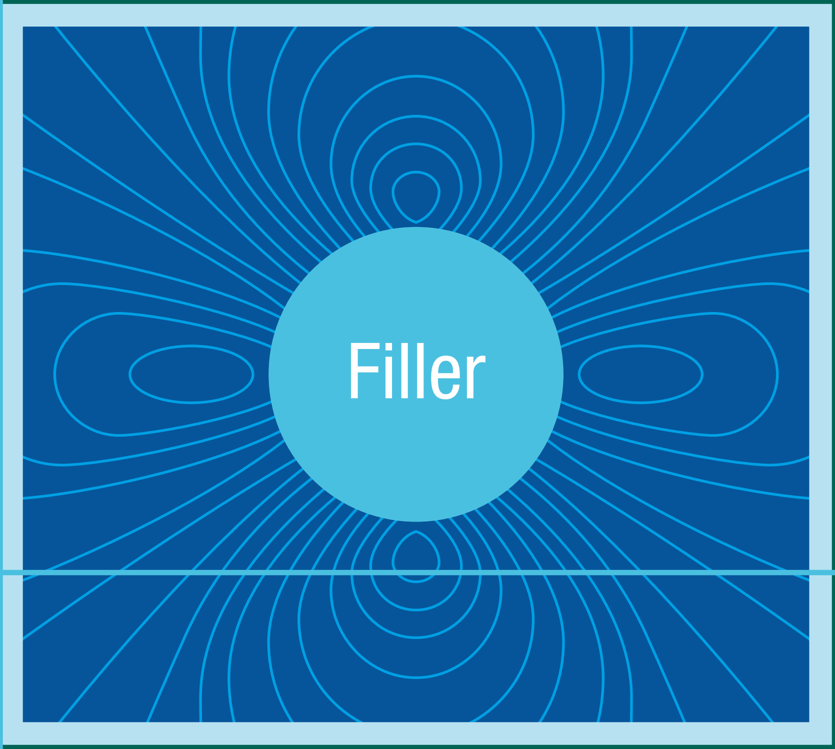
Meng-Jiao Wang
Michael Morris

Rubber Reinforcement with Particulate Fillers



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Preface

Soon after rubber's discovery as a remarkable material in the 18th century, the application of particulate fillers − alongside vulcanization − became the most important factor in the manufacture of rubber products, with the consumption of these particulate fillers second only to rubber itself. Fillers have held this important position not only as a cost savings measure by increasing volume, but more importantly, due to their unique ability to enhance the physical properties of rubber, a well-documented phenomenon termed "reinforcement." In fact, the term filler is misleading because for a large portion of rubber products, tires in particular, the cost of filler per unit volume is even higher than that of the polymer. This is especially true for the reinforcement of elastomers by extremely fine fillers such as carbon black and silica. This subject has been comprehensively reviewed in the monographs "Reinforcement of Elastomers," edited by G. Kraus (1964), "Carbon Black: Physics, Chemistry, and Elastomer Reinforcement," written by J.-B. Donnet and A. Voet (1975), and "Carbon Black: Science and Technology," edited by J.-B. Donnet, R. C. Bansal, and M.-J. Wang (1993). There has since been much progress in the fundamental understanding of rubber reinforcement, the application of conventional fillers, and the development of new products to improve the performance of rubber products.

While all agree that fillers as one of the main components of a filled-rubber composite have the most important bearing on improving the performance of rubber products, many new ideas, theories, practices, phenomena, and observations have been presented about how and especially why they alter the processability of filled compounds and the mechanical properties of filled vulcanizates.

This suggests that the real world of filled rubber is so complex and sophisticated that multiple mechanisms must be involved. It is possible to explain the effect of all fillers on rubber properties ultimately in similar and relatively nonspecific terms, i.e., the phenomena related to all filler parameters should follow general rules or principles. It is the authors' belief that, regarding the impact of filler on all aspects of rubber reinforcement, filler properties, such as microstructure, morphology, and surface characteristics, play a dominant role in determining the properties of filled rubbers, hence the performance of rubber products, via their effects in rubber. These effects, which include hydrodynamic, interfacial, occlusion, and agglomeration of fillers, determine the structure of this book.

