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CARBON

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STRUCTURE, TERMINOLOGY, AND HISTORY

Carbon [*7440-44-0*] occurs widely in its elemental form as crystalline or amorphous solids. Coal, lignite, and gilsonite are examples of amorphous forms; graphite and diamond are crystalline forms. Carbon forms chemical bonds with other elements, but is capable of forming compounds in which carbon atoms are bound to carbon atoms and, as such, is the chemical element that is the basis of organic chemistry. Carbon and graphite can be manufactured in a wide variety of products with exceptional electrical, thermal, and physical properties. They are a unique family of materials in that properties of the final product can be controlled by changes in the manufacturing processes and by raw material selection.

Crystallographic Structure

Elemental carbon exists in nature as two crystalline allotropes: diamond [*7782-40-3*] and graphite [*7782-42-5*]. The diamond crystal structure (see page 683) is face-centered cubic with interatomic distances of 0.154 nm. Each atom is covalently bonded to four other carbon atoms in the form of a tetrahedron. Diamond is transformed to graphite in the absence of air at temperatures above 1500°C.

The accepted ideal structure for graphite was proposed by Bernal in 1924 (1). This structure is described as infinite layers of atoms of carbon which are arranged in the form of hexagons lying in planes (see page 691). The stacking arrangement is ABAB so that the atoms in alternate planes align with each other. The spacing between the layers is 0.3354 nm, the interatomic distance within the planes 0.1415 nm, and the crystal density 2.266 g/cm^3. A less frequently occurring structure is rhombohedral with a stacking arrangement of ABCABC in which the atoms of every fourth layer align with each other (2). This rhombohedral form, which occurs only in conjunction with the hexagonal form, is less stable, and converts to the hexagonal form at 1300°C.

There are six electrons in the carbon atom with four electrons in the outer shell available for chemical bonding. Three of the four electrons form strong covalent bonds with the adjacent in-plane carbon atoms. The fourth electron forms a less-strong bond of the van der Waals type between the planes. Bond energy between planes is 17 kJ/mol (4 kcal/mol) (3) and within planes 477 kJ/mol (114 kcal/mol) (4). The weak forces between planes account for such properties of graphite as good electrical conductivity, lubricity, and the ability to form interstitial compounds.

Terminology

Although the terms carbon and graphite are frequently used interchangeably in the literature, the two are not synonymous. The terms carbon, formed carbon, manufactured carbon, amorphous carbon, or baked carbon refer to products that result from the process of mixing carbonaceous filler materials such as petroleum coke, carbon blacks, or anthracite coal with binder materials of coal tar or petroleum pitch, forming these mixtures by molding or extrusion, and baking the mixtures in furnaces at temperatures from 800–1400°C. The term carbon–graphite designates a formed, composite product in which the filler materials, in addition to a carbon, such as petroleum coke, contain a graphitized carbon that has been heat-treated to high temperatures. The filler is material that makes up the body of the finished product (see Fillers). Green carbon refers to formed carbonaceous material that has not been baked.

Graphite, also called synthetic or artificial graphite, electrographite, manufactured graphite, or graphitized carbon refers to a carbon product that has been further heat-treated at a temperature exceeding 2400°C. This process of graphitization, described in a later section, changes not only the crystallographic structure, but also the physical and chemical properties.

With the development of nuclear and aerospace technologies, several new forms of carbon and graphite are being commercially produced. Products that are deposited on a heated graphite substrate by vapor phase decomposition of gaseous hydrocarbons, usually methane, at 1800–2300°C, are termed pyrolytic carbons (5). Chemical vapor deposited (CVD) carbon or pyrocarbon are other terms used to designate pyrolytic carbons. Pyrolytic graphite is a product resulting from high temperature annealing, and has a crystallite interlayer spacing similar to that of ideal graphite (6) (see Ablative materials; Nuclear reactors).

The term polymeric carbon is a generic term for products that result when high polymers with some degree of cross-linking are heated in an inert atmosphere. These organic starting materials do not coke; instead, they result in chars that represent a distinct group of materials possessing a graphite ribbon-network structure rather than extensive graphite sheets (7). Vitreous or glassy carbon prepared by carbonization of cellulose and phenolic or polyfurfuryl resins is an example of a polymeric carbon. Carbonization of acrylic fibers to produce carbon fibers is another example.

Because of the diversity of carbon and graphite forms, British, French, and German carbon groups have agreed to cooperate in improving the characterization of carbon solids. The ultimate aim is to prescribe standard primary and secondary methods of characterization as well as making available standard samples (8). In the United States, the ASTM has issued standard definitions of terms relating to manufactured carbon and graphite (9).

There is no standard industry-wide system for designating the various grades of carbon and graphite that are commercially available. Each of the more than 20 manufacturers has its own nomenclature to describe grades, sizes, and shapes available for specific purposes. The *Directory of Graphite Availability* (10) characterizes many of the materials that were available in 1967, but the catalogues and technical literature issued by carbon and graphite manufacturers must be consulted for current grade and property data. The data cited in the following sections are representative average values for commercially available materials.

History of the Industry

Graphite as it is found in nature has been known for several centuries for its use in making clay–graphite crucibles and its lubricating properties. The first known use was for drawing or writing, and it was because of this attribute that the German mineralogist A. G. Werner named graphite after the Greek word *graphein*, which means to write (11).

Manufacture of artificial graphite did not come about until the end of the 19th century. Its manufacture was preceded by developments mainly in the fabrication

Table 1. Applications for Manufactured Carbon and Graphite[a]

Aerospace
- nozzles
- nose cones
- motor cases
- leading edges
- control vanes
- blast tubes
- exit cones
- thermal insulation

Chemical
- heat exchangers and centrifugal pumps
- electrolytic anodes for the production of chlorine, aluminum, and other electrochemical products
- electric furnace electrodes for making elemental phosphorus
- activated carbon
- porous carbon and graphite
- reaction towers and accessories

Electrical
- brushes for electrical motors and generators
- anodes, grids, and baffles for mercury arc power rectifiers
- electronic tube anodes and parts
- telephone equipment products
- rheostat disks and plates
- welding and gouging carbons
- electrodes in fuel cells and batteries
- contacts for circuit breakers and relays
- electric discharge machining

Metallurgical
- electric furnace electrodes for the production of iron and steel, ferroalloys, and nonferrous metals
- furnace linings for blast furnaces, ferroalloy furnaces, and cupolas
- aluminum pot liners and extrusion tables
- run-out troughs for molten iron from blast furnaces and cupolas
- metal fluxing and inoculation tubes for aluminum and ferrous furnaces
- ingot molds for steel, iron, copper, and brass
- extrusion dies for copper and aluminum

Nuclear
- moderators
- reflectors
- thermal columns
- shields
- control rods
- fuel elements

Other
- motion picture projector carbons
- turbine and compressor packing and seal rings
- spectroscopic electrodes and powders for spectrographic analyses
- structural members in applications requiring high strength-to-weight ratios

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[a] Ref. 15.

and processing of carbon electrodes. H. Davy is credited with using the first fabricated carbon in his experiments on the electric arc in the early 1800s. During the 19th century, several researchers received patents on various improvements in carbon electrodes. The invention of the dynamo and its application to electric current production in 1876 in Cleveland, Ohio, by C. F. Brush, provided a market for carbon products in the form of arc-carbons for street lighting. The work of a Frenchman, F. Carré, in the late 19th century, established the industrial processes of mixing, forming, and baking necessary for the production of carbon and graphite (12).

A significant development occurred when E. G. Acheson patented an electric resistance furnace capable of reaching approximately 3000°C, the temperature necessary for graphitization (13). This development was the beginning of a new industry where improved carbon and graphite products were used in the production of alkalies, chlorine, aluminum, calcium and silicon carbide, and for electric furnace production of steel and ferroalloys. In 1942 a new application for graphite was found when it was used as a moderator by E. Fermi in the first self-sustaining nuclear chain reaction (14). This nuclear application and subsequent use in the developing aerospace industries opened new fields of research and new markets for carbon and graphite. Carbon and graphite fibers are an example of a new form and a new industry. A list of major applications is shown in Table 1.

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J. C. LONG
Union Carbide Corporation

ACTIVATED CARBON

Activated carbon, a microcrystalline, nongraphitic form of carbon, has been processed to develop internal porosity. Activated carbons are characterized by a large specific surface area of 300–2500 m^2/g which allows the physical adsorption of gases and vapors from gases and dissolved or dispersed substances from liquids. Commercial grades of activated carbon are designated as either gas-phase or liquid-phase adsorbents. Liquid-phase carbons are generally powdered or granular in form; gas-phase, vapor-adsorbent carbons are hard granules or hard, relatively dust-free pellets. Activated carbons are widely used to remove impurities from liquids and gases and to recover valuable substances from gas streams (see Adsorptive separation).

Physical Properties

Surface area is the most important physical property of activated carbon. For specific applications, the surface area available for adsorption depends upon the molecular size of the adsorbate and the pore diameter of the activated carbon. Generally, liquid-phase carbons are characterized as having a majority of pores of 3 nm diameter and larger (1), whereas most of the pores of gas-phase adsorbents are 3 nm in diameter and smaller. Liquid-phase adsorbents require larger pores because of the need for rapid diffusion in the liquid and because of the large size of many dissolved adsorbates. Methods of testing adsorbency employ substances having a range of molecular sizes. Liquid-phase carbons are usually characterized by phenol, iodine, and molasses numbers. Gas-phase carbons are characterized by carbon tetrachloride and benzene adsorption activities.

The bulk density or apparent density of an activated carbon, together with its specific adsorptive capacity for a given substance, can be used to determine bed capacity in the design of an adsorption system or to determine grades of carbon required for an existing system.

The range of particle sizes of activated carbon is important: the rate of adsorption has been shown to depend inversely upon the particle size, (small particles having the fastest rates); however, in fixed beds pressure drop increases as particle size decreases.

The mechanical strength or hardness and the attrition resistance of the particles are important where pressure drop and carbon losses are a concern.

The kindling point of the carbon must be high enough to prevent excessive carbon oxidation in gas-phase adsorption where high heats of adsorption, particularly of ketones, are involved.

Chemical Properties

The most important chemical properties of activated carbon are the ash content, ash composition, and pH of the carbon. Discrepancies between the expected performance of an activated carbon, based upon surface area and pore-size distribution data, and actual adsorptive capacity can often be explained by oxygen-containing groups on the surfaces of the carbon. The pH or pK_a of the carbon, as a measure of surface acidity or basicity of the oxygen-containing groups, assists in predicting hydrophilicity and anionic or cationic adsorptive preferences of the carbon (2–5).

Manufacture and Processing

Almost any carbonaceous material of animal, plant, or mineral origin can be converted to activated carbon if properly treated. Activated carbon has been prepared from the blood, flesh, and bones of animals; it has been made from materials of plant origin, such as hardwood and softwood, corncobs, kelp, coffee beans, rice hulls, fruit pits, nutshells, and wastes such as bagasse and lignin. Activated carbon has also been made from peat, lignite, soft and hard coals, tars and pitches, asphalt, petroleum residues, and carbon black. However, for economic reasons, lignite, coal, bones, wood, peat, and paper mill waste (lignin) are most often used for the manufacture of liquid-phase or decolorizing carbons, and coconut shells, coal, and petroleum residues are used for the manufacture of gas-adsorbent carbons.

Activation of the raw material is accomplished by two basic processes, depending upon the starting material and whether a low or high density, powdered or granular carbon is desired: (*1*) Chemical activation depends upon the action of inorganic chemical compounds, either naturally present or added to the raw material, to degrade or dehydrate the organic molecules during carbonization or calcination. (*2*) Gas activation depends upon selective oxidation of the carbonaceous matter with air at low temperature, or steam, carbon dioxide, or flue gas at high temperature. The oxidation is usually preceded by a primary carbonization of the raw material.

Decolorizing carbons are coal- and lignite-based granules, or light, fluffy powders derived from low density starting materials such as sawdust or peat. Many decolorizing carbons are prepared by chemical activation. Some raw materials, such as bones, contain inorganic salts that impart some degree of activity to the carbon when the raw material is simply carbonized or heated in an inert atmosphere (2–3). Decolorizing carbons are usually prepared by admixing or impregnating the raw material with chemicals that yield oxidizing gases when heated or that degrade the organic molecules by dehydration. Compounds used successfully are alkali metal hydroxides, carbonates, sulfides, and sulfates; alkaline earth carbonates, chlorides, sulfates, and phosphates; zinc chloride; sulfuric acid; and phosphoric acid (2).

Gas- and vapor-adsorbing carbons may be prepared by the chemical activation process by using sawdust or peat as raw material and phosphoric acid, zinc chloride, potassium sulfide, or potassium thiocyanate as the activator (2–3). In some cases, the chemically activated carbon is given a second activation with steam to impart physical properties not developed by chemical activation.

Processes involving selective oxidation of the raw material with air or gases are also used to make both decolorizing- and gas-adsorbing carbons. In both instances, the raw material is activated in granular form. The raw material is carbonized first at 400–500°C to eliminate the bulk of the volatile matter and then oxidized with gas at 800–1000°C to develop the porosity and surface area. Some decolorizing carbons are oxidized with air at low temperature; however, because this reaction is exothermic, it is difficult to control and is suitable only for low activity carbon. The high temperature oxidation process with steam, carbon dioxide, or flue gas is endothermic, easier to control, and generally used more often (6–7).

Some gas-adsorbing carbons are made from hard, dense starting materials such as nutshells and fruit pits. These are carbonized, crushed to size, and activated directly to give hard, dense granules of carbon. In other cases, it is advantageous to grind the charcoal, coal, or coke to a powder, form it into briquettes or pellets with a tar or pitch binder, crush to size, calcine at 500–700°C, and then activate with steam or flue gas at 850–950°C. This method gives more easily activated particles because they possess more entry channels or macropores for the oxidizing gases to enter and for the reaction products to leave from the center of the particles.

The production of activated carbon from granular coal (8) as well as the activation of briquetted coal (9–10) has been described. In commercial plants, the raw material is carbonized in horizontal tunnel kilns, vertical retorts, or horizontal rotary kilns. Activation is accomplished in continuous internally or externally fired rotary retorts, or in large, cylindrical, multiple hearth furnaces where the charge is stirred and moved from one hearth to the next lower one by rotating rabble arms, or in large vertical retorts where the charge cascades over triangular ceramic forms as it moves downward through the furnace.

Fibrous activated carbon has been made by carbonizing infusible, cured phenolic fibers, air oxidizing, and then steam activating the fibers. The activated carbon fibers of 300–1000 m^2/g surface area are relatively strong and flexible with tensile strengths of at least 103 MPa (ca 15,000 psi). The manufacture of the activated fibers and of activated quilted fabrics has been reported (11).

Antipollution laws have increased the sales of activated carbon for control of air and water pollution (see Air pollution control methods). Pollution control regulations also affect the manufacture of activated carbons. Chemical activating agents have a large potential for the emission of corrosive acid gases during the activation process. If the emissions from chemical activation processes cannot be economically controlled, alternative selective oxidation methods will dominate. Selection of raw materials favoring low-sulfur materials will depend upon the local standards for permissible emission levels of sulfur oxides.

Economic Aspects

Activated carbon usage in the United States in 1976 was ca 90,000 metric tons valued at 9×10^7 dollars, or $0.99/kg. Of the total activated carbon usage, 45,000 t was powdered carbon at an average price of $0.62/kg and 45,000 t was granular carbon at an average price of $1.32/kg (12–13). The capacities of activated carbon production of United States companies in 1976 are shown below (14–16):

Company	*Location*	*Capacity, metric tons*
Westvaco Corp.	Covington, Ky.	38,500
ICI United States	Marshall, Tex.	34,000
Calgon Corp.	Catlettsburg, Ky. Pittsburgh, Pa.	39,000
Husky Industries	Romeo, Fla.	10,000
Barnebey-Cheney Co.	Columbus, Ohio	5,500
Union Carbide	Fostoria, Ohio	2,250
Witco Chemical	Petrolia, Pa.	2,250
Total		*131,500*

The 1976 production of gas- and vapor-adsorbent carbon in the United States is estimated to be 14,000 t. Gas-phase carbon consumption is much lower than liquid-phase carbon consumption, as there are fewer large volume applications and, in most applications, the carbon is regenerated repeatedly, remaining in service for several years. Prices were $1.10–4.08/kg with special grades running as high as $5.50/kg.

Since activated carbon manufacture is energy-intensive, prices increase with increases in the costs of fuels used to supply heat for calcination and activation of the carbon.

Regeneration of activated carbons is a major factor in the cost-effectiveness of the use of carbon (13). Liquid treatment costs can be minimized best by using the lowest effective carbon dosage of a carbon that retains its adsorptive capacity and mechanical strength after many thermal regeneration cycles (17).

Gas-phase activated carbons used for recovery of valuable process gases and solvents are responsible for the continued cost-effectiveness of many industrial processes, particularly solvent-based fiber and tape manufacture, dry cleaning, and rotogravure printing. Regeneration methods used are steam, thermal-vacuum, and pressure-swing desorption. Regeneration, pressure drop through carbon beds, carbon life, and system capital cost are the principal economic factors in gas and vapor recovery by activated carbon (18–19).

Specifications

Activated carbon is supplied on the basis of minimum values (eg, bulk density), maximum values (eg, moisture and ash content), and ranges of properties. In many cases, setting a narrow specification range for a property may considerably increase the price of the carbon. Specifications are based upon estimates and tests that indicate those properties of the carbon yielding the lowest cost of use or the maximum return on investment.

Table 1 shows some typical physical properties of activated carbons. These are approximate values; properties vary by grade and manufacturer within each raw material type.

Analytical and Test Methods

The American Society for Testing and Materials (ASTM), Committee D-28 on activated carbon, has defined several common property tests (20). These standard tests are listed in Table 2.

Many industrial activated carbon tests have not yet been standardized by ASTM but are in common use. The following are standard industrial tests: shaking a sample with several different sized steel balls for a standard time period reveals its hardness or strength; the percent hardness reported is based upon the decrease in average

Table 1. Physical Properties of Typical Activated Carbon Grades

	Liquid-phase carbon			Gas-phase carbon		
Property	Lignite base	Wood base	Bituminous coal base	Granular coal	Pelleted coke	Granular coconut
mesh (Tyler)	−100	−100	8–30	−4, +10	−6, +8	−6, +14
(mm)	(0.15)	(0.15)	(2.38–0.59)	(4.76, 1.70)	(3.36, 2.38)	(3.36, 1.18)
CCl_4 activity, % min	30	40	50	60	60	60
iodine no., min	500	700	950	1000	1000	1000
bulk density, g/mL, min	0.48	0.25	0.50	0.50	0.52	0.53
ash, % max	18	7	8	8	2	4

Table 2. ASTM Test Methods for Activated Carbon

Test	ASTM test no.
definition of terms relating to activated carbon	D2652
apparent density of activated carbon	D2854
liquid-phase evaluation of activated carbon	D2355
moisture in activated carbon	D2867
particle size distribution of granular activated carbon	D2862
total ash content of activated carbon	D2866

particle size of the carbon calculated from screen analyses before and after shaking with the steel balls.

Gas adsorptive properties of activated carbon may be statically determined by exposure to the desired substance at constant temperature and humidity levels in a bell jar. Adsorptive capacity is reported as weight percent pickup of the adsorbate by the carbon adsorbent. Gas adsorptive properties can be determined dynamically by blowing a test gas through a carbon bed or tube of a standardized depth and diameter. The equilibrium amount of adsorbate per unit weight of carbon is determined when the carbon bed becomes saturated with adsorbate. The most commonly applied gas adsorption tests are carbon tetrachloride and benzene activity tests. The carbon tetrachloride activity of a sample is its weight percent pickup, at equilibrium, of carbon tetrachloride from a dry air stream saturated with carbon tetrachloride. Benzene activity is based on the same principle, except that the benzene-saturated air stream is usually diluted to 10 vol % saturation (21). Another common gas-phase carbon test is retentivity. Both benzene and carbon tetrachloride retentivities measure the weight percent of adsorbate retained by a carbon sample first saturated with adsorbate and then subjected to air blowing for 6 h (2).

Activated carbon adsorption tests are useful in classifying carbons for general application areas and in manufacturing quality control. Although actual process fluids might appear more useful for testing the adsorptive powers of activated carbon than standard gas or liquid methods, process stream adsorbate and other impurity concentrations often vary within such wide limits that process fluid tests may be less reliable and less convenient than standard gas and liquid tests (2,22).

Storage

Activated carbon packaging includes bags, drums, cartons, railroad cars, and tank trucks. To avoid contamination and possible loss of properties, gas-phase activated carbon should not be exposed to vapors or moisture. Liquid-phase activated carbon may be stored as a water slurry. For storage of specially impregnated grades, activated carbon may be supplied in vapor-barrier drums.

Health and Safety Factors

Although activated carbon is not an easily combustible material (kindling points in pure oxygen are usually above 370°C), stored carbon should be kept away from heat, electricity, and flames. Dry carbon should not be allowed to contact strong oxidizing agents. Electrical controls used on or near activated carbon should be dust-tight and explosion-proof, and electrical motors should be totally enclosed. Foam or a fine water spray can extinguish activated carbon fires. When organic gases or vapors are adsorbed from an air stream, the carbon should be wet, steamed, or purged with inert gas prior to the first adsorption cycle since the initial heat of adsorption, especially for ketones, is sufficiently high to represent a fire hazard.

Use of activated carbon in protective masks does not protect the wearer from an oxygen depleted atmosphere's asphyxiation hazard (23). Also, an asphyxiation hazard exists inside activated carbon vessels because of adsorption of oxygen from the air onto the carbon. Proper ventilation and breathing equipment should be used by persons entering activated carbon vessels. Since flammable solvent vapors may be present, only explosion-proof lamps and spark-proof tools should be used inside the adsorber vessels. Dust-free loading of activated carbon into adsorbers may be accomplished by using special dry-loading equipment or by slurrying the carbon and wet-loading the adsorbers.

Uses

Liquid-Phase Carbon. Approximately 60% of the activated carbon manufactured for liquid-phase applications is used in powdered form. The two principal uses of powdered activated carbon are: (*1*) removal from solution of color, odor, taste, or other objectionable impurities such as those causing foaming or retarding crystallization, and (*2*) concentration or recovery from solution of a solute. Usually liquid treatment with powder is a batch process. The liquid to be treated is mixed with an appropriate amount of carbon predetermined by laboratory tests, heated if necessary to reduce viscosity, and agitated for 10–60 min. When the batch process is complete, the carbon is separated from the liquid by settling or filtration and is either discarded or eluted. The use of powdered carbons has been declining because granular carbons offer advantages in improved handling and reduced need for final filtering. The possibility of regenerating the carbon makes granular carbon more cost effective than powdered carbon. Increased exports to sugar-producing countries in Latin America mask the decline in domestic use of powdered carbon.

Granular carbon can be used in a continuous process where the liquid is slowly percolated through fixed beds of carbon until the carbon becomes saturated with adsorbate. The liquid stream is then diverted to a second adsorber, allowing the carbon in the first to be regenerated by hot gas or by solvent extraction. In applications where modest amounts of carbon are used, carbon saturated with adsorbed impurities is sent back to the manufacturer for regeneration in a multiple-hearth furnace.

Activated carbon is widely used to remove color from sugar (qv) (2). The use of carbon in glucose manufacture removes protein and hydroxymethylfurfural from the syrup, rendering it colorless and stable.

Although there are many chemical, physical, and biological methods of treating water contaminated with industrial and municipal wastes to produce safe and palatable drinking water, none have the potential of activated carbon treatment (24). Most methods require careful control for the effective removal of taste and odor contaminants. Activated carbon is a broad-spectrum agent that effectively removes toxic or biorefractive substances (25). Insecticides, herbicides, chlorinated hydrocarbons, and phenols, typically present in many water supplies, can be reduced to acceptable levels by activated carbon treatment. Powdered activated carbon is most effectively used in smaller water treatment systems where the equipment investment required for granular carbon would be prohibitive. Granular carbon systems may consist of moving beds, beds in series, beds in parallel, or expanded beds (26). Expanded-bed systems require water flow rates sufficient to expand the bed at least to 115% of static bed volume. Removal of organics by expanded-bed systems is comparable to fixed beds without the need for frequent backwashing required by fixed beds (27). Granular water-treatment carbons are thermally regenerated for reuse, thus reducing the cost of treatment.

Industrial and municipal waste water treatment will be an expanding market for liquid-phase activated carbons (14,28). *The 1972 Federal Water Pollution Control Act* expanded the authority of the EPA to conduct research for the improvement of municipal and industrial water treatment (29). Thus government and industry may cooperate through an EPA cost-sharing grant system in the improvement and application of activated carbon for effective, economical waste water treatment. The EPA program for advanced industrial waste water treatment will be especially concerned with activated carbon regeneration technologies (16) (see Water).

The dry cleaning industry uses powdered and granular carbons for reclaiming liquid solvent that has become contaminated with dyes and rancid extracted oils and grease. Carbon use is cheaper than distillation, and carbon more completely removes odor-causing substances.

Activated carbon has many applications in food and pharmaceutical manufacturing. Such uses include purification and color removal during the processing of fruit juices, honey, maple syrup, candy, soft drinks, and alcoholic beverages (2). Pharmaceutical uses include removal of pyrogens from solutions for injections, vitamin decolorizing and deodorizing, and insulin purification. Activated carbon (drug-pure grade) can be administered orally to poison victims (30). Research is being conducted for the development of activated carbon filters for artificial kidney devices and for the dialysis (qv) of poisons and drugs (31–32).

Activated carbon is used in electroplating (qv) to remove organic impurities from the bath. Carbon may also be used to allow the recovery of gold from cyanide-leach pulps (33). Gold may be recovered by burning the carbon or by eluting the gold (34). Activated carbon is not commonly used for the purification of inorganic chemicals (1,35).

Miscellaneous uses for liquid-phase carbons include laboratory uses, reaction catalysis, and aquarium water filters.

Gas-Phase Carbon. Gas-phase carbons typically have a surface area of 1000–2000 m^2/g and are made in larger particle sizes of greater strength and density than liquid-phase carbons. The small (3 nm and less) pores of gas-phase carbons provide high adsorptive capacity and selectivity for gases and organic vapors. Desirable characteristics of a good gas adsorbent carbon are: high adsorptive capacity per unit volume; high retentive capacity; high preferential adsorption of gases in the presence of moisture; low resistance to gas flow; high strength or breakage resistance; and complete release of adsorbates at increased temperatures and decreased pressures.

The largest single application for gas-phase carbon is in gasoline vapor emission control cannisters on automobiles. Evaporative emissions from both fuel tank and carburetor are adsorbed on the carbon (33,36). An evaporative control carbon should have good hardness, a high vapor working capacity, and a high saturation capacity (37). The working capacity of a carbon for gasoline vapor is determined by the adsorption–desorption temperature differential, the rate at which purge air flows through the carbon cannister, and by the extent to which irreversibly adsorbed, high molecular weight gasoline components accumulate on the carbon (15).

Another application for gas-phase carbons is the purification and separation of gases. Many industrial gas streams are treated with activated carbon to remove impurities or recover valuable constituents. Odors are removed from air in activated carbon air conditioning systems, and gas masks containing activated carbon are used to protect individuals from breathing toxic gases or vapors (38).

The purification of industrial gases is usually performed with gas under pressure in a two-bed system. The carbon is supported in tall vertical towers having one on stream as the other is regenerated, dried, or cooled. Regeneration is accomplished by temperature or pressure change or both, with or without a purge gas.

Activated carbon is used in air conditioning (qv) systems to remove industrial odors and irritants from building inlet air and to remove body, tobacco, and cooking odors, etc from recirculated building air (39). The use of carbon to remove odors allows more economical building operation by permitting higher percentages of recycled air to be used, thus minimizing the need for heating or cooling large amounts of fresh inlet air (40). Manufacturers use carbon to remove objectionable odors from process exhaust gases, and to remove corrosive gases and vapors, eg, sulfur compounds, from intake air to protect electrical switching equipment. Activated carbon also prolongs the storage life of fruits and flowers by adsorbing gases that contribute to odor and deterioration of these products (2).

Since air is circulated by low-pressure fans in air conditioning systems, activated carbon is always used in thin beds from 13–26 mm thick. The carbon is usually supported in cannisters of perforated sheet metal that are either flat, cylindrical, or corrugated. The effective life of the carbon depends on the application but may range from several months to 1.5 yr (41).

Activated carbon is used in nuclear reactor systems to adsorb radioactive gases in carrier or coolant gases, and from the air in reactor emergency exhaust systems (42). Radioactive gas adsorbers are very deep beds of carbon used to adsorb and retain radioactive materials long enough for isotopes to decay to safe levels of radioactivity before they are discharged into the atmosphere. Radioactive iodine and organic iodides are adsorbed by specially impregnated grades of high-activity carbon (43). The radioactive fission products, krypton and xenon, are adsorbed for decay to safe isotopes before they are released to the atmosphere (44–45).

The use of solvent recovery-grade activated carbon for the recovery of volatile organic compounds from process air streams is important to the operating economics of several industries (18,46). A simple activated carbon recovery system consists of an air filter, a blower, two horizontal adsorbers (each containing a bed of carbon 0.3–0.6 m deep), a vapor condenser, and a solvent decanter or continuous still (19).

Some solvent recovery plants are manually operated, but most are automatic, using a time–cycle controller. The newer, larger industrial units allow adsorption cycle times to be controlled according to variable vapor loadings in the process air stream (47).

Specially impregnated grades of activated carbon in cigarette filters adsorb some of the harmful components of tobacco smoke (48). Other applications for activated carbon include use in kitchen range hoods, gas sampling tubes (49), refrigerator deodorizers, and as getters used in pill bottles and vacuum equipment for adsorption of harmful contaminant vapors or to aid in attaining high vacuum.

The catalytic oxidation of compounds by activated carbon has been recognized for many years. It is generally conceded that this action results from the presence of irreversibly adsorbed oxygen on the carbon surface. Many salts, such as ferrous sulfate, sodium arsenite, potassium nitrite, and potassium ferrocyanide, are oxidized in solution by activated carbon; the reaction can be made continuous by passing both solution and air over granular carbon (50).

Hydrogen sulfide in air is oxidized to sulfur when passed over activated carbon. It can be removed from manufactured gas by adding a small amount of air to the gas before bringing it in contact with the carbon (51).

Activated carbon is used as the catalyst in the manufacturing of phosgene (qv) from carbon monoxide and chlorine, and sulfuryl chloride is produced by the reaction of sulfur dioxide with chlorine in the presence of activated carbon.

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R. W. SOFFEL
Union Carbide Corporation

BAKED AND GRAPHITIZED CARBON

Raw Materials

The raw materials used in the production of manufactured carbon and graphite largely determine the ultimate properties and practical applications of the finished products. This dependence can be attributed to the nature of carbonization and graphitization processes.

Throughout the entire process of the thermal conversion of organic materials to carbon and graphite, the natural chemical driving forces cause the growth of larger and larger fused-ring aromatic systems, and ultimately result in the formation of the stable hexagonal carbon network of graphite. Differences in the final materials depend upon the ease and extent of completion of these overall chemical and physical ordering processes.

The first few steps in the carbonization process can be considered as a dehydrogenative polymerization where hydrocarbon molecules lose hydrogen and combine to form larger planar molecular networks. As the process moves toward carbon, solid-state reorganization and recrystallization processes begin to take place. In these processes, a gradual improvement in both in-plane and stacking perfection occurs; the result is the three-dimensionally ordered graphite structure with ABAB stacking (see page 691).

The starting materials in the carbonization process may be partly or entirely aromatic hydrocarbons or heterocyclics derived from coal or petroleum. After some heat treatment, the partially-polymerized products constitute a pitch, which is a complex mixture of many hundreds or even thousands of aromatic hydrocarbons with 3–8 condensed rings and an average molecular weight of 300. Although the individual, pure compounds may melt at fairly high temperatures (>300°C), the pitch mixture acts as a eutectic and softens at a much lower temperature, eg, 50–180°C. Both liquid and solid pitches are isotropic materials, ie, perfectly random in their mutual molecular orientation.

Coke is the next stage in the process of carbonization. Coke consists of aromatic polymers of much higher molecular weights, >3000. In contrast to pitch, coke is a totally infusible solid and is generally anisotropic, ie, the flat molecules within fairly large domains can all have nearly the same orientation.

