CARBON BLACK

1. Introduction

Carbon black is a generic term for an important family of products used principally for the reinforcement of rubber, as a black pigment, and for its electrically conductive properties. It is a fluffy powder of extreme fineness and high surface area, composed essentially of elemental carbon. Carbon black is one of the most stable chemical products. In a general sense, it is the most widely used nano-material with its aggregate dimension ranging from tens to a few hundred nanometers (nm), and imparts special properties to composites of which it is a part. Plants for the manufacture of carbon black are strategically located worldwide in order to supply the rubber tire industry, which consumes 70% of carbon black production. About 20% is used for other rubber products and 10% is used for special nonrubber applications (1). World capacity in 2001 was estimated at >8 million metric tons (1). The U.S. capacity was ~2 million metric tons. Over 42 grades, listed in ASTM 1765-01 (2), are used by the rubber industry. Many additional grades are marketed in the nonrubber markets.

Carbon blacks differ from other forms of bulk carbon such as diamond, graphite, cokes, and charcoal in that they are composed of aggregates having complex configurations, quasigraphitic in structure, and are of colloidal dimensions. They differ from other bulk carbons in being formed from the vapor phase by homogeneous nucleation through the thermal decomposition and the partial combustion of hydrocarbons. Carbon black is the product of a technology incorporating state-of-the-art engineering and process controls. Its purity differentiates it from soots that are impure by-products from the combustion of coal and oils and from the use of diesel fuels. Carbon blacks are essentially free of the inorganic contaminants and extractable organic residues characteristic of most forms of soot.

A number of processes have been used to produce carbon black including the oil-furnace, impingement (channel), lampblack, the thermal decomposition of natural gas, and decomposition of acetylene (3). These processes produce different grades of carbon black and are referred to by the process by which they are made, eg, oil-furnace black, lampblack, thermal black, acetylene black, and channel black. A small amount of by-product carbon from the manufacture of synthesis gas from liquid hydrocarbons has found applications in electrically conductive compositions. The different grades from the various processes have certain unique characteristics, but it is now possible to produce reasonable approximations of most of these grades by the oil-furnace process. Since >95% of the total output of carbon black is produced by the oil-furnace process, this article emphasizes this process (1).

2. History of Manufacture

Carbon blacks' use as a pigment dates back to prehistoric times. Wall paintings from Paleolithic caves are the earliest known use. The Egyptians used carbon black to pigment paints and lacquers. In China, ~3000 BC, carbon black for pigment use was made by burning vegetable oils in small lamps and collecting the carbon on a ceramic lid.

Prior to 1870 the dominant carbon black manufacture was by the lampblack process where oil from animal or vegetable sources was burned in a shallow pan with a restricted air supply. Starting in 1870, natural gas began to be used as the feedstock for carbon black manufacture. The resulting blacks were much darker and better covering than lampblacks. Over a couple of decades, the channel process was developed in which small gas flames burning in restricted air supply impinged on iron channels. The black adhered to the cool channel surface and was recovered by scraping it from the channel. Carbon yields were poor—a few percent. In part this was from the inefficiency of methane as a feedstock, but it also reflects the very poor capture efficiency of the early channel black process. Reportedly, the smoke plumes from channel black plants could be seen for 50 miles. The last channel black plant in the United States was closed in 1976. Two plants remain in the former Soviet Union, and a related but much evolved process is still operated in Germany.

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 (4). As the automobile became ubiquitous during the decade of the 1920s, the application in pneumatic tires grew rapidly and soon by-passed other applications, causing rapid growth in consumption. During the 1920s, two other processes 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-work alternately absorbs heat from a natural gas air flame, and then gives up heat to crack natural gas to carbon and hydrogen. The other process was the gas furnace process that 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 this process fuel is burned with air in a primary combustion flame that contains excess air. A heavy, highly aromatic oil is then atomized in the hot gases leaving the primary combustion flame. A portion of the oil is burned by the excess oxygen providing the heat to maintain temperature and pyrolyze the remainder of the oil. In a modern version of the oil furnace process, carbon 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.

The wide adoption of radial tires during the decades of the 1970s and 1980s caused a major contraction in demand for blacks for tire use as the expected life of an automobile tire moved from 20,000 miles with bias ply tires to over 40,000 miles with radial tires. This brought about considerable consolidation in the carbon black industry, particularly in North America and Europe.

3. Properties and Characterization

The structure of carbon black is schematically shown in Figure 1. The primary dispersable unit of carbon black is referred as an “aggregate” that is a discrete, rigid colloidal entity. It is the functional unit in well-dispersed systems. The aggregate is composed of spheres that are fused together for most carbon blacks. These spheres are generally termed as primary “particles” or “nodules". These nodules are composed of many tiny graphite-like stacks. Within the nodule the stacks are oriented so that their c axis is normal to the sphere surface, at least near the nodule surface.

The carbon blacks are characterized by their chemical compositions, microstructure, morphologies, and the physical chemistry of the surface. Morphology is a set of properties related to the average magnitude and frequency distribution

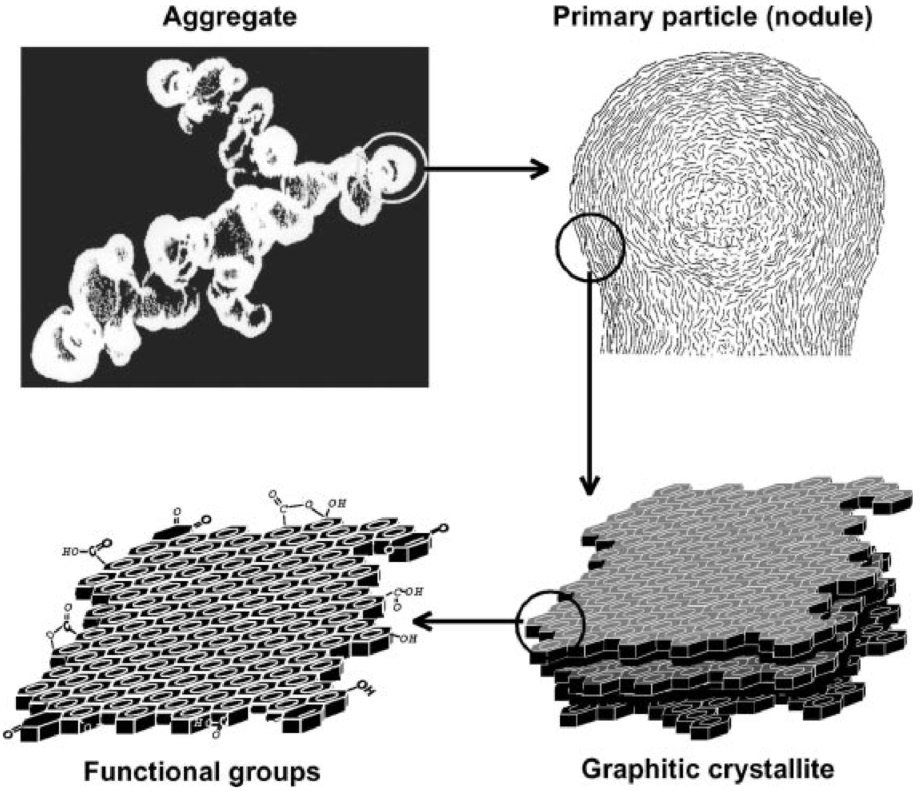

Fig. 1. Structure of carbon black.

of the nodule diameter, aggregate diameter, and the way nodules are connected in the aggregates.

3.1. Chemical Composition. Oil-furnace blacks used by the rubber industry contain >97% elemental carbon. Thermal and acetylene black consist of >99% carbon. The ultimate analysis of rubber-grade blacks is shown in Table 1. The elements other than carbon in furnace black are hydrogen, oxygen, sulfur, and nitrogen. In addition there are mineral oxides, salts and traces of adsorbed hydrocarbons. The hydrogen and sulfur are distributed on the surface and the interior of the aggregates. The oxygen content is located on the surface of the aggregates as C_xO_y complexes.

Since carbon blacks are produced from hydrocarbon materials, the dangling bonds at the edges of the basal planes of graphitic layers are saturated mostly by hydrogen. The graphitic layers are large polycyclic aromatic ring systems.

Oxygen-containing complexes are by far the most important surface groups. The oxygen content of carbon blacks varies from 0.2 to 1.5% in mass for furnace blacks to 3 to 4% for channel blacks. Some speciality blacks used for pigment purposes contain larger quantities of oxygen than normal furnace blacks. These blacks are made by oxidation in a separate process step using nitric acid, ozone, air, or other oxidizing agents. They may contain from 2 to 12% oxygen. The oxygen-containing groups influence the physicochemical properties, such

Table 1. **Chemical Composition of Carbon Blacks**

Type	Carbon, %	Hydrogen, %	Oxygen, %	Sulfur, %	Nitrogen, %	Ash, %	Volatile, %
furnace rubber-grade	97.3–99.3	0.20–0.80	0.20–1.50	0.20–1.20	0.05–0.30	0.10–1.00	0.60–1.50
medium thermal	99.4	0.30–0.50	0.00–0.12	0.00–0.25	NA[a]	0.20–0.38	
acetylene black	99.8	0.05–0.10	0.10–0.15	0.02–0.05	NA[a]	0.00	<0.40

[a] Not available = NA.

as chemical reactivities, wettability, catalytic, electrical properties, and adsorbability. Oxidation improves dispersion and flow characteristics in pigment vehicle systems such as lithographic inks, paints, and enamels. In rubber-grade blacks surface oxidation reduces pH and changes the kinetics of vulcanization, making the rubber compounds slower curing.

A convenient method for assessing the extent of surface oxidation is the measurement of volatile content. This standard method measures the weight loss of the evolved gases on heating up from 120 to 950°C in an inert atmosphere. The composition of these gases consists of three principal components: hydrogen, carbon monoxide, and carbon dioxide. The volatile content of normal furnace blacks is <1.5%, and the volatile content of oxidized special grades is 2–22%.

The origin of the volatile gases is the functional groups attached to carbon black, especially those on the surface. Surface oxides bound to the edges of the of carbon layers are phenols, hydroquinones, quinones, neutral groups with one oxygen, carboxylic acids, lactones, and neutral groups containing two oxygens (5,6). Figure 2 shows an idealized graphite surface layer plane with the various functional groups located at the periphery of the plane. Carbon blacks with few oxygen groups show basic surface properties and anion exchange behavior (7,8).

In addition to combined hydrogen and oxygen, carbon blacks may contain as much as 1.2% combined sulfur resulting from the sulfur content of the aromatic feedstock that contains thiophenes, mercaptans, and sulfides. The majority of the sulfur is not potentially reactive as it is inaccessibly bound in the interior of carbon black particle and does not contribute to sulfur cross-linking during the vulcanization of rubber compounds.

The nitrogen in carbon blacks is the residue of nitrogen heterocycles in the feedstocks. Thus carbon blacks derived from coal tars have far more nitrogen than petroleum derived blacks.