The first part of the book is dedicated to the basic properties of fillers and their characterization, followed by a chapter dealing with the effect of fillers in rubber. Based on these two parts, the processing of the filled compounds and the properties of the filled vulcanizates are discussed in detail. The last few chapters cover some special applications of fillers in tires, the new development of filler-related materials for tire applications, and application of fumed silica in silicone rubber. All chapters emphasize an internal logic and consistency, giving a full picture about rubber reinforcement by particulate fillers. As such, this work is intended for those working academically and industrially in the areas of rubber and filler.

We would like to express our heartfelt thanks to Wang's colleagues at the EVE Rubber Institute Mr. Weijie Jia, Mr. Fujin He, Dr. Bin Wang, Dr. Wenrong Zhao, Dr. Hao Zhang, Dr. Mingxiu Xie, Dr. Yudian Song, Dr. Feng Liu, Dr. Liang Zhong, Dr. Bing Yao, Dr. Dan Zhang, Dr. Kai Fu, and Mr. Shuai Lu for their assistance in preparing this book. Special thanks are due to the EVE Rubber Institute, Qingdao, China and Cabot Corporation, USA. Without their firm backing and continuous understanding, this effort could not have been accomplished.

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About the Authors

Meng-Jiao Wang began his career in rubber research in 1964 after graduating from Shandong University and joining the Beijing Research and Design Institute of the Rubber Industry, China, where his last position was a professor and chief engineer. In 1982, he moved to France to work at the CNRS in Mulhouse as an associate researcher. He was awarded a doctoral degree (Docteur d'Etat es Sciences) in 1984. He then spent a year and half as a visiting scientist working at the University of Akron. From 1988 to 1989 he worked at the German Institute for Rubber Technology (DIK) as a visiting scientist and later he joined Degussa as a Senior Scientist. In 1993, Dr. Wang moved again to the United States to join Cabot, and soon became a scientific fellow of the company. From 2011 onwards, he has been the scientific fellow of National Engineering Research Center for Rubber and Tire and the director of the EVE Rubber Institute, China.

Over his 56-year career in rubber research, Meng-Jiao Wang has published over 140 scientific papers and 10 book chapters, and he has 55 different US and Chinese patents and 24 equivalent international patents to his name. He co-edited the book "Carbon Black: Science and Technology" and co-authored 6 other books. He was previously a member of the Editorial Board of the journal *Rubber Chemistry and Technology* (USA).

Michael Morris is currently a Principal Scientist at Cabot Corporation in Massachusetts, USA. He was awarded a Ph.D. from the University of Southampton, UK, in 1985 and began his career in rubber research at the Malaysian Rubber Producers Research Association (MRPRA; now TARRC) the same year. In 1987, he was seconded to the Rubber Research Institute of Malaysia in Kuala Lumpur to work on various aspects of natural rubber research. After four years, in 1991, he returned to the MRPRA and continued research, mainly on NR latex. In 1996, Dr. Morris moved to the USA to join the R&D organization of Cabot Corporation. His research and applications development were initially focused on fumed silica, as part of the Cab-O-Sil division. Since 2005, he has been part of the rubber reinforcement group at Cabot, focused on carbon black reinforcement of rubber.

During his career, Michael Morris has published 18 journal papers, 2 book chapters, and 14 conference presentations. In addition, he is an inventor on 12 granted US patents and numerous other international patents.

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1

Manufacture of Fillers

The history of particulate fillers used in rubber is almost as long as that of rubber itself[1−3]. One aspect of filler addition has been improvement of rubber properties. Another aspect was extension of the rubber with less expensive materials. After Hancock developed the earliest device using rollers to crumb natural rubber (NR) in 1820, and the two-roll mill for NR mastication and compounding was patented by Chaffee in 1836 and 1841, incorporation of inert fillers in finely divided particulate form became standard practice. Fillers such as ground limestone, barites, clay, kaolin, etc. were used in order to extend and cheapen the compounds since it was found that in natural rubber, quite a bit of filler could be added without detracting too much from the final vulcanizate properties. Zinc oxide was originally used for its whiteness, and later was found to have some reinforcing effect, becoming known as an “active” filler. Carbon black, which was known as a black pigment, was also found to be able to improve the rubber properties significantly at low concentrations, especially the stiffness. Systematic studies of the effect of fillers had been reported by Heinzerling and Pahl in Germany in 1891. Part of this effect may be due to its activating effect on many vulcanization accelerators for which zinc oxide is still utilized. In 1904, Mote in England, discovered the reinforcing effect of carbon black. He reported that the tensile strength of the filled NR increased drastically, compared with the values obtained with the techniques of that time. Although automobiles had been around and running on rubber tires for more than a decade, the importance of this discovery was recognized and developed when black tires were demonstrated to have better wear resistance than white ones, which contained mainly zinc oxide as a filler. Carbon black is now the most important filler used in rubber. In the last century, the production techniques and designation of types of carbon black have developed rapidly.