Coke is well-oriented compared with pitch because an easily oriented liquid crystal or mesophase of aromatic molecules forms during the pitch-to-coke transformation. As isotropic pitch is heated above 400°C, small anisotropic mesophase spheres appear which grow, coalesce, and finally form large anisotropic regions (1). As polymerization continues, these anisotropic regions become very viscous or semisolid and are essentially coke. Such well-oriented coke retains this ordered structure and can be converted to crystalline graphite by high temperature heat treatment. Fine insoluble solids in the pitch are not incorporated within the growing mesophase sphere but tend, instead, to aggregate on the surfaces of the spheres and may modify the coalescence, usually resulting in a less anisotropic coke. Pitches that contain this mesophase material are now generally known as mesophase pitches; the term mesophase is derived from the Greek mesos or intermediate and indicates the pseudo-crystalline nature of this highly oriented anisotropic material.

In order to produce useful carbon and graphite bodies, filler and binder materials are mixed, formed by molding or extrusion, and finally baked, or baked and graphitized, to yield the desired shaped carbon or graphite bodies. More than 30 different raw materials are used in the manufacture of carbon and graphite products. The primary materials, in terms of tonnage consumed, are the petroleum coke or anthracite coal fillers and the coal-tar or petroleum pitch binders and impregnants. Other materials, called additives, are often included to improve processing conditions or to modify certain properties in the finished products.

Filler Materials. ***Petroleum Coke.*** Petroleum coke is produced in large quantities in the United States as a by-product of the petroleum cracking process used to make gasoline and other petroleum products. It is the largest commercially available source of synthetically produced carbon that can be readily graphitized by heating above 2800°C.

Most of the petroleum coke is produced by the delayed coking process (2). The properties of cokes vary according to the feedstock and to operating variables in the delayed coker unit such as operating pressure, recycle ratio, time, and coker heater outlet temperature.

The cokes to be used in any one product are selected to provide optimum quality. The major quality factors are sulfur content, volatiles, ash, and thermal expansion. High sulfur content is undesirable because of environmental concerns and because it leads to uncontrolled expansion (puffing) during graphitization, resulting in cracking of the product. The volatiles in raw cokes affect the quality of the calcined coke; high levels of volatiles lead to low density and low strength in the calcined product. High ash content is usually undesirable and leads to contamination of the finished product. Also, if these ash contaminants are present in the feedstock from which the coke is made, they impede the formation of desired crystal structure during the coking and lower the strength and density of the final coke product.

High-quality or needle cokes have low thermal expansion, low ash content, high density, and good crystal structure as indicated by x-ray analysis. Such needle cokes are used primarily in the manufacture of large graphite products such as electrodes for electric steel-making furnaces. Cokes of lower quality are known as metallurgical-grade cokes.

Needle cokes are produced from aromatic feedstocks such as decant oils from a refinery catalytic cracking unit or tars made by thermally cracking gas oils. Other feedstocks, such as atmospheric or vacuum residues from a refinery, usually produce sponge cokes. Usually the more aromatic the feedstock, the higher the coke quality will be, since larger, more highly ordered domains of oriented molecules will form during the mesophase stage of the coking reaction.

Sponge cokes are used primarily as fuel and in the manufacture of anodes for the aluminum industry. For every kilogram of aluminum produced, approximately 0.4 kg of petroleum coke is consumed (3).

The properties required in cokes for the aluminum industry are different from those required in needle cokes. Metallic impurities in the coke are more critical and a low ash content is essential since impurities from the coke tend to concentrate in the aluminum as the anode is consumed.

Particularly important impurities are vanadium, nickel, iron, and silicon; other impurities such as sulfur are slightly less critical. Since the carbon consumption per kilogram of aluminum produced affects the economics of the process, bulk density is also an important property (see Aluminum).

Table 1 shows a comparison of properties of typical sponge- and needle-grade cokes.

Natural Graphite. Natural graphite is a crystalline mineral form of graphite occurring in many parts of the world (see Carbon, natural graphite).

Carbon Blacks. Carbon blacks are commonly used as components in mixes to make various types of carbon products (see Carbon, carbon black).

Table 1. Typical Properties of Sponge and Needle Cokes

Property	Aluminum anode grade sponge coke		Graphite electrode-grade needle coke	
	Raw	Calcined[a]	Raw	Calcined[a]
sulfur, wt %	2.5	2.5	1.0	1.0
ash, wt %	0.25	0.50	0.10	0.15
vanadium, ppm	150[b]	200[b]	10	10
nickel, ppm	150[b]	200[b]		20–40
silicon, wt %	0.02	0.02	0.04	0.04
volatile matter, wt %	10–12		8	
resistivity, μΩ·m (particles, −35 mesh to +65 mesh Tyler, 0.49 to 0.23 mm)		890		965
real density, g/cm³		2.06		2.12
bulk density, g/cm³		0.80		0.88
coefficient of thermal expansion of graphite per °C (30–100°C)		20×10^{-7}		5×10^{-7}

[a] Calcining, discussed later in this section, is a thermal treatment which removes volatiles from the raw materials and shrinks the particles.

[b] Ref. 4.

Anthracite. Anthracite is preferred to other forms of coal in the manufacture of carbon products because of its high carbon-to-hydrogen ratio, its low volatile content, and its more ordered structure. It is commonly added to carbon mixes that are used for fabricating metallurgical carbon products to improve specific properties and reduce cost. Anthracite is used in mix compositions for producing carbon electrodes, structural brick, blocks for cathodes in aluminum manufacture, and in carbon blocks and brick used for blast furnace linings (see Coal).

Pitches. Carbon articles are made by mixing a controlled-size-distribution of coke filler particles with a binder such as coal tar or petroleum pitch. The mix is then formed by molding or extruding and is heated in a packed container to control the shape and set the binder. This brief description of the carbon-making process serves to identify the second most important raw material for making a carbon article, the pitch binder. The pitch binder preserves the shape of the green carbon and also fluidizes the carbon particles, enabling them to flow into an ordered alignment during the forming process. During the subsequent baking steps, the pitch binder is pyrolyzed to form a coke that bridges the filler particles and serves as the permanent binding material. These carbon bridges provide the strength in the finished article and also provide the paths for energy flow through thermal and electric conductance (see Tar and pitch).

A binder used in the manufacture of electrodes and other carbon and graphite products must (*1*) have high carbon yield, usually 40–60 wt % of the pitch; (*2*) show good wetting and adhesion properties to bind the coke filler together; (*3*) exhibit acceptable softening behavior at forming and mixing temperature, usually in the range of 90–180°C; (*4*) be low in cost and widely available; (*5*) contain only a minor amount of ash and extraneous matter that could reduce strength and other important physical properties; and (*6*) produce binder coke that can be graphitized to improve the electrical and thermal properties.

The primary binder material, coal-tar pitch, is produced primarily as a by-product of the destructive distillation of bituminous coal in coke ovens during the production of metallurgical coke. The second largest source of binder is petroleum pitch obtained from the cracking of petroleum in refinery processes. Manufacturers of carbon products require pitches with various softening points, depending upon the products to be made and the processing conditions required in forming and baking. The softening behavior and rheology of the pitch are important factors in establishing the forming conditions of the carbon product (see Rheological measurements). Baking schedules are then developed to improve the carbon yield and to reduce energy input to the furnace.

Petroleum Pitch. Although coal-tar pitch is a main source of binder pitch for the carbon industry, pitches from other precursors are becoming increasingly important. Petroleum pitch has been investigated extensively as a potential source of aluminum cell anode pitch (5). These studies have shown that pitch from petroleum sources, if produced from the proper charging stock, can be the approximate equivalent in quality of coal-tar pitch for manufacture of carbon products. Petroleum pitch is produced by cracking petroleum liquids at 450–500°C, 690–1380 kPa (100–200 psi). The cracking step produces both light and heavy feedstocks. The heavy feedstock is then processed by heat soaking at ca 350°C to form a viscous pitch.

The primary differences (shown in Table 2) between petroleum pitches and coal-tar pitches are in viscosity, benzene insolubles (BI), and quinoline insolubles (QI). In the graphite industry, petroleum pitch is used as an impregnant to increase the density of carbon and graphite products because of its low QI content.

Certain compounds found in some coal-tar and petroleum pitches are carcinogenic. Individuals working with pitches or exposed to fumes or dust should wear protective clothing to avoid skin contact. Respirators should be worn when pitch dust or fume concentrations in the air are above established limits (see Industrial hygiene and toxicology).

Additives. In addition to the primary ingredients in the mixes (the fillers and binders), minor amounts of other materials are added at various steps in the process. Although the amounts of these additives are usually in small percentages, they play an important role in the economics of the process and determine the quality of the final products. Light extrusion oils and lubricants, including light petroleum oils, waxes, and fatty acids and esters, are often added to the mix to improve the extrusion rates and structure of extruded products. Inhibitors are used to reduce the detrimental effects of sulfur in high sulfur cokes. Iron oxide is often added to high sulfur coke to

Table 2. Comparison of Typical Physical Properties of Petroleum and Coal-Tar Pitches

Property	Petroleum	Coal tar
softening point, cube-in-air, °C	120	110
sp gr, 15.5–26.7°C	1.22	1.33
coking value, wt %	51	58
benzene insolubles (BI), wt %	3.6	33
quinoline insolubles (QI), wt %	none	14
ash, wt %	0.16	0.10
sulfur, wt %	1.0	0.8
viscosity in Pa·s[a] at		
160°C	0.8	1.4
177°C	0.3	0.4
199°C	0.1	0.2

[a] To convert Pa·s to poise, multiply by 10.

prevent puffing, the rapid swelling of the coke caused by volatilization of the sulfur at 1600–2400°C. Iron from Fe_2O_3 or other iron compounds prevents this action by forming a more stable iron sulfide, which reduces the gas pressure in the coke particles. Other sulfide-forming compounds such as sodium, nickel, cobalt, and vanadium may also be used. Sodium carbonate is often used in applications requiring a low ash product.

Calcining

Coke and pitch purchased by carbon companies from suppliers must meet rigid specifications. Some materials, such as pitch and natural graphite, may be used as received from suppliers; other materials, such as raw coke and anthracite, require calcining, a thermal treatment to temperatures above 1200°C.

Calcining consists of heating raw filler to remove volatiles and to shrink the filler to produce a strong, dense particle. Raw petroleum coke, eg, has 5–15% volatile matter; when the coke is calcined to 1400°C, it shrinks approximately 10–14%. Less than 0.5% of volatile matter in the form of hydrocarbons remains in raw coke after it is calcined to 1200–1400°C. During calcination the evolving volatiles are primarily methane and hydrogen which burn during the calcining process to provide much of the heat required. The calcining step is particularly important for those materials used in the manufacture of graphite products, such as electrodes, since the high shrinkages occurring in raw coke during the baking cycle of large electrodes would cause the electrode to crack. To prevent partial fusion of the coke during calcining, the volatile content of the green coke is kept below 12%.

Anthracite is calcined at appreciably higher temperatures (1800–2000°C). The higher calcining temperatures for anthracite are necessary to complete most of the shrinkage and to increase the electrical conductivity of the product for use in either Soderberg or prebaked carbon electrodes for aluminum or phosphorus manufacture. Some other forms of carbon used in manufacturing of carbon products, such as carbon black, are also calcined.

The selection of calcining equipment depends upon the temperatures required and the materials to be calcined. Two major types of calcining units are used for cokes: the horizontal rotary drum-type calciner and the vertical rotary hearth-type calciner. Modifications of these have been developed for particular applications and to reduce energy input and product loss.

Rotary-type calciners for calcining raw petroleum coke are similar in design to those used for calcining limestone and cement (6–7).

The conventional rotary calciner is energy-intensive, and 10–15% loss of coke is experienced through oxidation. Newer calciners have been designed to prevent excessive loss of product and to reduce fuel consumption.

Since anthracite must be calcined at higher temperatures than can be reached reasonably in conventional gas-fired kilns, an electrically heated shaft kiln is used to calcine the coal (qv) at temperatures up to 2000°C (8).

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L. L. WINTER
Union Carbide Corporation

PROCESSING OF BAKED AND GRAPHITIZED CARBON

Raw Material Preparation

Crushing and Sizing. Calcined petroleum coke arrives at the graphite manufacturer's plant in particle sizes ranging typically from dust to 5–8 cm dia. In the first step of artificial graphite production the run-of-kiln coke is crushed, sized, and milled to prepare it for the subsequent processing steps. The degree to which the coke is broken down depends on the grade of graphite to be made. If the product is to be a fine-grained variety for use in aerospace, metallurgical, or nuclear applications, the milling and pulverizing operations are used to produce sizes as small as a few micrometers in diameter. If, on the other hand, the product is to be coarse in character for products like graphite electrodes used in the manufacture of steel, a high yield of particles up to 1.3 cm dia is necessary.

The wide variety of equipment available for the crushing and sizing operations is well-described in the literature (1–2). Roll crushers are commonly used to reduce the incoming coke to particles that are classified in a screening operation. The crushed coke fraction, smaller than the smallest particle needed, is normally fed to a roll or hammer mill for further size reduction to the very fine (flour) portion of the carbon mix. A common flour sizing used in the graphite industry contains particles ranging from 149 μm (100 mesh) to a few micrometers, with about 50% passing through a 74-μm (200-mesh) screen.

For a coarse-grained (particle-containing) graphite, the system depicted in Figure 1 is typical. The run-of-kiln coke is brought in on railroad cars and emptied into pits where the coke is conveyed to an elevator. The elevator feeds a second conveyer which empties the coke into any one of a number of storage silos where the coke is kept dry. The manufacturer usually specifies a maximum moisture content in the incoming coke, at about 0.1–0.2%, to ensure that mix compositions are not altered by fluctuations in moisture content.

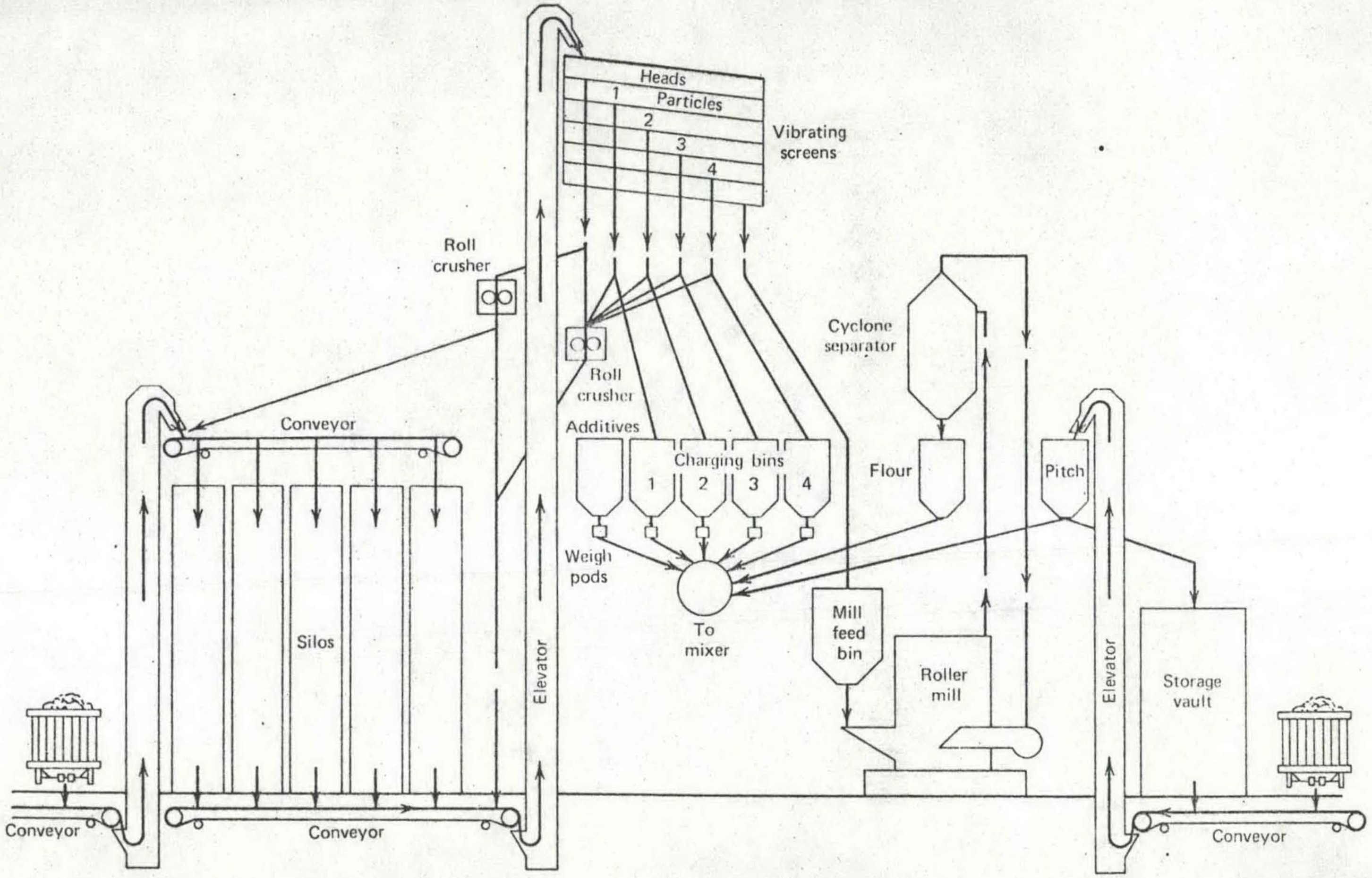

Figure 1. Raw materials handling system.

In the system shown in Figure 1, the oversized coke particles (heads) are diverted to a roll crusher. Most raw materials systems provide the option of further reducing the sizes of particles by passing them through a second crusher directly from the screens and recycling the resulting fractions through the screening system. The undersized coke fractions are transferred to a bin that supplies a mill for production of the flour portion of graphite composition. The mills used in this application may be of impact (hammer) variety or of roller variety. A commonly-used mill consists of a rotating roller operating against a stationary steel ring. The coke is crushed to very fine sizes that are air-classified by a cyclone separator. The sizes larger than those desired in the flour are returned to the mill and the acceptable sizes are fed to a charge bin.

The coal-tar-pitch binder used in graphite manufacture also arrives in railroad cars. If the pitch is shipped in bulk form, the large pieces must be crushed to ca 3 cm and smaller to facilitate uniform melting in the mixer and control of the weighing operation. Many vendors of binder pitches now form their product either by prilling, extruding, or flaking to ensure ease of handling and storage.

The pitch system shown in Figure 1 conveys the incoming pitch through a crusher to an elevator that deposits it into a charging bin. The graphite manufacturer tries to avoid long-term storage of 100°C-softening point pitch because of its tendency to congeal at ambient conditions into masses extremely difficult to break up and handle. Thus, whenever possible, cars of pitch are ordered and used as needed at the carbon plant.

In some plants the pitches are delivered in heated tank cars as liquids.

Proportioning. The size of the largest particle is generally set by application requirements. For example, if a smoothly-machined surface with a minimum of pits is required, as in the case of graphites used in molds, a fine-grained mix containing particles no larger than 0.16 cm with a high flour content is ordinarily used. If high resistance to thermal shock is necessary (eg, in graphite electrodes used in melting and reducing operations in steel plants), particles up to 1.3 cm are used to act as stress absorbers in preventing catastrophic failures in the electrode.

Generally, the guiding principle in designing carbon mixes is the selection of the particle sizes, the flour content, and their relative proportions in such a way that the intergranular void space is minimized. If this condition is met, the volume remaining for binder pitch and the volatile matter generated in baking are also minimized. The volatile evolution is often responsible for structural and property deterioration in the graphite product. In practice, most carbon mixes are developed empirically with the aim of minimizing binder demand and making use of all the coke passed through the first step of the system. From an economic standpoint, accumulation of one size component cannot be tolerated in making mixes for commonly used graphite grades since this procedure will amount to a loss of relatively costly petroleum coke. Typically, a coarse-grained mix may contain a large particle (eg, 6 mm dia), a small particle half this size or smaller, and flour. In this formulation, approximately 25 kg of binder pitch would be used for each 100 kg of coke.

Although binder levels increase as particle size is reduced, and they are greatest in all-flour mixes where surface area is very high, the principle of minimum binder level still applies. The application of particle packing theory to achieve minimum binder level in all-flour mixes is somewhat more complex because of the continuous gradation in sizes encountered (3).

For some carbon and graphite grades, particle packing and minimum pitch level concepts are not used in arriving at a suitable mix design. For relatively small products, eg, where large dimensional changes can be tolerated during the baking and graphitizing operations, high binder levels are often used. Increased pitch content results in greater shrinkage which gives rise to high density and strength in the finished products.

Mixing. Once the raw materials have been crushed, sized, and stored in charging bins and the desired proportions established, the manufacturing process begins with the mixing operation. The purpose of mixing is to blend the coke filler materials and to melt and distribute the pitch binder over the surfaces of the filler grains. The intergranular bond ultimately determines the property levels and structural integrity of the graphite. Thus the more uniform the binder distribution is throughout the filler components, the greater the likelihood for a structurally sound product.

The degree to which mixing uniformity is accomplished depends on factors such as time, temperature, and batch size. However, a primary consideration in achieving mix uniformity is mix design. A number of mechanically agitated, indirectly-heated mixer types are available for this purpose (4–5). Each mixer type operates with a different mixing action and intensity. Ideally, the mixer best suited for a particular mix composition is one that introduces the most work per unit weight of mix without particle breakdown. In practice, only a few mixer types are used in graphite manufacture.

The cylinder mixer is commonly used for coarse-grained mixes. It is equipped with an axial rotating shaft fitted with several radial arms where paddles are attached. The intensity of this mixer is relatively low to avoid particle breakdown, and long mixing times, such as 90 min, are therefore needed to complete the mixing operation. With fine-grained compositions, more intensive mixers may be used with a corresponding reduction in mixing time. Bread or sigma-blade mixers and the high intensity twin-screw mixers of the Werner-Pfleiderer and Banbury variety are examples of the equipment that can be used on fine-grained compositions. For both mixers, temperatures at the time of discharge are 160–170°C.

Following the mixing operation, the hot mix must be cooled to a temperature slightly above the softening point of the binder pitch. Thus the mix achieves the proper rheological consistency for the forming operation and the formed article is able to maintain its shape better as it cools to room temperature. At the end of the cooling cycle, which typically requires 15–30 min, the mix is at 100–110°C and is ready to be charged into an extrusion press or mold.

Forming. One purpose of the forming operation is to compress the mix into a dense mass so that pitch-coated filler particles and flour are in intimate contact. For most applications, a primary goal in the production of graphite is to maximize density; this goal begins by minimizing void volume in the formed (green) product. Another purpose of the forming step is to produce a shape and size as near that of the finished product as possible. This reduces raw material usage and cost of processing graphite that cannot be sold to the customer and must be removed by machining prior to shipment.

The two important methods of forming are extrusion and molding.

Extrusion. The extrusion process is used to form most carbon and graphite products. In essence, the various extrusion presses comprise a removable die attached by means of an adapter to a hollow cylinder, called a mud chamber. This cylinder is charged with mix that is extruded in a number of ways depending on the press design. For one type of press, the cooled mix is introduced into the mud chamber in the form of plugs which are molded in a separate operation. A second type of extruder, called a tilting press, makes use of a movable mud chamber–die assembly to eliminate the need for precompacting the cooled mix. Loading occurs directly from coolers with the assembly in the vertical position; the mixture is extruded with the assembly in the horizontal position. A third type of extrusion press makes use of an auger to force mix through the die. This press is used principally with fine-grained mixes because of its tendency to break down large particles.

The basic steps in the extrusion operation when a tilting press is used are depicted in Figure 2. The cooled mix is usually fed to the press on a conveyor belt where it is discharged into the mud chamber in the vertical position. A ram descends on the filled chamber, tamping the mix to compact the charge. A closing plate located in the pit beneath the press is often used to seal off the die opening thereby preventing the mix from extruding during the application of high tamping pressures. The filling and tamping procedures are repeated until the mud chamber is filled with tamped mix and then rotated back to the horizontal position. The extrusion ram then enters the mud cylinder forcing the mix through the die at 7–15 MPa (69–148 atm). A guillotine-like knife located near the die outlet cuts the extruded stock to the desired length. Round products are rolled into a tank of water where the outer portions are quickly cooled to prevent distortion of the plastic mass. Products having large rectangular cross sections may be transferred from the press to the cooling tank by means of an overhead crane. Water temperatures are regulated to avoid cracking as a result of too rapid cooling. Products with smaller cross sections, such as the $3.2 \times 15.2 \times 81$ cm plates used as anodes in chlorine cells, may be cooled in air on steel tables. Bulk densities of green products range typically from 1.75–1.80 g/cm^3.

The anisotropy, usually observed in graphite products, is established in the forming operation. In extruded products, the anisotropic coke particles orient with

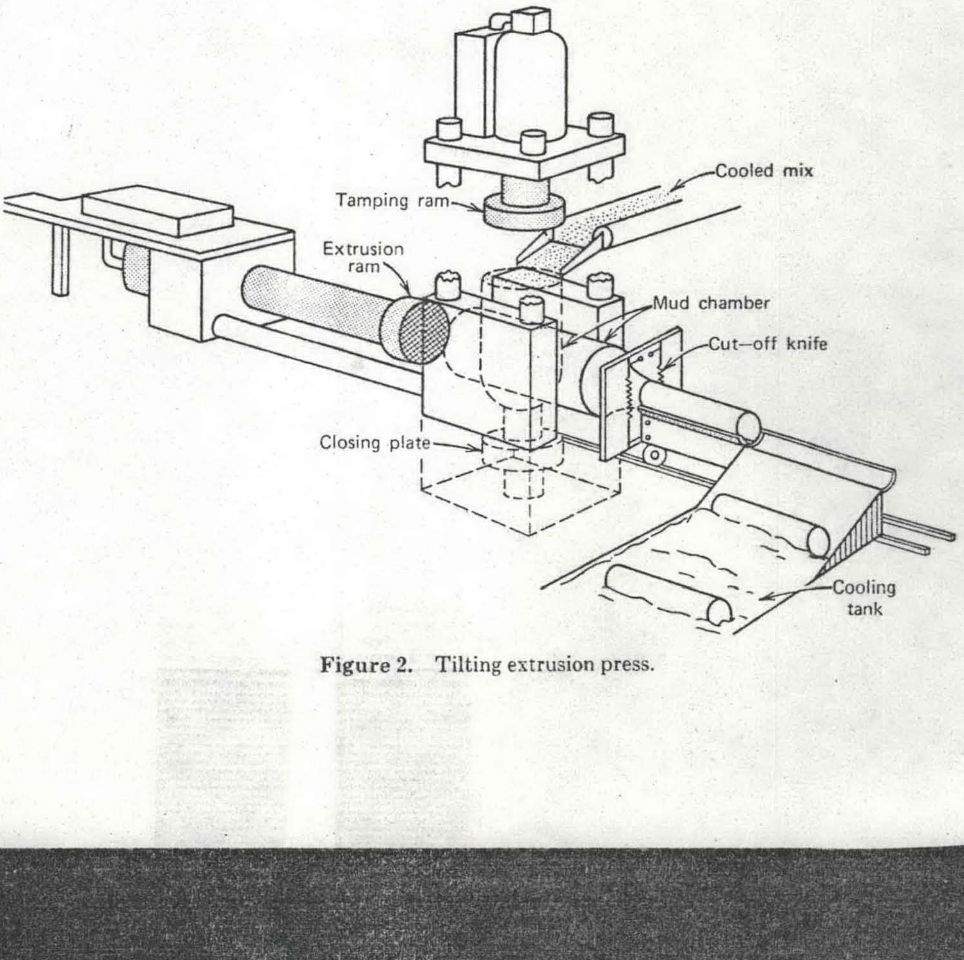

Figure 2. Tilting extrusion press.

their long dimensions parallel to the extrusion direction. The layer planes of the graphite crystals are predominantly parallel to the long dimension of the coke particle. Accordingly, the highly anisotropic properties of the single crystal are translated, to a greater or lesser degree depending on several factors, to the graphite product. The most important of these factors are coke type, particle size, and the ratio of die-to-mud chamber diameters. The more needlelike the coke particle, the greater the difference is between properties with-grain (parallel to the extrusion direction) and cross-grain. The use of smaller particles in the mix design also increases this property difference; the presence of large particles interferes with the alignment process. As the ratio of mud cylinder to die diameter increases, the with-grain to cross-grain ratios of strength and conductivity increase, while the with-grain to cross-grain ratios of resistivity and expansion coefficient decrease. Thus anisotropy is increased for the same coke type and mix design when going from a 0.60 m dia die to a 0.40 m dia die on the same extrusion press. As a result of particle orientation in extruded graphitized products, strength, Young's modulus, and thermal conductivity values are greater, whereas electrical resistivity and coefficient of thermal expansion are smaller in the with-grain direction than in the two cross-grain directions.

Molding. Molding is the older of the two forming methods and is used to form products ranging in size from brushes for motors and generators to billets as large as 1.75 m dia by 1.9 m in length for use in specialty applications.

Several press types are used in molding carbon products. The presses may be single-acting or double-acting, depending on whether one or both platens move to apply pressure to the mix through punched holes in either end of the mold. The use of single-acting presses is reserved for products whose thicknesses are small compared with their cross-sections. As thickness increases, the acting pressure on the mix diminishes with distance from the punch because of frictional losses along the mold wall. Acceptable thicknesses of molded products can be increased by using double-acting presses which apply pressures equally at the top and bottom of the product.

Jar molding is another method used to increase the length of the molded piece and keep nonuniformity within acceptable limits. By this technique the heated mold is vibrated as the hot mix is introduced, thus compacting the mix during the charging operation. Pieces as large as 2.5 m in diameter and 1.8 m in length have been molded in this way; the green densities are comparable with those obtained in extruded materials.

Smaller products, such as brushes and seal rings, are often molded at room temperature from mix that is milled after cooling. When binder levels exceed approximately 30% of the mix, the compacted milled mix has sufficient green strength to facilitate handling in preparation for the baking operation.

In a typical hot-molding operation to form a 1.7 m dia billet 1.3 m long, approximately 7200 kg of mix at 160°C is introduced into a steam-heated mold without cooling. The platens of the press compact the mix at ca 5 MPa (ca 50 atm), holding this pressure for 15–30 min. The cooling step for pieces of this size is the most critical part of the forming operation. Owing to the low thermal conductivity of pitch, 0.13 W/(m·K) (6), and its relatively high expansion coefficient (4.5×10^{-4}/°C at 25–200°C) (7), stresses build rapidly as the outer portions of the piece solidify. If cooling is too rapid, internal cracks are formed which are not removed in subsequent processing steps. As a result, a cooling schedule is established for each product size and is carefully followed by circulating water of various temperatures through the mold for specified time periods.

When the outside of the piece has cooled sufficiently, it is stripped from the mold and the cooling operation continued by direct water spray for several hours. If cooling is stopped too soon, heat from the center of the piece warms the pitch binder to a plastic state, resulting in slumping and distortion. The cooled piece is usually stored indoors prior to baking in order to avoid extreme temperature changes which may result in temperature gradients and damage to the structure. Bulk density of the green billet is usually 1.65–1.70 g/cm^3.

As with extruded products, molded pieces have a preferred grain orientation. The coke particles are aligned with their long dimensions normal to the molding direction. Thus the molded product has two with-grain directions, and one cross-grain direction which coincides with the molding direction. Strength, modulus, and conductivity of molded graphites are higher in both with-grain directions, and expansion coefficient is higher in the cross-grain direction.

Isostatic molding is a forming technique used to orient the coke filler particles randomly, thereby imparting isotropic properties to the finished graphite. One approach to isostatic molding involves placing the mix or blend into a rubber container capable of withstanding relatively high molding temperatures. The container is evacuated, then sealed and placed in an autoclave which is closed and filled with heated oil. The oil is then pressurized to compact the mass which may then be processed in the usual way to obtain isotropic graphite.

Baking. The next stage is the baking operation during which the product is fired to 800–1000°C. One function of this step is to convert the thermoplastic pitch binder to solid coke. Another function of baking is to remove most of the shrinkage in the product associated with pyrolysis of the pitch binder at a slow heating rate. This procedure avoids cracking during subsequent graphitization where very fast firing rates are used. The conversion of pitch to coke is accompanied by marked physical and chemical changes in the binder phase, which if conducted too rapidly, can lead to serious quality deficiencies in the finished product. For this reason, baking is generally regarded as the most critical operation in the production of carbon and graphite.