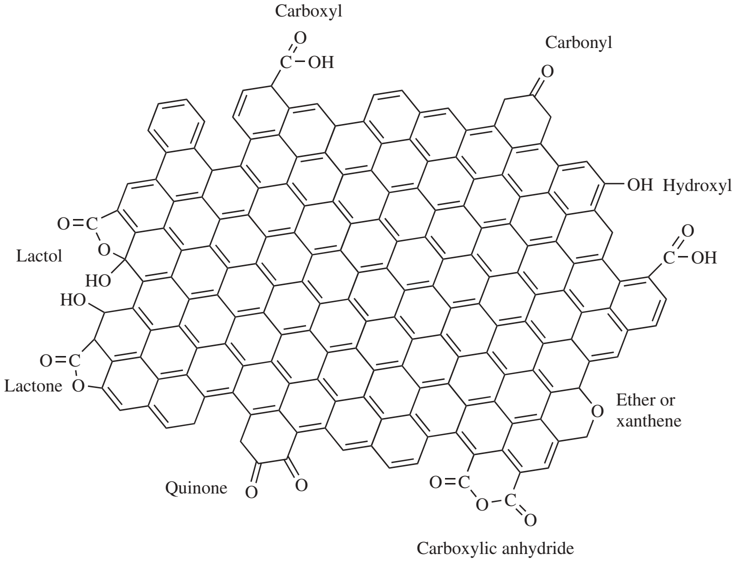

Fig. 2. Aromatic layer plane with functional groups.

The ash content of furnace blacks is normally a few tenths of a percent but in some products may be as high as one percent. The chief source of ash is the water used to quench the hot black from the reactors during manufacture and for wet pelletizing the black.

3.2. Microstructure: Molecular and Crystallite Structure. The arrangement of carbon atoms in carbon black has been well established by X-ray diffraction methods (9,10). The diffraction patterns show diffuse rings at the same positions as diffraction rings from pure graphite. The suggested relation to graphite is further emphasized as carbon black is heated to 3000°C. The diffuse reflections sharpen, but the pattern never approaches that of true graphite. Carbon black has a degenerated graphitic crystalline structure as defined above. Whereas graphite has three-dimensional order, as seen in the model structures of Figure 3, carbon black has two-dimensional order. The X-ray data indicate that carbon black consists of well-developed graphite platelets stacked roughly parallel to one another but random in orientation with respect to adjacent layers. As shown in Figure 3, the carbon atoms in the graphitic structure of carbon black form large sheets of condensed aromatic ring systems with an interatomic spacing of 0.142 nm within the sheet identical to that found in graphite. However, the interplanar distances are quite different. While graphite interplanar distance is 0.335 nm, which results in a relative density of 2.26, the interplanar distance of carbon black is larger, in the range of 0.350–0.365 nm, as a consequence of the random planar orientations or so-called turbostratic arrangement. The relative density of commercial carbon blacks are 1.76–1.90 depending on the grade. About one-half of the decrement in density is attributed to stacking height, L_c in the crystallites. X-ray diffraction data provide estimates of crystallite size. For a typical carbon black, the average crystallite diameter, L_a, is ~1.7 nm and average L_c is 1.5 nm, which corresponds to an average of four layer planes per crystallite containing ~375 carbon atoms.

It was originally suggested that these discrete crystallites were in random orientation within the particle. This view was later abandoned when electron microscopy of graphitized and oxidized carbon blacks indicated more of a

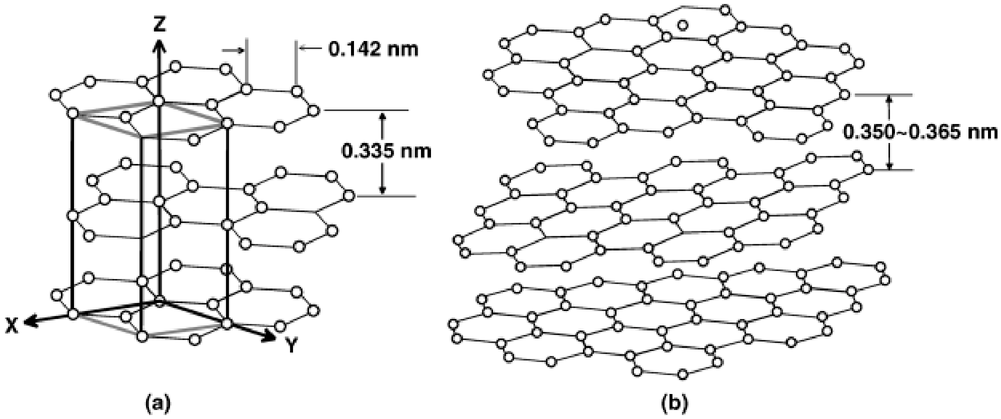

Fig. 3. Atomic structural models of (**a**) graphite, and (**b**) carbon black.

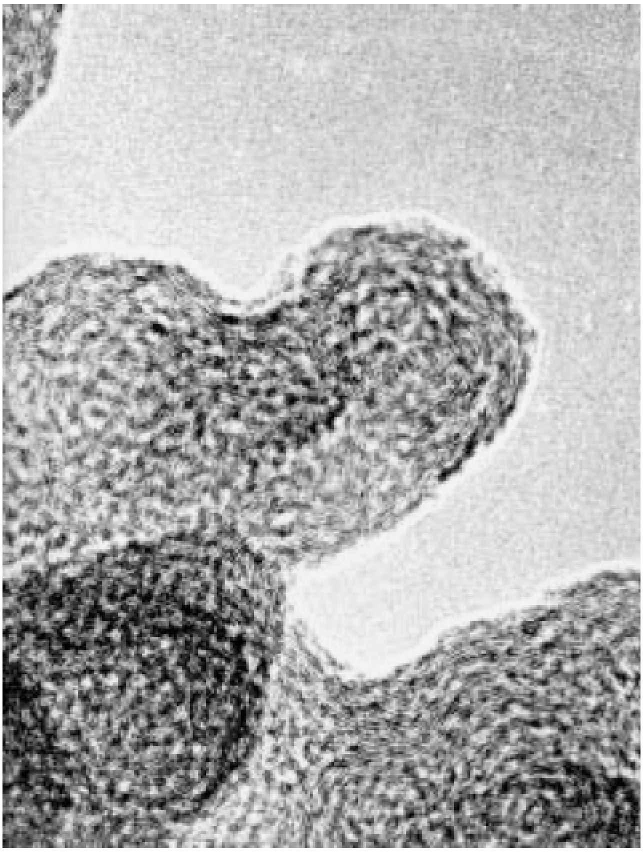

Fig. 4. High resolution (3,000,000 ×) electron micrograph of N220-grade carbon black. Courtesy of W. M. Hess.

concentric layer plane arrangement that can be described by a paracrystalline model. This structure has been confirmed by the use of high resolution phase-contrast electron microscopy that made possible the direct imaging of graphitic layer planes in carbon black (11). Figure 4 shows a phase-contrast electron micrograph of carbon black at high resolution that displays the marked concentric arrangement of the layer planes at the surface and around what appear to be growth centers.

More recently, the microstructure of the carbon black surface has been investigated by means of scanning tunneling microscopy (STM) (12,13). Figure 5 shows the STM images obtained in the current mode for graphite, graphitized carbon black and normal carbon black N234. Compared to graphite, the structure of carbon blacks graphitized for 24 h at a temperature of 2700°C in an inert atmosphere still remains in a certain inperfect state, shown by different tunneling current partterns in the organized domains. The surface structure of carbon black can be classified in two types: organized domains and unorganised domains. The organized domains occupy the majority of the carbon black surface, and its size generally decrease with decreasing particle size.

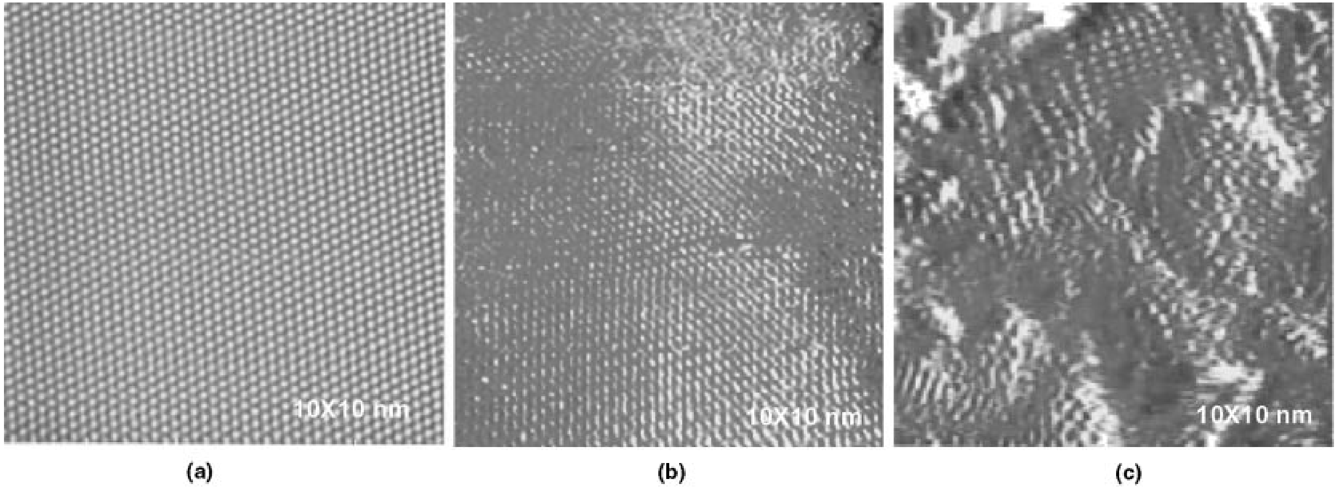

Fig. 5. STM images of (**a**) graphite, (**b**) graphitized carbon black, and (**c**) carbon black N234.

3.3. Morphology. Morphologically, carbon blacks differ in primary "particle" or nodule size, surface area, aggregate size, aggregate shape, and in the distribution of each of these.

Primary "Particle" (Nodule) Size. Although the smallest discrete entity of carbon black is the aggregate, the "particle" size, and its distribution is one of the most important morphological parameters with regard to its end-use applications, even though the particles do not exist as discrete entities except for thermal black. The "particle" size is of critical importance to the specific surface of the carbon blacks and has been taken as the principal parameter for grade classification of rubber blacks in ASTM. In almost all types of carbon black, the primary particles within a single aggregate are similar. However, the types of blacks can differ in the uniformity of the primary particles of different aggregates. While many types do show a quite narrow range of primary particles, others are clearly quite broad mixtures of aggregates of differing primary particle size or specific surface area. The electron microscope is the universally accepted instrument for measuring particle size, aggregate size, and aggregate morphology. Typical electron micrographs of rubber-grade carbon blacks are shown in Figure 6.

"Particle" size measurement is based on the visual electron microscope counts for several thousand particles on electromicrographs of known magnification (ASTM D3849). Automated image analyzers provide measurements of a variety of particle parameters.

Surface area. The surface area is one of the most important features influencing the performance of carbon blacks. It is an extensity factor that determines the interfacial area between carbon black and the medium in which a given volume of black is dispersed.

The surface area can be calculated from particle size measured with transmission electron microscope (TEM) (ASTM D3849). Generally, for rubber grade, the surface areas determined by TEM are in reasonable agreement with surface areas determined by nitrogen adsorption measurements. However, for those carbon blacks that have highly developed micropores, such as special pigment blacks and blacks used for electrical conductivity, the surface areas calculated from their particle diameters are smaller than those calculated from gas absorption as the internal surface area in the micropore is excluded.