In the meantime, non-black fillers have also developed. Among these non-black ones, the first reinforcing filler, calcium silicate, was introduced in 1939. It was prepared by wet precipitation from sodium silicate solution with calcium chloride. In further development of the process, the calcium was leached out by hydrochloric acid to yield a reinforcing silica pigment of comparable particle size. About 10 years later, direct precipitation of silica from sodium silicate solution had developed to a commercial process and this is still a major process today. In 1950, a different type of anhydrous silica appeared, which was made by reacting silicon tetrachloride or silica chloroform (trichlorosilane) with water vapor in a hydrogen-oxygen flame. Because of the high temperature at the formation (about 1400°C), this pyrogenic silica has a lower concentration of silanol groups on the surface than the precipitated silicas. The latter contain about 88%−92% SiO_2 and have ignition losses of 10%−14%, whereas pyrogenic silica contains 99.8% silica. Because of its lower surface concentration of silanols, ultra-high purity with total impurities in many cases below 100 ppm (parts per million), and much higher price, pyrogenic silica is mainly used as a filler for high cost compounds such as silicone rubber.

In contrast, since the beginning of the industrial-scale production of fine-particle silicas and silicates in 1948, precipitated silica manufacturers have always desired to find their products used in tires as well. Whereas silicas were rapidly able to replace up to 100 percent of carbon black in shoe sole materials and also made their way into the mechanical goods sector, mostly as blends with carbon blacks, their use in tires in any quantities worth mentioning has long been limited to two types of compounds: off-the-road tread compounds containing 10 phr to 15 phr of silica blended with carbon black in order to improve tear properties, and textile and steel cord bonding compounds containing 15 phr of silica, again blended with carbon black, in combination with resorcinol/formaldehyde systems[4].

During the two oil crises in the 1970s, which had led to a steep rise in the price of carbon black, the question arose whether silica in tires could be an alternative to carbon black. When the price of oil fell and the fear of a lack of availability of carbon blacks subsided, this question was soon forgotten, especially since the price of silica was always higher than that of carbon black, at least in Japan and the USA. Experience has shown that silicas only have a chance to be used in tires if they offer technological advantages which are superior to those of carbon blacks.

Two developments have created a new opportunity for silicas to be used in tires: the increased awareness of the pollution from industry and the necessity of protecting the environment have given rise to a call for tires combining a long service life with driving safety and low fuel consumption. The introduction of bifunctional organosilanes as coupling agents now permits the reinforcing mechanism of silicas to be controlled by chemical means[4,5]. Based on systematic studies of surface characteristics, polymer-filler interactions, and better understanding of compounding and processing, silica was successfully used to replace carbon black as the principal filler in the tread compound of the “green tire” patented in 1992[6]. Since then, the application of precipitated silica in tire has been continuously growing, not only in tread compounds, but also in other parts of tires.

In the last two decades, research on rubber reinforcement with particulate fillers and the development of new fillers have been very hot. Since the main fillers used in the rubber industry are still carbon blacks and silicas, the topics of this book will focus on these two materials and their derivatives.

1.1 Manufacture of Carbon Black

The history of carbon black manufacture is very long, such as in China, about 3000 B.C., carbon black for pigment use was made by burning vegetable oils in small lamps and collecting the carbon on a ceramic lid; in Egypt, carbon black was used as a pigment for paints and lacquers. Starting in 1870, natural gas began to be used as the feedstock for carbon black manufacture. Over a couple of decades, the channel process was developed in which small gas flames burning in restricted air supply impinged on iron channels. In 1976, the last channel black plant was closed in the USA, due to the pollution of smoke plumes.