Several studies discuss the kinetics of pitch pyrolysis and indicate, in detail, the weight loss and volatile evolution as functions of temperature (8–9). During this process weight losses of 30–40% occur, indicating that for every 500 kg of green product containing 20% pitch, 30–40 kg of gas must escape. In terms of gas volume, approximately 150 cm^3 of volatiles at standard conditions must be evolved per g of pitch binder during the baking operation. The product in the green state is virtually impermeable, and the development of a venting porosity early in the bake must be gradual to avoid a grossly porous or cracked structure. The generation of uniform structure during the bake is made more difficult by the poor thermal conductivity of pitch. Long firing times are usually needed to drive the heat into the center of the product which is necessary for pitch pyrolysis and shrinkage. If the heating rates exceed a value which is critical for the size and composition of the product, differential shrinkage leads to splitting scrap. Shrinkage during baking is of the order of 5% and increases with increasing pitch content. Added to these difficulties is the complete loss of mechanical strength experienced by the product in the 200–400°C range where the pitch binder is in a liquid state. To prevent slumping and distortion during this period, the stock must be packed in carefully sized coke or sand which provides the necessary support and is sufficiently permeable to vent the pitch volatiles.

A variety of baking furnaces are in use to provide the flexibility needed to bake a wide range of product sizes and to generate the best possible temperature control. One common baking facility is the pit furnace, so named because it is positioned totally or partially below ground level to facilitate improved insulation. In essence, the pit furnace is a box with ceramic brick walls containing ports or flues through which hot gases are circulated. Traditionally, natural gas has been the fuel used to fire pit furnaces; however, because of natural gas shortages, pit furnaces are being converted to use fuel oil (see Furnaces, fuel-fired).

Another common baking facility is the so-called ring furnace; one form of this is depicted in Figure 3. Two equal rows of pit furnaces are arranged in a rectangular ring. Ports in the furnace walls permit the heated gases from one furnace to pass to the next until the cooled gases are exhausted by a movable fan to a flue leading to a stack. A movable burner, in this case located above one furnace, fires it to a predetermined off-fire temperature. The firing time per furnace is 18–24 h. When the desired temperature has been reached, the burner is moved to the adjacent furnace which has been heated by gases from the most recently fired pit. At the same time, the fan is moved to a furnace that has just been packed. This process continues, with packing,

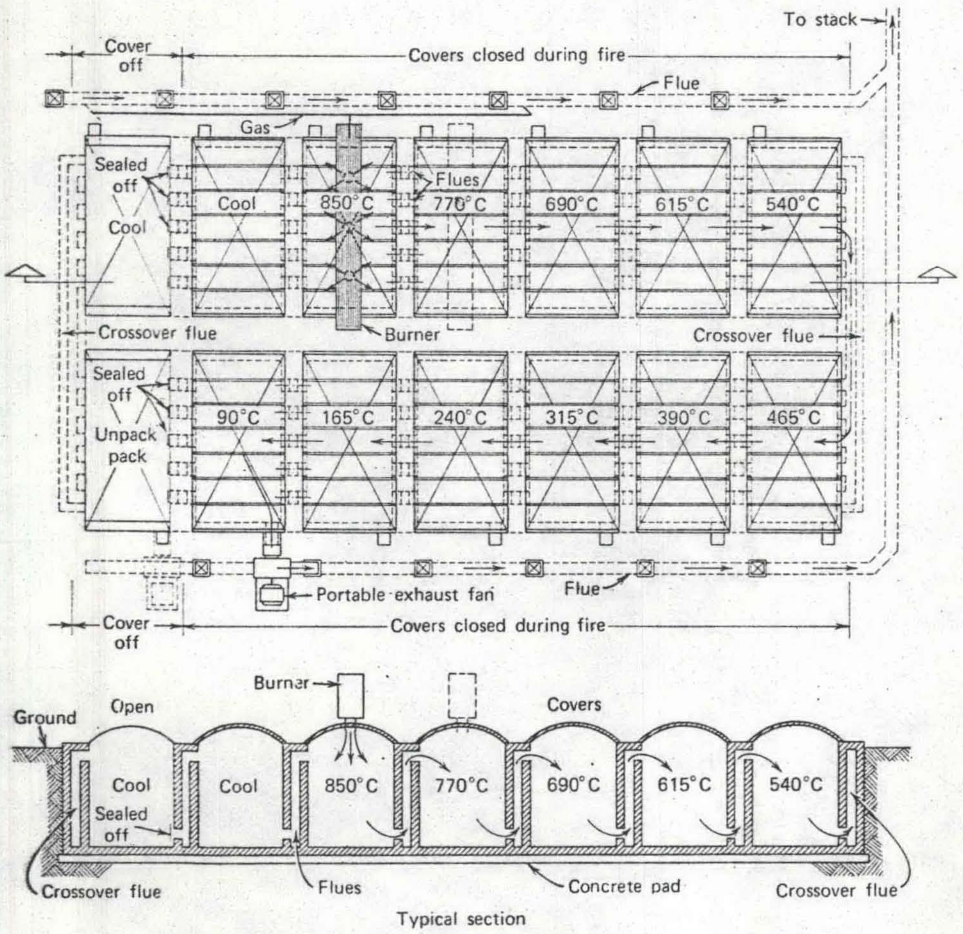

Figure 3. Ring furnace system.

unloading, and cooling stages separating the fan and the burner. Cycle times in this furnace are 3–4 wk. Thermally, the ring furnace is highly efficient but it has the disadvantage that very little control can be exercised over heating rates.

The firing schedules used in the baking operation vary with furnace type, product size, and binder content. A bulk furnace packed with 61 × 81 × 460 cm pieces of specialty graphite may require 6 wk to fire and an additional 3–4 wk to cool. In contrast, very small products, such as seal rings, may be baked in tunnel kilns in a few h. A sagger furnace containing electrodes may require 12–14 d to reach final temperature with an additional 3–5 d to cool. Firing rates early in the baking schedule are reduced to permit pitch volatiles to escape slowly, minimizing damage to the structure. For most carbon products, temperatures must be well below 400°C prior to unpacking to avoid cracking due to thermal shock. The product is scraped or sanded to remove adhering packing materials and is then weighed, measured, and inspected prior to being stored for subsequent processing. Some products that are sold in the baked state are machined at this stage. Baked products include submerged arc furnace electrodes, cathode blocks for the electrolytic production of aluminum, and blast furnace lining blocks.

Impregnation. In some applications the baked product is taken directly to the graphitizing facility for heat treatment to 3000°C. However, for many high performance applications of graphite, the properties of stock processed in this way are inadequate. The method used to improve those properties is impregnation with coal-tar or petroleum pitches. The function of the impregnation step is to deposit additional pitch coke in the open pores of the baked stock, thereby improving properties of the graphite product. Table 1 lists the graphite properties of unimpregnated and impregnated stock 15–30 cm dia and containing a 1.5 mm particle.

Further property improvements result from additional impregnation steps separated by rebaking operations. However, the gains realized diminish quickly, for the quantity of pitch picked up in each succeeding impregnation is approximately half of that in the preceding treatment. Many nuclear and aerospace graphites are multiply pitch-treated to achieve the greatest possible assurance of high performance.

Table 1. Effect of One Pitch Impregnation on Graphite Properties

Property		Unimpregnated	Impregnated
bulk density, g/cm³		1.6	1.7
	wg[b]	7.4	11.0
Young's modulus[a], GPa	ag[c]	4.4	6.3
	wg	10,000	17,000
flexural strength[a], kPa	ag	7,100	13,000
	wg	5,000	8,100
tensile strength[a], kPa	ag	4,400	7,300
	wg	21,000	34,000
compressive strength[a], kPa	ag	21,000	33,000
	wg	0.40	0.19
permeability, Darcys	ag	0.35	0.16
	wg	1.3	1.5
coefficient of thermal expansion, 10^{-6}/°C	ag	2.7	3.1
	wg	8.8	7.6
specific resistance, μΩ·m	ag	13	11

[a] To convert Pa to atm, divide by 101×10^3.

[b] With the grain.

[c] Across the grain.

During the baking operation, binder pitch exuding the product surface creates a dense impermeable skin. In addition, the exuding pitch causes packing material to adhere to the baked stock. The skin and the packing material must be removed by sanding, scraping, or machining before the stock can be impregnated on a reasonable time cycle. Unless this operation is properly performed, the impregnant may not reach the center of the product and a so-called dry core will result. When this condition exists, the product usually splits during graphitization as a consequence of the greater concentration of pitch and greater shrinkage in the outer portions of the stock. The likelihood of a dry core increases with the quinoline-insoluble solids content of the impregnant. During the impregnation process, the insolubles form a filter cake of low permeability on the stock surface, reducing the penetrability of the impregnant. Quinoline insolubles significantly greater than 5% reduce the penetration rate and increase the incidence of dry cores.

A schematic diagram of the pitch impregnation process is shown in Figure 4. Before it is placed in an autoclave, the skinned baked stock is preheated to 250–300°C to thoroughly dry it and to facilitate free flow of the molten impregnant into the open pores. The first step in the impregnation process is to evacuate the stock to pressures below 3.5 kPa (26 mm Hg) for a period of 1 h or more depending on the size and permeability of the stock. Unless the stock is adequately evacuated, the remaining air prevents thorough penetration of the impregnant to the center of the product. Heated pitch is then introduced by gravity flow into the autoclave from a holding tank until the charge is completely immersed. The system is then subjected to pressures of 700–1500 kPa (6.9–14.8 atm) for several hours to shorten the time for pitch penetration. When the pressure cycle has been completed, the pitch is blown back to the holding tank by means of compressed air. The autoclave is then opened, and the stock is transferred to a cooler where water and circulating air accelerate the cooling process. After cooling, the stock is weighed to determine the quantity of pitch picked up. If the pickup is below a specified limit, the stock is scrapped. Depending on the density of the baked stock, the pickup is 14–16% on the first impregnation and 7–8% on the second impregnation.

If the stock is to receive a second impregnation, it must be rebaked. In the past, stock containing raw impregnating pitch could be graphitized directly. However, the air polluting effect caused by this practice has made rebaking a necessary preliminary step to graphitization in order to meet the requirements of the EPA.

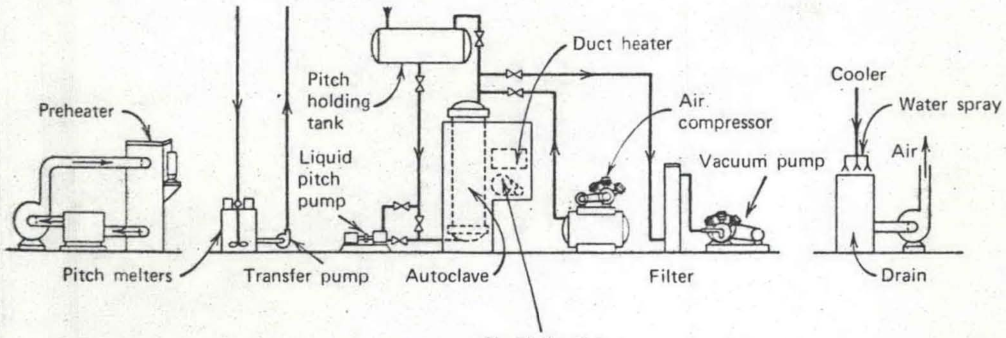

Figure 4. Pitch impregnation system.

Graphitization. Graphitization is an electrical heat treatment of the product to ca 3000°C. The purpose of this step is to cause the carbon atoms in the petroleum coke filler and pitch coke binder to orient into the graphite lattice configuration. This ordering process produces graphite with the intermetallic properties that make it useful in many applications.

Very early in the carbonization of coker feeds and pitch, the carbon atoms are present in distorted layers of condensed benzene ring systems formed by the polymerization of the aromatic hydrocarbons in these materials. The x-ray studies of raw coke, for example, show that two-dimensional order exists at that early stage of graphite development (10). As the temperature of coke increases, the stack height of the layer planes increases. The layers are skewed about an axis normal to them, however, and it is not until a temperature of ca 2200°C is reached that three-dimensional order is developed. As the graphitizing temperature is increased to 3000°C, the turbostratic (see pp. 690–691) arrangement of the layer planes is effectively eliminated, and the arrangement of the carbon atoms approaches that of the perfect graphite crystal. Depending on the size and orientation of these crystals, the properties of manufactured graphites can be varied controllably to suit a number of critical applications.

The furnace that made the graphite industry possible was invented in 1895 by Acheson (11) and is still in use today with only minor modifications. It is an electrically-fired furnace capable of heating tons of charge to temperatures approaching 3000°C. The basic elements of the Acheson furnace are shown in Figure 5. The furnace bed is made up of refractory tiles supported by concrete piers. The furnace ends are

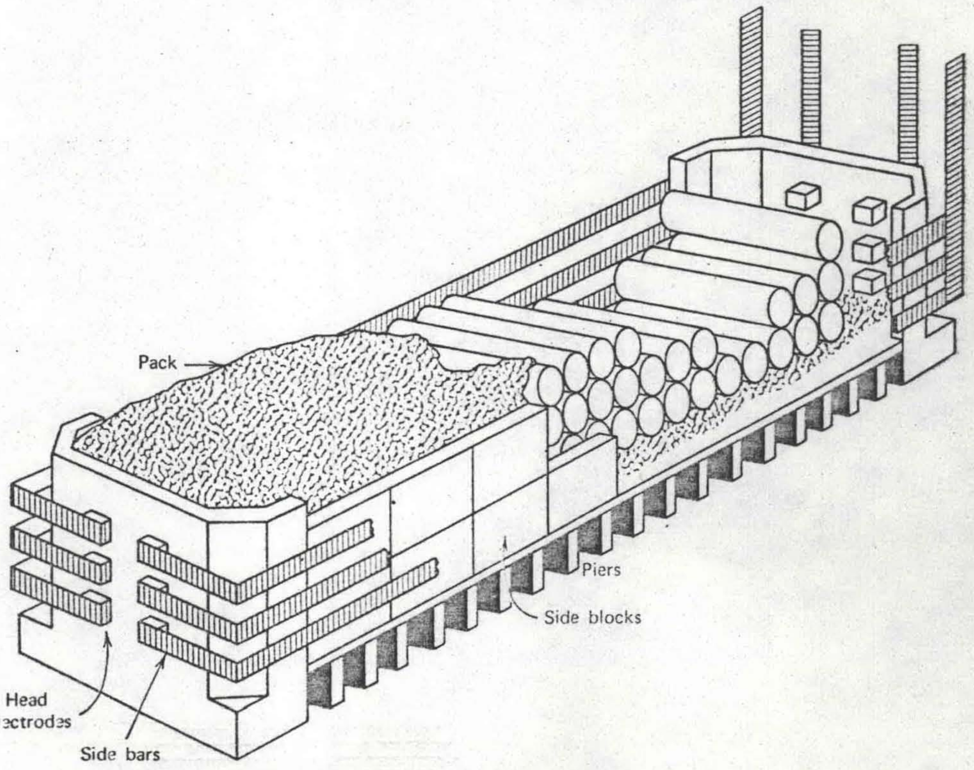

Figure 5. The Acheson furnace.

U-shaped concrete heads through which several graphite electrodes project into the pack. These electrodes, which are water-cooled during operation, are connected by copper bus work to the secondary of a transformer. The product is placed on a layer of metallurgical coke with its long axis transverse to current flow. Although a cylindrical product is shown in Figure 5, any product shape can be graphitized in the Acheson furnace so long as the product pieces are carefully spaced. This feature of the Acheson furnace makes it extremely versatile. The spacing between pieces may vary from less than a centimeter to several centimeters, depending on the shape and size of the product. With the product in place, a coarsely-sized metallurgical coke, called resistor pack, is used to fill the interstices between pieces; most of the heat needed to reach graphitizing temperatures is generated in the resistor material. Once the charge and resistor material are loaded, the furnace is covered with a finer blend of metallurgical coke, sand, and silicon carbide to provide thermal and electrical insulation. Concrete side blocks, usually 0.5–1 m from the charge ends, are used to retain the insulation. The procedure for loading a furnace usually requires one day.

Acheson furnace sizes may vary, depending on the product size and the production rate desired. Typically, the furnace may be 12–15 m by 3–3.5 m. Loads ranging from 35–55 metric tons of product are charged to these furnaces. The transformers used are rated 4000–6000 kW and are capable of delivering up to 60,000 A to the charge. Heating rates are usually 40–60°C/h, the total firing time being approximately three days. At the end of this time, the product temperatures are 2800–3000°C. Total power input varies, depending on the product and load size; for graphite electrodes, total power (energy) inputs average 4.5 kW·h/kg, and total power inputs in excess of 9 kW·h/kg may be used in the thermal purification of nuclear graphites. Following the heating cycle, 8–10 d are needed to cool and unload the furnace. The total cycle time on an Acheson furnace is ca two weeks. The cooling procedure is hastened by the gradual removal of pack with care to leave sufficient cover to prevent oxidation of the product. The insulation and resistor materials are screened to specified sizes and proportions for reuse, and new materials added as necessary. The product is cleaned and inspected prior to being measured and weighed for bulk density and resistivity determinations. If the properties are within specified limits, the product is stored and is ready for machining.

Furnaces other than the Acheson furnace are used commercially, but on a much smaller scale and usually for smaller products. For example, electrographitic brushes are graphitized in tube furnaces, wherein a current-carrying graphite tube is the heating element. These furnaces are particularly useful in the laboratory because of the ease with which they can be loaded and unloaded without the need for handling large quantities of packing material. Inductively-heated furnaces are also used commercially to graphitize a limited number of products, such as some aerospace grades and graphite fibers. These furnaces, also popular in the laboratory, consist basically of a cylindrical graphite shell susceptor positioned inside a water-cooled copper coil. High frequency power supplied to the coil induces current to flow in the susceptor, heating it and causing it to radiate heat to the contained charge (see Furnaces, electric).

More recently, several patents (12–15) have been issued describing a process for graphitization where the carbon charge to be heated is placed in a longitudinal array and covered with insulation to prevent heat losses and oxidation of the charge. An electric current is passed directly through the carbon array, generating within the carbon the heat required to raise the carbon to the graphitization temperatures. These patents describe reduced energy requirements and reductions in process time.

Puffing. In the temperature range of 1500–2000°C, most petroleum cokes undergo an irreversible volume increase known as puffing. This effect has been associated with thermal removal of sulfur from coke and increases with increasing sulfur content. Because of the recent emphasis on the use of low sulfur fuels, many of the sweet crudes that had been used as coker feeds are now being processed as fuels. Desulfurization of the sour crudes available for coking is possible but expensive. The result is an upward trend in the sulfur content of many petroleum cokes, leading to greater criticality in heating rate in the puffing temperature range during graphitization.

Many studies of the puffing phenomenon and of means for reducing or eliminating it have been made (16–18). As a general rule, puffing increases as particle size increases and is greater across the product grain. Depending on particle size and on the product size, heating rates must be adjusted in the puffing range to avoid splitting the product. Fortunately, the use of puffing inhibitors (discussed in the previous section) has eased the problem and has permitted the use of graphitization rates greater than would otherwise be possible.

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E. L. Piper
Union Carbide Corporation

PROPERTIES OF MANUFACTURED GRAPHITE

Physical Properties

The graphite crystal, the fundamental building block for manufactured graphite, is one of the most anisotropic bodies known. Properties of graphite single crystals illustrating this anisotropy are shown in Table 1 (1). Anisotropy is the direct result of the layered structure with extremely strong carbon–carbon bonds in the basal plane and weak bonds between planes. The anisotropy of the single crystal is carried over in the properties of commercial graphite, although not nearly to the same degree. By the selection of raw materials and processing conditions, graphites can be manufactured with a very wide range of properties and degree of anisotropy. The range of room temperature properties, attainable for various forms of graphite, is shown in Figures 1 and 2 (1). The range extremities represent special graphites having limited industrial utility, whereas the bulk of all manufactured graphites fall in the bracketed areas marked conventional.

The directional properties of graphite arise in the following way. When the coke aggregate is crushed and sized, the resulting coke particles tend to have one axis longer than the other two. As the plastic mix of particles and binder pitch is formed into the desired shape, the long axis of particles tends to align perpendicularly to the molding force in molded graphites and parallel to the extrusion force in extruded graphites. The particle alignment is preserved during the subsequent processing so that properties of the finished graphite have an axis of symmetry that is parallel to the forming force. Properties in the plane perpendicular to the axis of symmetry are essentially independent of direction. Samples cut parallel to the molding force for molded graphites or perpendicular to the extrusion force for extruded graphites are designated as cross-grain. Samples cut parallel to the molding plane of molded graphites or parallel to the extrusion axis for extruded graphites are designated as with-grain. A number of special test procedures for determining the properties of carbon and graphite have been adopted by ASTM (2).

Manufactured graphite is a composite of coke aggregate (filler particles), binder carbon, and pores. Most graphites have a porosity of 20–30%, although special graphites can be made that have porosity well outside this range. Manufactured graphite is a highly refractory material that has been thermally stabilized to as high as 3000°C. At atmospheric pressure, graphite has no melting point but sublimes at 3850°C, the triple point being approximately 3850°C and 12.2 MPa (120 atm) (3). The strength of graphite increases with temperature to 2200–2500°C; above 2200°C, graphite becomes

Table 1. Room Temperature Properties of Graphite Crystals[a]

Property	Value in basal plane	Value across basal plane
resistivity, Ω·m	40×10^{-4}	ca 6000×10^{-4}
elastic modulus[b], TPa	0.965	0.034
tensile strength (est)[b], TPa	0.096	0.034
thermal conductivity, W/(m·K)	ca 2000	10
thermal expansion, °C^{-1}	-0.5×10^{-6}	27×10^{-6}

[a] Ref. 1.

[b] To convert TPa to psi, multiply by 1.45×10^8.

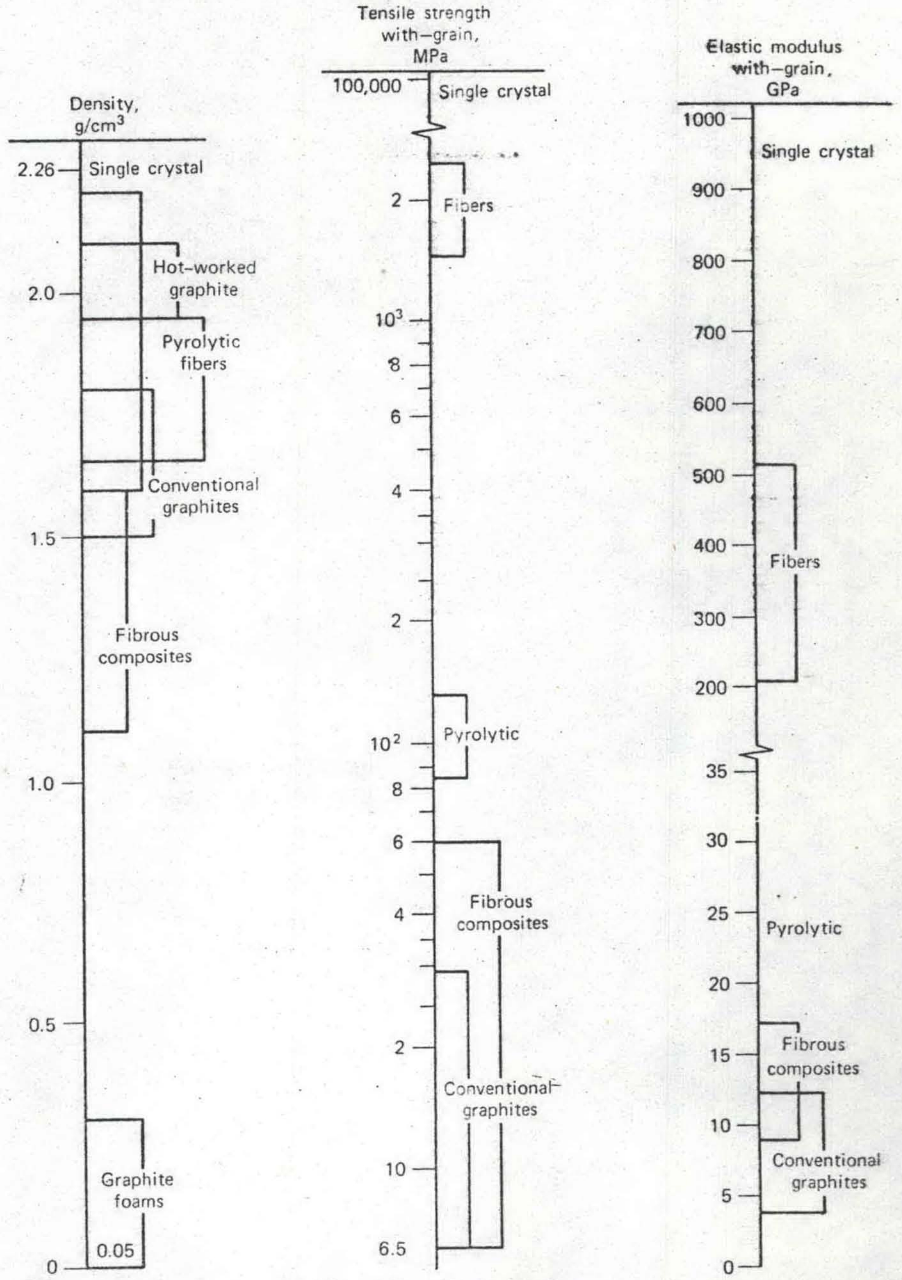

Figure 1. Mechanical properties of artificial graphite (1). To convert Pa to psi, multiply by 145 × 10^{-6}.

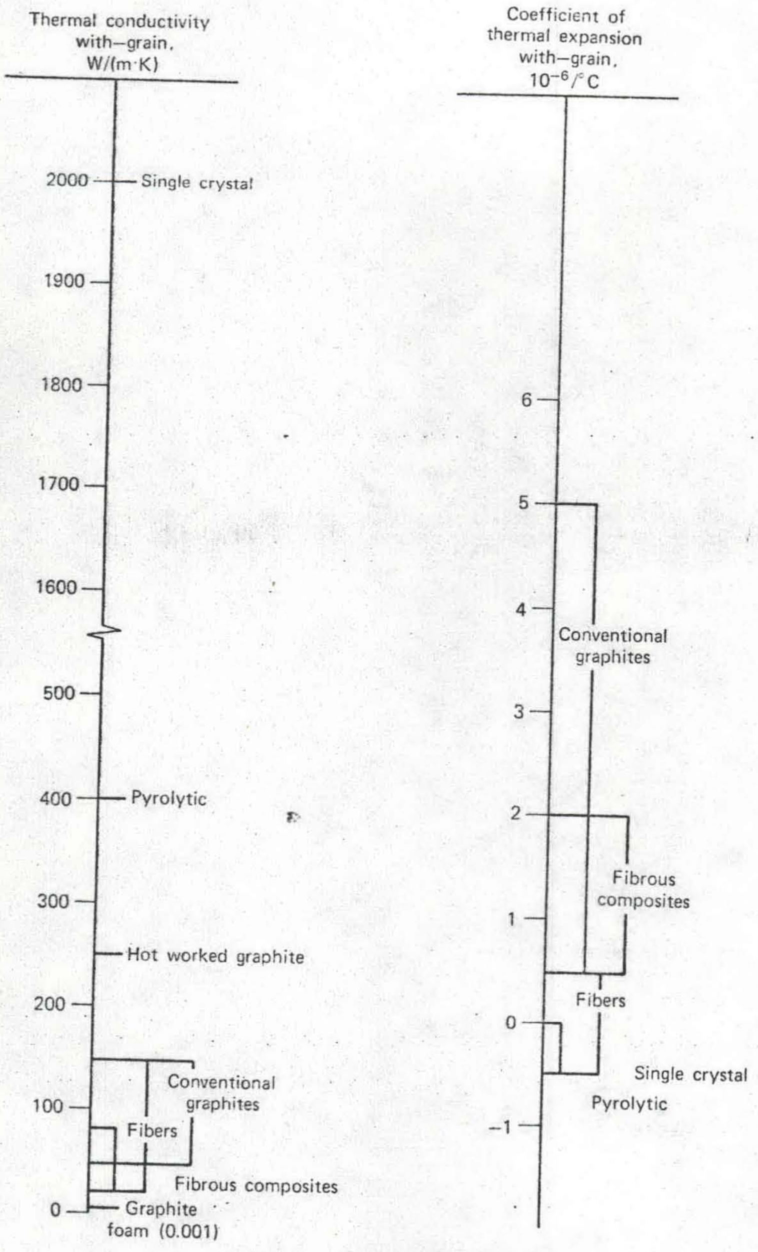

Figure 2. Thermal properties of artificial graphites (1).

plastic and exhibits viscoelastic creep under load (4). Graphite has high resistance to thermal shock, a property that makes it a valuable structural material at higher temperatures than most metals and alloys. For many applications of graphite, one or more of the following characteristics are important: density, elastic modulus, mechanical strength, electrical and thermal conductivity, and thermal expansion.

Electrical Properties. Manufactured graphite is semimetallic in character with the valence and conduction bands overlapping slightly (5–7). Conduction is by means of an approximately equal number of electrons and holes that move along the basal planes. The resistivity of single crystals as measured in the basal plane is approximately 4[illegible] Ω·m; this is several orders of magnitude lower than the resistivity across the layer planes (8–10). Thus the electrical conductivity of formed graphite is dominated by the conductivity in the basal plane of the crystallites and is dependent on size, degree of perfection, and orientation of crystallites and on the effective carbon–carbon linkages between crystallites. Manufactured graphite is strongly diamagnetic and exhibits a Hall effect, a Seebeck coefficient, and magnetoresistance. The green carbon body is practically nonconductive; however, heat treatment at 1000°C decreases the resistivity by several orders of magnitude, and thereafter resistivity decreases slowly. After graphitization to over 2500°C, the room temperature electrical resistivity may range from a few hundred to a few tenths Ω·m, depending upon the type of raw materials used. Graphites made from petroleum coke usually have a room temperature resistivity range of 5–15 Ω·cm and a negative temperature coefficient of resistance to about 500°C, above which it is positive. Graphites made from a carbon black base have a resistivity several times higher than those made from petroleum coke, and the temperature coefficient of resistance for the former remains negative to at least 1600°C.

Thermal Conductivity. Compared with other refractories, graphite has an unusually high thermal conductivity near room temperature (11); above room temperature, the conductivity decreases exponentially to approximately 1500°C and more slowly to 3000°C (12). With the grain the thermal conductivity of manufactured graphite is comparable with that of aluminum; against the grain it is comparable to that of brass. However, graphite is similar to a dielectric solid in that the principal mechanism for heat transfer is lattice vibrations. The electronic component of thermal conductivity is less than 1%. Graphite does not obey the Wiedemann-Franz Law; however, at room temperature the ratio of thermal and electrical conductivities is equal to approximately 0.126 when the thermal conductivity is in W/(m·K) and the electrical conductivity is in S(=1/Ω) (13–14). For most graphites, a value of thermal conductivity at room temperature accurate to ±5% can be obtained from the measured value of the electrical conductivity.

Coefficient of Thermal Expansion. The volumetric thermal expansion of manufactured graphite is anomalously low when compared to that of the graphite single crystal. At room temperature, the volume coefficient of thermal expansion of a single crystal is approximately $25 \times 10^{-6}/°C$ (15–16), whereas those of many manufactured graphites fall in the range of $4–8 \times 10^{-6}/°C$. There are exceptions, and some commercially available, very fine-grain, near-isotropic graphites have a volumetric expansion as high as two thirds the value for the single crystal. The low value of volume expansion of most manufactured graphite has been related to the microporosity within the coke particles. The microcracks within the coke particle accommodate the large c-axis expansion of graphite crystallites (17–19) and effectively neutralize it. The coefficient of thermal expansion (CTE) is somewhat sensitive to the filler particle sizing and to the method of processing, but the anisotropy and perfection degree of filler carbon particles largely determine the expansion characteristics of the finished graphite. Except for differences in absolute values, plots of the CTEs of manufactured graphite vs temperature are essentially parallel to each other, showing that the change in CTE with temperature is approximately the same for all graphites at high temperatures. The mean linear coefficient of thermal expansion between room temperature and any final temperature can be obtained by adding the value of CTE for the temperature interval 20–100°C to the appropriate factor which varies from 0 at 100°C to 2.52×10^{-6} at 2500°C (20). This method is valid for stock of any grain orientation.