While the TEM images contain very detailed statistical information, such images are expensive and time consuming to obtain. Direct measurement of specific surface area is much faster and cheaper. Such measurements are most easily made by gas- and liquid-phase adsorption techniques that depend on the amount of adsorbate required to form a surface monolayer. If the area occupied by a single-adsorbate molecule is known, a simple calculation will yield the surface area.

A low temperature nitrogen adsorption method, based on the original method of Brunauer, and co-workers (BET) (14), has been adopted by ASTM as standard method D 6556. It is not sensitive to changes in the surface chemistry of carbon black such as those resulted from surface oxidation and presence of trace amount of tarry material. With a molecular diameter of <0.5 nm, nitrogen is small enough to enter the micropore space so that the surface measured by BET is the total area, inclusive of micropore. For some applications such as, eg, rubber reinforcement, the internal surface area in the micropore with <2-nm

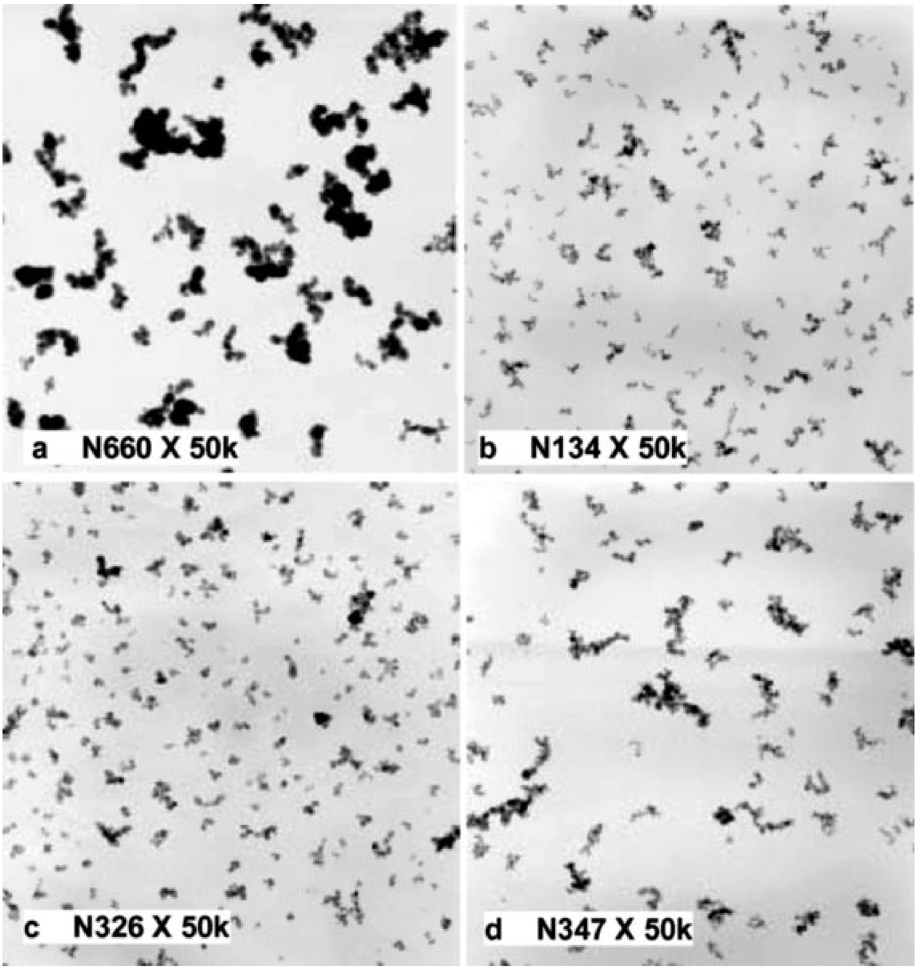

Fig. 6. Electron micrographs of rubber-grade carbon blacks.

diameter is inaccesible to large rubber molecules, thus it plays no part or has a negative effect on rubber reinforcement. The specific surface area that is accesible to rubber is defined as "external" surface area. This is conveniently measured by a multilayer nitrogen adsorption, also defined in ASTM 6556 and known as the statistical thickness surface area (STSA) (15).

Liquid-phase adsorption methods are also widely used. The adsorption of iodine from potassium iodide solution is the standard ASTM method D1510. The surface area is expressed as the iodine number whose units are milligrams of iodine adsorbed per gram of carbon blacks. The test conditions such as adsorbate concentration and the amount of carbon black sample used are specified in such a way that the values of iodine numbers turn out to be about the same as the values for surface areas in square meters per gram that are measured by nitrogen adsorption for nonporous and nonoxidized furnace carbon blacks. The iodine number is raised by porosity and decreased by surface oxygen or adsorbed organics. Still it is the most easily measured surface area estimate and is used extensively, especially for process control.

Another standard industry method for surface area measurement is based on the adsorption of cetyltrimethylammonium bromide (CTAB) from aqueous solution, which is ASTM method D3765 and has largely been replaced by STSA in the last decade.

Aggregate Morphology (Structure). The aggregate morphology is another important characteristic that influences performance. The term “structure” is widely used in the carbon black and rubber industries to describe the aggregate morphology. It was originally introduced in 1944 (16) to describe the ensemble of aggregates that is a stochastic distribution of the number and arrangement of the nodules that make up the aggregates.

Structure comparisons of grades with different surface areas cannot be made. It is now known that the properties associated with structure are associated principally with the bulkiness of individual aggregates. Aggregates of the same mass, surface area, and number of nodules have high structure in the open bulky and filamentous arrangement and a low structure in a more clustered compact arrangement. Therefore, the structure is now used to describe the relative void volume characteristics of grades of black of the same surface area. Structure is determined by aggregate size and shape, and their distribution. They are geometrical factors that affect aggregate packing and the volume of voids in the bulk material. Therefore, in composite systems, structure is also a principal feature that determine the performance of carbon black as a reinforcing agent and as a pigment (17). In liquid media, structure affects rheological properties such a viscosity and yield point. In rubber, viscosity, extrusion die swell, modulus, abrasion resistance, dynamic properties, and electrical conductivity are affected by structure.

The direct method for structure measurement of carbon black is TEM (ASTM D3849). This method is unique in furnishing information about the aggregate size, shape and the distribution of these. Typical electron micrographs of rubber-grade carbon blacks are shown in Figure 6. There is an enormous range in aggregate size. The size of the aggregates is generally related to the size of the particles. The shapes of the aggregates have infinite variety from tight grapelike clusters to open dendritic or branched arrangements to fibrous configurations.

A useful method for determining relative aggregate sizes and distributions is by centrifugal sedimentation. For a sphere, the diameter can be derived from the sedimentation rates in the gravitational field according to Stokes equation. For the nonspherical particles such as carbon black aggregates, an equivalent Stokes diameter, D_{st} can be obtained as the diameter of a sphere of carbon black having the same settling behavior. A convenient instrument for these measurements is the Joyce Loebl disk centrifuge photosedimentometer (DCP) (18). Large aggregates sediment at a faster rate than smaller ones. The sedimentation rate is also influenced by the bulkiness of the aggregates. At constant volume or mass, a bulky aggregate sediments more slowly than a compact aggregate because of frictional drag. The DCP curve is characteristic of the black structure but the measured diameters need to be viewed with suspicion.

Table 2 lists average D_{st} values and the weight mean diameter, D_{wm}, for the aggregates calculated from their estimated volumes measured by TEM. There is

Table 2. **Carbon Black Morphology**

ASTM designation	Particle size[a], D_{wm},[b] nm	Aggregate size[a], D_{wm},[b] nm	D_{st}[c], nm	Surface area[a], m^2/g
N110	27	93	76–111	143
N220	32	103	95–117	117
N234	31	109	74–97	120
N326	41	108	98	94
N330	46	146	116–145	80
N339	39	122	96–125	96
N351	50	159	127	75
N375	36	106	91	105
N550	93	240	220–242	41
N660	109	252	227–283	34
N774	124	265	261	30
N990	403	593	436	9

[a] Measured by TEM.

[b] D_{wm} = weight mean diameter = $\Sigma nd^4/\Sigma nd^3$.

[c] Stokes diameter by centrifugal sedimentation from various sources.

reasonable agreement between the two diameters. Aggregate size distributions from centrifugal sedimentation analysis are very useful for assessing the differences in this characteristic within a given grade or at constant surface area.

By far the most intensively investigated measure of structure is the maximum packing fraction. In fact, the amount of void at the maximum packing has almost become synonymous with carbon black “structure”. At least two approaches are widely used. The first determines the amount of liquid that is needed to just fill all the spaces between aggregates when the aggregates are pulled together by the surface tension forces of that liquid. This measurement is done by means of an absorptometer with dibutyl phthalate (DBP) as the liquid (ASTM D 2414). This is based on the change in torque during mixing of carbon black and the liquid as there is a sharp increase in viscosity of the mixture, when it changes from free flowing powder to a semiplastic continuous paste. The viscosity, hence the torque, will drop as the liquid is continually added, due to the lubrication effect. The volume of DBP needed for a unit mass of carbon blacks to reach a predetermined level of torque is termed the DBP number. In order to eliminate the effects of pelletizing conditions, the DBP absorption test has been modified to use a sample that has been pre-compressed at a pressure of 165 MPa (24,000 psi) and then broken up four successive times (24M4) (ASTM D 3493). This procedure causes some aggregate breakdown and is claimed to more closely approximate the actual breakdown that occurs during rubber mixing. The DBP numbers measured for compressed samples are also termed crush DBP (CDBP) number.

The maximum random packing for mono-sized spheres is a volume fraction of 68 percent, which is equivalent to a DBP number of 25 mL/100 g of carbon black.

The types of blacks with the lowest DBP number, and therefore highest packing, have values ~30–35 mL/100 g. The types with the highest structure, and therefore lowest packing, have DBP number of ~140 mL/100 g. Grades with significantly higher DBP number do not have solid primary particles and the fluid is absorbed both within the primary particles and between the aggregates.

The second way of estimating the maximum packing fraction is mechanical compression. Most commonly this is practiced in uniaxial compression. The test is termed the void volume measurement (ASTM D6086). With both liquid and mechanical compaction, the measured value can be influenced to some degree by either the speed of the compaction, ie, the time the aggregates have to rearrange, and the final pressure to which they are subjected.

Tinting strength, adopted by ASTM as D3265, is another industry method used for the classification of carbon blacks. In this test, a small amount of carbon black is mixed with zinc oxide and an oil vehicle to produce a black or gray paste. The reflectance of this paste is measured and compared to the reflectance of a paste made with a reference black. The ratio of the reference black paste reflectance to the sample black multiplied by 100 is the tint strength. It provides a rough estimate of the reinforcing potential of carbon black in rubber. Tint strength is closely related to carbon black morphology. The carbon blacks with smaller particle size, ie, larger surface area and smaller size of the aggregates, ie, lower structure show a greater ability to cover the typically larger size zinc oxide particles, giving higher tinting strength. The tinting strength is also related to the aggregate size distribution. The narrower the aggregate size distribution, the higher is the tinting strength.

3.4. Surface Activity. Surface activity is also an important factor in performance. This factor can, in a chemical sense, be related to different chemical groups on the carbon black surface. In a physical sense, variations in surface energy determine the adsorptive capacity of the carbon blacks and their energy of adsorption. However, compared with the morphologies, a satisfactory description of surface properties of carbon black is still lacking because only a limited number of tools have been available to assess the carbon black surface in terms of ensemble properties.