A critical event in the development of the carbon black industry was the discovery of the benefits of carbon black as a reinforcing agent for rubber in 1904[1]. As the automobile became ubiquitous during the 1920s, the application of pneumatic tires grew rapidly and soon by-passed other applications, causing rapid growth in consumption of carbon black. Also in the 1920s, two other processes concerning carbon black production were introduced, both using natural gas as feedstock, but having better yields and lower emissions than the channel process. One was the thermal black process, in which a brick checker is employed and works alternately by absorbing heat from a natural gas air flame, and then giving up heat to crack natural gas to carbon and hydrogen. The other process was the gas furnace process, which is no longer practiced.

The oil furnace process was first introduced by Phillips Petroleum at its plant in Borger, Texas, in 1943. This process rapidly replaced all others for the production of carbon black for use in rubber. In a modern version of the oil furnace process, carbon black yields range from 65% downward depending on the surface area of the product. Product recovery is essentially 100% as a result of high efficiency bag filters. The overwhelming majority of carbon black reactors today are based on the oil furnace process.

1.1.1 Mechanisms of Carbon Black Formation

The formation of particulate carbon involves either pyrolysis or incomplete combustion of hydrocarbon materials. Enormous literature has been published to describe the mechanism of carbon black formation, from a series of lectures by Michael Faraday at the Royal Institution in London in the 1840s[2], to a more recent intensive review[7]. Since Faraday's time, many theories have been proposed to account for carbon formation, but controversy still exists regarding the mechanism.

Mechanisms of carbon black formation must account for the experimental observations of the unique morphology and microstructure of carbon black. These include the presence of nodules, or particles, multiple growth centers within some nodules, the fusion of nodules into large aggregates, and the paracrystalline or concentric layer plane structure of the aggregates. It is generally accepted that the mechanism of formation involves a series of stages as follows:

Formation of gaseous carbon black precursors at high temperature – This involves dehydrogenation of primary hydrocarbon molecular species to atomic carbon or primary free radical and ions which condense to semi-solid carbon precursors (or poly-nuclear-aromatic sheet) and/or formation of large hydrocarbon molecules by polymerization which then is dehydrogenated to particle precursors[3]. Taking production of furnace black with high aromatic feedstock as an example, Figure 1.1 represents several of the possible paths that feedstock can take as it is mixed with the primary fire in the reactor at the early stage. The primary fire has excess oxygen, carbon dioxide, and water, all of which act as combustion (or oxidation) reactants to the feedstock molecules. These molecules can react with and break up any feedstock molecules into small combustion species; any feedstock that goes this route is lost for carbon black production. As there is a limit to oxidative species, the remaining feedstock can either be broken down by pyrolysis or survive and become directly involved in carbon black formation reactions. Typical pyrolysis species are hydrogen, acetylene, and polyynes, which are essentially chained acetylenes. At least two formation paths are thought to occur. The first one is ring growth from acetylene, polyyne,or polycyclic aromatic hydrocarbon (PAH) collision with PAH molecules. When the number of rings reaches five or six, the molecules become thermally stable and will only be attacked by remaining oxidant molecules. These PAH molecules will