Mechanical Properties. The hexagonal symmetry of a graphite crystal causes the elastic properties to be transversely isotropic in the layer plane; only five independent constants are necessary to define the complete set. The self-consistent set of elastic constants given in Table 2 has been measured in air at room temperature for highly ordered pyrolytic graphite (21). With the exception of c_{44}, these values are expected to be representative of those for the graphite single crystal. Low values of shear and cleavage strengths between the layer planes compared with very high C–C bond strength in the layer planes, suggest that graphite always fails through a shear or cleavage mechanism. However, the strength of manufactured graphite depends upon the effective network of C–C bonds across any stressed plane in the graphite body. Until these very strong bonds are broken, failure by shear or cleavage cannot take place. Porosity affects the strength of graphite by reducing the internal area over which stress is distributed and by creating local regions of high stress. Because of the complexity of the graphite structure, a simple analytical model of failure has not been derived (22). The stress–strain relation for bulk graphite is concave toward the strain axis. The relaxation of the stress leads to a small residual strain; repeated stressing to larger loads followed by gradual relaxation leads to a set of hysteresis loops contained within the stress–strain envelope (4,23–26). Each successive load causes an increase in the residual strain and results in a decreased modulus for the sample. The residual strain can be removed by annealing the sample to the graphitizing temperature after which its original stress–strain response is restored. In the limit of zero stress, the elastic modulus of graphite is the same in compression and tension, and is equal to the modulus derived from dynamic measurements (27). The modulus of graphite is weakly dependent upon temperature, increasing with temperature to approximately 2000°C and decreasing thereafter. The strain at rupture of most graphites is 0.1–0.2%; however, values of strain at rupture approaching 1.0% have been obtained for specially-processed, fine-grain graphites (28). Graphite exhibits measurable creep under load and at temperatures above 1600°C, but for most applications creep can be neglected below 2200°C. As the temperature is increased above 2500°C, the creep rate increases rapidly and the short-time strength decreases rapidly.

Thermal shock resistance is a primary attribute of graphite and a number of tests have been devised in attempts to establish a quantitative method of measurement (29–30). These tests, which establish very large thermal gradients in small specially shaped samples, continue to give only qualitative data and permit one to establish only the relative order of shock resistance of different graphites. A commonly used thermal shock index is the ratio of the thermal conductivity and strength product to the expansion coefficient and modulus product (31). At high temperatures, values of this index for graphite are higher than for any other refractory material. To show the range of property values of graphite, several properties for a very coarse grain graphite and a very fine grain graphite are given in Table 3 (27,32).

Table 2. Elastic Constants of Graphite[a]

$c_{11} = 1.06 \pm 0.002$	$s_{11} = 0.98 \pm 0.03$
$c_{12} = 0.18 \pm 0.02$	$s_{12} = 0.16 \pm 0.06$
$c_{13} = 0.015 \pm 0.005$	$s_{13} = 0.33 \pm 0.08$
$c_{33} = 0.0365 \pm 0.0010$	$s_{33} = 27.5 \pm 1.0$
$c_{44} = 0.00018 - 0.00035$	$s_{66} = 2.3 \pm 0.2$

[a] Units c_{ij} (stiffness constant) in TPa, s_{ij} (compliance constant) in $(\text{TPa})^{-1}$. To convert TPa to psi, multiply by 1.45×10^8.

Table 3. Properties of Fine and Coarse Grain Graphites[a]

Temperature, °C	Thermal cond, W/(m·K)		CTE[b], cm/cm ×10⁶/°C		Specific heat[c] kJ/(kg.K)	Tensile[d]				Compression[d]			
						Modulus, GPa		Strength, MPa		Modulus, GPa		Strength, MPa	
	wg	cg	wg	cg		wg	cg	wg	cg	wg	cg	wg	cg
Fine-grained graphite, 180 μm maximum grain size													
21.1	150	114	2.15	3.10	0.63	11.5	7.9	17.4	15.0	9.7	7.2	26.6	20.1
260	117	93	2.50	3.46	1.30	11.6	8.0	19.3	17.2	10.0	7.4	27.9	21.7
538	91	72	2.82	3.84	1.63	11.7	8.1	21.7	19.7	10.3	7.6	29.3	23.4
816	73	57	3.16	4.12	1.80	11.9	8.3	24.1	22.1	10.6	7.9	30.9	25.2
1093	60	46	3.45	4.45	1.95	12.1	8.6	26.0	24.3	11.4	8.3	32.4	26.9
1371	52	40	3.70	4.69	2.03	12.5	9.0	28.3	26.2	12.4	9.0	35.2	29.3
1649	46	35	3.95	4.91	2.11	13.2	9.6	29.9	27.9	13.4	9.7	38.1	31.6
1927	42	32	4.17	5.16	2.16	13.7	10.5	31.0	29.3	13.4	9.7	32.2	37.2
2204	40	29	4.35	5.39	2.18	11.5	8.4	31.7	30.1	12.1	9.0	37.9	32.6
2482	38	28	4.58	5.71	2.20	8.0	5.9	31.0	29.3	10.0	7.9	32.4	26.6
2760	36	28	4.83	6.04	2.20	5.2	4.3	26.9	24.8	7.9	6.2	26.6	19.1
Coarse-grained graphite, 6400 μm maximum grain size													
21.1	156	108	0.46	1.03		4.2	2.6	3.75	2.91	3.0	2.6	9.3	12.1
1371	30	22	2.4	3.2		5.8	2.9	5.34	4.54	3.4	2.8	12.0	14.7
1927	24	19	2.7	2.85		6.5	3.7	5.39	4.36	4.3	3.3	14.1	17.4
2427	24	20	3.0	4.2		5.6	3.0	7.32	5.17				

[a] wg = with-grain; cg = cross-grain.

[b] CTE = coefficient of thermal expansion.

[c] To convert J to cal, divide by 4.184.

[d] To convert Pa to psi, multiply by 145 × 10^{-6}.

Chemical Properties

The impurity (ash) content of all manufactured graphite is low, since most of the impurities originally present in raw materials are volatilized and diffuse from the graphite during graphitization. Ash contents vary from 1.5% for large diameter graphites to less than 10 ppm for purified graphites. Iron, vanadium, calcium, silicon, and sulfur are major impurities in graphite; traces of other elements are also present (33). Through selection of raw materials and processing conditions, the producer can control the impurity content of graphites to be used in critical applications. Because of its porosity and relatively large internal surface area, graphite contains chemically and physically adsorbed gases. Desorption takes place over a wide temperature range, but most of the gas can be removed by heating in a vacuum at approximately 2000°C.

Graphite reacts with oxygen to form CO_2 and CO, with metals to form carbides, with oxides to form metals and CO, and with many substances to form laminar compounds (34–35). Of these reactions, oxidation is the most important to the general use of graphite at high temperatures. Oxidation of graphite depends upon the nature of the carbon, the degree of graphitization, particle size, porosity, and impurities present (36). These conditions may vary widely among graphite grades. Graphite is less reactive at low temperatures than many metals; however, since the oxide is volatile, no protective oxide film is formed. The rate of oxidation is low enough to permit the effective use of graphite in oxidizing atmospheres at very high temperatures when a modest consumption can be tolerated. A formed graphite body alone will not support combustion. The differences in oxidation behavior of various types of graphite are greatest at the lowest temperatures, tending to disappear as the temperature increases. If an oxidation threshold is defined as the temperature at which graphite oxidizes at 1% per day, the threshold for pure graphite lies in the range of 520–560°C. Small amounts of catalyst, such as sodium, potassium, vanadium, or copper, reduce this threshold temperature for graphite by as much as 100°C but greatly increase the oxidation rate in the range of 400–800°C (33). Above 1200°C, the number of oxygen collisions with the graphite surface controls the oxidation reaction. Oxidation of graphite is also produced by steam and carbon dioxide; general purpose graphite has a temperature oxidation threshold of approximately 700°C in steam and 900°C in carbon dioxide. At very low concentrations of water and CO_2, there is also a catalytic effect of impurities on the oxidation behavior of graphite (37).

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J. T. MEERS
Union Carbide Corporation

APPLICATIONS OF BAKED AND GRAPHITIZED CARBON

Aerospace and Nuclear Reactor Applications

Graphite is an important material for aerospace and nuclear reactor applications because of a unique combination of thermal, chemical, and mechanical properties that enable its survival under the extremely hostile environments encountered.

Graphite is a lightweight structural material that retains good mechanical strength to extremely high temperatures and is readily machinable and commercially available. It also demonstrates good neutron interaction characteristics and stability under irradiation. The most troublesome problem is oxidation at high temperatures.

Aerospace and nuclear reactor applications of graphite demand both high reliability and reproducibility of properties, and physical integrity of the product. The manufacturing processes require significant additional quality assurance steps that result in high cost.

Aerospace. Graphite has long been employed in rocket nozzles, as wing leading edges, as nose cones, and as structural members for both ballistic and glider types of reentry vehicles (see Ablative materials). Graphite is unique in that it can be used both as a heat sink and as an ablation–sublimation material.

The erosion of graphite in nozzle applications is the result of both chemical and mechanical factors. Changes in temperature, pressure, or fuel-oxidizing ratio markedly affect erosion rates. Graphite properties affecting the erosion resistance include density, porosity, and pore size distribution.

The entrance cap, throat, and exit cone sections in a typical nozzle are frequently made or lined with conventional bulk graphite, especially in small nozzles because a small change in dimension causes a relatively large change in performance. In other designs, the throat may be made of conventional graphite with the entrance cap and exit cone molded of carbon or graphite fibrous materials that serve as reinforcement in conjunction with high-temperature plastic resins. In larger nozzles, all three sections might be made of fibrous, reinforced material owing to the ease of construction as well as the entire assembly being lighter in weight.

Nose cones and wing leading-edge components fabricated of graphite are used on both ballistic and glider types of reentry vehicles. Ballistic missiles are subjected to short-duration and extremely severe friction heating and oxidizing conditions when reentering the atmosphere, whereas glider-type reentry vehicles are exposed to less severe conditions for longer periods. Design technology has overcome any adverse effects of high anisotropy relative to thermal stress.

Nuclear Reactors. Manufactured graphite is the most extensively used material for moderator and reflector materials in thermal reactors. Since its use in the first reactor, CP-1, constructed in 1942 at Stagg Field, University of Chicago, many thousands of metric tons of graphite have been used for this purpose. Recently, great interest has been shown in the use of graphite as a construction material in the High-Temperature Gas-Cooled Reactor (HTGR) system.

Graphite is chosen for use in nuclear reactors because it is the most readily available material with good moderating properties and a low neutron capture cross section. Other features that make its use widespread are its low cost, stability at elevated temperatures in atmospheres free of oxygen and water vapor, and its good heat transfer characteristics, good mechanical and structural properties, and excellent machinability.

Neutron economy in graphite occurs since pure graphite has a neutron capture cross section of only $0.0032 \pm 0.0002 \times 10^{-24}$ cm^2. Taking into account the density of reactor grade graphite (bulk density 1.71 g/cm^3), the bulk neutron absorption coefficient is 0.0003/cm. Thus a slow neutron may travel >32 m in graphite without capture.

The purity of reactor-grade graphite is controlled by raw material selection and subsequent processing and purification. Although high temperature purification is most commonly used, some moderator applications require considerably higher purity levels. This objective is accomplished by halogen purification to remove extremely stable carbides, especially of boron, as volatile halides. The actual purity requirements are determined by the reactor design.

The major effect of high temperature radiation (1) over a long period of time is to produce dimensional changes in the graphite involved. When graphite initially contracts upon exposure to fast neutron doses, the rate of contraction decreases with exposure until it reaches a minimum volume; further exposure causes volume expansion, with the rate of expansion increasing rapidly at neutron doses above 3×10^{22} neutrons/cm^2 (>50 keV) in all bulk graphite tested to date. This behavior is caused by atomic displacements that take place when graphite is exposed to fast neutrons, resulting in anisotropic crystallite growth rates. The crystal expands in the c-axis direction and contracts in the a-axis directions (see page 691). The bulk dimensional change depends upon the geometrical summation of the individual crystallite changes and, hence, is dependent upon the starting materials and the method of fabrication. The extent of radiation damage is also strongly dependent upon the temperature of the graphite during irradiation. The severity of graphite radiation damage at high temperatures was underestimated since the magnitude of this temperature dependence was not recognized until about 1965.

Figure 1 shows the volume change in a conventional nuclear graphite during irradiations at various temperatures of relatively high fluxes. Figure 2 shows the length change in an isotropic nuclear graphite during irradiations at various temperatures at relatively high fluxes. The actual changes in dimensions are, of course, different from grade to grade and depend largely on the degree of anisotropy present in the graphite (1).

Table 1 (2) lists some useful properties of several graphites used for moderators or reflectors in nuclear reactors.

Reactor designers have taken advantage of graphite's properties in applying the material to other than moderator and reflector components, usually in conjunction with some other material.

Combined as an admixture with some forms of boron or other high-neutron-absorbing elements, graphite offers advantages as a neutron shield, control rod, or secondary shutdown material of high temperature stability, without danger of meltdown. In fast reactors, where high-energy neutrons reach the shield region, the presence of carbon atoms slows these neutrons down to energy levels where the probability of capture in the neutron absorber greatly increases. Graphite also serves as a stable matrix for the neutron absorber because it is able to withstand neutron and localized alpha recoil damage, offering protection against gross shield degradation.

Bulk graphites are also used in the HGTR concept to support and surround the active fuel core. These components tend to be large, complex-shaped blocks and have been produced from commercial grades of molded graphites.

In combination with compounds of uranium or thorium, graphite offers advantages as a matrix for fissile or fertile reactor fuel in thermal reactors. In this instance, the graphite serves a dual purpose, as a moderator and as a stable disbursing phase for fuel. Its stability under irradiation and at high temperature aids in minimizing fuel degradation and permits longer useful fuel life. Because of its excellent thermal properties and mechanical integrity, graphite offers an exceptional heat transfer medium for heat removal and also resists thermal shock.

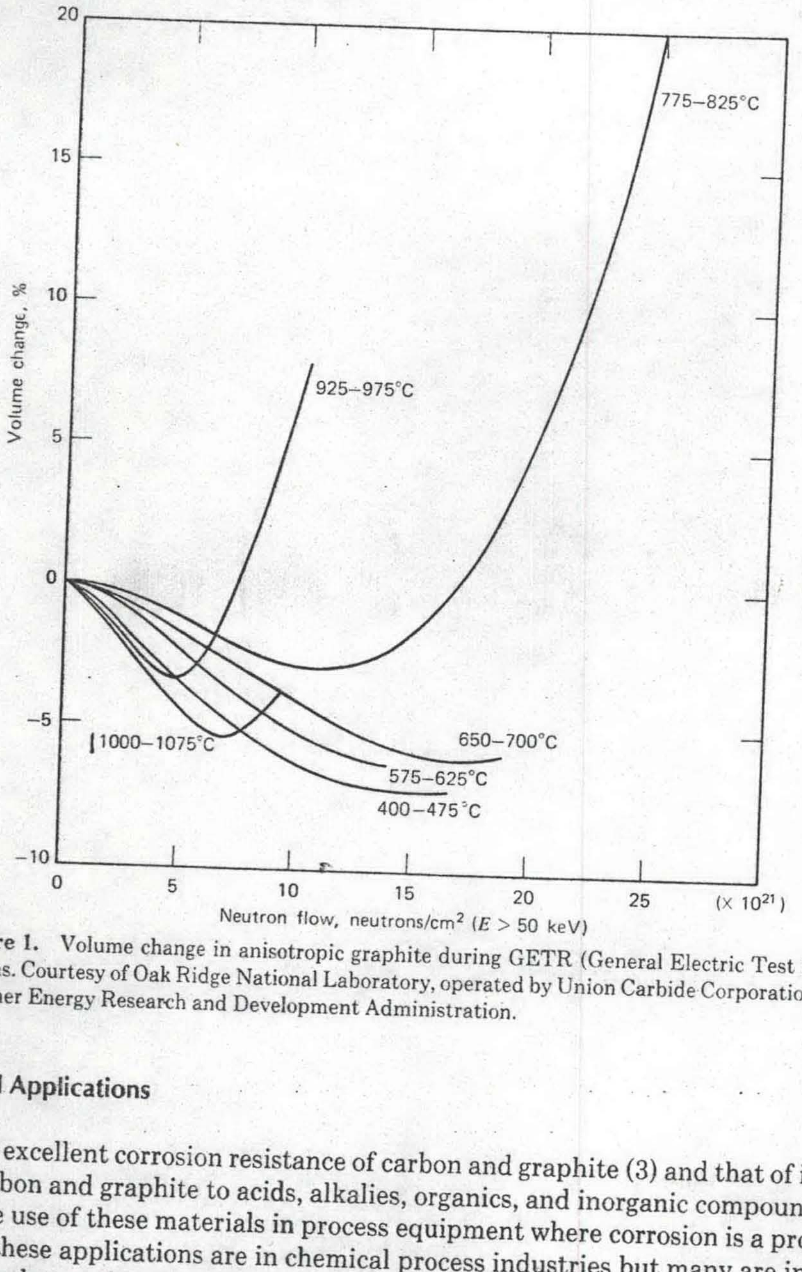

Figure 1. Volume change in anisotropic graphite during GETR (General Electric Test Reactor) irradiations. Courtesy of Oak Ridge National Laboratory, operated by Union Carbide Corporation for the DOE, former Energy Research and Development Administration.

Chemical Applications

The excellent corrosion resistance of carbon and graphite (3) and that of impervious carbon and graphite to acids, alkalies, organics, and inorganic compounds has led to the use of these materials in process equipment where corrosion is a problem. Most of these applications are in chemical process industries but many are in steel, food, petroleum, pharmaceutical, and metal finishing industries.

Other properties, such as the high thermal conductivity of graphite, excellent high temperature stability, and immunity to thermal shock, make these materials useful in applications involving combinations of heat and corrosion, such as heat exchange and high-temperature gas-spray cooling.

Carbon and graphite exhibit varying degrees of porosity, depending on grade, and equipment fabricated of these materials must be operated essentially at atmospheric pressure; otherwise, some degree of leakage must be tolerated. A good example is the carbon brick used to line tanks and vessels handling acids such as hydrofluoric,

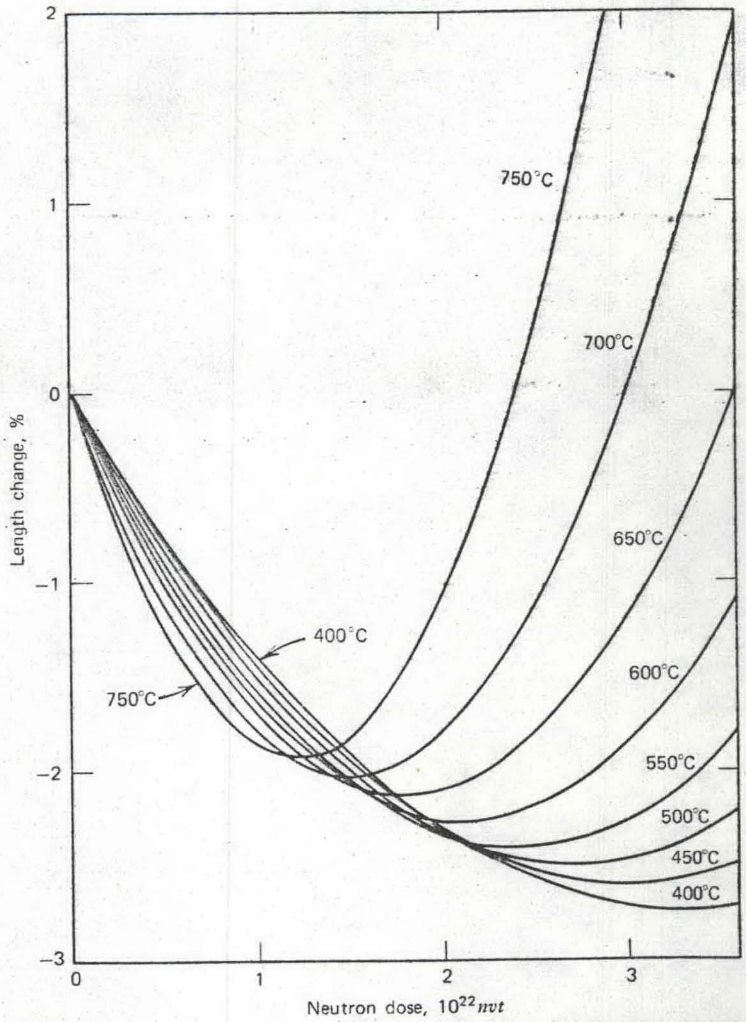

Figure 2. - Radiation induced dimensional changes in isotropic graphite at various temperatures. *nvt* = neutron (density) velocity time. Courtesy of Oak Ridge National Laboratory, operated by Union Carbide Corporation for the DOE, former Energy Research and Development Administration.

nitric–hydrofluoric, phosphoric, sulfuric, and hydrochloric (3). An impervious backing membrane of lead (4), elastomer, or plastic stops the seepage through the brick lining at the outside of the brick. These membrane materials, by themselves, may not withstand the corrosive and temperature conditions in the vessel; however, as a membrane behind the carbon lining, they are protected from adverse temperature and abrasion effects. Carbon linings have provided indefinite life with a minimum of maintenance.

Self-Supporting Structures. Self-supporting structures of carbon and graphite are used in a variety of ways. Water-cooled graphite towers serve as chambers for the burning of phosphorus in air or hydrogen in chlorine. The high thermal conductivity of graphite allows rapid heat transfer to the water film, thus maintaining inside wall temperatures below the graphite threshold oxidation temperature of ca 500°C.

Table 1. Properties of Nuclear Graphites[a]

Property	Anisotropic graphite	Isotropic graphite
density, g/cm^3	1.71	1.82
resistance, $\mu\Omega$-cm	735	1,000
tensile strength, kPa[b]	9,930	16,550
coefficient of thermal expansion (CTE), 10^{-6}/°C		
with grain	2.2	4.8
against grain	3.8	4.6
ansiotropy ratio (CTE ratio)	1.73	0.96
total ash, ppm	740	500
boron content, ppm	0.4	0.3

[a] Ref. 2.

[b] To convert kPa to psi, multiply by 0.145.

Phosphorus combustion chambers for the production of thermal phosphoric acid using cemented graphite block construction have been built 6 m in diameter and 11 m high (5). In other thermal phosphoric acid systems, cement–carbon block structures are used as spray-cooling, hydrating, and absorbing towers.

The immunity of graphite to thermal shock, its high temperature stability, and its corrosion resistance, permit its use for the fabrication of high temperature (800–1650°C), self-supporting reaction vessels such as those used in direct chlorination of metal and alkaline earth oxides. Cemented joints are vulnerable in the units, and it is necessary to machine the graphite components to close tolerances (±0.10 mm) to minimize the cement joint thickness. Graphite is easily machined on commercial metal-machining equipment.

Carbon Raschig-ring tower packing is available in sizes of 10–75 mm dia. Bubble-cap trays up to 3 m dia for hydrochloric–organic stripping towers and packing support structures up to 5.5 m dia for scrubbing towers in pulp and paper mill liquor recovery processes have been installed. Because none of these components requires complex machining or a high degree of imperviousness, carbon rather than graphite is often used in these applications because of its lower cost.

Impervious Graphite. For those applications where fluids under pressure must be retained, impregnated materials are available (3). Imperviousness is attained by blocking the pores of the graphite or carbon material with thermosetting resins such as phenolics, furans, and epoxies. Because the resin pickup is relatively small (usually 12–15 wt %), the physical properties exhibited by the original graphite or carbon material are retained. However, the flexural and compressive strengths are usually doubled. Graphite is also made impervious in a vacuum impregnation process.

Because carbon is difficult to machine, very little impervious carbon equipment is made. However, impervious graphite has been accepted as a standard material of construction by the chemical process industry for the fabrication of process equipment, such as heat exchangers, pumps, valves, towers, pipe, and fittings (6–7).

Many types of impervious graphite shell and tube, cascade, and immersion heat exchangers are in service throughout the world (8). The most common is the shell and tube design where an impervious graphite tube bundle with fixed and floating covers is employed in combination with a steel shell. Whenever parts must be joined, such as the tube to the tube sheet in a shell and tube heat exchanger, very thin resin cement joints are used. These resin cements have the same corrosion-resistant characteristics as the resins used to impregnate the graphite. Because of the high thermal conductivity of graphite, heat exchangers fabricated of impervious graphite have thermal efficiencies equal to metal heat exchangers of equivalent heat transfer area. Heat exchangers up to 1.8 m dia with areas up to 1300 m^2 are commercially available with operating pressures to 690 kPa (100 psi) and temperatures to 170°C (9–11).

Impervious graphite shell and tube heat exchangers are used in boiling, cooling, condensing, heating, interchanging, and cooling–condensing. Large units are used extensively for cooling–condensing wet sulfur dioxide gas in sulfuric acid production plants that burn sludge acid (4). The operation of six units was analyzed to compare actual operation with the calculated design using the Colburn-Hougen analogy; good agreement was reported (12).

These heat exchangers are also used for evaporation of phosphoric acid and rayon spin bath solution; cooling electrolytic copper cell liquor; heating pickle liquor used for descaling sheet steel; boiling, heating, cooling, and absorbing hydrochloric acid and hydrogen chloride; and in many heating and cooling applications involving chlorinated hydrocarbons and sulfuric acid.

Impervious graphite heat exchangers machined from solid blocks are also available (13–14). The solid block construction is less susceptible to damage by mechanical shock, such as steam and water hammer, than are shell and tube exchangers. Block exchangers are limited in size and cost from 50–100% more than shell and tube units on an equivalent area basis.

For in-tank heat exchange, a variety of immersion heat exchangers, such as plate, coil, and steam injection types, are available in impervious graphite. These units are highly efficient, and the heat transfer area required for most services can be easily determined from manufacturers' monographs.

Impervious graphite centrifugal pumps, pipe fittings, and valves were developed because most chemical processes require the movement of liquids.

Impervious graphite pipe and fittings of 25–635 mm ID are used to convey corrosive fluids.

Towers, entrainment separators, thermowells, and rupture disks are fabricated of impervious graphite material. Many equipment items are available from stock. Special equipment can be custom-designed and built, and both standard and special items can be integrated to handle a complete process step. Systems for the absorption of hydrogen chloride in water to produce hydrochloric acid use impervious graphite equipment throughout. Usually, absorption is done in a falling-film absorber (15), a special design adaption of the shell and tube heat exchanger. This approach to absorption of hydrogen chloride (16) was developed and expanded in the United States and is now accepted as the standard.

Stripping hydrogen chloride (13–19) from aqueous hydrochloric acid, and the subsequent production of anhydrous hydrogen chloride, can be efficiently and economically achieved with a series of impervious graphite shell and tube heat exchangers that operate as falling-film reboiler, water and brine-cooled condensers, and bottoms acid cooler. In plants with available chlorine and hydrogen, the production of hydrogen chloride in any form or concentration can be achieved in a system that combines the burning of hydrogen in chlorine in a water-cooled graphite combustion chamber; absorption is carried out in an impervious graphite falling-film absorber, and a train of impervious graphite exchangers is used for stripping and drying (20).

Low Permeability Graphite. Most resin-impregnated impervious graphite materials have a maximum operating temperature limit of 170°C because of resin breakdown above this temperature. Certain special grades with a temperature limitation of 200°C are on the market (21). The chemical industry has developed high temperature processes (370°C and above) where equipment corrosion is a serious problem. Graphite equipment could solve the corrosion problem, but complete fluid containment is usually needed. To meet this need, graphite manufacturers have developed low permeability graphite materials where permeability is reduced by deposition of carbon and graphite in the pores of the base material (21). This material is not limited in its operating temperature, except in oxidizing conditions, and it is used to fabricate high-temperature interchanger ejectors, fused salt cells, fused salt piping systems, and electric resistance heaters.

Several grades of carbon and graphite are commercially available. A controlled combination of high permeability and porosity characterizes these materials. Average pore diameters for typical grades are 0.03–0.12 mm with a total porosity of 48%. Porous graphite is manufactured by graphitizing the amorphous material.

Porous carbon and graphite are used in filtration of hydrogen fluoride streams, caustic solutions, and molten sodium cyanide; in diffusion of chlorine into molten aluminum to produce aluminum chloride; and in aeration of waste sulfite liquors from pulp and paper manufacture and sewage streams.

Electrical Applications

Arc Carbons. A current of electricity produces carbon arc light by leaping across a gap between two carbon electrodes. The typical arc light for visible radiation uses direct current which produces a relatively uniform ball of light across the crater of the positive electrode. The core of the positive electrode contains rare earth compounds to produce white light in the visible portion of the radiation spectrum.

The carbon arc can produce the highest useful brightness of any known artificial light source and provides a color quality matching that of sunlight. The size and shape of the carbon arc light source and the distribution of brilliancy bear an important relation to the optical problems involved in its use. The flat light source at the crater of the positive electrode produces a relatively even brilliancy distribution over a considerable portion of the area. This characteristic permits the light to be collected and directed with a simple reflector or lenses.

The carbon rods used in carbon arc lighting usually consist of two parts, the shell and the core. The shell forms the outer wall and has a central longitudinal hole throughout its length where the core is inserted. The core hole is formed during the extrusion process. The core is usually inserted into the shell after the shell is baked, or alternatively, the shell and core may be extruded simultaneously (22). The core contains, in addition to the conventional carbon filler–binder mix, small percentages of an arc-supporting material, such as potassium, and a flame material such as the metals of the cerium group. For some applications, the carbons are copper-plated to increase electrical conductivity.

Carbon arcs have been used for motion picture projection since the earliest days of the motion picture industry. Owing to the simplicity and reliability of the carbon arc system, thousands of carbon arc lamps are still in use after 20–30 yr. The quantity of light projected by the arc lamps is 10,000–50,000 lm. The amount of light depends on the carbon size and required brightness.

Projector carbon electrodes are manufactured in 7–13.6 mm dia. The diameter of the light ball at the positive crater is proportional to the carbon diameter. Carbon diameters are selected so that the light image at the projector aperture has a side to center brightness of at least 80%.

Peak crater brightness of the d-c high-intensity arc is near 1.8 ncd/m^2. The luminous efficiency is on the order of 25–35 lm/W. Color temperature of the carbon arc light is ca 4000–7000 K, and is dependent on the composition of the core of the positive electrode.

Carbon arc lighting is also used for spotlighting, for searchlights, and in the graphic arts industry for photoengraving, photolithography, and other mechanical reproduction processes. The light sensitized materials, such as dichromates, used for transferring the photographic negative image for subsequent graphic arts operations are affected by radiation in the 0.3–0.5 μm range. Carbon electrodes are specially designed to give a high spectral response in this spectral range.

Light from the carbon arc is used to simulate outdoor exposure for measuring the relative lightfastness, fading, and deterioration of materials such as clothing, paint, plastics, etc. Materials can be tested under precisely controlled conditions which may be repeated often (23–24).

Simulation of the solar radiation in space, by means of the carbon arc, is used for environmental testing of space vehicles, missiles, and their components (25).

Brushes for Motors, Generators, and Slip Rings. Electric motors and generators employ carbon and graphite brushes to maintain electrical contact between an external circuit and the windings of the machine's rotating element. Brushes have several functions, each being essential to the satisfactory operation of the particular machine (26). The brushes must provide electrical contact: they must be good conductors of electricity. The brushes must maintain firm mechanical contact with the rapidly revolving surface of the commutator and function as a bearing material, and they must control the currents resulting from commutation (27). These functions must be fulfilled without destructive sparking, serious commutator wear, or excessive electrical or frictional losses. The brushes must also maintain a smooth commutator surface and a commutator film of suitable characteristics. Only carbon and graphites are capable of meeting all these requirements.

The brushes currently manufactured may be classified into four general types: electrographitic, carbon–graphite, resin-bonded graphite, and metal–graphite. Electrographitic brushes are generally made from calcined blacks and coal-tar pitch. These composites may be supplemented by the addition of graphites and other additives. Mixing and forming follow conventional carbon processing procedures. The final baking temperature approaches 3000°C. Electrographitic brushes have exceptionally good commutating properties and low friction coefficients; they are also efficient in high speed, high current density applications. Carbon–graphite brushes are made from calcined carbon black, calcined coke, graphite, or any combination of the three. They are more abrasive than electrographitic brushes and are generally adapted to lower speed and lower current density applications. Resin-bonded graphite brushes are made from graphite flours and polymeric resins. These brushes have high electrical resistance and are used in applications where very low current densities are required. Metal–graphite brushes can be classified into two general types: those where powdered metal and graphite are mixed and bonded mechanically or chemically and those where carbon–graphite base stock is impregnated with molten metal. Because of the lowered electrical resistance of metal–graphite brushes, they are usually used where high current carrying capacity is required. Table 2 lists typical physical properties of each type of brush.

