steam. The temperatures reached in the flame are 1200 to 1600°C (2200 to 2990°F), dependent on the type of carbon black manufactured. The finer particle size blacks require a higher flame temperature, achieved by means of a higher combustion ratio. The hydrocarbon feedstock, generally preheated to about 250°C (480°F) is injected into the flame zone, causing decomposition and carbon black formation. The feedstock is atomized by introduction under pressure through specially designed nozzles. The turbulence required in the process is obtained by the furnace design selected, frequently involving tangential injection.

The carbon black formed in the flame zone is passed through the furnace section at a high, precalculated velocity, resulting in a residence time of the order of milliseconds. The hot carbon stream is quenched with a spray of water at a carefully determined distance from the flame, dependent on the type of black produced. Quenching reduces the temperature to about 650°C (1200°F).

Usually six furnaces are joined to a single collection system. The carbon stream is generally first passed through an electrostatic precipitator, of the Cottrell type, at 60,000 V dc. Thereafter, it is passed through primary, secondary and often tertiary cyclone collectors. The remaining black is retained in bag filters made from silicone-treated glass fiber fabric. It is pulverized thereafter in a micropulverizer, to remove grit. Magnetic grit is taken out by means of magnetic separators.

Occasionally a mixed oil-gas system is used in which the feedstock is partly natural gas, partly oil.

Low-structure blacks, characterized by a low degree of agglomeration of carbon particles into persistent (primary) aggregates, are advantageously produced by introducing trace quantities of alkali metals, preferably potassium derivatives, into the flame zone [9-10]. This may be done in the form of aqueous salt solutions injected directly into the furnace or by the use of an oil-soluble alkali metal compound, such as alkali salts of 2-ethyl hexanoic acid [11] or by other methods [12-13]. Quantities as little as 5 to 25 ppm (parts per million) of potassium, calculated as metal per unit of weight of carbon black may be used to reduce the particle structure significantly. Smaller quantities of alkali metals, usually at concentrations below 5 ppm and, more frequently, at 0.5 to 1.5 ppm, are used to maintain quality control of the black produced [9]. In the processes currently used there are certain more or less inexactly controllable factors, which tend to make quality control a major problem. As an example, the readily available economical hydrocarbon feedstock used, a byproduct of petroleum refining, consists of many different types of hydrocarbons, varying widely in quantities and in structures, not only from one source to the next but even from the same source. The additions of precisely measured trace quantities of alkali metal are an important aid in overcoming the influence of feedstock variations on carbon black manufacture.

High-structure blacks, characterized by a high degree of particle aggregation into persistent, fused (primary) aggregates are advantageously produced by controlling the turbulence of the combustible mixture in the furnace to a desired pattern. For instance, feedstock may be atomized in a relatively quiet, heated precombustion chamber and thereafter rapidly passed into the combustion zone, resulting in an increased structure [14]. Equally, by injecting the atomized feedstock tangentially into a precombustion chamber, a spiral path is followed by the gases. Upon passing the gas stream into the reaction chamber, centrifugal forces will cause the carbon particles formed to enrich along the walls, resulting in an increased degree of structure formation [15]. Other patterns of controlled turbulence may lead to a greatly increased coalescence of the black particles into persistent aggregates. Increased aromatic contents of the feedstock leads to increased structure of the blacks.

Other processes to increase the particle structure include the addition of free oxygen in the furnace [16], or of sulfur [17]. Another approach is by heat treatment of the black in the furnace immediately after formation at temperatures of 1310 to 1430°C (2400 to 2600°F), just prior to quenching [18]. A recent modification of the furnace process yields the so-called "new technology" blacks [18a] for which superior reinforcing properties for rubber have been claimed [18b]. A review of recent developments in high and low structure blacks was given by Powell [19].

The feedstock used in the oil must fulfill a number of requirements, such as:

1. High contents of aromatics
2. Low contents of asphaltenes
3. Low contents of free carbon
4. Low contents of sulfur
5. Low contents of alkaline metal compounds
6. Low contents of water
7. Low contents of sediments
8. Limited boiling range

The aromatic contents is the most important criterium, since it largely controls the all-important yield. A typical number used to characterize a feedstock is the Bureau of Mines Correlation Index (BMCI) [20] defined as follows:

$$\mathrm{BMCI} = 100\left(\frac{876}{\mathrm{BP}_{50} + 460°\mathrm{F}} + \frac{670}{131.5 + °\mathrm{API}} - 4.568\right)$$

where

BP_{50} = 50% boiling point at 760 mm in °F

$°API = 141.5/D^{60}_{60} - 131.5$

D^{60}_{60} = specific gravity at 60°F

The BMCI, empirically derived, is a function of the specific gravity and the boiling range of the feedstock. It emphasizes the importance of the aromatic contents, which is directly related to the density of the feedstock. It also indicates the importance of the boiling point, since a good feedstock should be completely vaporized in a fraction of a second at prevailing conditions in the furnace. As a result, oils distilling above 180°C (350°F) and below 350°C (660°F) are desirable. For practical purposes, oils with a BMCI number above 120 are preferred as feedstock.

Chemically speaking, highly aromatic hydrocarbons of molecular weights up to 500 fulfill the requirements. Particularly, polynuclear aromatics are very useful, while short side chains with many double bonds enhance the quality of feedstock. Long paraffinic side-chains are not desirable.

Asphaltenes, the toluene-soluble, hexane-insoluble fractions are relatively nonvolatile and carbonize easily to form highly undesirable gritty material. Maximum quantities tolerated are 5 to 8%, although occasionally feedstocks with a somewhat higher asphaltene content are used. Ash and sulfur accumulate in the black and must be avoided. Alkaline metals reduce the structure in an uncontrolled manner, while water and sediment impede normal processing and transport of feedstock to the furnace. A review of properties of feedstock for carbon black manufacture was given by Beede and Stokes [20] and recently by Powell [19]. An example of a commercial feedstock specification is given in Table 1.1.

While feedstocks have generally been derived from refinery cracking operations [2], the major part of feedstock used at present is obtained from the bottoms of petroleum fractions cracked under high severity conditions. Petroleum extracts are also used, such as