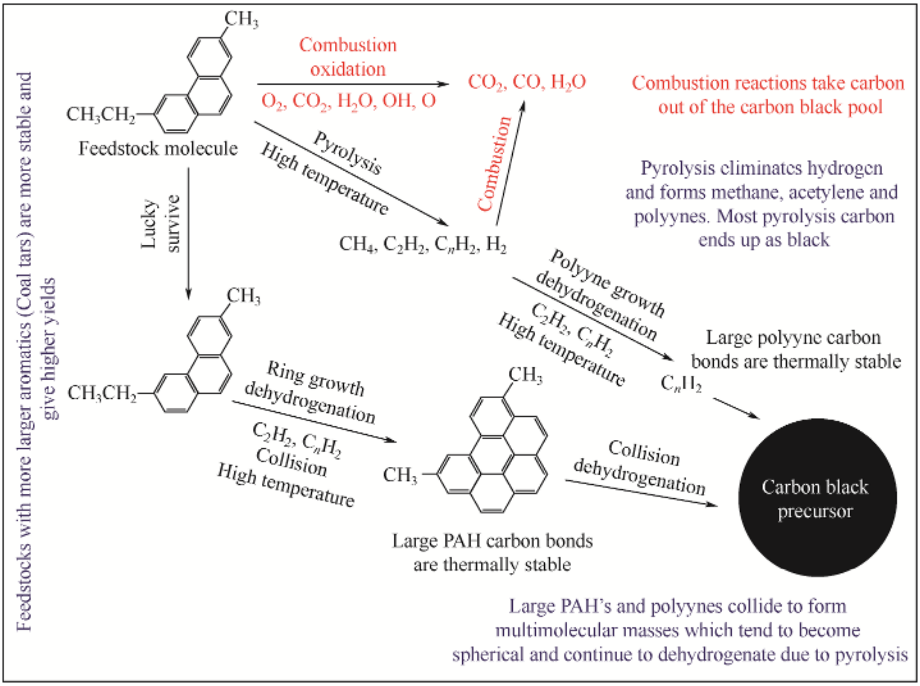

Figure 1.1 Formation of gaseous carbon black precursors

eventually stack up after collisions and then begin to form the crystallites which are found in the finished primary particles. The other route to carbon black occurs as the acetylene polymerizes (polyacetylene) to form long chain polyynes which also reach a thermally stable size and begin to collide with the large PAH molecules. These polyynes can then restructure themselves to increase the crystallite size or provide the amorphous portion of the carbon black particles. Once these particles grow to about one to two nanometers they tend to become spherical and are referred to as carbon black precursors.

Nucleation – Because of increasing mass of the carbon particle precursors through collision, the larger fragments are no longer stable and condense out of the vapor phase to form nuclei or growth centers.

Particle growth and aggregation – In this period, three processes go on simultaneously as shown in Figure 1.2: condensation of more carbon precursors on the existing nuclei, coalescence of small particles into larger ones, and formation of new nuclei. Coalescence and growth seem to predominate. The products of this stage are “proto-nodules”.

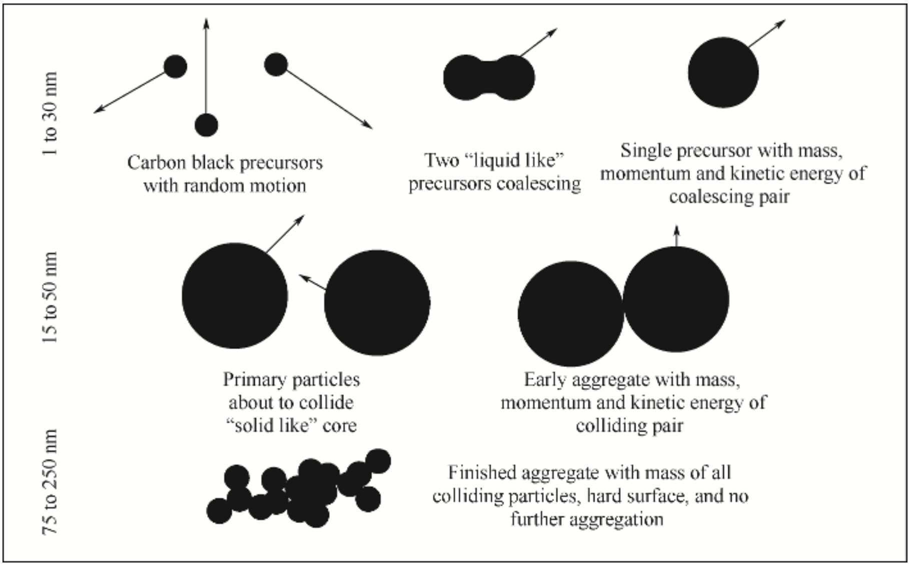

Figure 1.2 Particle growth and aggregation

Surface growth – Surface growth includes the processes in which the small species attach to or deposit on the surfaces of existing particles or aggregates, forming the nodules and aggregates with their characteristic onion micro-structure (note: aggregates are permanent structures cemented by carbon). The surface growth represents about 90% of total carbon yield. It is responsible for the stability of the aggregates because of the continuous carbon network formation. Aggregates are formed and cemented in this stage.

Agglomeration – Once no more carbon is forming and aggregation ceases, aggregates collide and adhere by van der Waals forces but there is no material to cement them together, hence they form temporary structures (agglomerates).

Aggregate gasification – After its formation and growth, the carbon black surface undergoes reaction with the gas phase, resulting in an etched surface. Species such as CO_2, H_2O, and of course any residual oxygen attack the carbon surface. The oxidation is determined by gas phase conditions, such as temperature, oxidant concentration, and flow rates.