The performance of brushes in terms of wear and commutation is dependent upon environmental, electrical, and mechanical aspects of each particular application. The environmental aspects which most affect the commutator surface film and consequent performance are temperature and atmosphere. In the absence of water vapor or oxygen, the brushes lose their self-lubricating quality and some impregnant is generally employed to make up for this deficiency. Performance is also dependent on the electrical design of the commutating machine: the location of the brushes with respect to the electrical neutrality of the field poles, the current density required by the application, and the number of commutator bars bridged by the brush face. The mechanical features that affect brush performance include commutator design, brush configuration, holder design, and wear of the moving parts on the commutating machine.

Spectroscopic Electrodes and Powders. Electrodes made of some form of carbon or graphite are employed extensively in optical emission spectrochemical analysis (28–35). The sample to be analyzed (in powder, solid, or liquid form) is excited by means of an electric arc at 5,000–8,000°C or by a spark source at 7,000–20,000°C between two electrodes. At these temperatures, most chemical compounds are dissociated and elements are excited. The chemical elements present are determined qualitatively, semiquantitatively, or quantitatively by measurements of the wavelength and intensity of spectral lines produced by such excitation and dispersed by a suitable optical device.

Graphite and carbon electrodes are used in spectrochemical analysis for several reasons: they are available in high purity grades at reasonable cost; graphite electrodes are easily machinable; they have a uniform structure; they have reasonable electrical and thermal properties; they emit few spectral lines or bands; they do not absorb appreciable moisture; they are chemically inert at room temperature and not wetted even at arc temperatures by most materials; they are porous; they produce an arc with a high excitation potential; they produce a chemically reducing atmosphere in the arc discharge; and they sublime rather than melt.

Graphite is the most universally employed material for spectroscopic electrodes because it is easier than carbon to machine into desired shapes and ship without breakage. Graphite electrodes are available in rods of different diameters and in a variety of preforms, whereas carbon is offered only in rod form. Spectroscopic electrodes are usually supplied in several grades of graphite and one grade of carbon. The graphite grades are of various densities and of different purity levels. The carbon grade is a low crystallinity, high purity material of moderate density. A given spectroscopic grade of graphite or carbon is determined by selection of raw materials and processing conditions.

High purity graphite and carbon powders are also used extensively in spectroscopic techniques as matrix material, either in powder form or as spectroscopic pellets. Graphite carries the sample into the arc thus eliminating excessively long burn times; in addition, fractional distillation of elements from the sample is reduced during exposure. Artificial or synthetic graphite has excellent mixing properties because its almost spherical particles flow more easily and can be transferred and mixed thoroughly with other powders. Natural graphite is specially suited for pelletizing applications because of its flat platelets or needles (depending on whether it is of the

Table 2. Typical Physical Properties of Brushes

Type	Resistivity, μΩ·m	Apparent density, g/cm^3	Scleroscope hardness	Flexural strength, MPa[a]	Current capacity, kA/m^2	Contact drop[b]	Coefficient of friction[b]	Abrasiveness[b]
electrographitic	10	1.72	35	14	93	*M*	*M*	*VL*
	63	1.43	60	34	124	*H*	*L*	*L*
carbon–graphite	20	1.80	40	25	62	*M*	*M*	*M*
resin-bonded	1400	1.60	9	6	47	*VH*	*L*	*VL*
graphite	13	1.90	30	31	101	*L*	*M*	*L*
metal–graphite	0.05	6.60	8	103	232	*VL*	*VL*	*VL*
	8	2.50	45	21	116	*L*	*M*	*M*

[a] To convert MPa to psi, multiply by 145.

[b]

	VL = very low	*L* = low	*M* = medium	*H* = high	*VH* = very high
contact drop, V	<0.05	ca 0.2	ca 0.4	ca 0.6	≥0.8
coefficient of friction	≤0.15	≤0.22	≤0.3	≥0.3	

Madagascar or Sri Lanka (Ceylon) type) which compress along their long slippage plane and cohere to a large contact area.

The areas where optical emission spectrochemical analysis and graphite or carbon spectroscopic products are employed are varied; they include: metallurgy, geology and prospecting, agriculture, wear, metal analysis, the petroleum industry, medicine, forensics, customs work, and astronomy (see Analytical methods).

The temperature of the electrode, the temperature distribution, and the processes occurring in the arc are of concern to the spectroscopist. Vaporization of the electrode material into the arc is a very complex mechanism affected by particle size, particle shape, particle bonding, the degree of crystallization, and other factors. It is possible to control these properties by manufacturing techniques. Selected raw materials are blended under special conditions to prevent contamination. The blend is extruded into rods and subsequently graphitized. From the graphitized rod stock, preformed electrodes are machined to specific dimensions with precision tools and then purified by a halogen gas process that removes the last traces of nearly all contaminants. After the purified electrodes are tested by means of a very sensitive cathode layer spectrographic technique to make sure they meet the purity requirements, they are packed in spectroscopically clean containers. Each step must be carefully executed and controlled to assure a consistent and uniform product, with a total impurity level of less than 6 ppm.

Miscellaneous Electrical Applications. Carbon and graphite can be processed to have the electrical, mechanical, chemical, and thermal properties required for many electrical and electronic applications. Graphite is an ideal electrode material for electrical discharging machining (EDM). Ultrafine grain, high strength grades that are readily machinable to complex shapes are used as electrodes in the EDM process. Fine-grain graphites are used as EDM electrodes in roughing applications where rapid metal removal and electrode cost are of primary concern (see Electrolytic machining methods).

Graphite is employed in a variety of electronic tube applications. The low inherent gas evolution of graphite makes it easily outgassed; it is pure, free from melting and distortion at high temperatures, and conforms closely in radiating characteristics to the theoretical black body (36). Graphite is used for many electronic tube applications (37). Combinations of the electrical and mechanical properties of carbon and graphite make these materials useful in such diverse applications as pantograph contacts and collector shoes, rheostat disks and plates, high-temperature furnace heating elements, telephone and microphone components, and lightning arrestor parts (27).

Electrode Applications

With the exception of carbon use in the manufacture of aluminum, the largest use of carbon and graphite is as electrodes in electric-arc furnaces. In general, the use of graphite electrodes is restricted to open-arc furnaces of the type used in steel production, whereas carbon electrodes are employed in submerged-arc furnaces used in phosphorus, ferroalloy, and calcium carbide production.

Graphite Electrodes. Graphite electrodes are commercially produced in many sizes ranging from 32 mm dia by 610 mm length to 700 mm dia by 2800 mm length. Such electrodes are used in open-arc furnaces for the manufacture of steel (38), iron and steel castings, brass, bronze, copper and its alloys, nickel and its alloys, fused cast refractories, and fused refractory grain. By far the largest use of graphite electrodes is in the manufacture of steel and, as a consequence, the growth of graphite production has been closely related to the growth in electric furnace steel production. A cutaway sketch of an open-arc furnace is shown in Figure 3. Steel is produced by filling the cylindrical shell with ferrous scrap, metallized iron ore, or occasionally, molten pig iron, then melting and refining the metallic charge with the heat derived from the electric arc generated at the tips of the electrodes.

Prior to the mid 1940s, the arc furnace was used almost exclusively for the production of low tonnage, high quality steels such as stainless and alloy steels. Since then its use has been extended to production of the more common high-tonnage steel grades (see Steel). Domestic growth of arc furnace steel production has been dramatic, rising

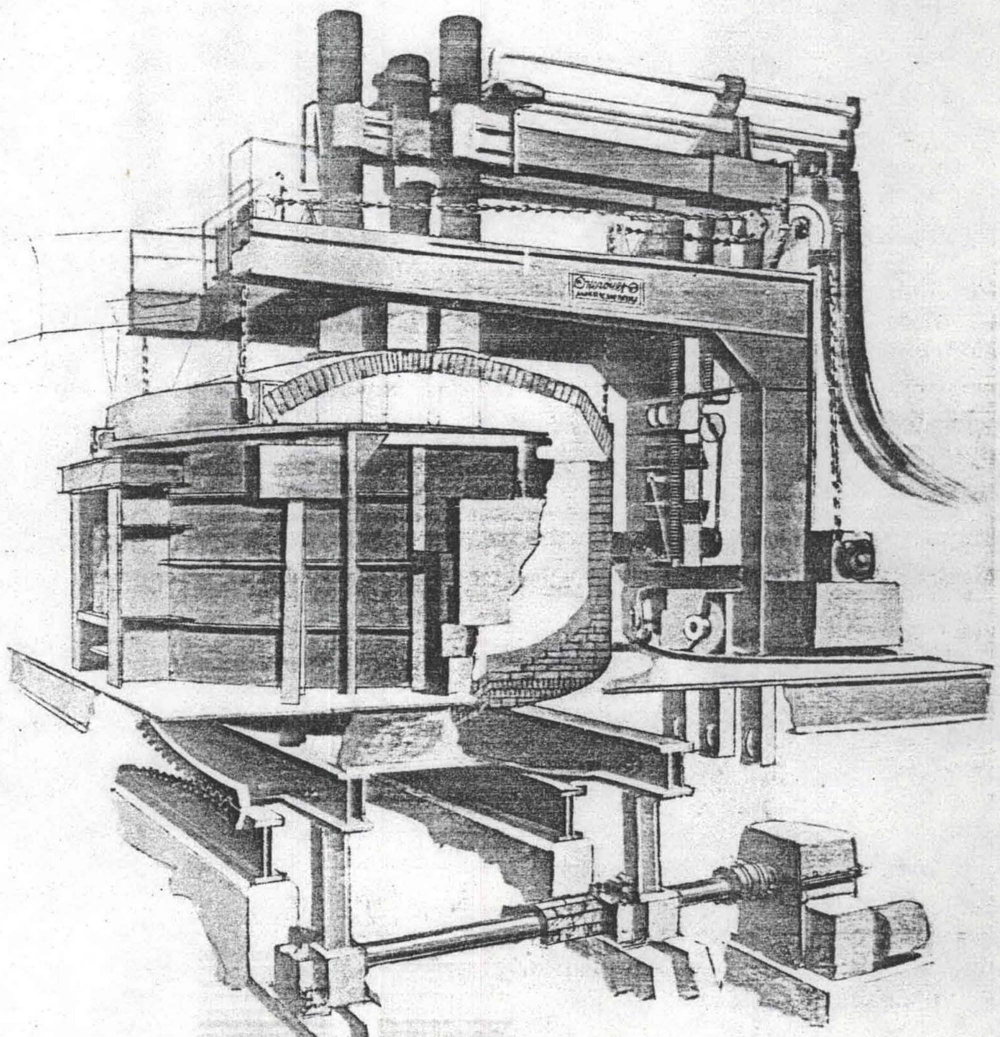

Figure 3. Overall sketch of an electric-arc furnace, cut away to show sections of bottom, sidewall, and roof. Courtesy of American Bridge Division, U.S. Steel Corporation.

from 6% of total domestic steel production in 1950 to 20% in 1975. Over 100 million metric tons of steel were produced in 1975 in electric-arc furnaces in the free world, approximately 20% of total world steel production (39), and these furnaces consumed over 600,000 metric tons of graphite electrodes.

Graphite electrodes are consumed in the melting process. For iron and steel production, the average consumption is ca 5–8 kg/t, depending upon the quality of charge material, the quality of electrodes, and numerous factors related to the operation of the furnace (22). Electrode consumption can be classified into three broad categories: tip consumption, sidewall consumption, and breakage. Roughly half of the observed consumption occurs at the electrode tip where the intensely hot and rapidly moving arc spot produces both vaporization of the graphite and some ejection of small graphite particles. In addition, the electrode tip is eroded by contact with the liquid metal and slag. The rate of incremental tip consumption generally increases when operating currents or power are increased. However, since increased current or power levels generally result in higher productivity, the electrode consumption when expressed in terms of kg/t of metal produced, may exhibit little or no increase. The periphery or sidewall of the hot electrode is slowly consumed by reaction with oxidizing atmospheres both inside and outside the furnace, resulting in a tapering of the electrode toward the arc tip. Sidewall consumption is time dependent and is greatest for low productivity furnaces (40). It is also increased by the use of many fume removal systems and by the use of oxygen in the furnace for assisting melting or refining. Since sidewall consumption may account for 40% or more of total electrode consumption, extensive efforts have been made to reduce this component of consumption through the use of oxidation retardants and electrode coatings. Such efforts have had little success to date, primarily because of the extreme thermal and chemical environment to which the electrode is exposed. A third form of consumption consists primarily of electrode breakage resulting from excessive movement of large masses of scrap during melting or the presence of nonconductors in the charge. Although such breakage usually accounts for less than 10% of net electrode consumption, excessive thermal shock, improper joining practice, and incorrect phase rotation can magnify this form of electrode consumption (41). Although attempts have been made to correlate electrode consumption with relatively small changes in electrode properties, it is apparent that charge quality and furnace operating practice exert a more profound influence on electrode performance. Most notable is the established inverse relationship between furnace productivity and electrode consumption (40).

Graphite electrodes are produced in two broad classifications, regular grade and premium grade. Typical properties of these grades are given in Table 3.

The major differences between the two grades are that the premium grade is made from needle-grade coke and is pitch-impregnated prior to graphitization. The premium grade electrode is used where very high performance is required, such as in the high current operation typical of ultrahigh-powered arc furnaces. The current carrying capacity of an electrode column depends on many characteristics of the furnace operation as well as the characteristics of the electrode and electrode joint. Over the years, significant progress has been achieved in improving the current carrying capacity of electrode columns. For example, the 510 mm dia electrode first introduced in 1938 was designed to carry 26,000 A; by 1961, this same size electrode carried ≤45,000 A and, by 1975, permitted >55,000 A. Such improvements stem primarily from improved raw materials and process technology advancements that are not fully reflected in changes in electrode properties (42).

Table 3. Typical Properties of Regular and Premium Grade Graphite Electrodes[a]

Property	Regular grade	Premium grade
bulk density, g/cm^3	1.58	1.68
resistivity, $\mu\Omega\cdot$m	7.7	6.0
flexural strength, kPa[b], wg	6900	10350
cg	5865	8300
elastic modulus, GPa[b], wg	6.2	7.6
cg	3.5	5.5
coefficient of thermal expansion (CTE), 10^{-6}/°C		
wg	0.8	0.9
cg	1.7	1.5
thermal conductivity W/(m·K), wg	134	168
cg	67	101
thermal shock parameter[c], wg	186×10^3	254×10^3
cg	66×10^3	102×10^3

[a] wg = with-grain; cg = cross-grain.

[b] To convert Pa to psi, multiply by 1.45×10^{-4}.

[c] $$\text{Thermal shock parameter} = \frac{\text{thermal conductivity} \times \text{strength}}{\text{CTE} \times \text{elastic modulus}}$$

In service, graphite electrodes operate at up to 2500 K and are subject to large thermal and mechanical stresses and extreme thermal shock. Graphite is unique in its ability to function in this extreme environment. The relatively low electrical resistance along the length of the electrode minimizes the power loss owing to resistance heating and helps keep the electrode temperature as low as possible. This characteristic is most important in ultrahigh-power furnaces. For such furnaces approximately 30% lower electrode resistivity of premium grade electrodes is usually essential. A high value of the thermal shock parameter is also important (see Table 3); this is enhanced by high strength and high thermal conductivity combined with low elastic modulus and low coefficient of thermal expansion.

The joints between electrodes are an extremely important part of the electrode system, both from the standpoint of resisting the mechanical forces of scrap caves and of carrying high current density without localized overheating (42a). Such joints should possess high strength, especially in flexure, and possess low electrical resistance. Careful assembly and proper torque are vital to good performance (41).

Carbon Electrodes. Carbon electrodes are used primarily in submerged-arc furnaces for the manufacture of ferroalloys, phosphorus, silicon metal, calcium carbide, pig iron, and fused refractory grain. There are two broad types of carbon electrodes. The self-baking Soderberg type consisting of carbon paste is used extensively in the production of calcium carbide and electric-furnace pig iron; and the prebaked electrode finds its major use in production of phosphorus, silicon metal, and several ferroalloys. Prebaked carbon electrodes are produced in sizes ranging from 250 mm dia by 1520 mm length to 1400 mm dia by 2800 mm length. In general, the sizes up to 1140 mm dia are extruded; the larger sizes are molded.

Submerged-arc furnaces (see Fig. 4) differ significantly from open-arc furnaces in both function and operation. The name submerged-arc furnace is derived from the fact that the high temperature reaction zone in such furnaces is always isolated from the walls and roof by cooler charge material, ie, the reaction zone is submerged. As

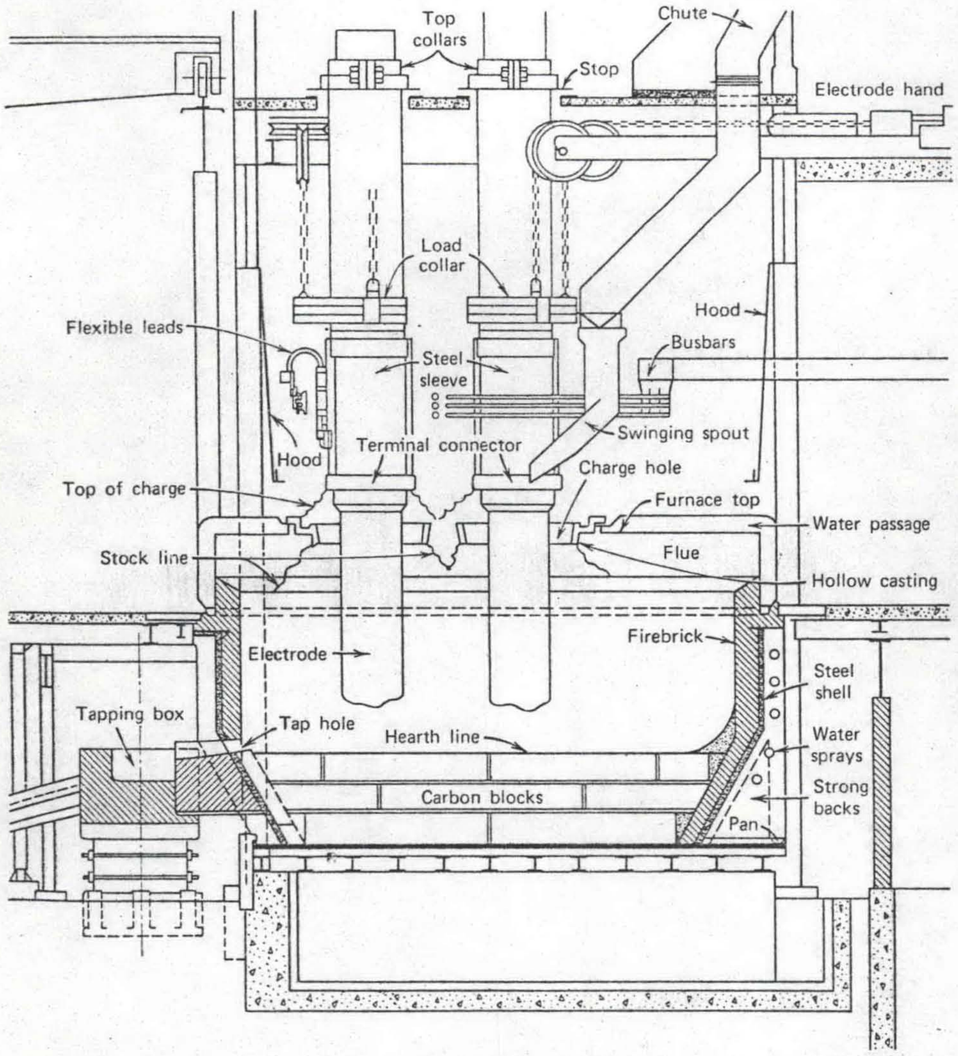

Figure 4. Design of a submerged-arc ferroalloy furnace. Courtesy of Union Carbide Corporation (3).

charge material is consumed in the reaction zone, fresh charge material is added to keep the furnace nearly full. In addition to melting the charge, the furnace also performs the function of a reaction vessel where reduction of oxides is achieved, usually by reaction with carbon. Electrode carbon consumption by reduction reactions varies greatly with the type of product produced and the amount of reducing agent added to the charge. Thus a broad range of specific electrode consumption rates is found in commercial practice, extending from approximately 20 kg/t product for phosphorus or standard ferromanganese to more than 140 kg/t for silicon metal. Unlike open-arc furnaces, the tip of the electrodes in submerged-arc furnaces is often a few meters above the hearth floor so that the volume beneath and around the electrode tip is heated by a combination of resistance heating and arcing (43). Temperatures in this region may reach 2200 K. The volume of this heated reaction zone largely determines furnace productivity. Therefore, to attain the largest possible reaction zone, large diameter electrodes are employed. In many cases, owing to the relatively low electrical currents involved, relatively low cost carbon electrodes may be used rather than graphite which might be prohibitively expensive in the sizes required. However, in certain cases, such as the modern phosphorus furnaces operating at up to 90,000 kW (see Phosphorus), semigraphite electrodes are required. This type of electrode is produced primarily from graphite raw materials bonded with a carbonized pitch binder. In addition to possessing significantly lower electrical resistance, semigraphite electrodes are more easily machined than carbon and have superior thermal shock resistance.

Typical properties of carbon and semigraphite electrodes are shown in Table 4. Strength is an important factor, especially in the larger size electrodes, because of the massive weight of the electrode columns used on many furnaces. Low resistance is an advantage in reducing joule heating losses, although such losses are relatively minor except for very highly powered furnaces. Since relatively large thermal gradients can exist in the submerged electrode, thermal shock or thermal stress resistance is also important in cases of furnaces subjected to transient or intermittent operation and especially where large diameter electrodes are used.

Anode Applications

Graphite has served as the primary material for electrolysis anodes in which chlorine or chlorates are produced at the anode (see Alkali and chlorine products). Recent technological advances, however, have resulted in a dimensionally stable anode (DSA) consisting of precious metal oxides deposited on a titanium substrate that is replacing graphite as the primary anode in mercury cells used in the chlor–alkali industry (40–46).

Although the particles and binder of graphite anodes are subject to oxidative attack under anodic conditions, graphite anodes can provide 270 days of service in diaphragm cell applications. Diaphragm cells account for 75% of the chlor–alkali capacity in the United States (47–48).

Graphite anodes meet the requirements for electrolytic cell applications which include: high degree of insolubility, low initial cost, availability in almost unlimited quantities, few limitations as to size and shape, good electrical conductivity, and high purity to prevent contamination of cell products.

The two basic types of graphite anodes used are plain and impregnated. The purpose of impregnation is to prevent anolyte penetration of the pores in graphite and attendant corrosion inside the anode. For impregnated anodes, base graphite with an initial porosity of 20–30% is given a vacuum-pressure impregnation usually with an oil such as linseed to fill or coat the accessible pores. Proper impregnation provides a 20–50% increase in anode life over unimpregnated graphite.

The electrolysis of fused magnesium chloride for the production of magnesium metal is the second largest use for graphite anodes. The electrolytic process is the current principal method of magnesium production although developments in the metallothermic process and the carbothermic process show potential for economical alternatives (49).

Other applications of graphite anodes include electrolysis of fused chlorides for the production of sodium, lithium, tantalum, and columbium. Graphite anodes are also used for electrolysis of aqueous manganese sulfate and for the anodic deposition of manganese dioxide used as dry battery depolarizer. Carbon anodes are utilized in the electrolytic production of fluorine.

Table 4. Average Properties of Carbon and Semigraphite Electrodes (Measured With the Grain at Room Temperature)

Electrode diameter range, mm	Bulk density, g/cm^3	Compressive strength[a], kPa	Flexural strength[a], kPa	Elastic modulus[a], GPa	Specific resistance, $\mu\Omega\cdot m$	Coefficient of thermal expansion (CTE), $10^{-6}/°C$	Thermal conductivity, W/(m·K)
				Carbon			
425–1125	1.63	11700	4830		50	3.2	16
1250–1375	1.62	11700	3860	3.3	46	3.2	12
				Semigraphite			
875–1125	1.64	12400	5400		24	3.0	34
1250–1375	1.64	12400	4660	3.7	30	3.0	34

[a] To convert Pa to psi, multiply by 1.45×10^{-4}.

Graphite anodes are also used in cathodic protection applications for corrosion prevention of underground and underwater metal structures where low cost, light weight, and excellent electrical conductivity are required. Life of treated graphite ranges from 3–30 yr in cathodic protection applications (50).

Mechanical Applications

Carbon–graphite finds use in many mechanical applications where its natural lubricity, high-temperature mechanical strength, and corrosion resistance give it important advantages over other materials. This lubricity, strength, and corrosion resistance, together with ease of machining, dimensional stability, and high thermal conductivity, make carbon–graphite the material of choice for mechanically supporting loads in sliding or rotating contact. The mechanical applications are: mechanical seals—face, ring, and circumferential types; bearings—carbon cages for roller and ball bearings, carbon sleeve bearings and bushings, carbon thrust bearings or washers, and combination sleeve and thrust bearings; packing rings—steam and water shaft packing rings, and compressor tail-rod packing rings; nonlubricated compressor parts—piston rings, wear rings, segments, scuffer shoes, shaft tail-rod packing rings, pistons, and piston skirts; and miscellaneous applications—flat plate slider parts for support of apparatus and facilitating sliding movement under load, rotor vanes, and metering device parts such as the metering ball and plates.

Carbon–graphite materials employed for mechanical applications are prepared by mixing selected sizes and types of carbon and graphite with binder materials such as pitches and resins. The mixtures are formed into compacts and baked to temperatures of ca 1000–3000°C. Specific raw materials and processing techniques are employed to obtain desired properties for the finished carbon–graphite materials (51).

The successful application of carbon–graphite as a sliding contact is dependent upon the proper use of proprietary additives or impregnants, or both, in the carbon–graphite materials. Carbon–graphite, long considered to be self-lubricating, depends on the presence of adsorbed films of water vapor and/or oxygen for its low friction and low wear properties. This adsorbed boundary layer is soon lost when the operation is conducted at high altitude, high temperature, or in cold, dry air. A substitute boundary layer can be formed by incorporating certain additives or impregnants, or both, such as thermoplastic or thermosetting resins, or metallic sulfides, oxides, or halides. In addition to reducing the friction and wear of the carbon–graphite materials, the additives and impregnants can serve to improve oxidation resistance, provide impermeability to high pressure gases and liquids, and even permit operation under high vacuum conditions (52). Successful operation under high vacuum conditions is a primary requirement of equipment used for exploring outer space.

Carbon–graphite materials will not gall or weld even when rubbed under excessive load and speed. Early carbon materials contained metal fillers to provide strength and high thermal conductivity, but these desirable properties can now be obtained in true carbon–graphite materials that completely eliminate the galling tendency and other disadvantages of metals.

Maintenance of flat faces in rotating and stationary mating seals is important for successful operation. Dimensional stability is necessary in high speed, high-load face seal applications, and carbon–graphite materials with high elastic moduli have been developed to meet the requirements. Distortion of face seals caused by unequal loading or thermal stress leads to high unit loads at contact points, causing high localized friction and additional heat which produces further distortion (53–54).

Carbon–graphite materials are compatible with a wide range of mating materials, such as chrome-plated steel, 440-C stainless, and 300 series stainless (for corrosion resistance) steel, fine-grained cast iron, flame-plated oxides and carbides, ceramics, cermets, and at times, with themselves. However, the importance of rubbing contact has been minimized for certain applications that employ face seals equipped with self-acting lift augmentation (55). For this new generation of seals, pads are machined on the seal face which, during operation, act as a thrust bearing and cause the seal to lift from the counter face and ride on a thin gas film. Ideally, the self-acting seal will experience mechanical wear only during startup and shutdown of the equipment on which it is installed. The advent of this new seal design will enhance the ability of carbon–graphite materials to meet the ever increasing speed, pressure, and temperature requirements for certain applications (56–57).

Metallurgical Applications

Because of their unique combination of physical and chemical properties, manufactured carbons and graphites are widely used in several forms in high temperature processing of metals, ceramics, glass, and fused quartz. A variety of commercial grades is available with properties tailored to best meet the needs of particular applications (58). Industrial carbons and graphites are also available in a broad range of shapes and sizes.

Structural Graphite Shapes. In many metallurgical and other high temperature applications, manufactured graphite is used because it neither melts nor fuses to many common metals or ceramics, exhibits increasing strength with temperature, has high thermal shock resistance, is nonwarping, has low expansion, and possesses high thermal conductivity. However, because of its tendency to oxidize at temperatures above 750 K, prolonged exposure at higher temperatures frequently necessitates use of a nonoxidizing atmosphere. In addition, prolonged contact both with liquid steel and with liquid metals that rapidly form carbides should be avoided.

Some of the more common applications for structural graphite shapes are: (*1*) hot-pressing molds and dies (59) for beryllium at 1370 K and 6.9 MPa (1000 psi); diamond-impregnated drill bits and saw tooth segments at 1250 K and 13.8 MPa (2000 psi); tungsten and other refractory metals and alloys up to 2370 K and 6.9 MPa (1000 psi); and boron nitride and boron carbide up to 2060 K; (*2*) molds for metal casting steel railroad car wheels made by the controlled-pressure pouring process (60); steel slabs and billets made by the controlled-pressure pouring process (61); continuous casting of copper and its alloys, aluminum and its alloys, bearing materials, zinc, and gray iron (62–63); centrifugal casting of brasses, bronzes, steels, and refractory metals (64); nickel anodes; welding rods and thermite welding molds; shapes of refractory metals (Ti, Zr, Mo, Nb, W) and carbides; and shapes of gray, ductile and malleable irons (65); (*3*) foundry accessories including: mold chill plates, core rods, and riser rods; crucible skimmer floats; plunging bells for magnesium additions to ductile iron and desulfurization of blast-furnace hot metal (66–67); stirring rods for nonferrous metals; and railroad brake shoe inserts; (*4*) injection tubes and nozzles for purifying molten aluminum (68) and other nonferrous metals, desulfurization of blast furnace and foundry iron with calcium carbide or magnesium, and carbon raising of foundry iron with graphite powders; (*5*) aluminum extrusion components including dies, guides from die openings, run-out table boards, and cooling-rack inserts; (*6*) rolls for handling metal sheets are used in certain processes because they are self-lubricating and reduce surface marring; (*7*) immersion thermocouple protection tubes for nonferrous metals; (*8*) welding electrodes for welding, gouging, and cutting iron and steel, particularly with the aid of an air blast (69); (*9*) crucibles, either induction or resistance heated, for producing tungsten carbide, beryllium fluoride and beryllium, titanium and zirconium fluoride, semiconductor crystals of germanium and silicon, and for laboratory chemical analysis equipment; (*10*) ceramic and glass production including: casting molds for fused cast refractories of alumina, magnesia, and chrome–magnesite compositions up to 2650 K (70); mold susceptors for fabricating fused magnesia crucibles; susceptors, electrical resistor elements, fusion crucibles, molds and dies for the production of fused quartz (71); linings for float-glass tanks (72); take-out pads for automatic glass-blowing machines; diablo-wheels for glass tubing production; and linings for hydrofluoric acid tanks for glass etching; (*11*) boats, trays, and plates for sintering clutch plates, brake disks, and cemented carbides and for the manufacture of semiconductor material and transistors; and (*12*) furnace jigs for brazing honeycomb panels, automotive ignition points and arms, automotive radiator cores, transistor junction assembly, and glass-to-metal seals.

Electric Heating Elements. Machined graphite shapes are widely used as susceptors and resistor elements to produce temperatures up to 3300 K in applications utilizing nonoxidizing atmospheres. The advantages of graphite in this type of application include its very low vapor pressure (lower than molybdenum), high black body emissivity, high thermal shock resistance, and increasing strength at elevated temperatures with no increase in brittleness. Graphites covering a broad range of electrical resistivity are available and can be easily machined into complex shapes at lower cost than refractory metal elements. Flexible graphite cloth is also used widely as a heating element since its low thermal mass permits rapid heating and cooling cycles. Porous carbon or graphite, and flexible carbon or graphite felts are used for thermal insulation in many high temperature furnaces. Typical applications include molten-iron or steel-holding furnaces, continuous-casting tundishes, liquid-steel degassing units, chemical-reaction chambers, quartz-fusion apparatus, zinc-vaporization chambers, sintering furnaces, vapor deposition units; the felts are also used in the manufacture of semiconductors (qv) (73–74).