With regard to rubber reinforcement, the surface activity of carbon black has traditionally been measured by bound rubber. Bound rubber, sometimes termed “carbon gel”, is defined as the rubber portion in an uncured compound that cannot be extracted by a good solvent of the polymer due to the adsorption of the rubber molecules onto the filler surface. This phenomenon has been studied extensively and is recognized as a typical feature of carbon black surface activity. For given polymer systems and for the carbon black with comparable surface area, the higher the bound rubber content, the higher is the polymer-filler interaction, and hence the higher is the surface activity of carbon black. Generally speaking, bound rubber is a parameter that is simple to measure, but the factors that influence the test results are highly complicated. It has been recognized that carbon black–polymer interaction leading to the formation of bound rubber involves physical adsorption, chemisorption, and mechanical interaction.

It is generally found that the surface energy of carbon blacks have a much greater effect on the mechanical properties of filled elastomers than the chemical composition, particularly when general-purpose hydrocarbon rubbers are concerned. The surface energy, γ, is defined as the work, necessary to create a unit new surface of liquid or solid. This energy is caused by different types of cohesive forces, such as dispersive, dipole–dipole, induced dipole–dipole, and hydrogen-bond forces. In the case of all these cohesive forces being involved in independent ways, the surface energy can be expressed as the sum of several components, each corresponding to a type of molecular interaction (dispersive, polar, hydrogen bond, etc). Since the effect of the dispersive force is universal, the dispersive component of the surface free energy, γ^d, is particularly important. If a solid substance can have only dispersion interaction with its environment, its surface energy, γ_s, is identical with its dispersive component, $\gamma_s{}^d$. For most substances, the surface energy of a solid is the sum of $\gamma_s{}^d$ and $\gamma_s{}^{sp}$ that is the sum of the other components of surface energy and is termed "specific component" or "polar" component. The higher the $\gamma_s{}^d$ of the carbon black, the stronger is the interaction between carbon black and non- or less-polar polymers such as hydrocarbon rubbers. The higher polar component of the surface energy leads to higher interaction with polar polymer or polar groups in the polymer chains.

Several methods to measure the solid surface energy can be used for carbon black. However, inverse gas chromatography (IGC) has recently been shown to be one of the most sensitive and convenient methods for measuring carbon black surface energy (19). In IGC, the filler to be characterized is used as the stationary phase and the solute injected is called a probe. When the probe is operated at infinite dilution, the adsorption energy of the probe on the carbon black surface, and hence the surface energy of the black can be calculated from the net retention volume (19). If, however, the surface is energetically heterogeneous, the values of parameters obtained from IGC measurement are mean values over the whole surface of the fillers, but they are "energy-weighted", ie, the high energy sites play a very important role in the determination of adsorption parameters measured (20). When the probe is operated at finite concentration, the adsorption isotherms of the probes on carbon black surface can be generated from the pressure dependence of the retention volume and, hence, the distribution of free energy of adsorption of the probe chemicals can be derived from the isotherm (20).

3.5. Other Methods for Carbon Black Characterization. There are many other test methods used to characterize carbon blacks for quality control and specification purposes. Table 3 lists some of these methods that, with a few exceptions, have been adopted by ASTM.

4. Classification

Carbon blacks have been classified by their production process, by their production feedstocks such as acetylene blacks, by their application field, such as rubber blacks, color blacks, electric conductive blacks, and by properties of end use products such as high abrasion furnace black (HAF) and fast extrusion furnace black (FEF). From their applications, the carbon black is classified into two groups: one used for rubber products, and another for non-rubber applications. They are referred as special blacks. Generally, special carbon blacks cover a wider range of morphology and surface chemistry than rubber blacks.

Table 3. **Special Analytical Test Methods for Carbon Black**

Test method	Standard	Comment
iodine adsorption, mg/g	ASTM D1510	amount of iodine adsorbed from aqueous solution as a measure for the specific surface area; not applicable for oxidized or highly porous carbon blacks
N_2 surface area, and external surface area, m^2/g	ASTM D6556	determination of the total surface area (NSA) by B.E.T. theory of multilayer gas adsorption behavior using multipoint determinations and the external surface area based on the statistical thickness surface area (STSA) method
CTAB surface are, m^2/g	ASTM D3765	amount of cetytrimethylammonium bromide adsorbed from aqueous solution as measure of specific nonporous (outer) surface area
aggregate dimension and aggregate size distribution	ASTM D3849	determination of aggregate dimensions (unit length, width, etc) by electron microscope image analysis
aggregate size distribution		diameters of equivalent solid spheres that sediment at same rate as aggregates during centrifuging
DBP absorption, mL/100 g	ASTM D2414	determination of the void volume with dibutyl phthalate in a special kneader as measure of structure
24 M4-DBP absorption, mL/100 g	ASTM D3493	determination of DBP absorption after four repeated compressions at 165 MPa (24,000 psi)
compressed volume index	ASTM D6086	determination of compressed volume of carbon black under a specified compression force.
jetness		light absorption of a carbon black paste in linseed oil; determination by visual comparison against standard blacks or by measuring the absolute light emission
tint strength, %	ASTM D3265	ability of a carbon black to darken a white pigment in an oil paste. The tinting strength is the reflectance of the tested carbon black paste with respect to the reflectance of the reference carbon black paste.
volatiles, %		weight loss when calcined at 950°C for 7 min
heating loss (moisture), %	ASTM D1509	weight loss on drying at 125°C for 1 h
pH	ASTM D1512	pH of an aqueous slurry of carbon black; pH is mainly influenced by surface oxides
extractables, %	ASTM D1618	amount of material that can be extracted by a boiling solvent, usually toluene
extractables, %	ASTM D4527	determination of the total material extracted from carbon black by toluene under specified conditions. The procedure is also applicable to other solvents

Table 3 (*Continued*)

Test method	Standard	Comment
ash content, %	ASTM D1506	amount of noncombustible material after burning the carbon black at 675°C
sulfur content, %	ASTM D1619	
sieve residue, %	ASTM D1514	amount of coarse impurities that cannot be purged through a testing sieve by water
pour density, g/L	ASTM D1513	measure for the densification of carbon black
tamped density, g/L		similar to bulk density; however, void volume is reduced by temping
pellet crush strength	ASTM D5230	automated individual pellet crush strength
pellet crush strength	ASTM D3313	individual pellet crush strength
pellet mass strength	ASTM D1937	pellet mass strength
pellet size distribution	ASTM D1511	determination by means of sieve shaker
fines content, %	ASTM D1508	only for pelletized blacks; percentage passing through a sieve of 125 μm (mesh) width

The rubber industry is by far the major consumer of carbon black. For rubber grades, a classification system issued by ASTM is based essentially on particle size, structure and their effect on the cure rate of filled rubber compounds which is related to the degree of surface oxidation (ASTM D1765). It is composed of a letter followed by three numbers. The N series are for the normal-curing furnace and thermal blacks and S for "slow-curing" blacks with higher degree of oxidation, such as channel black and oxidized furnace blacks that are acidic in nature. The first number of three digit suffix identifies particle size and is inversely related to the surface area. The range of particle sizes from 0 to 500 nm has been grouped into 10 categories, covering surface areas from 0 to 150 m^2/g. The remaining two digits are assigned arbitrarily by the carbon black manufacturers. A selected list of typical properties, taken from ASTM D1765 of rubber-grade carbon blacks, is shown in Table 4. In addition to the assigned ASTM N-numbers, the list includes structure, surface areas, and tint data. The structure–surface area relationships of these grades, called the carbon black spectrum, is illustrated in Figure 7, which shows a diagram of DBP numbers for compressed samples versus the nitrogen surface areas.

5. 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 1860s (21), to a recent

Table 4. **Typical Properties of Rubber-Grade Carbon Blacks**

ASTM classification	Iodine No., mg/g	DBP No. mL/100 g	CDBP No[a], mL/100 g	NSA, m^2/g	STSA m^2/g	Tint strength,%
N110	145	113	97	127	115	123
N115	160	113	97	137	124	123
N120	122	114	99	126	113	129
N121	121	132	111	122	114	119
N125	117	104	89	122	121	125
N134	142	127	103	143	137	131
N135	151	135	117	141		119
S212		85	82	120	107	115
N220	121	114	98	119	106	116
N231	121	92	86	111	107	120
N234	120	125	102	119	112	123
N293	145	100	88	122	111	120
N299	108	124	104	104	97	113
N315		79	77	89	86	117
N326	82	72	68	78	76	111
N330	82	102	88	78	75	104
N335	92	110	94	85	85	110
N339	90	120	99	91	88	111
N343	92	130	104	96	92	112
N347	90	124	99	85	83	105
N351	68	120	95	71	70	100
N356	92	154	112	91	87	106
N358	84	150	108	80	78	98
N375	90	114	96	93	91	114
N539	43	111	81	39	38	
N550	43	121	85	40	39	67
N582	100	180	114	80		
N630	36	78	62	32	32	
N642	36	64	62	39		
N650	36	122	84	36	35	
N660	36	90	74	35	34	
N683	35	133	85	36	34	
N754	24	58	57	25	24	
N762	27	65	59	29	28	
N765	31	115	81	34	32	
N772	30	65	59	32	30	
N774	29	72	63	30	29	
N787	30	80	70	32	32	
N907		34		9	9	
N908		34		9	9	
N990		43	37	8	8	
N991		35	37	8	8	

[a] For compressed samples.

intensive review (22). 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

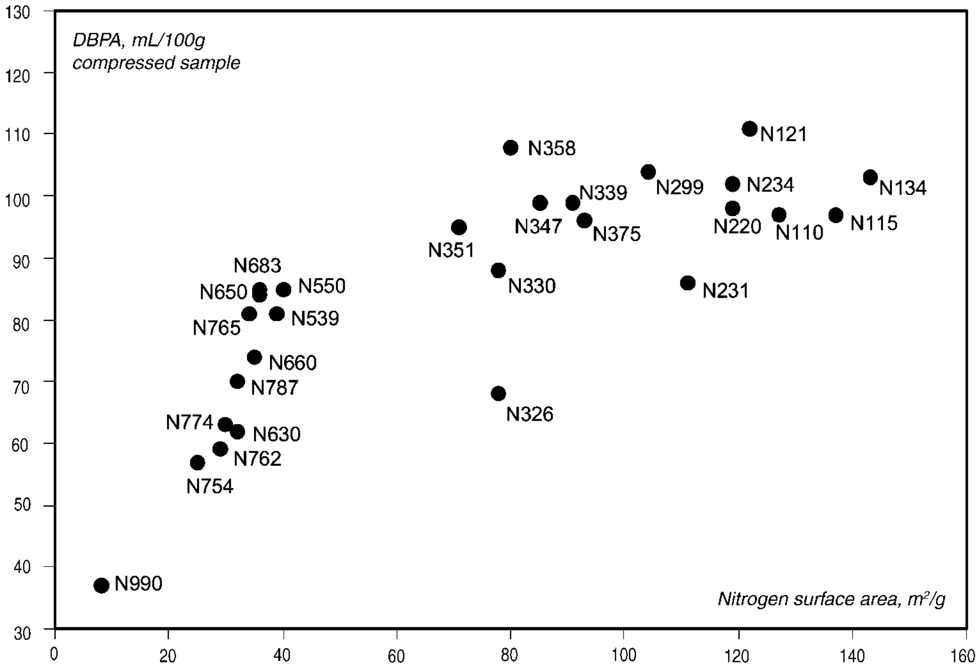

Fig. 7. Rubber grades carbon black spectrum.