Practically, the carbon black morphology and surface chemistry can be well-controlled by changing the reaction parameters. For furnace carbon blacks, the reaction temperature is the key variable that governs the surface area. The higher the temperature, the higher is the pyrolysis rate and the more nuclei are formed, resulting in an earlier stop of the growth of the particles and aggregates due to the limitation of starting materials. Therefore, with higher reaction temperature, achieved by adjusting air rate, fuel rate, and feedstock rate, the surface area of carbon black can be increased. Addition of alkali metal salts into the reactor can modify the aggregation process, influencing carbon black structure. At the reactor temperature, the salts of alkali metals, such as potassium, are ionized. The positive ions adsorb on the forming carbon black nodules and provide some electrostatic barrier to internodule collisions, resulting in lower structure[8].

The time scale of carbon black formation varies substantially across the range of particle sizes found in commercial furnace blacks. For blacks with surface areas around 120 m^2/g, the carbon black formation process from oil atomization to quench takes less than 10 milliseconds. For blacks with surface areas around 30 m^2/g, formation times are a few tenths of a second.

1.1.2 Manufacturing Process of Carbon Black

1.1.2.1 Oil-Furnace Process

The oil-furnace process accounts for over 95 percent of all carbon black produced in the world. It was developed in 1943 and rapidly displaced previous gas-based technologies because of its higher yields and the broader range of blacks that could be produced. It also provides highly effective capture of particulates and has greatly improved the environment around carbon black plants. As indicated in the mechanism discussion, it is based on the partial combustion of residual aromatic oils. Because residual oils are ubiquitous and are easily transported, the process can be practiced with little geographic limitation. This has allowed construction of carbon black plants all over the world. Plants are typically located in areas of tire and rubber goods manufacture. Because carbon black is of relatively low density, it is far less expensive to transport feedstock oil than to transport the black.

For nearly 80 years since its invention, the oil-furnace process has undergone several cycles of improvement. These improvements have resulted in increased yields, larger process trains, better energy economy, and enhanced product performance. A simplified flow diagram of a modern furnace black production line is shown in Figure 1.3[9]. This is intended to be a generic diagram and contains elements from several operators' processes. The principal pieces of equipment are the air blower, process air and oil preheaters, reactors, quench tower, bag filter, pelletizer, and rotary dryer. The basic process consists of atomizing the preheated oil in a combustion gas stream formed by burning fuel in preheated air. The atomization is carried out in a region of intense turbulent mixing. Some of the atomized feedstock is combusted with excess oxidant in the combustion gas. Temperatures in the region of carbon black formation range from 1400°C to over 1800°C. The details of reactor construction vary from manufacturer to manufacturer and are confidential to each manufacturer. Leaving the formation zone, the carbon black containing gases are quenched by spraying water into the stream. The partially cooled smoke is then passed through a heat exchanger where incoming air is preheated. Additional quench water is used to cool the smoke to a temperature consistent with the life of the bag material used in the bag filter. The bag filter separates the unagglomerated carbon black from the by-product tail gas which contains nitrogen, hydrogen, carbon monoxide, carbon dioxide, and water vapor. It is mainly nitrogen and water vapor. The tail gas is frequently used to fuel the dryers in the plant, to provide other process heat, or sometimes is burned to manufacture steam and electric power either for internal plant use or for sale.

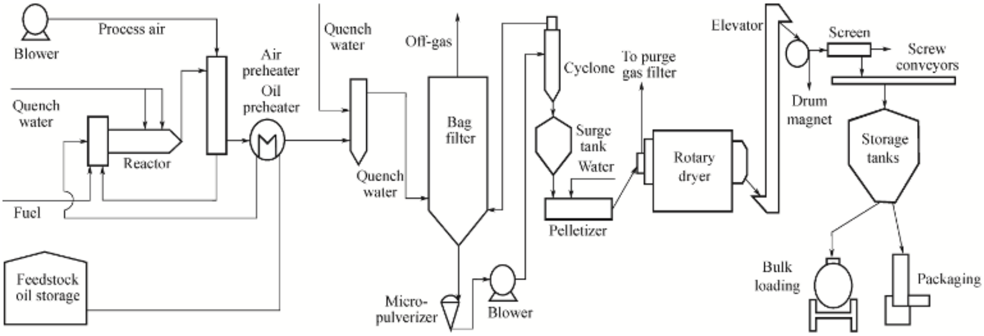

Figure 1.3 Flow diagram of a modern furnace black process

The fluffy black from the bag filter is mixed with water, typically in a pin mixer, to form wet granules. These are dried in a rotary dryer, and the dried product is conveyed to bulk storage tanks. For special purposes, dry pelletization in rotary drums is also practiced. Most carbon black is shipped by rail or in bulk trucks. Various semi-bulk containers are also used including IBC's and large semi-bulk bags. Some special purpose blacks are packed in paper or plastic bags.