Graphite Powder and Particles. Manufactured graphite powders and particles are used extensively in metallurgical applications where the uniformity of physical and chemical characteristics, high purity, and rapid solubility in certain molten metals are important factors (75). The many grades of graphite powders and particles are classified on the basis of fineness and purity. Applications for these materials include facings for foundry molds and steel ingot molds, additives to molten iron to control carbon level and chill characteristics, covering material for molten nonferrous metals and salt baths to prevent oxidation, additives to sintered materials to control carbon level and frictional characteristics of oil-less bearings, and as charge-carbon in steels made in electric arc furnaces.

Refractory Applications

Various forms of carbon and graphite materials have found wide application in the metals industry, particularly in connection with the production of iron and aluminum. Carbon has been used as a refractory material since 1850, although full commercial acceptance and subsequent rapid increase in use has taken place only since 1945 (see Refractories).

Carbon as a Blast Furnace Refractory. The first commercial use of carbon as a refractory for a blast furnace lining took place in France in 1872, followed in 1892 by a carbon block hearth for a blast furnace of the Maryland Steel Company at Sparrows Point, Md. After a period of abated interest, the excellent results obtained with several carbon hearths in Germany and the United States during the late 1930s and early 1940s renewed enthusiasm for this approach. Although initially used only for the hearth floor of blast furnaces, carbon and graphite refractories have been applied successfully to hearth walls, lower and upper boshes, and most recently, to the lower stack of modern high-performance blast furnaces throughout the world (76). More than 360 individual carbon or graphite blast furnace linings have been installed in North America through the end of 1975. Carbon is also used extensively for blast furnace slag troughs and iron runners.

Experience has shown that carbon and graphite refractories have several characteristics contributing to their successful use in blast furnaces. (*1*) They show no softening or loss of strength at operating temperatures. (*2*) They are almost immune to attack by either blast furnace slags or molten iron. (*3*) Their relatively high thermal conductivity, when combined with adequate external cooling, assures solidification of iron and slag far from the furnace exterior, thus promoting long life while maintaining safe lining thicknesses (77). (*4*) A high level of thermal shock resistance avoids cracking or spalling in service. (*5*) A positive, low thermal expansion provides both dimensional stability and a tightening of joints in the multiblock linings. However, because of their poor oxidation resistance such refractories must not be exposed to air, carbon dioxide, or water vapor at elevated temperatures (78–79).

The prime requirement for linings in blast furnace hearths or hearth walls is to contain liquid iron and slag safely within the crucible throughout extended periods of continuous operation. This requirement is most readily achieved by providing sufficient cooling of the lining to assure solidification of penetrating iron and slag far from the furnace exterior (80). Where only peripheral cooling is used, a thick carbon bottom is required, the thickness of which is approximately one-quarter of the furnace diameter between the cooling system (77). In North and South America, such hearth bottoms are made from 3 or 4 horizontal layers of long carbon beams, each of which may be up to 6.5 m long and weigh as much as 5 metric tons. Anchoring the ends of these long beams beneath the furnace sidewall prevents flotation of the blocks in the denser molten iron, a phenomenon that has been observed in other parts of the world where long carbon beams are not used. Where short carbon blocks are used in the hearth, whether in a vertical or horizontal orientation, extensive interlocking, keying, and cementing must be employed to prevent loss by flotation. The application of carbon hearth and hearth wall refractories has virtually eliminated the once-prevalent danger of breakouts, a phenomenon that represents a serious threat to both life and property. As of 1976, carbon hearth walls were used in virtually all blast furnaces in North America, and of these, 80 had carbon hearth floors. One such furnace remained in operation after 22 years of service on the original carbon hearth, and another produced over 13 million metric tons of iron on its carbon hearth. In recent years, there has been an increasing tendency to incorporate some form of underhearth cooling in the larger furnaces to enhance hearth life. Medium size furnaces generally use a layer of high conductivity graphite beneath the carbon hearth for improved cooling. Larger furnaces incorporate tightly sealed steel plenums beneath the hearth through which air (or infrequently water) is passed to effect cooling of the hearth (81).

During 1960–1975 the use of carbon and graphite as bosh refractories has tripled. In 1976 ninety North American blast furnaces were operating with carbon boshes, and record performance on a single carbon bosh has exceeded 8 million metric tons of pig iron. As in the hearth and hearth wall, long life is assured by efficient cooling of the carbon bosh lining. 100% External shower cooling is used, and special cements are employed to assure that the high conductivity refractory is in good thermal contact with the cooled bosh shell. Long life of carbon bosh refractories also necessitates a high level of resistance to abrasion and alkali attack (82).

The success of carbon bosh linings has prompted several operators in Europe and Japan to extend the use of this refractory into the lower stack of several large modern blast furnaces where design permits this feature (76).

Refractories in the Aluminum Industry. The Hall-Heroult aluminum cell uses carbon materials for the anode, cathode, and sidewall, since carbon is the only material able to withstand the corrosive action of the molten fluorides used in the process (see Aluminum). The aluminum industry uses more carbon per metric ton of virgin metal than any other industry. Production of 1 t of molten aluminum requires about 500 kg of anode carbon and 7.5–10 kg of cathode carbon.

Because of the very large consumption of anode carbon, aluminum plants usually contain an on-site carbon plant for the manufacture of anodes.

Two types of cathodes are used in aluminum cells: both are produced from blends of calcined anthracite, metallurgical coke, and pitch. Compared with a tamped lining, prebaked carbon block linings provide higher operating strength, higher density, lower porosity, and longer life. Their lower resistance results in a lower voltage drop through the lining that improves the overall electrical efficiency of the cell (83). Prebaked cathodes also exhibit more predictable starting characteristics and possess greatly improved ability to restart successfully after a shutdown. This characteristic helps increase production and service life and usually more than compensates for the higher initial cost of prebaked cathode blocks. The service life of a prebaked cathode is usually 3–4 yr.

Refractories for Cupolas. In many ways, the use of carbon cupola linings has paralleled the application of carbon in the blast furnace. Carbon brick and blocks are used to form the cupola well (84), or crucible, up to the tuyeres. When properly installed and cooled, carbon linings last for many months, or even years of intermittent operation. Their resistance to molten iron and both acid and basic slags provides not only insurance against breakouts but also operational flexibility to produce different iron grades without the necessity of changing refractories. Carbon is also widely used for tap holes, breast blocks, slagging troughs, and dams.

Refractories for Electric Reduction Furnaces. Carbon hearth linings are used in submerged-arc electric reduction furnaces producing phosphorus, calcium carbide, all grades of ferrosilicon, high carbon ferrochromium, ferrovanadium, and ferromolybdenum. They are also used in the production of beryllium oxide and beryllium copper, where temperatures up to 2273 K are required.

Most of the principles pertaining to carbon blast furnace hearths apply as well to hearths for submerged-arc furnaces, although the fact that carbon is an electrical conductor is of importance in the case of electric reduction furnaces. The very long life of carbon linings in this application is attributable to their exceptional resistance to corrosive slags and metals at relatively high temperatures.

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R. M. BUSHONG (Aerospace and Nuclear Applications)
R. RUSSELL (Chemical Applications)
B. R. JOYCE (Electrical Applications, Arc Carbons)
P. M. SCHERER (Electrical Applications, Brushes; Anode Applications; and Mechanical Applications)
N. L. BOTTONE (Electrical Applications; Spectroscopic Electrodes)
R. L. REDDY (Electrode Applications; Metallurgical Applications; and Refractory Applications)
Union Carbide Corporation

CARBON FIBERS AND FABRICS

Carbon fibers are filamentary forms (fiber dia 5–15 μm) of carbon (carbon content exceeding 92 wt %) and are characterized by flexibility, electrical conductivity, chemical inertness except to oxidation, refractoriness, and in their high performance varieties, high Young's modulus and high strength. Considerable confusion exists over the terms carbon and graphite fibers. The term graphite fibers should be restricted to materials with the three-dimensional order characteristic of polycrystalline graphite; essentially all commercial fibers are carbon fibers.

Carbon fibers were first made intentionally in 1878 by Edison (1) who pyrolyzed cotton to make incandescent lamp filaments. Interest in carbon fibers remained at a very low level until the late 1950s when commercially useful products, made by carbonizing rayon cloth and felt, were introduced (2). These relatively low strength, low modulus products were followed in 1964 by the development of high modulus, high strength, rayon-based carbon yarns (3) and of intermediate modulus, high strength, polyacrylonitrile (PAN)-based carbon yarns (4). High modulus, intermediate strength fibers made from a mesophase (liquid crystal) pitch precursor were introduced in 1974 as a mat product (5) and in 1975 as continuous yarns (6–7). Carbon fibers can also be made from ordinary (nonmesophase) pitch, but they generally have low strength and low modulus. Other precursor materials, including phenolics, polyacetylene, poly(vinyl alcohol), and polybenzimidazole, have been investigated (8–9). As of early 1977 no evidence was available to indicate that fibers from these latter precursors would become commercially significant.

Most desirable properties of carbon fibers, eg, Young's modulus, electrical and thermal conductivity, and to a lesser extent tensile strength, depend on the degree of preferred orientation. In a high modulus fiber, the carbon layer planes are predominantly parallel to the fiber axis; however, when viewed in cross section, the layers in most carbon fibers are oriented in all directions, although mesophase pitch-based fibers with concentric layers (onionskin structure) and with layers radiating from the fiber axis (radial structure) have been made (7). The high strength, high modulus properties are found only along the fiber axis. Very highly oriented carbon fibers possess a Young's modulus of nearly 900 GPa (130 × 10^6 psi), very close to that of the graphite single crystal, and tensile strength of over 3.4 GPa (500,000 psi). In commercial production, Young's moduli are usually held below 550 GPa (80 × 10^6 psi) for three principal reasons: the tensile strength does not always increase proportionally with the modulus, leading to unacceptably low strain-to-failure ratios; the interlamellar shear strength (adhesion between the fiber and the matrix resin) decreases with increasing modulus; and the production costs for very high modulus fibers are high.

Detailed discussions of the carbon fiber structure and the methods of structure determination are reported (10–13). The Young's modulus of carbon fibers depends entirely upon the degree of preferred orientation, as shown in Figure 1. Since carbon fibers of different origin can vary greatly in density, the data in Figure 1 have been normalized to correct for these differences.

The electrical and thermal conductivity also increase with increased orientation (11). The elastic constants of rayon- and PAN-based carbon fibers with Young's moduli ranging from 41–551 GPa (6–80 × 10^6 psi) and of epoxy-matrix composites made from

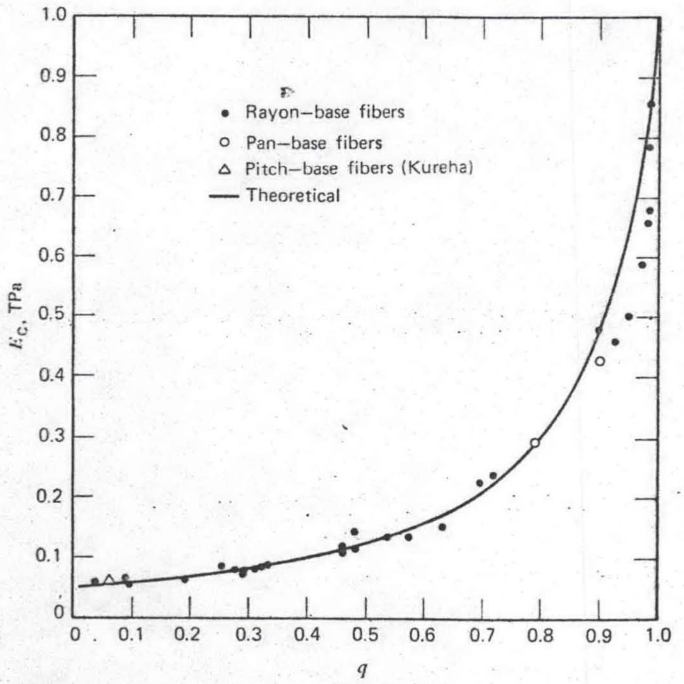

Figure 1. Young's modulus corrected for porosity E_c as a function of preferred orientation q; curve is based on theoretical model (10). To convert TPa to psi, multiply by 145 × 10^6.

these fibers have been determined (14). The relation between the axial thermal expansion of a variety of commercial carbon fibers to their preferred orientation was measured (15) and the transverse thermal expansion was determined (16).

The tensile strength of highly oriented carbon fibers should, in theory, be approximately 5% of the Young's modulus. Graphite whiskers with tensile strength of over 21 GPa (3×10^6 psi) have been made (17). For commercially produced carbon fibers, the tensile strength is controlled by defects in the fiber structure; these include stress risers in the form of surface irregularities, voids, and particulate inclusions (18–25). The nature and frequency distribution of these limiting defects vary for different carbon fibers, but all fibers show significant increases in single-filament tensile strength (frequently over 100%) when the test-gage length is reduced from 5 cm to 1 mm. The useful tensile strength (translatable into composite properties) of commercial carbon yarn rarely exceeds 3.8 GPa (550,000 psi). In 1977 the standard, low cost, PAN-based carbon fibers had a modulus of 207 GPa (30×10^6 psi) and tensile strengths of 2.4–2.9 GPa (350,000–425,000 psi).

The interlamellar shear strength of carbon fiber composites tends to decrease with increasing fiber modulus. This property is important because a low shear strength results in low transverse composite properties and possibly low compressive strength (26–27). A large number of surface treatments to improve shear strength have been published. Most processes (28) depend on some form of oxidative etching in air, nitric acid, or other oxidizing liquids, anodic oxidation, or the deposition of a low temperature carbon char (29) on the fiber surface. The actual processes used by various producers are closely guarded trade secrets.

There are considerable differences in the process chemistry, production economics, and properties of rayon-, PAN-, and pitch-based carbon fibers. These processes and products are, therefore, discussed separately.

Rayon-Based Carbon Fibers

The production process for rayon-based carbon yarn and cloth involves three distinct steps: preparation and heat treating, carbonization, and optional high temperature heat treatment. Heat treating at 200–350°C to form a char with thermal stability is required for rapid subsequent carbonization. Principally, water evolves during this stage although complex thermal tars also form. These tars can redeposit on the yarn or cloth and render the material brittle upon carbonization. To reduce tar formation and to quicken the process, the heat treatment is frequently carried out in a reactive atmosphere, such as air, or with the aid of chemical impregnants (9). The weight loss during this step is approximately 50–60% and any structure or preferred orientation that may have existed in the starting material is destroyed during the formation of the amorphous char. The yarn or cloth is carbonized next at 1000–2000°C during which additional weight is lost and an incipient carbon layer structure is formed. The material may then be heat treated at temperatures approaching 3000°C. The overall carbon yield is approximately 20–25%. The products have densities of 1.43–1.7 g/cm^3, filament tensile strengths of 345–690 MPa ($5\text{–}10 \times 10^4$ psi), and Young's moduli of 21–55 GPa ($3\text{–}8 \times 10^6$ psi). They are usually used in the form of cloth for aerospace applications, eg, phenolic impregnated heat shields, and in carbon–carbon composites for missile parts and aircraft brakes. Production statistics are not available; estimated consumption for 1970–1976 was 100,000–250,000 kg/yr. Through 1975 the volume of rayon-based, low modulus yarn and cloth probably exceeded that of all other carbon fibers combined. The price for cloth is \$60–120/kg (see Ablative materials).

To produce high modulus, high strength rayon-based fiber, it is necessary to stretch the yarn during the heat treatment process at 2700–3000°C. The high temperature increases the size, perfection, and parallel stacking of the carbon layers, and stretching orients them parallel to the fiber axis. The tensile strength of rayon-based yarn also increases with increasing stretch and Young's modulus, resulting in an almost constant strain-to-failure of approximately 0.5%. The density of the yarn is 1.65 g/cm^3 at a modulus of 345 GPa (50×10^6 psi) or 1.82 g/cm^3 at a modulus of 517 GPa (75×10^6 psi). There are comprehensive reviews of production processes (10), and the structure and properties of rayon-based yarn (8).

The hot-stretching process is very costly, and the price of high modulus rayon-based yarn is \$600–1300/kg. Production volume is relatively low and applications are confined to aerospace uses.

The long range future availability of all rayon-based carbon fiber products depends on the continued production of suitable continuous filament rayon yarn. The rapid decline in the tire cord use of rayon has caused several major rayon manufacturers to discontinue production. Many applications of rayon-based carbon fibers depend on their stability at very high temperatures and the high carbon content of over 99%. In these areas, they are not readily replaceable by the standard PAN-based fibers that have a lower carbon content and change when heated beyond the original process temperature. Mesophase pitch-based fibers can be made with properties very similar to those of rayon-based products and may be expected to replace them in many applications.

PAN-Based Carbon Fibers

Production of PAN-based carbon fibers also involves the three steps of low temperature heat treatment, carbonization, and optional high temperature heat treatment. The principal differences from the rayon-based fiber process are that a well-oriented ladder polymer structure is developed during oxidative heat treatment under tension, and the orientation is essentially maintained through carbonization.

Most producers probably use copolymer PAN fibers containing at least 95% acrylonitrile units. Textile PAN yarns with a high percentage of copolymer content and those containing appreciable quantities of brighteners, such as TiO_2, are not considered suitable precursors. To improve the alignment in the polymer structure and reduce the fiber diameter, the as-spun PAN fibers are frequently stretched by 100–500% at approximately 100°C. Stretching of the polymer also increases the tensile strength and Young's modulus of the resulting carbon fibers (30).

Heat treatment is carried out in an oxidizing atmosphere (usually air) at 190–280°C for 0.5–5 h. Sufficient tension must be applied at this stage to prevent the yarn from shrinking and to develop a high degree of alignment of the ladder polymer chain. Heat treatment is an exothermic process, and precautions against a runaway reaction are required. After heat treatment, the yarn is black, infusible, and can be rapidly carbonized in an inert atmosphere, usually at 1000–1300°C, where the tensile strength reaches a maximum. Hydrogen cyanide is evolved during carbonization, and suitable precautions must be taken for combustion of volatiles. The yield from raw to carbonized yarn is approximately 45–50%. At this stage, the material consists of 92–95%

carbon and most of the remainder is nitrogen. This yarn has a Young's modulus of ca 210 GPa (30×10^6 psi). The modulus can be further increased to 350–520 GPa ($50–75 \times 10^6$ psi) by heating to above 2500°C, but the tensile strength tends to decrease. In at least one type of PAN-based fiber this decrease in strength is caused by impurities in the raw PAN fibers (24). Fibers spun under clean-room conditions increased in strength as well as modulus upon heating above 2500°C.

The tensile strength of some fibers with 210 GPa (30×10^6 psi) Young's modulus is apparently limited by stress-rising surface irregularities (24), and etching to remove or blunt these flaws can increase the strength (31). PAN-based fibers can also be hot-stretched, with a resulting increase in both tensile strength and Young's modulus. However, because of the high cost, this process is not the usual commercial practice. Detailed reviews of the PAN-based fiber process and fiber characteristics have been published (8–9,32).

Most PAN-based fibers produced in 1976 had a tensile strength of ca 2.4–2.75 GPa (350,000–400,000 psi) and a Young's modulus of 193–241 GPa ($28–35 \times 10^6$ psi), although fibers with moduli up to 482 GPa (70×10^6 psi) and generally lower strength are available. Fiber densities are usually 1.7–1.8 g/cm^3. Product forms include yarns of 1,000, 3,000, 6,000, and 10,000 filaments, tows up to 500,000 filaments, and fabrics of various styles and weave construction.

Although official production statistics are not available, it is estimated that the combined production in the three principal producing countries (United States, Japan, and England) may have risen from 10 metric tons in 1970 to 250 t in 1976. With increased production, the price of the standard 207 GPa (30×10^6 psi) Young's modulus fibers has decreased from approximately $1000/kg before 1970 to $40–80/kg in 1977, although higher modulus fibers and low denier yarns, such as 1000-filament products, are sold at premium prices.

Until about 1972 PAN-based carbon fibers were used almost exclusively in epoxy "prepregs" where structures for the aerospace industry were fabricated. The higher costs had to be justified by weight savings and performance improvements. Long-time reliability experience was meager and aircraft structures were mostly limited to noncritical parts. Fiber price reductions and significant advances in composite fabrication technology had, by 1976, made carbon fiber composites cost competitive with many metal parts in aircraft construction. Confidence in design and reliability has been established; composites are currently used in major flight-critical structures. During the same time period, a second major market for PAN-based carbon fibers developed in the sporting goods industry, first in golf clubs, then in fishing rods, tennis rackets, bows and arrows, skis, and sailboat masts and spars. Applications for textile and computer machinery, automotive and general transportation, and musical instruments are rapidly emerging (see Composite materials).

Mesophase Pitch-Based Fibers

The process for these fibers starts with commercial coal tar or petroleum pitch which is converted through heat treatment into a mesophase or liquid crystal state. Since the mesophase is highly anisotropic, the shear forces acting on the pitch during spinning and drawing result in a highly oriented fiber, with the essentially flat aromatic polymer molecules oriented parallel to the fiber axis. The spun yarn is then thermoset in an oxidizing atmosphere which renders the fibers infusible and amenable to rapid carbonization. The original preferred orientation is maintained during thermosetting, which does not require tensioning, and is further enhanced during carbonization and graphitization. Mesophase pitch-based fibers have a Young's modulus over 690 GPa (100×10^6 psi) when heated (without stretching) to 3000°C. These are the only fibers that can truly be called graphite. The carbon yield from spun to carbonized fiber is 75–85%, depending on the molecular weight of the mesophase pitch and the heat treatment conditions. Fibers with a Young's modulus over 345 GPa (50×10^6 psi) are almost pure (over 99.5%) carbon. Lower modulus fibers may contain small amounts (ca 1%) of sulfur. The fiber density is approximately 2 g/cm^3.

The tensile strength of mesophase pitch-based fibers increases with increasing carbonization temperatures until a modulus of 345 GPa (50×10^6 psi) is reached. It then remains essentially flat to 550 GPa (80×10^6 psi) and rises again with further heat treatment. Single-filament tensile strengths (2 cm gage length) over 3.5 GPa (5×10^5 psi) have been measured. In 1977 the commercial yarn with a 345 GPa (50×10^6 psi) modulus had a tensile strength of approximately 2.0 GPa (3×10^5 psi). The strength-limiting defects consist primarily of voids of 1–2 μm dia and, at this stage of development, of particulate inclusions similar to but more severe than those found in PAN-based fibers. Considerable process details and the microstructure of mesophase pitch-based fibers are described in the literature (7,33).

In 1977 mesophase pitch-based fibers were produced in three forms. One form is a low modulus (138 GPa or 20×10^6 psi), low cost ($17/kg) mat product that is not recommended for structural reinforcement. This material is useful as a veil mat for sheet molding to provide an electrically conductive surface for electrostatic spraying or improved surface appearance or both. Milled mat with a fiber length of ca 1.0 mm is used in injection molding to achieve electrical conductivity, resistance to heat distortion, and improved wear characteristics (for bearing applications).

The second form consists of pitch-based carbon fiber fabrics (12) that have filament moduli of 138–517 GPa ($20–75 \times 10^6$ psi), depending on process temperature, and present an attractive, low cost alternative to rayon-based cloth.

The third form, a continuous filament yarn with a Young's modulus of 345 GPa (50×10^6 psi) and 2.0 GPa (3×10^5 psi) tensile strength, is by far the lowest priced high modulus carbon yarn. Initial uses are in stiffness-critical applications.

Health and Environmental Considerations

Carbon fibers, like other forms of carbon, are very inert. For this reason they are now used in medical research for body implant studies such as pacemaker leads (see Prosthetic and biomedical devices). The only known medical hazard is a possible skin irritation caused by broken filaments, similar to that caused by glass fibers. Carbon fibers are good electrical conductors. Broken filaments can remain airborne over considerable distances and can cause short circuits in electrical equipment.

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H. F. VOLK
Union Carbide Corporation

OTHER FORMS OF CARBON AND GRAPHITE

The many forms and applications of graphite already mentioned illustrate the versatility and unique character of this material. Several other forms of graphite with specialized properties have been developed during recent years (1), and although all are characterized by relatively high cost, the specialized properties are sufficiently intriguing that applications have been found resulting in sales of a few millions of dollars in each category.

Carbon and Graphite Foams

The earliest foamed graphite was made from exfoliated small crystals of graphite bound together and compacted to a low density (2–4). This type of foam is structurally weak and will not support loads of even a few newtons per square meter. More recently, carbon and graphite foams have been produced from resinous foams of phenolic or urethane base by careful pyrolysis to preserve the foamed cell structure in the carbonized state. These foams have good structural integrity and a typical foam of 0.25 g/cm^3 apparent density has a compressive strength of 9,300–15,000 kPa (1350–2180 psi) with thermal conductivity of 0.87 W/(m·K) at 1400°C. These properties make the foam attractive as a high-temperature insulating packaging material in the aerospace field and as insulation for high temperature furnaces (see Insulation, thermal). Variations of the resinous-based foams include the syntactic foams where cellular polymers or hollow carbon spheres comprise the major volume of the material bonded and carbonized in a resin matrix.

Pyrolytic Graphite

The carbon commercially produced by the chemical vapor deposition (CVD) process is usually referred to as pyrolytic graphite (5–6). The material is not true graphite in the crystallographic sense, and wide variations in properties occur as a result of deposition methods and conditions; nevertheless, the term pyrolytic graphite is generally accepted and used extensively. Pyrolytic graphite was first produced in the late 1800s for lamp filaments yet received little further attention until the 1950s. Since then pyrolytic graphite has been studied extensively and has been commercially produced in massive shapes by several companies. Commercial applications for pyrolytic graphite, limited by the price of $18 or more per kg, include rocket nozzle parts, nose cones, laboratory ware, and pipe liners for smoking tobacco. Pyrolytic graphite coated on surfaces or infiltrated into porous materials is also used in other applications such as nuclear fuel particles and prosthetic devices (qv).

The greatest quantity of commercial pyrolytic graphite is produced in large, inductively-heated, low pressure furnaces for which natural gas is used as the carbon source. Temperature of deposition is ca 1800–2200°C on a carefully prepared substrate of fine-grained graphite. The properties of pyrolytic graphite are highly anisotropic. The ultimate tensile strength in the *ab* direction is five to ten times greater than that of conventional graphite, and the *c* direction strength is proportionally weaker. The thermal conductivity is even more anisotropic. In the *ab* direction, pyrolytic graphite is one of the very best conductors among elementary materials, whereas in the *c* direction conductivity is quite low. At room temperature the thermal conductivity values are approximately three hundred times as high in the *ab* direction as in the *c* direction. The commercially produced pyrolytic graphite is quite dense, usually 2.0–2.1 g/cm^3, and is quite low in porosity and permeability.

A special form of pyrolytic graphite is produced by annealing under pressure at temperatures above 3000°C. This pressure-annealed pyrolytic graphite exhibits the theoretical density of single crystal graphite; and although the material is polycrystalline, the properties of the material are close to single-crystal properties. The highly reflective, flat faces of pressure-annealed pyrolytic graphite have made the material valuable as an x-ray monochromator (see X-ray techniques).

Glassy Carbon

When carbon is produced from certain nongraphitizable carbonaceous materials, the material resembles a black glass in appearance and brittleness; hence, the terms glassy carbon or vitreous carbon (7–8). Nongraphitizing carbons are obtained from polymers that have some degree of cross-linking, and it is believed that the presence of these cross-linkages inhibits the formation of crystallites during subsequent heat treatments. By pyrolyzing polymers such as cellulosics, phenol–formaldehyde resins, and poly(furfuryl alcohol) under closely controlled conditions, glassy carbon is produced. These carbons are composed of random crystallites, of the order of 5.0 nm across, and are not significantly altered by ordinary graphitization heat treatment to 2700°C.

The properties of glassy carbon are quite different from those of conventional carbons and graphites. The density is low (1.4–1.5 g/cm^3), but the porosity and permeability are also quite low. The material has approximately the same hardness and brittleness as ordinary glass, whereas the strength and modulus are higher than for ordinary graphite. The extreme chemical inertness of glassy carbon, along with its impermeability, make it a useful material for chemical laboratory glassware, crucibles, and other vessels. It has found use as a susceptor for epitaxial growth of silicon crystals and as crucibles for growth of single crystals. Applications have been limited because of high cost owing to technological difficulties in manufacturing, although recently billets of reasonable size and with good properties have become available (9).

Carbon Spheres

Carbon and graphite have been produced for many years in roughly spherical shape in small sizes (1–2 mm dia). Globular carbon of this type was used in telephone receivers in the mid 1930s. Carbon of nearly spherical shape can be produced by mechanically tumbling or rolling a mixture of finely divided carbon or graphite with a resinous binder, screening to select the desired size balls, and carefully carbonizing the selected material. Graphite balls in small sizes have also been made from manufactured graphite by crushing, milling in a chopping-type mill, sizing, and tumbling to abrade away the irregular corners. Usage of these nearly spherical carbon balls has been limited to specialized applications where flowability was at a premium or uniform contact area was important. The telephone resistor already mentioned and shim particles for use in nuclear reactor fuel applications are examples.

Recently, a new type of carbon sphere, usually hollow, has been made from pitch. This technology, developed in Japan (10), produces carbon spheres available in 40–400 μm dia. The spheres are of uniform, very nearly spherical shape and are graphitizable. The particle density is usually 0.20–0.25 g/cm^3, and consequently, attention has been given to application in syntactic carbon foam for high temperature insulation and for lightweight composite structures. The spheres can be activated to produce an adsorptive material of high flow-through capacity. At present, cost has limited the application of these spheres. Although the spheres can be produced for about $1/kg, the cost is greater than for most starting materials for carbon.

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R. M. Bushong
Union Carbide Corporation

CARBON BLACK

Carbon black is an important member of the family of industrial carbons. Its various uses depend on chemical composition, pigment properties, state of subdivision, adsorption activity and other colloidal properties. The basic process for manufacturing carbon black has been known since antiquity. The combustion of fuels with insufficient air produces a black smoke containing extremely small carbon black particles which, when separated from the combustion gases, comprise a fluffy powder of intense blackness. The term carbon black refers to a wide range of such products made by partial combustion or thermal decomposition of hydrocarbons in the vapor phase, in contrast to cokes and chars which are formed by the pyrolysis of solids.

This printed page was made with an ink containing a pigment grade of carbon black. Prehistoric cave wall paintings and objects from ancient Egypt were decorated with paints and lacquers containing carbon black. Carbon black was made in China about 3000 BC and records show that it was exported to Japan about 500 AD. The original process consisted of the partial burning of specially purified vegetable oils in small lamps with ceramic covers. The smoke impinged on the covers from which the adhering carbon black was painstakingly removed. Thus carbon black is one of the oldest industrial products. In the United States carbon black has been manufactured for over 100 years. Its use as a pigment continues as an important and growing application, but the major market for the last 50 years has been as a strengthening or reinforcing agent for rubber products, particularly tires.

Relationship of Carbon Black to Other Forms of Industrial Carbons

Carbon exists in two crystalline forms, and numerous so-called amorphous, less-ordered forms. The crystalline forms are diamond and graphite, and the less-ordered forms are mainly cokes and chars. Diamond has a cubic structure in which every carbon atom in the space lattice is bonded by its four valences to adjacent atoms situated in the apexes of a regular tetrahedron around the central atom. The carbon–carbon distance is 0.154 nm, similar to that in aliphatic hydrocarbons. The diamond structure is shown in Figure 1**a**. Diamond has a specific gravity of 3.54 (high for such a low atomic weight element), high refractive index, brilliance and clarity, electrical insulating properties, and a hardness greater than any other known material (see Hardness). The graphite form of carbon has a completely contrasting set of properties: lower density, a grayish-black appearance, softness, slipperiness, and electrical conductivity.