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 that condense to semisolid carbon precursors (or polynucleararomatic sheet) and/or formation of large hydrocarbon molecules by polymerization, which then is dehydrogenated to particle 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 the system, three processes go on simultaneously; 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”.
- 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 microstructure. The surface growth represents ∼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 from van der Waals forces but there is no material to cement them together, hence they form temporary structures.
- Aggregate gassification: 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 at given feedstock. Therefore, with higher reaction temperature, that can be 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 (23).

The timescale of carbon black formation varies substantially across the range of particle sizes found in commercial furnace blacks. For blacks with surface areas $\sim$120 m^2/g, the carbon black formation process from oil atomization to quench takes $<$10 ms. For blacks with surface areas $\sim$30 m^2/g, formation times are a few tenths of seconds.

6. Manufacture

6.1. Oil-Furnace Process.

The oil-furnace process accounts for $>$95% of all carbon black produced in the world. It was developed in 1943 and rapidly displaced prior 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 than to transport the black.

Over the 50 years since its invention, the oil-furnace process has undergone several cycles of improvement. These improvements have resulted in improved yields, larger process trains, better energy economy, and improved product performance. A simplified flow diagram of a modern furnace black production line is shown in Figure 8 (24). This figure 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 to $>1800^\circ$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, and sometimes is burned to manufacture steam and electric power either for internal plant use or for sale.

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 semibulk containers are also used including IBCs and large semibulk 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.

The pricing of carbon black feedstocks depends on their alternate market as residual fuel oil, especially that of high sulfur No. 6 fuel oil. The actual price is determined by the supply–demand relationships for these two markets. Feedstock cost contributes $\sim$60% of the total manufacturing cost. The market price of carbon black is strongly dependent on the feedstock cost as shown in Figure 9.

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

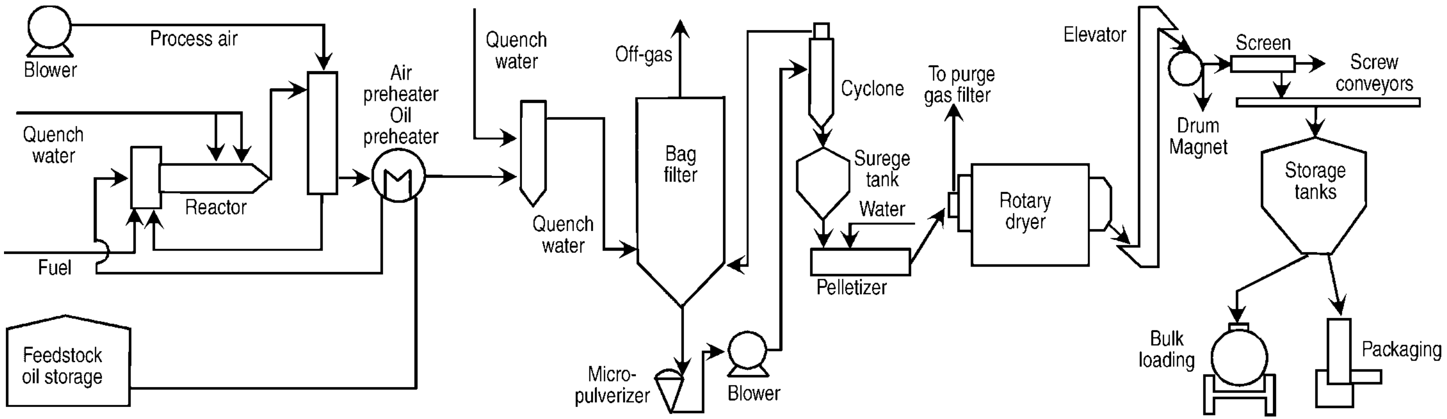

Fig. 8. Flow diagram of oil furnace black process.

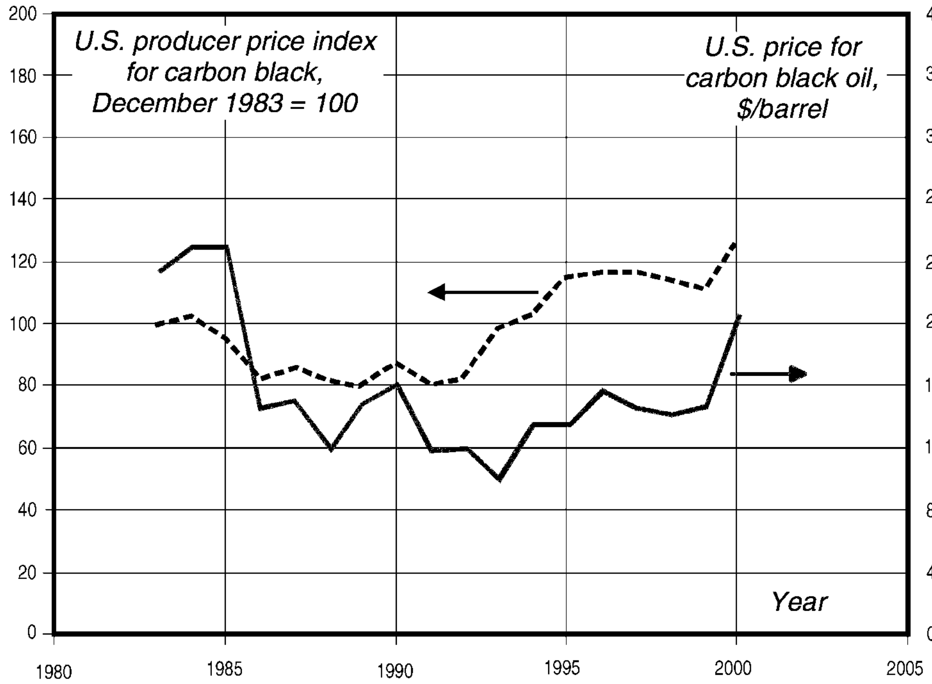

Fig. 9. Carbon black price and raw material cost in the United States (1983–2001) (1).

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 5 lists carbon formation temperatures, and residence times for the various grades of rubber blacks.

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 (23). The reactor consists of three zones. The first zone is a combustion zone in which

Table 5. **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

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 thereof. 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/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. Figures 10 and 11 show the designs of commercial reactors based on the patent literature.

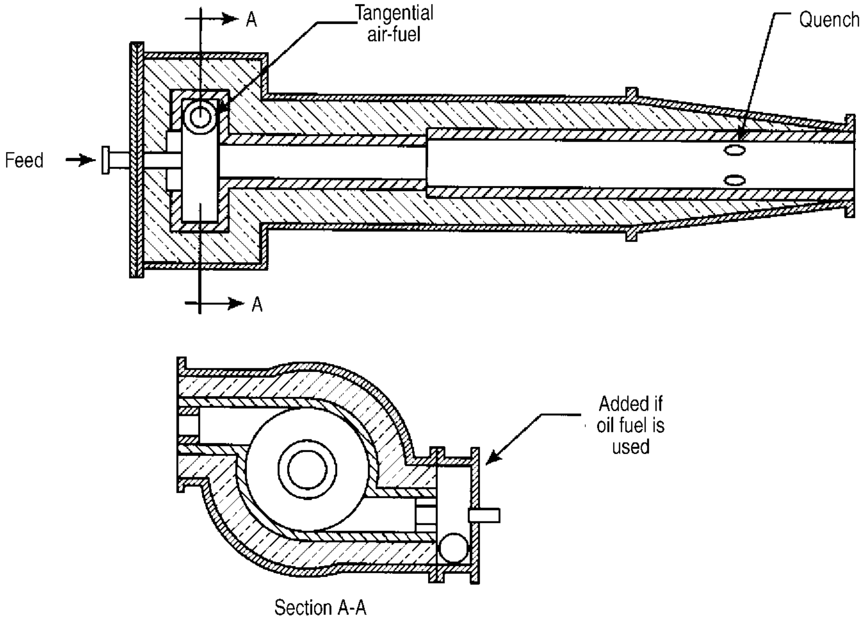

Fig. 10. Reactor for N300–N200 carbon blacks (25).

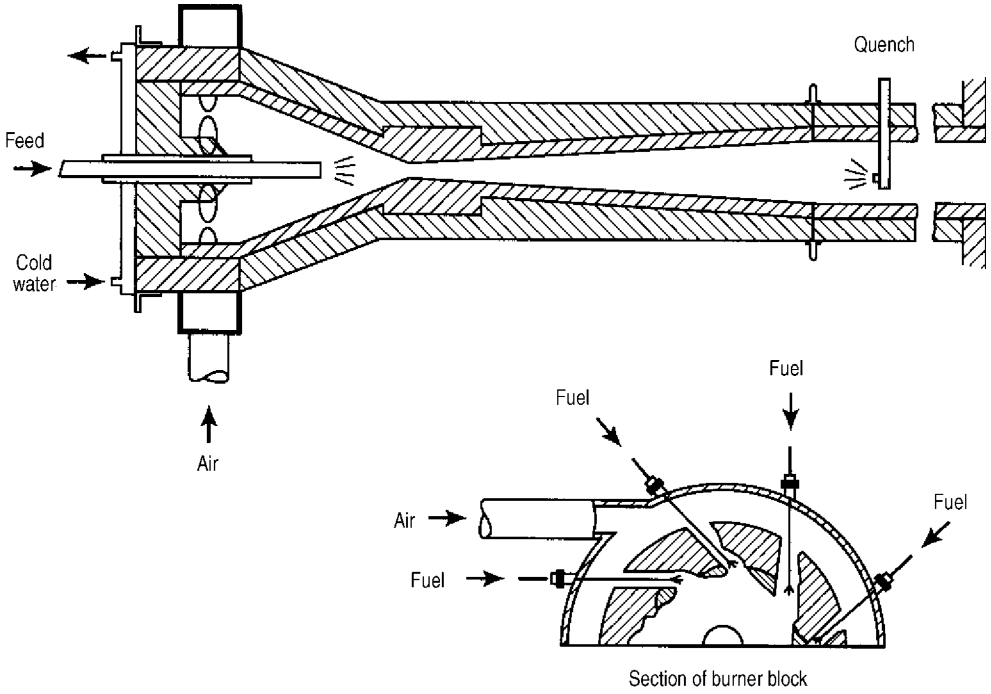

Fig. 11. Reactor for tread blacks (26).

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.

The energy utilization in the production of one kilogram of oil-furnace carbon black is in the range of $9–16 \times 10^7$ 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, heat loss by radiation to atmosphere, and the heat transferred to preheat the primary combustion air.

6.2. The Thermal Black Process. Thermal black is a large particle size, 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 innerliners, 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 ~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 make generation 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 5 min 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 ~90% hydrogen, carries the black to a quench tower where water sprays lower the temperature before entering the bag filter. The effluent gas is cooled and dehumidified in a water scrubber for use as fuel in the heating cycle. The collected black from the filters is conveyed to a magnetic separator, screened, and hammermilled. It is then bagged or pelletized. The pelletized form is bagged or sent to bulk loading facilities.

There are thermal black plants in Canada, the United States, the United Kingdom (1) and Russia. Two common grades are manufactured. These are Medium Thermal Black, N990, and Fine Thermal Black N880.