While the reactor and its associated air-moving and heat-exchange equipment are where the properties of the black are determined, they tend to be dwarfed by the bag collectors, the dryers, and particularly the storage tanks.

Feedstocks

Feedstocks for the oil-furnace process are heavy fuel oils. Preferred oils have high aromaticity, are free of suspended solids, and have a minimum of asphaltenes. Suitable oils are catalytic cracker residue (once residual catalyst has been removed), ethylene cracker residues, and distilled heavy coal tar fractions. Other specifications of importance are freedom from solid materials, moderate to low sulfur, and low alkali metals. The ability to handle such oils in tanks, pumps, transfer lines, and spray nozzles is also a primary requirement.

Reactor

The heart of a furnace black plant is the furnace or reactor where carbon black formation takes place under high temperature, partial combustion conditions. The reactors are designed and constructed to be as trouble-free as possible over long periods of operation under extremely aggressive conditions. They are monitored constantly for signs of deterioration in order to ensure constant product quality. The wide variety of furnace black grades for rubber and pigment applications requires different reactor designs and sizes to cover the complete range, though closely related grades can be made in the same reactor by adjusting input variables. Reactors for higher surface area and reinforcing grades operate under high gas velocities, temperatures, and turbulence to ensure rapid mixing of reactant gases and feedstock. Lower surface area and less reinforcing grades are produced in larger reactors at lower temperatures, lower velocities, and longer residence time. Table 1.1 lists carbon formation temperatures, and residence times for the various grades of rubber blacks.

Table 1.1 Reactor conditions for various grades of carbon blacks

Black	Surface area/(m^2/g)	Temperature/°C	Residence time/s	Maximum velocity/(m/s)
N100 series	145	1800	0.008	
N200 series	120		0.010	180−400
N300 series	80	1550	0.031	
N500 series	42		1	30−80
N700 series	25	1400	1.5	0.5−1.5
N990 thermal	8	1200−1350	10	10

A key development in the carbon black reactor technology was the development of the zoned axial flow reactor for reinforcing blacks in the early 1960s[8]. The reactor consists of three zones. The first zone is a combustion zone in which fuel and air are completely burned to produce combustion gases with excess oxygen. This gas flow is accelerated to high velocity in a throat zone with intense turbulent mixing. The feedstock is injected either into this throat zone or just ahead; therefore, the reacting gases issue from the throat into a second cylindrical zone as a turbulent diffusion jet.

Depending on the desired black, the jet may be allowed to expand freely, or may be confined by bricking. Downstream of the reaction zone is a water quench zone. The throughput of a single reactor train varies from manufacturer to manufacturer and with grade of black. The largest reactors in operation have capacities of over 30,000 metric tons per year. Many producers operate smaller reactors in parallel. Reactors are typically designed to make a series of related blacks. Air and gas may be introduced to the primary combustion zone either axially, tangentially, or radially. The feedstock can be introduced into the primary fire either axially or radially in the high velocity section of the mixing zone. The high velocity section may be Venturi-shaped or consist of a narrow diameter choke. Plants may have from one to several operating trains.

Carbon black reactors are made of carbon steel shells lined with several courses of refractory. The most severe services are in the combustor and in the throat zone. Different manufacturers take different approaches to these elements, some using exotic materials or selected water cooled metal surfaces, others using conventional materials and limiting temperatures to what their materials can stand. Most manufacturers achieve refractory life of one to several years. For the rubber grade carbon blacks, at least three different reactor designs must be used to make this range of furnace blacks. Figure 1.4 and Figure 1.5 show the designs of commercial reactors found in patents.

The quality and yield of carbon black depend on the quality and carbon content of the feedstock, the reactor design, and the input variables. Surface area in particular is controlled by adjusting the temperature in the reaction zone. Structure is adjusted by introducing potassium into the combustion gas. This may be done in any of a variety of ways.