In Figure 1**b** the carbon atoms of the graphite structure are strongly bonded forming large sheets of hexagonal rings in which the electrons are quite mobile. The layer planes are stacked on each other in an ABAB arrangement, ie, layers in which every atom has an atom directly above it separated by one layer. Within a layer plane the carbon atoms are separated by 0.142 nm, comparable to the aromatic carbon separation distance of 0.139 nm in benzene. The mobility of electrons within the layer planes results in a 250-fold higher electrical conductivity in the planar direction than perpendicular to the planes. The bond strengths within the layer planes are over one hundred times stronger than the interlayer van der Waals bonding. The large graphite interplanar distance of 0.335 nm results in a specific gravity of 2.26.

All forms of industrial carbons other than diamond and graphite, including carbon black, can be classified as amorphous carbons characterized by degenerate or imperfect graphitic structures. The parallel layer planes in these carbons are not perfectly oriented with respect to their common perpendicular axis; the angular displacement of one layer with respect to another is random and the layers overlap one another irregularly. This arrangement has been termed turbostratic structure. In this arrangement a separation distance of 0.350–0.365 nm is found for the layer planes. A schematic model of the short-range crystalline order in carbon black is shown in Figure 1**c**. Table 1 lists some of the basic structural and crystallite properties of the various carbons.

Microstructure

X-ray diffraction patterns of carbon black show two or three diffuse rings similar to the more intense rings of natural graphite. Analysis of these patterns by Warren (1) yielded the first model of carbon black microstructure consisting of a random arrangement of crystallites within the particles. A diffuse (002) reflection band provided an estimate of the interplanar spacing and the thickness of the crystallites in the direction perpendicular to the planes. The weak (10) and (11) bands yielded values of the average diameter of the parallel layers. For most furnace and channel-type carbon blacks these values are about 0.35 nm for interplanar spacing (d), 1.2–1.5 nm for average crystallite thickness (L_c), and 1.7 nm for average diameter (L_a). Later studies of carbon black graphitization (2), electron diffraction analysis (3), oxidation studies (4), and high resolution diffracted-beam electron microscopy (5) have led to the conclusion that the microstructure of carbon black consists of a more concentric ar-

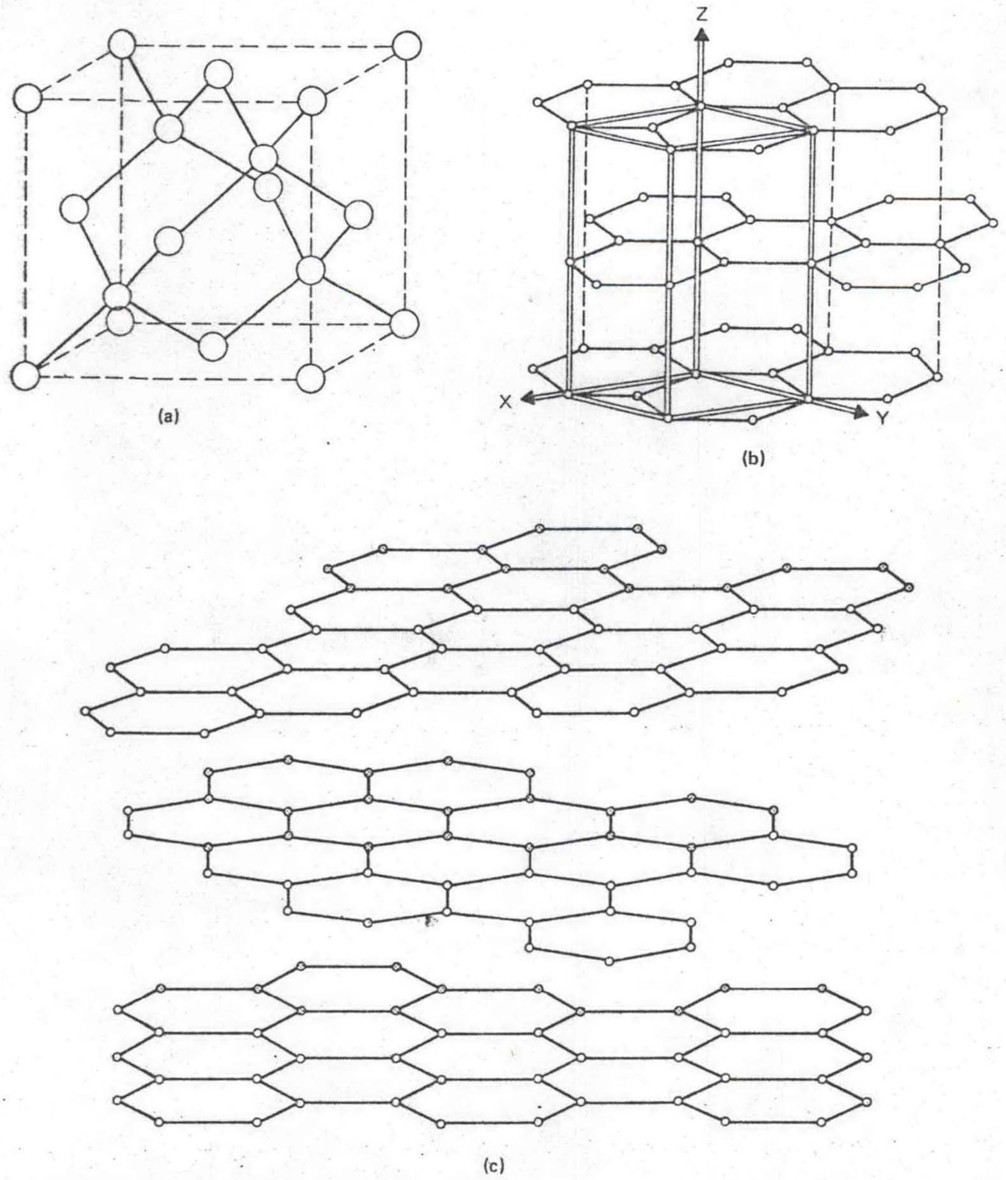

Figure 1. Crystallographic arrangement of carbon atoms in: (**a**) diamond, face-centered cubic structure; (**b**) graphite, parallel layers of hexagons in ordered positions (every third layer is in the same position as the first layer, the second layer corresponds with the fourth, etc); (**c**) carbon black, hexagonal layers are parallel but farther apart and arranged without order—turbostratic arrangement.

rangement of layer planes. Ordinary transmission electron microscopy provides information on the size and shape of carbon black aggregates from their two-dimensional projections as shown in Figure 2 for a rubber-reinforcing grade (N339). High resolution electron microscopy provides information on the microstructure of the aggregates from interference patterns caused by electron diffraction. These patterns are due to a concentric-layer configuration, with an interplanar distance of 0.35 nm, somewhat

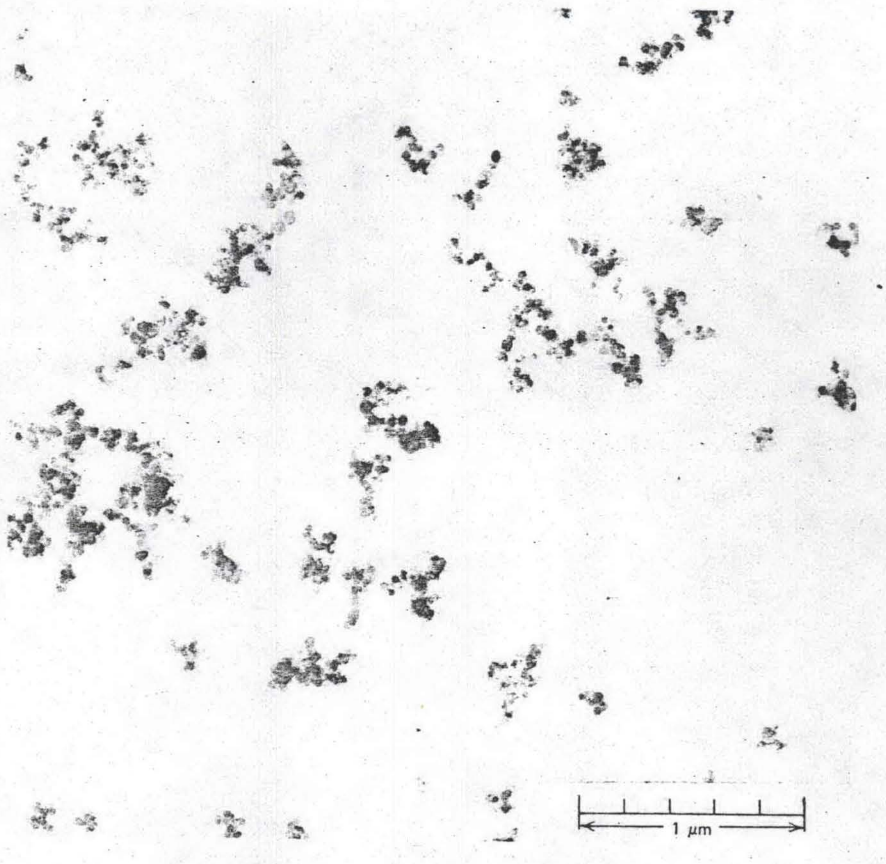

Figure 2. Electron micrograph of furnace black N339 (HAF-HS).

Table 1. Forms of Carbon and Characteristics

Form	Crystal system	Sp gr	C—C distance, nm	Layer distance, nm
diamond	cubical	3.52	0.155	
graphite	hexagonal	2.27	0.142	0.335
carbon black	hexagonal-turbostratic[a]	1.86–2.04	0.142	0.365
cokes (oven and calcined)	hexagonal-turbostratic[a]	1.3–2.1		
chars and activated carbons	hexagonal-turbostratic[a]	1.1–1.3		
fibrous carbon	hexagonal-turbostratic[a]	1.65		
vitreous carbon	hexagonal-turbostratic[a]	1.47		
pyrolytic graphite	hexagonal-turbostratic[a]	1.2–2.2		

[a] Turbostratic crystals have randomly oriented layer planes, see pp. 690–691.

larger than in graphite. Figure 3 shows a high resolution electron micrograph of a portion of a carbon black aggregate. A structural model with concentric-layer orientation proposed by Harling and Heckman (6) is shown in Figure 4. According to this model the interior of the aggregate is less ordered than the surface, has a lower density,

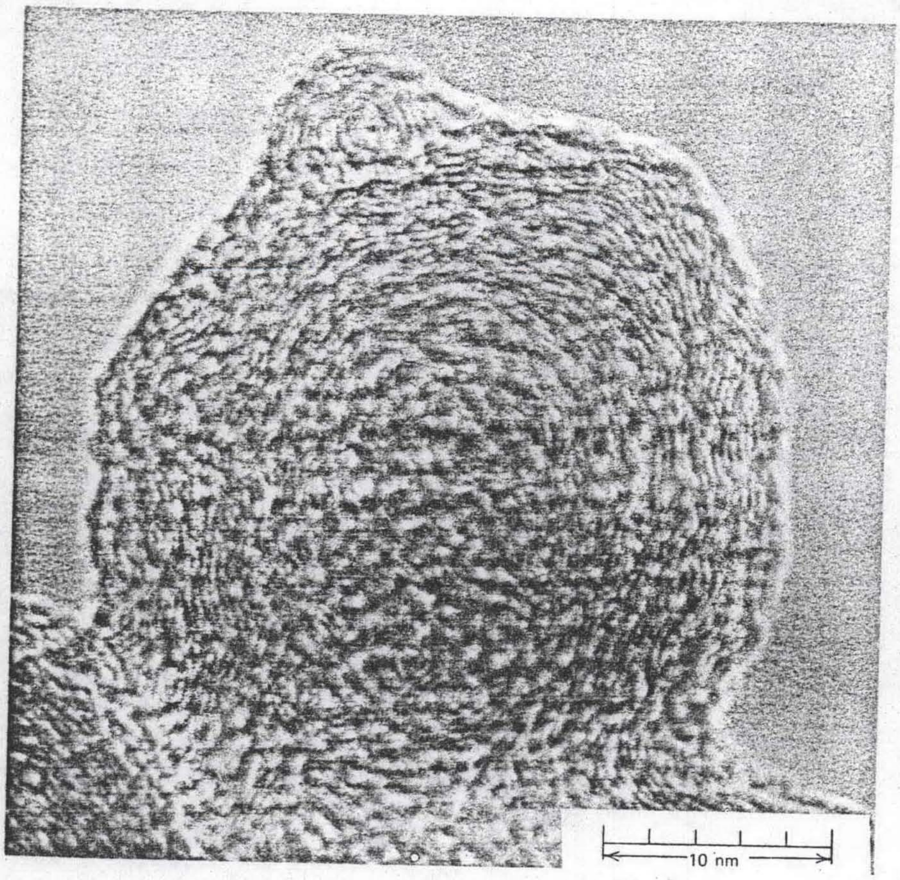

Figure 3. High resolution electron micrograph of carbon black primary aggregate nodule showing concentric orientation of layer planes.

and is chemically more reactive. Graphitization and oxidation studies confirm this view as illustrated by electron micrographs of oxidized and graphitized carbon blacks. Figure 5 shows that during oxidation the more reactive interior carbon is burned away leaving hollow shells of the less reactive surface layers. Figure 6 shows that graphitization causes increased crystallinity. The aggregates take on a capsule-like appearance with hollow centers. These changes are consistent with a concentric-layer structure.

High resolution electron microscopy also reveals that the interiors of some aggregates contain smaller concentric-layer regions which may have been separate entities at some stage of the carbon formation process. This can be seen in Figure 3. These have been called growth centers, and it is assumed that early in the carbon formation process they agglomerated, and continued to grow. The surface layers of these aggregates are distorted and folded in order to conform to aggregate geometry. This structure is clearly evident in the high resolution electron micrograph of graphitized N330 (HAF) in Figure 7.

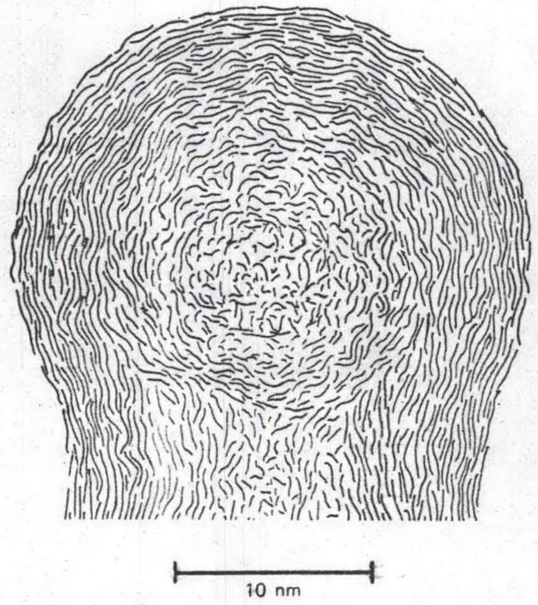

Figure 4. Concentric layer plane model of carbon black microstructure.

Characterization

Carbon blacks differ in particle size or surface area, average aggregate mass, particle and aggregate mass distributions, morphology or structure, and chemical composition. The form of these products, loose or pelleted, is another feature of some special grades. The ultimate colloidal units of cabon black, or the smallest dispersible entities in elastomer, plastic, and fluid systems are called aggregates, fused assemblies of particles. The particle size is related to the surface area of the aggregates. The oil furnace process produces carbon blacks with particle diameters of 10–250 nm and the thermal black process, 120–500 nm.

A primary aggregate is further characterized by its size, the volume of carbon comprising the aggregate, and its morphology. Aggregates have a variety of structural forms. Some are clustered like a bunch of grapes, whereas others are more open, branched, and filamentous.

Figure 8 illustrates the wide range of particle and aggregate sizes of commercial carbon blacks used for rubber reinforcement and for pigment applications.

Surface Area. The three most important properties used to identify and classify carbon blacks are surface area, structure, and tinting strength. Surface areas are measured by both gas- and liquid-phase adsorption techniques and depend on the amount of adsorbate required to produce a monolayer. If the area occupied by a single adsorbate molecule is known, a simple calculation will yield the surface area. The most familiar method is the procedure developed by Brunauer, Emmett, and Teller (BET). All commercial carbon blacks provide well-defined S-shaped isotherms with nitrogen as adsorbate at −193°C; the break in the isotherm (B point) corresponding to monolayer coverage V_m is determined and used to calculate the surface area. A useful extension of the BET method, called the "t" (adsorbed layer thickness) method, distinguishes between internal (or porous) surface area and external surface area (8). Most

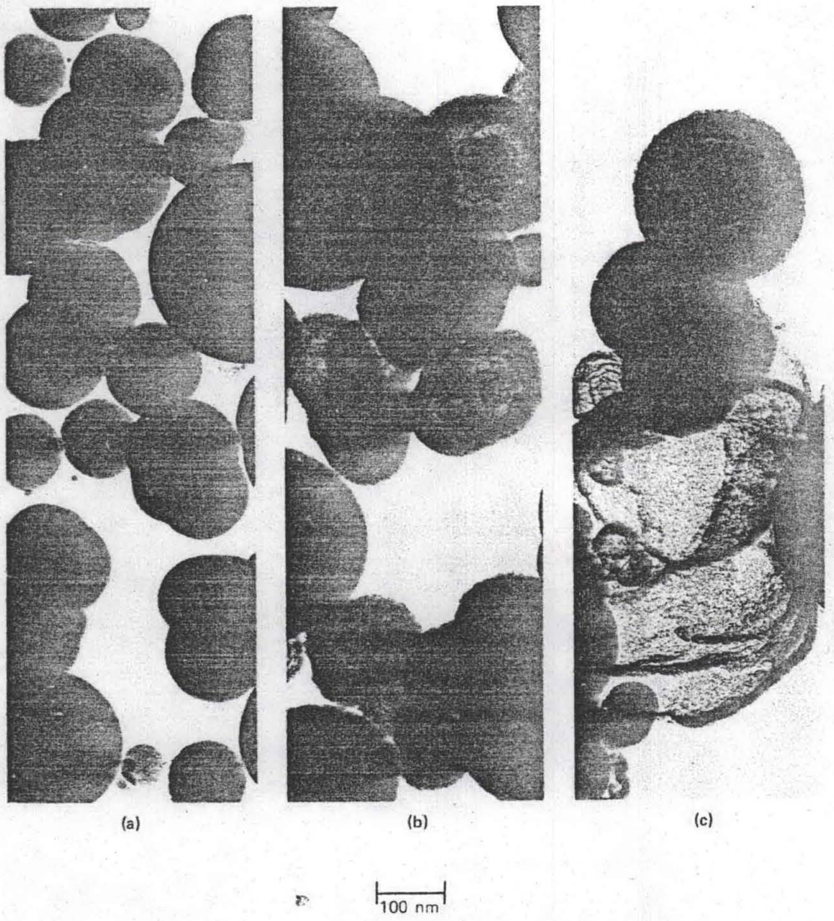

Figure 5. Electron micrographs of medium thermal carbon black particles: (**a**) original; (**b**) air-oxidized to 33% weight loss; (**c**) air-oxidized to 51% weight loss.

rubber-grade carbon blacks are nonporous, so that the BET and "t" methods give identical results. For some porous carbon blacks used for pigments and electrical applications, the "t" method is useful to assess their internal surface areas.

Liquid-phase adsorption methods are widely used for product control and specification purposes. The adsorption of iodine from potassium iodide solution is the standard ASTM method for classification of rubber-grade carbon blacks (9). The method is simple and precise, but its accuracy is affected by the presence of adsorbed hydrocarbons and the degree of surface oxidation. More recently developed surface area methods based on the adsorption of cetyltrimethylammonium bromide (CTAB) or Aerosol OT from aqueous solution are not affected by the same factors as the iodine adsorption test (10). These adsorbate molecules are so large that they cannot penetrate into micropores, and therefore provide an estimate of external surface area. The CTAB surface area method gives values in good agreement with the BET method for nonporous rubber grade blacks.

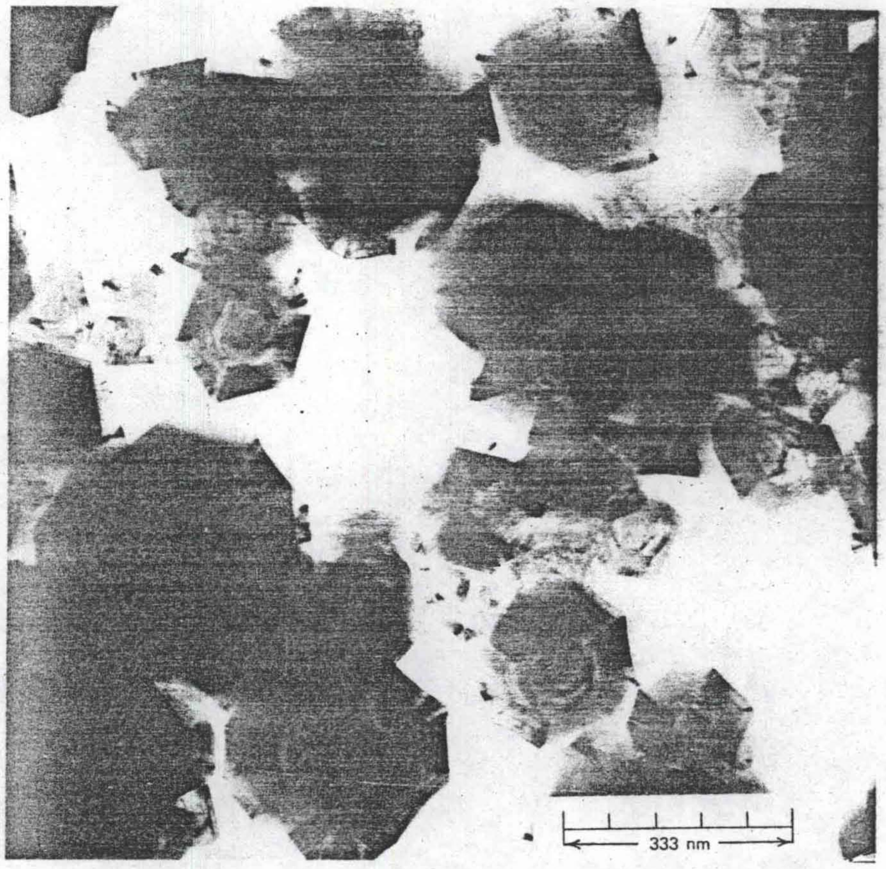

Figure 6. Electron micrograph of graphitized medium thermal carbon black.

Structure. The second most important property of carbon blacks is structure. Structure is determined by aggregate size and shape, the number of particles per aggregate, and their average mass. These characteristics affect aggregate packing and the volume of voids in the bulk material. The measurement of void volume, a characteristic related to structure, is a useful practical method for assessing structure. It is measured by adding linseed oil or dibutyl phthalate (DBP) to carbon black until the consistency of the mixture suddenly changes, at which point almost complete absorption or filling of the voids has occurred. Automated laboratory equipment is used to measure void volume by the DBP absorption (DBPA) method, a standard industry procedure (11). A modification of this procedure uses samples that have been preconditioned by four successive compression and grinding steps to fracture the weaker aggregate structures and more nearly represent the state of carbon black in rubber mixtures (12).

Tinting Strength. Tinting strength is another test method widely used to classify carbon blacks. In this test, a small amount of carbon black is mixed with a larger amount of white pigment, usually zinc oxide or titanium dioxide, in an oil or resinous vehicle to give a gray paste (13) and its diffuse reflectance measured. A carbon black with high tinting strength has a high light absorption coefficient and a low reflectance value. Tinting strength is related to average aggregate solid volume. Centrifugal sed-

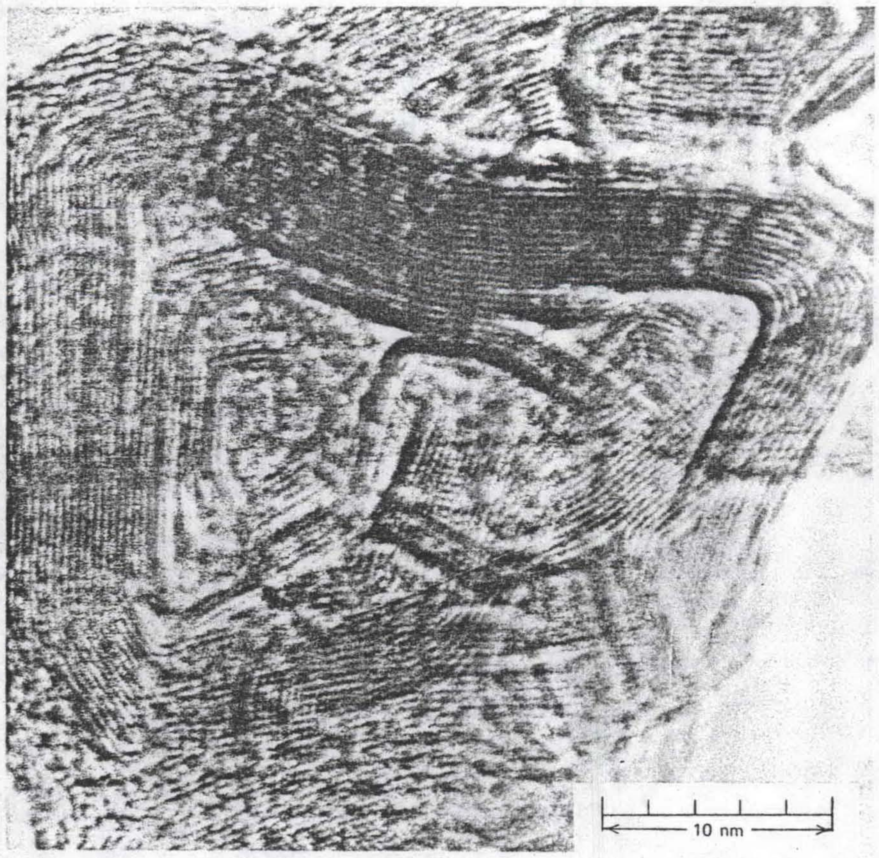

Figure 7. High resolution electron micrograph of graphitized N330 (HAF) carbon black.

imentation of aqueous carbon black suspensions has been used to estimate average aggregate volume and volume distributions (14). Figure 9 shows the correlation of tinting strength with average aggregate Stokes diameter, D_{St}. The Stokes diameter defines a sphere which sediments at the same rate as the actual aggregate.

Properties. Most commercial rubber-grade carbon blacks contain over 97% elemental carbon. A few special pigment grades have carbon contents below 90%. In addition to chemically combined surface oxygen, carbon blacks contain varying amounts of moisture, solvent-extractable hydrocarbons, sulfur, hydrogen, and inorganic salts. Hygroscopicity is increased by surface activity, high surface area, and the presence of salts. Extractable hydrocarbons result from the adsorption of small amounts of incompletely burned hydrocarbons. The combined sulfur content of carbon black has its origin in the sulfur content of the feedstocks. Most of the inorganic salt content comes from the water used for quenching and pelletizing. Table 2 lists the chemical composition of a few typical carbon blacks. Table 3 lists other analytical properties for rubber-grade carbon blacks. Table 4 lists analytical properties of carbon blacks for the ink, paint, plastics, and paper industries.

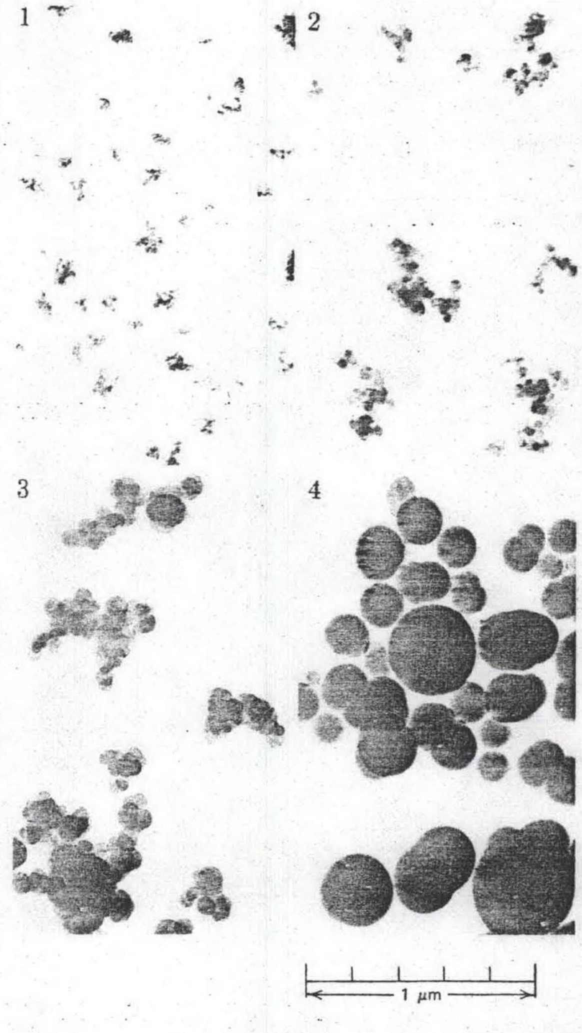

Figure 8. Electron micrographs of a range of carbon blacks: (1) high color pigment grade, 240 m^2/g; (2) rubber reinforcing grade, 90 m^2/g; (3) general purpose rubber grade, 36 m^2/g; (4) medium thermal grade. 7 m^2/g.

Formation Mechanisms

Carbon black is made by partial combustion processes involving flames, and by thermal decomposition processes in the absence of flames. Whether partial combustion or thermal decompsition methods are used, the basic reaction is represented by:

$$C_xH_y \xrightarrow{\Delta} x\,C + \frac{y}{2}H_2$$

With some hydrocarbon gases, such as methane, the reaction is endothermic, whereas with acetylene it is highly exothermic. The decomposition of heavy aromatic feedstocks in the furnace process is slightly endothermic, so that more energy is required than necessary to vaporize and heat the feedstock to reaction temperatures. The actual energy requirement will vary according to the process used, the average temperature of the carbon black formation reaction, the heat losses from the reactors, the degree

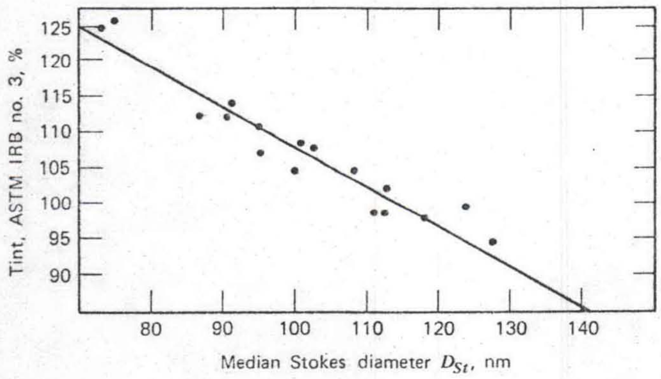

Figure 9. Tinting strength vs Stokes diameter D_{St}.

Table 2. Chemical Composition of Carbon Blacks

Symbol	Carbon, %	Hydrogen, %	Oxygen, %	Sulfur, %	Ash, %
medium thermal (N990) MT	99.4	0.3	0.1	0.0	0.3
semireinforcing furnace (N770) SRF	98.6	0.4	0.2	0.6	0.2
general purpose furnace (N660) GPF	98.6	0.4	0.2	0.6	0.2
fast extruding furnace (N550) FEF	98.4	0.4	0.4	0.7	0.2
high abrasion furnace (N330) HAF	98.0	0.3	0.8	0.6	0.3
superconducting furnace SCF	97.4	0.2	1.2	0.6	0.6
acetylene	99.8	0.1	0.1	0.0	0.0

of preheating of the input streams, the amount of heat recovery from the flue gases, and the extent to which the flue gases are used as auxiliary fuel. Modern furnace carbon black manufacture is quite efficient, reaching levels of 50–70% carbon recovery. The energy required to produce a kilogram of carbon black by the furnace process is in the range of $9\text{–}16 \times 10^7$ J/kg ($4\text{–}7 \times 10^4$ Btu/lb) depending on the grade of carbon black (see Burner technology).

The mechanism of carbon formation is not well defined. It is likely that no single mechanism can explain carbon black formation from different raw materials and by different processes. The manufacturing process has more of an influence on product quality than the raw material from which it is made. Thus natural gas or liquid aromatic hydrocarbons used in the channel black process produce the same type of carbon black. The decomposition of natural gas and benzene in a thermal process also will produce similar products. Thus a mechanism is called for in which different hydrocarbons in the vapor phase break down into smaller fragments at high temperature and recombine quickly to form particulate carbon. The temperatures and concentrations of reacting species determine the types of carbon black formed. There are several reviews of carbon formation theories (15–18).