6.3. Acetylene Black Process. The high carbon content of acetylene (92%) and its property of decomposing exothermically to carbon and hydrogen make it an attractive raw material for conversion to carbon black. Acetylene black is made by a continuous decomposition process at atmospheric pressure and 800–1000°C in water-cooled metal retorts lined with refractory. The process consists of feeding acetylene into the hot reactors. The exothermic reaction is self-sustaining and requires water cooling to maintain a constant reaction temperature. The carbon black-laden hydrogen stream is then cooled followed by separation of the carbon from the hydrogen tail gas. The tail gas is either flared or used as fuel. After separation from the gas stream, acetylene black is very fluffy with a bulk density of only 19 kg/m^3. It is difficult to compact and resists pelletization. Commercial grades are compressed to various bulk densities up to 200 kg/m^3.

Acetylene black is very pure with a carbon content of 99.7%. It has a surface area of ~65 m^2/g, an average particle diameter of 40 nm, and a very high but rather weak structure with a DBP number of 250 mL/100 g. It is the most crystalline or graphitic of the commercial blacks. These unique features result in high electrical and thermal conductivity, low moisture adsorption, and high liquid absorption.

A significant use of acetylene black is in dry cell batteries where it contributes low electrical resistance and high capacity. In rubber it gives electrically conductive properties to heater pads, tapes, antistatic belt drives, conveyor belts, and shoe soles. It is also useful in electrically conductive plastics such as electrical magnetic interference (EMI) shielding enclosures. Its contribution to thermal conductivity has been useful in rubber curing bags for tire manufacture.

6.4. Lampblack Process. The lampblack process has the distinction of being the oldest and most primitive carbon black process still being practiced. The ancient Egyptians and Chinese employed techniques similar to modern methods collecting the lampblack by deposition on cool surfaces. Basically, the process consists of burning various liquid or molten raw materials in large, open, shallow pans 0.5–2 m in diameter and 16 cm deep under brick-lined flue enclosures with a restricted air supply. The smoke from the burning pans passes through low velocity settling chambers from which the carbon black is cleared by motor-driven ploughs. In more modern installations the black is separated by cyclones and filters. By varying the size of the burner pans and the amount of combustion air, the particle size and surface area can be controlled within narrow limits. Lampblacks have similar properties to the low surface area oil-furnace blacks. A typical lampblack has an average particle diameter of 65 nm, a surface area of 22 m^2/g, and a DBP number of 130 mL/100 g. Production is small, mostly in western and eastern Europe. Its main use is in paints, as a tinting pigment where blue tone is desired. In the rubber industry lampblack finds some special applications.

6.5. Impingment (Channel, Roller) Black Process. From World War I to World War II the channel black process made most of the carbon black used worldwide for rubber and pigment applications. The last channel black plant in the United States was closed in 1976. Operations still exist and are even being expanded in Europe. The demise of channel black was caused by environmental problems, cost, smoke pollution, and the rapid development of oil-furnace process grades that were equal or superior to channel black products particularly for use in synthetic rubber tires.

The name channel black came from the steel channel irons used to collect carbon black deposited by small natural gas flames impinging on their surface iron channels. Today tar fractions are used as raw material in addition to natural gas. In modern installations channels have been replaced by water cooled rollers. The black is scraped off the rollers, and the off-gases from the steel box enclosed rollers are passed through bag filters where additional black is collected. The purified exhaust gases are vented to the atmosphere. The oils used in this process must be vaporized and conveyed to the large number of small burners by means of a combustible carrier gas. Yield of rubber-grade black is 60% and 10–30% for high quality color grades.

The characteristics of roller process impingement blacks are basically similar to those of channel blacks. They have an acidic pH, a volatile content of ~5%, surface area of ~100 m^2/g, and an average particle diameter of 10–30 nm. The smaller particle size grades are used as color (pigment) blacks, and the 30 nm grade is used in rubber.

6.6. Recycle Blacks. The pyrolysis of carbon black containing rubber goods has been promoted as a solution to the accumulation of waste tires. In the processes in question, tires are pyrolyzed in the absence of oxygen, usually in indirect fired rotary kiln type units. The rubber and extender oils are cracked to hydrocarbons that are collected and sold as fuels or petrochemical feedstocks. The gaseous pyrolysis products are burned as fuel for the process. Steel tire cord is removed magnetically and the remainder of the residue is milled into a “pyrolysis black”. This contains the carbon black, silica, and other metal oxides from the rubber and some newly created char. Typically these materials have 8–10% ash, and contain a lot of coarse residue. Most are difficult to pelletize. They have on average, the reinforcing properties of a N300 black but because they are a mixture of N600 and 700 blacks with N100 and N200 blacks they are not particularly suitable for either reinforcing or semireinforcing applications. To date they find application in relatively nondemanding uses such as playground and floor mats.

6.7. Surface Modification of Carbon Blacks.

For most of its long history, the carbon black industry had concentrated on the morphlogy as the key factor controlling product performance and grade differentiation. Recently, the importance of the composition of the interface between the carbon blacks and the medium in the composite in which the carbon black is used has been recognized.

The early stages of surface modification can be traced back to 1940s and 1950s. The approaches include physical adsorption of some chemicals on carbon black surface, heat treatment, and frequently oxidation. During 1980s and 1990s, some work on plasma treatment was reported. For chemical and polymer grafting modifications, a great deal of academic work was done in 1950s and 1960s in France, United States, and Japan, using surface oxygen groups as functional groups. However, because of rapid development applications of carbon black in different areas and the challenge from other reinforcing particles in its traditional applications, the surface modification technology for carbon black has been developing very rapidly over the last decade. These include surfactant treated surfaces, chemically modified surfaces, and deposition of other phases during or after black formation. Today there is active commercial development and new product introduction in all areas.

Attachments of the Aromatic Ring Nucleus to Carbon Black. Two approaches characterize this area. A number of patents have been issued to Cabot Corporation (27,28), which describe that the decomposition of a diazonium compound derived from a substituted aromatic or aliphatic amine results in the attachment of a substituted aromatic ring or chain onto the surface of the carbon black. This results in a stable attachment that is not sensitive to moisture. Examples show attachment of amines, anionic and cationic moieties, polysulfide moieties that can be attached into an elastomer network, and alkyl, polyethoxyl, and vinyl groups. Practically, the surface chemistry and physical chemistry can be tailored according to the applications of carbon blacks. Some applications are claimed in aqueous media for dispersion (29), in oil based coatings and inks for dispersion (30), and in rubbers for reduction of hysteresis and wear resistance improvement (31). The initially attached groups can also function as sites for further chemical substitution. Another approach has been developed by Xerox Corporation in which oligomers of the polymer are prepared using stable free radical polymerization and these are attached to the carbon black surface by reaction of the stable radical (32).

Attachments to the Aromatic Ring Structure Through Oxidized Groups. The acidic surface groups that result from surface oxidation of carbon black are natural synthons for the attachment of functionality. Generally, chemistry is done through either phenolic or carboxylic acid groups on the surface. Some of these groups are present in most blacks, but their density can be increased by treating with various oxidants such as ozone, nitric acid, or hypochlorite (33–35). Compared to the previous class, these C–O attachments are somewhat more labile, being particularly susceptible to hydrolysis. The concept of using phenolic groups as points of attachment for conventional silane treating agents has been described in several patents with the particular aim of attaching polysulfide moieties that can be vulcanized into elastomer networks for hysteresis reduction (36). Recently, patents have been issued on using the acidic sites on carbon black surfaces as points of reaction of amines. In the particular case in point, the attachment was used to improve compound stability and dispersion in conductive plastics applications (37).

Metal Oxide Treatments. The carbon black industry has worked on ways to respond to the challenge of silica in tire treads for low rolling resistance (replacing all or some of the carbon black). Cabot has filed on and widely published a class of dual phase fillers in which silica or other metal oxides and carbon are coformed in a carbon black like reactor (38). In the particular product they describe, the carbon black and silica are intimately intermixed on a scale that is about the same size as the carbon black crystallite. In more recent variants, materials where the silica location is more on the exterior of the particle are described (39). In these materials, the silica is the minor constituent. The main characteristics of these carbon blacks are their lower filler–filler interactions. Filler–polymer interactions are also increased, but by incorporating coupling agents these interactions can be adjusted as required. These materials are used as fillers for low rolling resistance, higher wet skid resistance and improved wear resistance in tire treads when used with conventional sulfide–silane coupling agents (40,41), or as fillers for silicone rubber when used with alkyl silane and vinyl silane agents (42). The patent literature suggests that other applications have been considered as well (43). Patents have also been issued on coated carbon black by depositing silica on the black surface in an aqueous solution of sodium silicate by adjusting pH with acid (44,45).

7. Economic Aspects

7.1. Manufacturers and Production. Starting with the oil crisis of 1973, consumption of carbon black in the United States decreased to 1.2 million tons in 1986 (1). A number of events had contributed to decreased consumption by the rubber and tire industries including tire radialization, increased tire mileage, downsizing of tires, and increased imports of foreign cars. The negative influence of these events have pretty much run their course, and during the last two decades there has been a modest growth in carbon black production. Production for the period 1971–2000 is shown in Table 6.

Table 6. **U.S. Production of Carbon Black (1971–2000)**[a]

Year	Millions of metric tons
1971	1.380
1976	1.415
1981	1.285
1986	1.200
1991	1.230
1994	1.475
1997	1.660
2000	1.665

[a] Ref. 1.

Table 7. **U.S. Carbon Black Manufacturers and Capacities, 2000**[a]

	Furnace black		Total carbon black	
	Millions of metric tons	% of capacity	Millions of metric tons	% of capacity
Cabot Corporation	0.451	24	0.451	24
Columbian Chemicals Co.	0.361	19	0.361	19
Continental Carbon Co.	0.254	14	0.254	13
Degussa-ECI	0.463	25	0.484	25
Sid Richardson Carbon Co.	0.340	18	0.340	18
other	0.000		0.014	1
Total	*1.869*	*100*	*1.903*	*100*

[a] Ref. 1.

The shrinkage in demand has resulted in a restructuring of the carbon black-industry. Several of the principal multinational oil companies have left the business including Ashland, Cities Service Co., Phillips, and Conoco. Some plants have changed ownership. Decreased margins, rising feedstock and environmental compliance costs have led to further restructuring in the late 1990s and early 2000 time period. ECI and Degussa consolidated their operations in 2002. Today's U.S. industry consists of five principal producers. Rated capacities of the five U.S. manufacturers is shown in Table 7. Cabot Corp., ECI-Degussa and Columbian Chemicals are the leading producers, followed by Continental Carbon Co. and Sid Richardson.

World carbon black rated capacities are shown in Table 8. North America has the largest capacity, and Africa and the Middle East have only a small production. The growth areas are predicted to be the Asian and Eastern European markets.

Table 8. **World Carbon Black Capacities of July 1, 2001 (1)**

	Millions of metric tons	% of total
North America[a]	2.4	28
South America	0.5	6
Western Europe	1.5	17
Japan	0.8	9
other Asia	2.0	24
other[b]	1.3	16
Total	*8.5*	*100*

[a] Including Mexico.

[b] Including eastern Europe, Africa, and the Middle East.