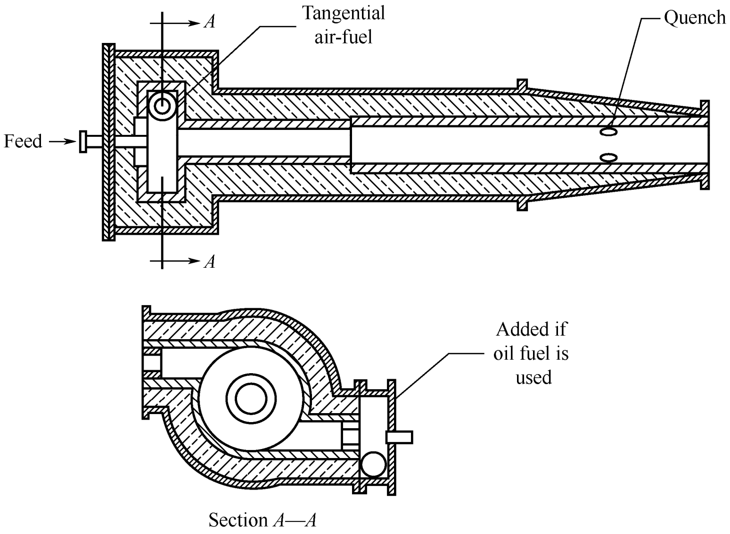

Figure 1.4 Reactor for N300−N200 carbon blacks[10]

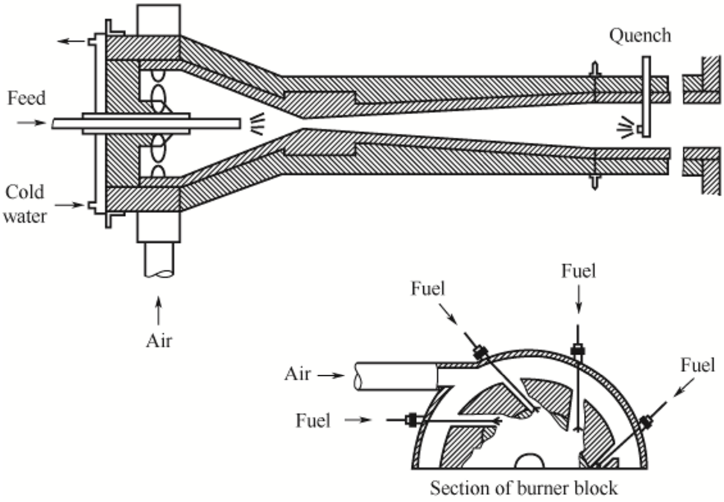

Figure 1.5 Reactor for tread blacks[11]

The energy utilization in the production of one kilogram of oil-furnace carbon black is in the range of $(9-16)\times10^7$ J, and the yields are 300–660 kg/m^3 depending on the grade. The energy inputs to the reactor are the heat of combustion of the preheated feedstock, heat of combustion of natural gas, and the thermal energy of the preheated air. The energy output consists of the heat of combustion of the carbon black product, the heat of combustion and the sensible heat of the tail gas, the heat loss from the water quench, the heat loss by radiation to atmosphere, and the heat transferred to preheat the primary combustion air.

1.1.2.2 The Thermal Black Process

Thermal black is a large particle size and low structure carbon black made by the thermal decomposition of natural gas, coke oven gas, or liquid hydrocarbons in the absence of air or flames. Its economic production requires inexpensive natural gas. Today it is among the most expensive of the blacks regularly used in rubber goods. It is used in rubber and plastics applications for its unique properties of low hardness, high extensibility, low compression set, low hysteresis, and excellent processability. Its main uses are in O-rings and seals, hose, tire inner liners, V-belts, other mechanical goods, and in cross-linked polyethylene for electrical cables.

The thermal black process dates from 1922. The process is cyclic using two refractory-lined cylindrical furnaces or generators about 4 m in diameter and 10 m high. During operation, one generator is being heated with a near stoichiometric ratio of air and off-gas from the making generator whereas the other generator, heated to an average temperature of 1300°C, is fed with natural gas. The cycle between black production and heating is five minutes alternating between generators, resulting in a reasonably continuous flow of product and off-gases to downstream equipment. The effluent gas from the make cycle, which is about 90% hydrogen, carries the black to a quench