8. Health and Safety Factors

8.1. Health. There is a long history of health studies, many of them sponsored by the carbon black manufacturing industry and a number of authoritative publications on carbon black SH&E aspects. In particular, Patty's Handbook chapter on Industrial Hygiene and Toxicology of carbon black is a recent authoritative reference (46). Mortality and worker health have been extensively studied, often in studies sponsored by the carbon black industry. These studies have included mortality (47,48) and health (49–50) in workers in the carbon black industry against unexposed controls in the same industry as well as those in nonindustry populations. The North American mortality studies (47) have logged ~55,000 worker exposure years since the first studies were first undertaken in 1939. They show no elevation in death rate among carbon black workers and no elevation in cancers of the respiratory organs because of occupational exposure to carbon black. In the United Kingdom a study of workers in five carbon black plants (48) shows that among this population there is an elevation of the death rate from cancers of the respiratory organs, which is significant versus the U.K. population, but the study indicated clearly that there was no correlation of the incidence of disease with exposure to carbon black. In other words, some other factors rather than carbon black exposure appeared to be the source of the excess cancers. Studies of worker health among both U.S. and European workers have been completed in the last decade and publications of the results of these studies continue to appear. These show no evidence of clinically significant health effects due to occupational exposure to carbon black. While there are some differences in the exposure metric between the North American Studies and the European studies, they show very similar effects. Over the course of time covered by these various studies, there has been a marked improvement in the work place air quality.

In 1995, IARC (International Agency for Research on Cancer) revised its evaluation of carbon black from category 3, "not classifiable as to its carcinogenicity to humans" to category 2B, "possibly carcinogenic to humans" based on lung tumor formation in two long term inhalation studies in rats (51–53). Comparable studies in mice and golden hamsters have failed to find any elevation of tumor incidence of lung or any other tissue (54). Other insoluble respirable materials have shown similar positive responses in rats, but not in other rodent species.

There are two major areas of carcinogenic concern with carbon black. Of these, the one that has historically attracted the most attention is the few tens to hundreds of pasts per million (ppms) of polynuclear aromatic hydrocarbons (PAH) that are adsorbed on the surface of most blacks. An extract made by exhaustive extraction of these materials with aromatic solvent has been shown to cause skin tumors in rodents. The PAH on carbon black is very tightly adsorbed and is not liberated by biological fluids. Hence, this material is believed to have little or no bioavailability (55). This is supported in the companion studies to those referenced by IARC (52,56). Attempts were made to get a dose response to PAH by using PAH free black and doping it with high levels of PAH. There was no statistically significant difference in the tumor incidence or type between the two groups.

The second carcinogenic mechanism seems to be common to all inert respirable insoluble particles. Positive carcinogenic responses have been shown with TiO_2, talc, carbon black, and diesel soot in the female rat (57). There is evidence that a common mechanism is at work in all these cases involving a process of damage to the lung epithelium, inflammatory response, saturation of the body's defense mechanisms, proliferation of new epithelial cells, recruitment of activated polymorphonuclear (PMN) cells, secretion of radical forming species by the PMN cells, and damage to the DNA in the dividing epithelial cells. Studies by Driscoll and co-workers are building a strong case for this mechanism and are ongoing (58). These data indicate that the distinction between the rat and other rodents is the nature of the inflammatory response that appears quite intense in the rat compared to other species. If indeed this proves to be the explanation, a strong case can be made for a threshold and establishment of a no observed adverse effect level (NOAEL). It is also clear that in the rat, an overload mechanism is at work in which above a certain critical loading, the mechanisms which normally clear dust particles from the lung lose effectiveness. Again this suggests a threshold and a no observed adverse effect level.

Carbon black inhalation is currently regulated by Occupational Safety and Health Administration (OSHA) in the United States at 3.5 mg/m^3 (total dust), by the Health and Safety Executive (HSE) in the United Kingdom at 3.5 mg/m^3 (inhalable dust), by the MAK Commission in Germany at 6.0 mg/m^3 (inhalable dust) for an 8 h time-weighted average (46). Reviews of these occupational exposure levels are currently underway by the MAK Commission, the HSE, and the American Conference of Governmental Industrial Hygienists (ACGIH). It is unlikely that any of these reviews will be completed before 2005.

8.2. Safety. Carbon blacks will burn in air if ignited and once ignited, are difficult to extinguish. In bulk storage, local hot spots can exist for very long periods. Great care needs to be exercised where a smoldering fire is suspected as there can be accumulations of carbon monoxide in enclosed spaces.

Carbon black dust clouds in air are not considered flammable. Carbon blacks have a high ignition energy requirement, and entrained dust clouds do not propagate flame, nor exhibit substantial overpressures. The reason is that they presumably have essentially no combustible volatile matter. Carbon black in air can be incinerated but only with difficulty, requiring long burnout times.

9. Environmental Concerns

The carbon black industry takes extreme efforts to confine the product during all stages of manufacturing and transport. Highly efficient bag filters are used to collect the product. After collection the fluffy carbon black is densified and pelletized to minimize dusting during shipment and use by customers. The process gas leaving the bag filter contains primarily water, nitrogen, carbon monoxide, carbon dioxide, and hydrogen. There are also traces of hydrogen sulfide, carbon disulfide, carbonyl sulfide, and various nitrogen-containing species. A portion of these gases is burned for internal plant fuel, and the residual gas is generally burned in a flare or incinerator. Where local conditions warrant, the remaining gas may be used to generate power or steam, either for the plant itself, or for merchant sale.

Like all other operators of combustion equipment, carbon black plants are subject to the usual pressures for reduced sulfur and nitrogen oxide emissions. It appears that the use of lower sulfur feedstock is the most economic way of reducing sulfur emissions. Redesign of combustion equipment for nitrogen oxide reduction is showing some promise. The primary NO_x issues arise from the combustion of tail gas since the carbon black production process is exceedingly fuel-rich.

10. Uses

The U.S. consumption of carbon black in 2000 by various market sectors is shown in Table 9. About 89% of total consumption is in the rubber industry and 70% for tires. About 10% is consumed for other automotive products and 9% for rubber products unrelated to the automotive industry. The automotive industry accounts for 80% of consumption and 11% of the blacks is for nonrubber uses. Its main applications are related to pigmentation, ultraviolet (uv) absorption, and electrical conductivity of other products such as plastics, coating, and inks. These carbon blacks are also termed special blacks (1).

10.1. Rubber-Grade Carbon Blacks.

Carbon black is a major component in the manufacture of rubber products, with a consumption second only to rubber itself. It is by far the most active rubber reinforcing agent owing to its unique ability to enhance the physical properties of rubbers. Table 10 lists the principal rubber grades by their N-number classification, general rubber properties, and typical uses.

The consumption of the various carbon black grades can be divided into tread grades for tire reinforcement and nontread grades for nontread tire use and other rubber applications. Table 11 shows the distribution of production of types for these uses. A typical passenger tire has several compounds and uses five to seven different carbon black grades.

Table 9. **U.S. End Use Consumption of Carbon Black in 2000 (1)**

	Millions of metric tons	Percent of total
automotive rubber uses tire and tire products	1.17	70
belts, hoses and other automotive products	0.17	10
industrial rubber products	0.16	9
non-rubber uses	0.18	11
Total	*1.67*	*100*

Table 10. **Application of Principal Rubber-Grade Carbon Blacks**

Designation	General rubber properties	Typical uses
N110, N121	very high abrasion resistance	special tier treads, airplane, off-the-road, racing
N220, N299, N234	very high abrasion resistance, good processing	passenger, off-the-road, special service tire treads
N339, N347, N375, N330	high abrasion resistance, easy processing, good abrasion resistance	standard tire treads, rail pads, solid wheels, mats, tire belt, sidewall, carcass, retread compounds
N326	low modulus, good tear strength, good fatigue, good flex cracking resistance	tire belt, carcass, sidewall compounds, bushings, weather strips, hoses
N550	high modulus, high hardness, low die swell, smooth extrusion	tier innerliners, carcass, sidewall, innertubes, hose, extruded goods, v-belts
N650	high modulus, high hardness, low die swell, smooth extrusion	tire innerliners, carcass, belt, sidewall compounds, seals, friction compounds, sheeting
N660	medium modulus, good flex fatigue resistance, low heat buildup	carcass, sidewall, bead compounds, innerliners, seals, cable jackets, hose, soling, EPDM compounds
N762	high elongation and resilience, low compression set	mechanical goods, footwear, innertubes, innerliners, mats

The behavior of different grades in rubber is dominated mainly by surface area, structure (DBPA), and surface activity. All these parameters play a role in rubber reinforcement through different mechanisms, such as interfacial interaction between rubber and carbon black, occlusion of the polymer in the internal voids of the aggregate, and the agglomeration of carbon black aggregates in the polymer matrix.

One of the consequences of the incorporation of carbon blacks into a polymer is the creation of an interface between a rigid solid phase and a soft elastomer phase. For rubber-grade carbon blacks, whose surfaces exhibit very little

Table 11. **Carbon Black Production by Grade in United States for 2000 (K metric tons) (1)**

N330 high abrasion	0.623
N550 fast extruding	0.138
N762 semireinforcing	0.129
N660 general purpose	0.356
N110 super abrasion	0.061
N220 intermediate super abrasion	0.170
N990 thermal	0.014
Total	*1.493*

porosity, the total area of the interface depends on both filler loading and the specific surface area of the filler. Due to the interaction between rubber and filler two phenomena are well documented: the formation of bound rubber and a rubber shell on the carbon black surface. Both are related to the restriction of the segmental movement of polymer molecules.

The effect of filler structure on the rubber properties of filled rubber has been explained by the occlusion of rubber by filler aggregates (59). When structured carbon blacks are dispersed in rubber, the polymer portion filling the internal void of the carbon black aggregates, or the polymer portion located within the irregular contours of the aggregates, is unable to participate fully in the macrodeformation. The partial immobilization in the form of occluded rubber causes this portion of rubber to behave like the filler rather than like the polymer matrix. As a result of this phenomenon, the effective volume of the filler, with regard to the stress–strain behavior and viscoelastic properties of the filled rubber, is increased considerably.

The filler aggregates in the polymer matrix have a tendency to associate to agglomerates, especially at high loadings, leading to chain-like filler structures or clusters. These are generally termed secondary structure or, in some cases, filler network, even though the latter is not comparable to the continuous polymer network structure. The formation of filler network is dependent on the intensity of interaggregate attractive potential, the distance between aggregates and polymer–filler interaction (60).

From the point of view of carbon black morphology, high surface area produces high reinforcement as reflected in high tensile and tear strengths, high resistance to abrasive wear, higher hysteresis, and poorer dynamic performance, while high structure leads to higher viscosity, lower die swell, and high modules. The hysteresis is a measure of the loss of mechanical energy as heat during cyclical deformation of a rubber body. Listed in Table 12 are the effects of surface area and structure that can be a guideline for choice of carbon blacks according to the processability and property requirements of rubber products.

A present day challenge to carbon black technologists is to optimize the balance between tire wear, tire hysteresis that determines the rolling resistance, and wet skid resistance. It is now recognized that besides the morphology, while the wear resistance is closely related to the polymer–filler interaction and dispersion of the carbon blacks, the hysteresis is mainly deterimined by filler

Table 12. **Effect of Carbon Black Morphologies on the Properties of Filled Compounds**

Surface area increase	Rubber properties	Structure increase
higher	abrasion resistance	depend on severity
higher	hardness	higher
higher	tensile strength	lower
not main factor	modulus	higher
lower	elongation	lower
lower	rebound	not main factor
higher	viscosity	higher
lower	dispersibility	higher
not main factor	dimensional stability	higher

networking or agglomeration. For tread compounds of tire, depression of filler networking results in lower hysteresis at the temperatures from 50 to 80°C, leading to low rolling resistance, and in higher hysteresis at lower temperature that is in favor of wet skid resistance. Some progress on this problem has been made by using new furnace designs and other process variables that broaden the aggregate size distributions and lower the tint strength while maintaining surface area and structure (61,62). A substantial improvement in global tire performance can be achieved through surface modification of carbon blacks, such as carbon–silica dual phase fillers (40,41,63).

10.2. Special-Grade Carbon Blacks. Besides reinforcement for rubber, the principal functions that carbon black imparts to a compound material are color, uv damage resistance, electrical conductivity, nondegradation of polymer physical properties, and ease of dispersion. The carbon blacks used for these purposes are classified as special-grade blacks. Smaller volume applications exploit other principal attributes, such as chemical inertness, thermal stability, and an open porous structure. The secondary attributes include chemical and physical purity, low affinity for water adsorption, and ease of transportation and handling.

In 2000, 11% of the U.S. consumption of carbon black was special blacks. About 51% of special blacks are used in plastics, 32% in printing inks, 5% in paint, 3% in paper, and 9% in miscellaneous applications (1).

Dispersion. The ability to disperse the special grades is an important consideration in almost all applications. The customer's milling costs can be comparable to the purchase price of the carbon black. In other cases, the inability to achieve an excellent dispersion impairs the ability to realize the full performance of the blacks or it creates other undesirable characteristics. For example, a black plastic part will not appear as dark nor have a smooth surface if the black cannot be fully dispersed.

The term "dispersion" is used in several ways in actual applications. It may refer to the amount of work that required to achieve a specified level imperfections or it may refer to the level of imperfections per se. When a black is referred to as "easily dispersed" it can mean that relatively low shear mixers can achieve a compound that is relatively free of imperfections. Or it may mean that with a given mixing protocol the compound achieves an imperfection count below a specified level.

The "level of imperfections" is most often assessed in one of two ways. Most often it refers to the size distribution of surface imperfections on an extruded or injection molded part. It may also refer to the rate of pressure buildup on an extrusion screen pack.

Undispersed material is one of three types. The first is non-carbon contaminants that come either in the feedstock or the result of corrosion of the manufacturing train. The second are carbon contaminants that occur when the feedstock droplets fail to evaporate. If the residual material in the droplet fails to evaporate, but is pyrolyzed in place, the contaminant is referred to as a coke ball. If the droplet reaches the wall before it is completely pyrolyzed, the resulting build up is termed wall coke and it can flake off and contaminate the carbon black product. Finally, the aggregates of carbon black can remain agglomerated or undispersed. Too often the concepts of contaminant free and the difficulty of separating agglomerates into aggregates are not clearly distinguished. Detailed microscopy is required to determine the nature of defects and therefore resolve if the problem is contamination or true difficulty in dispersion.

In most cases the properties of special carbon black aggregates that engender performance are antagonistic to achieving a good dispersion. High pigmenting strength for both light and uv implies high surface area. High surface area increases the difficulty of dispersion. Achieving an electrically conductive network at low concentration implies a black with high structure. High structure, per se, is an asset in dispersion. However, most carbon black formation technologies will not make high structure blacks unless the surface area is also high and the trade-off means that the best conducting grades are difficult to disperse.

Pigmentation. Carbon black is an excellent pigment. It is considerably more effective in absorbing light than any other material on either a weight or a cost basis. It is also environmentally stable.

Black pigments are used both alone and with other pigments. In the first the measure of performance is termed mass tone and is simply the ability to prevent the transmission or reflection of light. The second is called tint tone and it is the ability to soften or darken other colors.

How black is black? Two aspects can be important. The first is the total amount of white light that is either transmitted or reflected by a black material. The second is variation in these values with the frequency or color of the light. In almost all cases, relatively higher red light adsorption is valued as it gives the material a blue “undertone”. Various measures are used to equate blue tone with overall absorption. These color metrics are based on subjective judgments and are most highly developed for automotive paints.

Surface area and structure, or aggregate size, play a role in determining color strength. Pigmenting carbon blacks are used at quite low concentrations. Single particle Mie scattering theory is reasonably applicable. In applying the theory, an aggregate of carbon black is viewed as a composite of carbon and the resin or polymer. The refractive index of the carbon is taken as 1.84(1-0.46i) (64). And the index of refraction of the composite particle is the volume average of the carbon black and polymer values. The difficulty in using single particle scattering theory is in evaluating the size and carbon content of the “scattering particle”. Various methods are used to estimate aggregate size and to divide the CDBP value into “intra-” and “inter-” aggregate parts. The “intra-aggregate” part is considered to form part of the composite scattering particle.

Because aggregate and primary particle size cannot be controlled independently in carbon black reactors, and because the ability to achieve complete dispersion depends on morphology, the coloring properties of carbon blacks are often treated empirically.

The theory works best when carbon black is used with other pigments, ie, in tinting applications. In these applications, both theory and experiments indicate that smaller primary particles and aggregates absorb more light and have a bluer tone.

Table 13 shows the entire range of properties of blacks sold for color applications. Blacks with large primary particle sizes are used in news inks and other

Table 13. **Types and Applications of Special Pigment Grades of Carbon Blacks**

Type	Surface area, m^2/g	DBP number, mL/100 g	Volatile, %	Uses
		Normal grades		
high color	230–560	50–120	2	high jetness for alkyl and acrylic enamels, lacquers, and plastics
medium color	220–220	70–120	1–1.5	medium jetness and good dispersion for paints and plastics; uv and weathering protection for plastics
regular color	80–140	60–114	1–1.5	for general pigment applications in inks, paints, plastics, and paper; gives uv protection in plastics, high tint, jetness, gloss, and dispersibility in inks and paints
	46	60	1.0	good tinting strength, blue tone, low viscosity; used in gravure and carbon paper inks, paints, and plastics
	45–85	73–100	1.0	main use is in inks; standard and offset news inks
low color	25–42	64–120	1.0	excellent tinting black–blue tone; used for inks-gravure, one-time carbon paper inks; also for paints, sealants, plastics, and cements
thermal blacks	7–15	30–35		tinting-blue tone; plastics and utility paints
lamp blacks	20–95	100–160	0.4–0.9	paints for tinting-blue tone
		Surface oxidized grades		
high color	400–600	105–121	8.0–9.5	used for maximum jetness in lacquers, coatings, plastics, fibers, record disks
medium color, long flow	138	55–60	5	used in lithographic, letterpress, carbon paper, and typewriter ribbon inks; high jetness, excellent flow, low viscosity, high tinting strength, gloss, and good dispersability
medium color, long flow	96	70	2.5	used for gloss printing and carbon paper inks; excellent jetness, disper sibility; tinting strength, and gloss in paints
low color	30–40	48–93	3.5	used for tinting where flooding is a problem; easy dispersion

nondemanding applications. The extremely fine blacks are used in high performance enamels and automotive paints.

An emerging application is as the colorant in jet printer inks. The requirement of extremely high quality dispersion meant that the original black inks were dyes. The image permanence of carbon blacks lead to the displacement of dyes when techniques were developed that assured the stability of excellent, water-based dispersion.

The blacks used for uv protection of polymers have very small primary particle sizes. The industry standard for uv protection is primary particle sizes of <20 nm.

Conductivity. Carbon black is added to polymer or resin compounds to achieve electrical conductivity. If their concentrations are high enough, carbon black aggregates will form interconnected paths through the compound material. These networks can have resistivities in the range of 1–10 Ω-cm.

Concentrations that are too low will not form percolation networks. The Jansen equation (65) predicts that the critical concentration occurs when volume of polymer equals four times the volume of the CDBP value. The compounds are continuous when the amount of polymer is the CDBP value or greater and contain continuous carbon networks when the volume of polymer is between the crush DBP value and four times that amount.

In general it is desirable to achieve percolation at low loading to reduce the negative effects of the presence of the carbon black on the physical properties of the compound. Therefore blacks with high CDBP values are used in conducting application. Figure 12 shows the percolation threshold of a number of carbon blacks with widely varying CDBP values.

One of the most demanding applications for conducting compounds is as a layer around the center conductor of a high voltage cable. The purpose of the

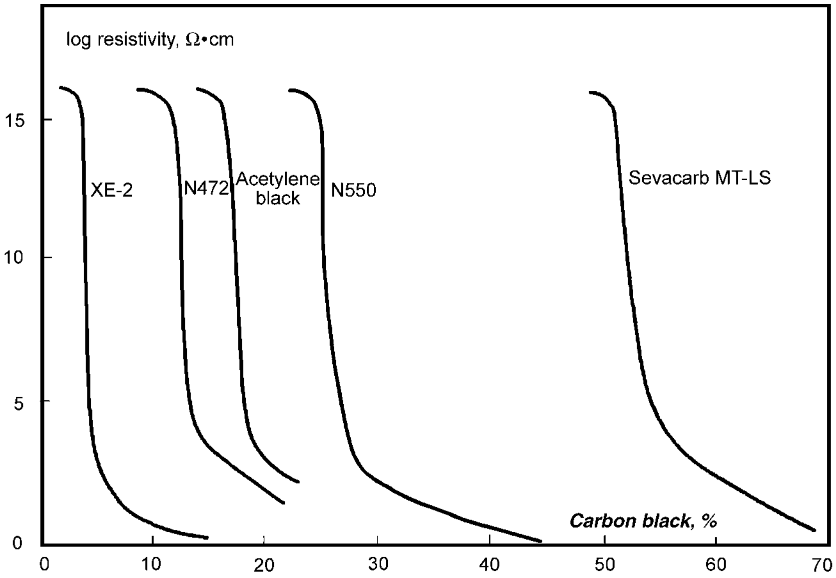

Fig. 12. Electrical resistivity-concentration curves for various carbon blacks (66).

compound is to smooth any surface imperfection that would otherwise result in high electric field gradients and the breakdown of the insulating layers. These compounds have the highest loading of carbon blacks to achieve the lowest possible resistance. Two very important secondary requirements are that the black is quite hydrophobic, free of inorganic salts, and has extremely low contaminant levels.

Other applications of carbon black filled polymers do not require as high a level of conductivity. The purpose is the dissipation of static electricity. These types of compounds are used in carrying containers for microelectronic components and in containers and pipes for combustible liquids such as gasoline. The newest application is adding enough conductivity to automobile panels to enable coatings of electrostatically charged paint particles.

Other Uses. Carbon blacks are used to make highly porous structures for catalyst supports. Most supports are metal oxides rather than carbon, but in certain circumstances a chemically inert support is required. The open structure of the carbon black aggregates allows control of the pore size distribution within the consolidated carbon body.

Fuel cell electrodes are a particularly interesting catalyst application. The active layers of the proton conducting membrane fuel cells must have the ability to transport both gases and hydrogen ions to the catalyst as well as conducting water away. Mixtures of carbon blacks with special polymers create the desired hydrophilic and hydrophobic pore structures.

The so-called boundary layer capacitors are also electrochemical devices that rely carbon blacks to achieve the appropriate pore structures.

Special carbon blacks are also used in batteries, with the largest use in old technology nonrechargeable cells.

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