Many of the proposed mechanisms of carbon black formation do not account for the microcrystalline morphology of the products. A model reaction mechanism of carbon formation involves sequentially: (*1*) the raw material hydrocarbon molecules decompose into smaller units or radicals with a loss of hydrogen; (*2*) these units, which may be monatomic carbon, C_2, C_3, C_6, or C_xH_y radicals, recombine into nuclei or

Table 3. Properties of Rubber-Grade Carbon Blacks

ASTM[a]	Type	Typical I_2 adsptn no.[b] D1510, mg/g	Surface area (BET), m^2/g	Particle size, nm[c]	Typical DBPA, mL/100 g D2414	Volatile content, %	Typical pour density, kg/m^3 (lb/ft^3) D1513	Tinting strength[d], % IRB 3 D3265
N110	SAF	145			113		336 (21.0)	128
N121	SAF–HS	120			130		320 (20.0)	
N219	ISAF–LS	118			78		441 (27.5)	124
N220	ISAF	121	115	22	114	1.5	344 (21.5)	114
N231	ISAF–LM	125			91		392 (24.5)	
N234		118			125		320 (20.0)	130
N242	ISAF–HS	123			126		328 (20.5)	119
N293	CF	145			100		376 (23.5)	
N294	SCF	205			106		368 (23.0)	
N326	HAF–LS	82	80	27	71	1.0	465 (29.0)	109
N330	HAF	82	80	27	102	1.0	376 (23.5)	104
N339	HAF–HS	90			120		344 (21.5)	114
N347	HAF–HS	90	90	26	124	1.0	336 (21.0)	104
N351		67			120		344 (21.5)	100
N358	SPF	84			150		288 (18.0)	
N363		66			68		481 (30.0)	
N375	HAF	90			114		344 (21.5)	116
N440	FF	50			60		481 (30.0)	
N472	XCF	270	254	31	178	2.5	256 (16.0)	
N539		42				9		384 (24.0)
N542		44			67		505 (31.5)	
N550	FEF	43	42	42	121	1.0	360 (22.5)	63
N568	FEF–HS	45			132		336 (21.0)	
N650	GPF–HS	36			125		368 (23.0)	
N660	GPF	36			91		424 (26.5)	51
N683	SPF	30			132		336 (21.0)	
N741		20			105		368 (23.0)	
N762		26			62		505 (31.5)	
N765	SRF–HS	31			111		376 (23.5)	54
N774		27			70		497 (31.0)	
N880	FT	13	12	200	35	0.5	673 (42.0)	29
N990	MT	7	8	450	35	0.5	673 (42.0)	17
acetylene black			67	40	260	0.3		

[a] ASTM designations are determined according to *Recommended Practice D2516, Nomenclature for Rubber-Grade Carbon Blacks.*

[b] In general, Method D1510 can be used to estimate the surface area of furnace blacks but not channel, oxidized, and thermal blacks.

[c] Approximate number-average particle size d_n in nm, based on electron microscopy.

[d] Industry reference black, IRB 3, an HAF grade, is taken as 100.

droplets by polymerization and condensation from the vapor phase; (*3*) the droplets continue to lose hydrogen and grow by further condensation on their surfaces of polymerized species, or the carbon nuclei grow into particles by further condensation of carbon from the vapor phase; (*4*) carbon particles or droplets flocculate; and (*5*) further carbon deposition on the carbon particle flocculates or continued loss of hydrogen from the agglomerated droplets result in the formation of primary aggregates. Higher reaction temperatures favor the formation of nuclei, smaller particle size within

Table 4. Properties of Furnace Process Carbon Blacks for Inks, Paints, and Plastics

	Nigrometer index[a]	Surface area (BET), m²/g	Particle size, nm	Oil (DBP) absorption, mL/100 g		Tinting strength index	Volatile content, %	Fixed carbon, %	pH	Toluene extract, %
				Fluffy	Pellets					
High Color Furnace										
HCF-1	64	560	13	121	105	100	9.5	90.5	3.3	0.08
HCF-2	65	240	14	65	50	115	2.0	98.0	7.0	0.08
HCF-3	69	230	15	70	65	120	2.0	98.0	7.0	0.08
Medium Color Furnace										
MCF-1	74	220	16	120	110	122	1.5	98.5	8.0	0.08
MCF-2	74	210	17	75	68	120	1.5	98.5	8.0	0.08
MCF-3	78	200	18	122	117	118	1.0	99.0	8.0	0.08
Long Flow Furnace	83	138	24	60	55	112	5.0	95.0	3.4	0.10
Medium Flow Furnace	84	96	25	72	70	112	2.5	97.5	4.5	0.10
Conductive Furnace	87	254	30	185	178	82	2.0	98.0	5.0	0.10
Regular Color Furnace										
RCF-1	84	140	19		114	114	1.5	98.5	7.0	0.10
RCF-2	83	112	24	62	60	116	1.0	99.0	7.5	0.10
RCF-3	83	86	25	65		112	1.0	99.0	8.0	0.30
RCF-4	84	94	25	62	70	110	1.0	99.0	8.5	0.10
RCF-5	87	80	27		72	104	1.0	99.0	7.5	0.10
RCF-6	90	46	36		60	92	1.0	99.0	7.0	0.10
RCF-6A	90	85	27	103		100	1.0	99.0	9.0	0.10
RCF-7	93	45	37	95		73	1.0	99.0	9.0	0.10
Low Color Furnace										
LCF-1	94	30	60		64	59	1.0	99.0	8.5	0.10
LCF-2	95	42	41		120	61	1.0	99.0	7.5	0.10
LCF-3	96	35	50		91	49	1.0	99.0	7.5	0.10
LCF-4	99	25	75	71	70	49	1.0	99.0	8.5	0.10

[a] A method for measuring the diffuse reflectance from a black paste with a black tile standard. The low numbers represent the jettest or most intense black grades.

the aggregates, and higher surface area. Aggregate formation is favored by increasing feedstock aromaticity. Particles are formed in close proximity, agglomerate, and form aggregates. The particles within an aggregate are remarkably monodisperse compared to the wide range of sizes apparent for aggregates (Figs. 2 and 8). In practice the various steps described above do not occur in an ideal sequence. For this reason carbon blacks are characterized by broad particle and aggregate size distributions.

Manufacture

Carbon black manufacture has evolved from primitive methods to continuous, high capacity systems using sophisticated designs and control equipment. About 1870 channel black manufacture began in the United States in natural gas producing areas to replace lampblack for pigment use. The discovery of rubber reinforcement by carbon black about 1912 and the growth of the automobile and tire industries transformed carbon black from a small-volume specialty product to a large-volume basic industrial raw material. Today's carbon black production is almost entirely by the oil furnace black process, which was introduced in the United States during World War II. However, the unique relationship of manufacturing process to special performance features of products has prevented the total abandonment of the older processes. The thermal, lamp black, channel black, and acetylene black processes account for less than 10% of the world's production. The easy sea and land transportation of feedstocks for the oil furnace process has made possible worldwide manufacturing facilities convenient to major consumers.

There are currently 30 furnace plant locations in the United States, 25 in Western Europe, 12 in the Eastern bloc countries, and 32 in the rest of the world. Eight United States companies produce carbon black. A recent estimate of their capacities (19) is shown in Table 5. Distribution of world carbon black manufacturing capacities is shown in Table 6.

Oil Furnace Process. The oil furnace process was developed during World War II by the Phillips Petroleum Company. The first grade of black produced was FEF (N500 type), followed by an HAF grade (N300 type) a few years later. The first successful carbon black reactor (Fig. 10) was introduced in the early fifties (20).

The oil furnace process was preceded by the gas furnace process. Gas furnace blacks were manufactured from about 1922 to the 1960s. In this process gas underwent partial combustion in refractory-lined retorts or furnaces, and carbon black was separated from the combustion gases with electrostatic precipitators and cyclone separators. Temperatures in the range of 1200–1500°C were used to produce carbon black grades designated as semireinforcing (SRF), high modulus furnace (HMF), fine furnace (FF), and high abrasion furnace (HAF). Some of these letter designations have been retained for oil furnace blacks. The gas furnace blacks were characterized by low structure levels and low-to-medium reinforcing performance. The carbon recovery of the process depended on the grade of black. The low-surface-area semireinforcing grades had yields of 25–30%, and the yields of the higher-surface-area reinforcing grades were 10–15%. The remarkable success of the oil furnace process was due to its improved yield performance in the range of 50–70%, higher capacities, and its ability to produce a wide range of products.

The use of petroleum oil for the manufacture of carbon black was patented as early as 1922 (21). The reactor contained many of the basic features of present oil

Table 5. United States Carbon Black Capacity, 1976

Manufacturer	Capacity, thousands of metric tons Furnace	Thermal
Ashland Chemical	*304*	
Arkansas Pass, Tex.	68	
Baldwin, La.	116	
Belpre, Ohio	45	
Mojave, Calif.	27	
Shamrock, Tex.	48	
Cabot Corp.	*425*	
Big Spring, Tex.	113	
Franklin, La.	91	
Pampa, Tex.	29	
Parkersburg, W. Va.	74	
Ville Platte, La.	118	
Cities Service	*343*	
Conroe, Tex.	44	
El Dorado, Ark.	37	
Eola, La.	32	
Franklin, La.	71	25
Hickok, Kan.	23	
Mojave, Calif.	24	
Moundsville, W. Va.	71	
Seagraves, Tex.	41	
Continental Oil	*194*	
Bakersfield, Calif.	35	
Ponca City, Okla.	61	
Sunray, Tex.	43	
Westlake, La.	54	
J. M. Huber Corp.	*179*	*19*
Baytown, Tex.	117	
Borger, Tex.	62	
Phillips Petroleum	*219*	
Borger, Tex.	130	
Orange, Tex.	52	
Toledo, Ohio	36	
Richardson Co.	*95*	
Addis, La.	45	
Big Spring, Tex.	50	
Thermatomic Carbon		
Sterlington, La.[a]		59
Total	*1759*	*94*

[a] Plant closed in 1977.

furnace processes including feedstock preheating and atomization, and water quenching. Another important oil furnace process was patented in 1942 (22). Table 7 compares yields for various processes. Energy requirements for each process are also shown.

Feedstocks. The feedstocks (qv) used by the carbon black industry are viscous, residual aromatic hydrocarbons consisting of branched polynuclear aromatic types mixed with smaller quantities of paraffins and unsaturates. Feedstocks are preferred that are high in aromaticity, free of coke or other gritty materials, and contain low levels of asphaltenes, sulfur, and alkali metals. For a particular plant location, other limi-

Table 6. Distribution of World Carbon Black Capacity[a]

Country	Number of plants	Estimated annual capacity, thousands of metric tons
North America		
Canada	3	164
Mexico	2	88
Total	5	*252*
South America		
Argentina	1	54
Brazil	3	152
Colombia	2	32
Peru	1	15
Venezuela	1	23
Total	*8*	*276*
Europe		
Great Britain	5	300
France	3	197
West Germany	5	269
Holland	2	116
Italy	4	175
Spain	3	91
Sweden	1	33
Yugoslavia	1	20
Total	*24*	*1201*
Australia, S. E. Asia		
Australia	3	89
India	5	111
Indonesia	1	3
Japan	9	479
Korea	1	23
Malaysia	1	13
Philippines	1	12
Taiwan	1	15
Total	*22*	*745*
Africa	1	60
Middle East		
Iran	1	15
Israel	1	11
Turkey	2	30
Total	*4*	*56*
United States	32	1888
remainder of the world[b]		680
Total		*5158*

[a] Including announced expansions through 1978.

[b] Estimated capacity.

tations usually involve the quantities available on a long-term basis, uniformity, ease of transportation, and cost.

In 1975 over 1.9 GL (5×10^8 gal) of feedstock was used for carbon black production in the United States. Sources of feedstock include petroleum refineries, ethylene plants, and coal coking plants. As a result of the introduction of more efficient petroleum cracking catalysts, decant oil from gasoline production has now become

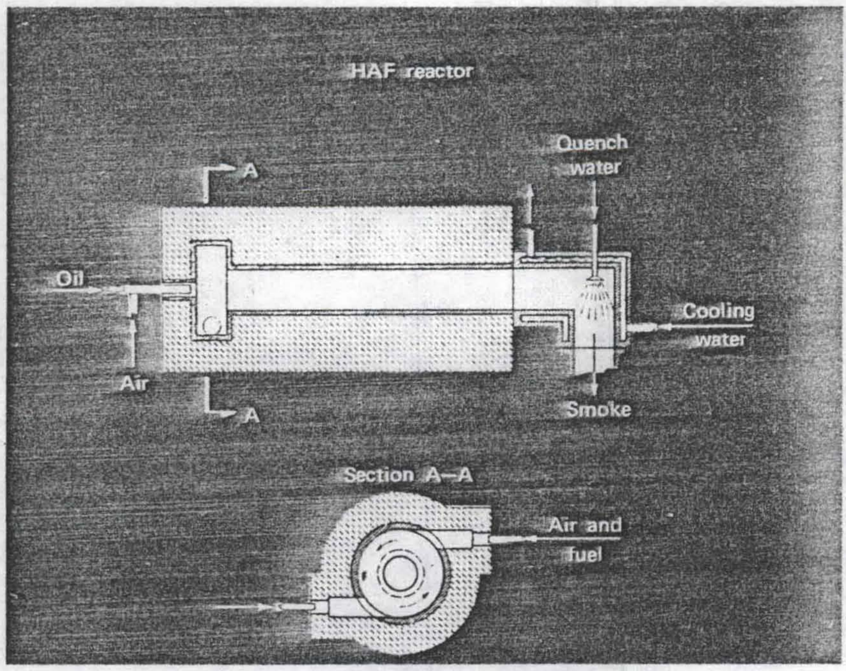

Figure 10. Phillips HAF black reactor (20).

Table 7. Yields from Different Processes

Process	Raw material	Commercial yields, g/m³ [a]	Yield % of theoretical carbon content	Energy utilization in manufacture, J/kg [b]
channel	natural gas	8–32	1.6–6.0	$1.2–2.3 \times 10^9$
gas-furnace	natural gas	144–192	27–36	$2.3–3.0 \times 10^8$
thermal	natural gas	160–240	30–45	$2.0–2.8 \times 10^8$
oil-furnace	liquid aromatic hydrocarbons	300–660[c]	23–70	$9.3–16 \times 10^7$

[a] To convert g/m³ to lb/1000 ft³, divide by 16.

[b] To convert J/kg to Btu/lb, multiply by 0.43×10^{-3}.

[c] In kg/m³ (2.5–5.5 lb/gal).

the most important feedstock in the United States, displacing residual thermal tars, and catalytic cycle stock extracts. Another important raw material is the steam pyrolysis residual tar from the manufacture of ethylene based on naphtha or gas oil. It is expected that ethylene tars will become more important as ethylene capacity increases. In Europe more ethylene process pyrolysis tars are used than in the United States. Coal tars, naphthalene and anthracene oils from coal tars, are also used for carbon black manufacture, but quantities are limited and prices are high.

Equipment. Figure 11 is a flow diagram (23) of an oil furnace process. The reactor feeds are preheated feedstock, preheated air, and gas. The carbon-containing combustion products are quenched with water sprays and pass through heat exchangers which preheat the primary combustion air. The product stream is again cooled by a secondary water quench in vertical towers. Carbon black in light fluffy form is separated in bag filters and conveyed to micropulverizers discharging into a surge tank. From the surge tank the carbon black is fed to dry drums for dry pelletization (not shown in Fig. 11) or pin-type wet pelletizers, followed by dryers, to produced pelleted products (see Pelleting).

Different grades of carbon black are made by changing reactor temperatures and residence times as shown in Table 8. The long residence time for thermal black, the largest particle size grade, is obtained with large volume reactors and relatively low gas velocities. The shortest residence times for the highest-surface-area reinforcing grades are obtained using small, high velocity reactors.

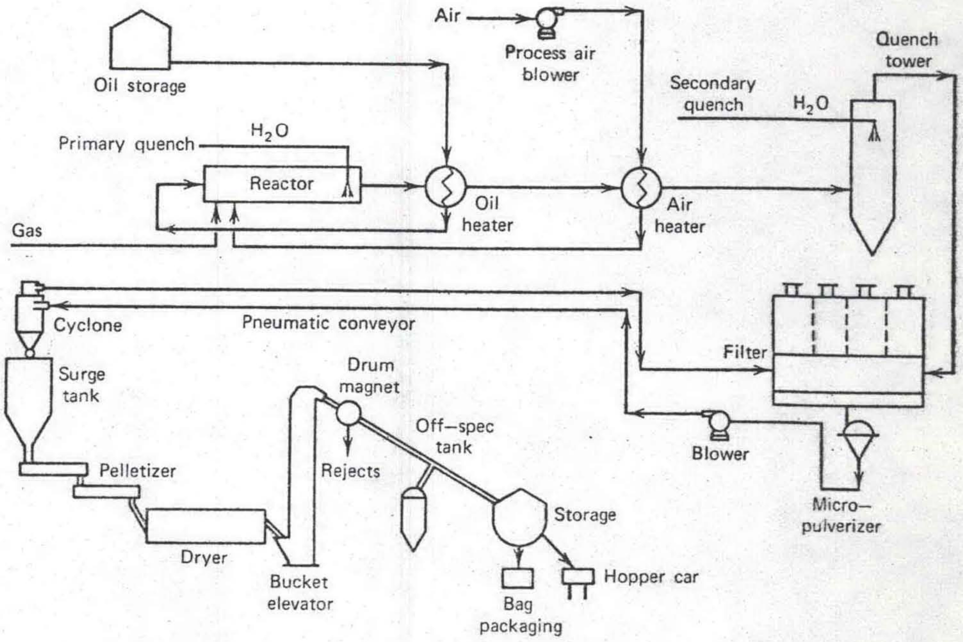

Figure 11. Flow diagram of oil furnace process.

Table 8. Time–Temperature Conditions in Carbon Black Reactors

Black grade	Residence time, s	Temperature, °C
thermal (N990)	10	1200–1350
SRF (N700 series)	0.9	1400
HAF (N300 series)	0.031	1550
SAF (N100 series)	0.008	1800

Reactors. The design and construction features of reactors are determined by economics and product specifications. Some reactors can produce over 45 metric tons of carbon black per day. At least two different types of reactors are required to make all the furnace grades for the rubber industry: one for the reinforcing and another for the less reinforcing grades. Additional types are used to produce special pigment grades. During the last decade reinforcing furnace black reactors have undergone substantial design changes to give higher gas velocities and turbulence, more rapid mixing of reactant gases and feedstock, and increased capacity (24–27). There have been fewer advances in the design of the larger reactors used for the less reinforcing, lower-surface-area grades. A notable exception has been the commercial use of huge vertical reactors having a more precise control of turbulence (28–29). Some of the latest reactor designs have refractory-lined metal construction, increased thermal efficiency, more efficient feedstock atomization, and improved quenching.

Carbon black properties, yield, and production rate can be adjusted by controlling the reactor feed variables. Combustion air and primary fuel rate are set to provide 20–50% excess air in the primary combustion flame. The desired temperature determines the feedstock rate. Lowering the feedstock rate produces higher temperatures, lower yields, and higher surface area products. In the mixing zone of the reactor a portion of the feedstock reacts with the excess air to give the required temperature. From 30 to 40% of the feedstock is burned to raise the temperature from 1450°C to 1500–1600°C when producing the most reinforcing types of carbon black. The temperature declines from this level as energy is used in the slightly endothermic hydrocarbon decomposition reactions.

In addition to the control of surface area, it is necessary to control average aggregate size, assessed by the dibutyl phthalate adsorption method (DBPA). Increasing the aromaticity of the feedstock increases the degree of aggregation. One of the most effective methods for reducing carbon black aggregation is by the injection of trace quantities of alkali metal salts into the carbon formation zone (30). This technique is useful for maintaining product DBPA specifications and for the production of low aggregation grades. The effectiveness of alkali metal addition is in the order of ionization potentials. The most commonly used alkali metal is potassium.

Post-reactor processing. The newly-formed carbon black aggregates are protected from attack by the water vapor in the hot reactor stream by rapidly reducing the temperature from 1300–1600°C to about 1000°C with a water spray. The primary water quench represents an unrecoverable energy loss and has the disadvantage of diluting the tail gas with moisture and lowering its heating value. Attempts to use indirect cooling methods to conserve heat energy have not been successful. The product stream is passed through heat exchangers to preheat the primary combustion air. The product is further cooled by a secondary water quench in a vertical tower, lowering its temperature to about 270°C before entering the bag filters. Glass cloth is commonly used in the bag filters. The product stream enters the inside of the bag filter tubes depositing carbon black and the tail gas is redistributed for use as fuel, or is flared or vented to the atmosphere. Periodically a bag filter compartment of tubes is repressurized with tail gas from the outside, releasing the carbon black.

The carbon black is collected in hoppers at the bottom of the bag filter unit, conveyed to grinders or micropulverizers which break up lumps, then conveyed to a cyclone and into the surge tank. The surge tank accumulates and partially compacts the fluffy carbon black and provides a reservoir for maintaining a constant flow to the pelletizers.

Most of the carbon black used by the rubber industry is wet pelletized. Dry pelletization is practiced for some rubber applications and for pigmentation. In the dry process the slightly compacted loose black is conveyed to large rotating steel drums whose rolling motion causes a steady increase in bulk density and the formation of pellets. A fraction of the pelletized product is recirculated and added to the loose black at the drum entry to increase the density of the bed and provide seed material to increase the formation rate.

The wet pellet process uses pin-type agitators enclosed in tubes about 0.5 m dia and about 3 m in length. The pins are arranged as a double helix, or other configuration, around a rotating shaft extending through the center of the tube. Water is added to the loose black through sprays downstream of its entry, resulting in a rapid increase in density while forming wet pellet beads. The water–carbon black ratio is critical; an insufficient amount of water results in a dusty product, and an excess causes a sticky paste which can clog the equipment. The optimum water–black ratio increases with increasing aggregation. For normal aggregation blacks about equal amounts by weight of water and black are used. There are many different types of wet pelletizers. Their water spray pressures, nozzle locations, and rotating shaft speeds influence the characteristics of the pellets.

The wet pellets are conveyed to a dryer which consists of a long, slowly-revolving cylindrical drum heated by natural gas or tail gas burners located under its entire length. A fraction of the heater exhaust gases may be passed over the moving bed of pellets in the drier drum to purge liberated moisture and remove small amounts of carbon black dust formed by pellet breakdown. The wet pellets have an initial moisture content of about 50% on entry to the drier, and after about one hour residence time exit with less than 0.5% moisture. The dried product is screened to remove oversized pellets which are recycled through the pelletization system. The product is conveyed to storage bins for bulk shipment or for bag packing. In the United States as much as 90% of carbon black production is shipped in bulk.

Good pellet quality is necessary for easy loading and unloading of bulk cars, for conveying without appreciable pellet breakdown and dustiness, and for automatic weighing in rubber factories. High bulk density is preferred for economical transportation, cleanliness, and rapid incorporation into rubber mixtures. The maximum bulk density is however limited by the requirement for good dispersion in rubber. Bulk densities of commercial furnace carbon black grades are 256–513 kg/m^3 (16–32 lb/ft^3). Their pellet size distributions are in the range of 125–2000 μm.

New Process Technology. During the early 1970s the industry adopted improved reactor and burner designs which provided more rapid and uniform feedstock atomization, more rapid mixing, and shorter residence times (27). Higher capacities and increases of 6–8% in yields for products rated at equivalent roadwear levels have been reported (31). These new carbon blacks have lower surface areas than the standard grades. Electron microscopy shows fewer large aggregates, a smaller average aggregate size, a narrower aggregate size distribution, and the individual aggregates appear to be more open, branched, and bulky. In addition to these changes in aggregate morphology, the new carbon blacks have higher tinting strengths and give evidence of higher surface activity as shown by an increase in bound rubber formation (14). In rubber, enhanced surface-polymer interaction results in higher tensile strength, modulus, hysteresis, and treadwear. The improvements in pigment and rubber performance are described in recent patents (32) (see Rubber compounding).

Thermal Decomposition Process. The high temperature decomposition of hydrocarbons in the absence of air or flames is the basis for the manufacture of thermal blacks and acetylene black. Thermal black is made by a strongly endothermic reaction requiring a large heat energy input, whereas the acetylene black decomposition reaction is strongly exothermic.

In the thermal process two refractory-lined cylindrical furnaces, or generators, alternate on about a 5-minute cycle between black production and heating, making the overall production continuous from the two generators. The generators are about 4 m in diameter and 10 m high and are nearly filled with an open checkerwork of silica brick. During operation one generator is fired with a stoichiometric ratio of air and fuel, while the other generator, heated in the previous cycle to an average temperature of 1300°C, is fed with natural gas. The product stream contains suspended carbon black, hydrogen, methane, and other hydrocarbons. This stream is cooled with water sprays and the black removed by a bag filter. Carbon recovery is about 30–45% of the total carbon content of the gas used for the heating and production cycles. The gas from the bag filter containing about 90% hydrogen is cooled, dehumidified, compressed, and used as fuel for reheating the generators. It is also used to dilute the natural gas feed for the production of a smaller particle size grade known as Fine Thermal (N880), as well as to fire boilers for plant steam and electricity. The fluffy black is passed through a magnetic separator, screened, and micropulverized. Most of the production is pelletized, packed in paper bags, or loaded directly into bulk hopper cars. Table 9 lists commercial grades of thermal blacks. The N900 series of medium thermal grades are the most widely used. The nonstaining grades N907 and N908 are made at higher average generator temperatures and longer contact times. This virtually eliminates residual hydrocarbon residues which cause staining by diffusion to the surface of many rubber products. A comparison of the analytical properties of medium and fine thermal blacks with carbon blacks made by other processes is shown in Table 10. Thermal blacks have the lowest surface area and lowest aggregation of the commercial carbon blacks. Medium thermal black particles are 400–500 nm and fine thermal blacks 120–150 nm in diameter. The electron micrograph of medium thermal black in Figure 8 shows a predominance of spherical particles in marked contrast to the aggregate nature of furnace black.

A medium thermal carbon black variety is produced in England by a cyclic process similar to the thermal process. This process uses oil for both the heating and production cycles. During the production cycle steam and oil are fed to the hot generator producing a gas containing suspended carbon black. The gas contains about 60% H_2, 25% CH_4, and 15% CO. After water cooling, about 85–90% of the black is removed with cyclones,

Table 9. Thermal Black Grades

ASTM classification	Industry type	Description
N880	FT–FF	fine thermal black, free flowing
N881	FT	fine thermal black
N990	MT–FF	medium thermal black, free flowing
N907	MT–NS–FF	medium thermal, nonstaining, free flowing
N908	MT–NS	medium thermal, nonstaining
N991	MT	medium thermal black

Table 10. Typical Analyses of Carbon Black Grades from Five Different Processes

Type:	Furnace	Thermal		Acetylene	Channel	Lampblack
Symbol:	HAF	MT	FT	Shawinigan	EPC	Lb
ASTM No.:	N-330	N-990	N-880		S300	
Property						
average particle diameter, nm	28	500	180	40	28	65
surface area (BET), m^2/g	75	47	13	65	115	22
DBPA, mL/100 g	103	36	33	250	100	130
tinting strength, % SRF	210	35	65	108	180	90
benzene extract, %	0.06	0.3	0.8	0.1	0.00	0.2
pH	7.5	8.5	9.0	4.8	3.8	3.0
volatile material, %	1.0	0.5	0.5	0.3	5	1.5
ash, %	0.4	0.3	0.1	0.0	0.02	0.02
Composition, %						
C	97.9	99.3	99.2	99.7	95.6	98
H	0.4	0.3	0.5	0.1	0.6	0.2
S	0.6	0.01	0.01	0.02	0.20	0.8
O	0.7	0.1	0.3	0.2	3.5	0.8

and the remainder is removed as a wet slurry used in the manufacture of carbon electrodes (33).

Thermal black has had wide use as a low-cost extender for rubber, as well as a functional filler for specially engineered rubber products (see Fillers). Substantial price increases during the last few years, caused by the rise in natural gas prices, have discouraged the extender use. It remains an essential ingredient in many specialty rubber products. The market share of thermal black has been as high as 11%, but in 1976 had declined to less than 5% due to the closing of some production facilities.

Acetylene Black Process. The high carbon content of acetylene (qv) (92%) makes it attractive for conversion to carbon. It decomposes exothermically at high temperatures, a property which was the basis of an explosion process initiated by electrical discharge (34). Acetylene black is made by a continuous decomposition process at 800–1000°C in water-cooled metal retorts lined with a refractory. The process is started by burning acetylene and air to heat the retort to reaction temperature, followed by shutting off the air supply to allow the acetylene to decompose to carbon and hydrogen in the absence of air. The large heat release requires water-cooling in order to maintain a constant reaction temperature. The high carbon concentration, high reaction temperature and relatively long residence time produce a unique type of carbon black. After separation from the gas stream it is very fluffy with a bulk density of only 19 kg/m^3 (1.2 lb/ft^3). Acetylene black is difficult to compact by compression and resists pelletization. Commercial grades are compressed to various bulk densities up to a maximum of 200 kg/m^3 (12.5 lb/ft^3).

Table 10 lists the properties of acetylene black in comparison with carbon blacks from other processes. It is the purest form of carbon black listed in Table 10 with a carbon content of 99.7%, and a hydrogen content of 0.1%. It has the highest aggregation with a DBPA value of 250 $cm^3/100$ g. X-ray analysis indicates that it is the most crystalline or graphitic of the commercial blacks (35). These features result in a product with low surface activity, low moisture adsorption, high liquid adsorption, and high electrical and thermal conductivities.

A major use for acetylene black is in dry cell batteries because it contributes low electrical resistance and high capacity. In rubber it gives electrically conductive properties to heater pads, heater tapes, antistatic belt drives, conveyor belts, and shoe soles. It is also used in electrically conductive plastics. Some applications of acetylene black in rubber depend on its contribution to improved thermal conductivity, such as rubber curing bags for tire manufacture.

Lampblack Process. Early lampblack processes used large open shallow pans from 0.5 to 2 m in diameter and 16 cm deep for burning various oils in an enclosure with a restricted air supply. The smoke from the burning pans was allowed to pass at low velocities through settling chambers from which it was cleared by motor-driven ploughs. Yields of ca 480–600 kg/m^3 (4–5 lb/gal) of oil were obtained when making rubber grades. Today lampblack substitutes are made by the furnace process. Traditional lampblack manufacture is still practiced, but the quantities produced are small.

Channel Black Process. The channel black process has had a long and successful history, beginning in 1872 and ending in the United States in 1976. Small quantities are still produced in a few scattered plants operating in Germany (roller-process using oil), Eastern Europe, and Japan. Rising natural gas prices, smoke-pollution, low yield, and the rapid development of furnace process grades caused the termination of channel black production in the United States.

The name channel black came from the use of steel channel irons whose flat side was used to collect carbon black deposited from many small flames in contact with its surface. The collecting channels and thousands of flames issuing from ceramic tips were housed in sheet metal buildings, each 35–45 m long, 3–4 m wide, and about 3 m high. The air supply came from the base of these buildings; the waste gases, containing large quantities of undeposited product, were vented to the atmosphere as a black smoke. Carbon black was removed from the channels by scrapers and fell into hoppers beneath the channels. Yields were very low, in the range of 1–5%. The blackest pigment grades had the lowest yields. The product was conveyed from the hot houses to a processing unit where grit, magnetic scale, coke, and other foreign material were removed. From an initial bulk density of 80 kg/m^3 (5 lb/ft^3) it was compacted and pelletized to over 400 kg/m^3 (25 lb/ft^3) for use in rubber. Lower bulk densities were used for pigment applications.

Table 10 lists the properties of easy processing channel black (EPC), a long-time favorite of the rubber industry for tire tread reinforcement. Channel blacks are surface oxidized as a result of their exposure to air at elevated temperatures on the channel irons. Due to surface oxidation, the particles are slightly porous. These features influence performance in most applications. In rubber, the acidity of the oxygen-containing surface groups has a retarding effect on rate of vulcanization. In polyethylene, where carbon black is used as an uv absorber (see Uv absorbers) and to improve weathering resistance, the phenol and hydroquinone surface groups have antioxidant properties (see Antioxidants). In inks, oxygen-containing groups contribute to flow and printing behavior.

Trends in Carbon Black Manufacture (36–37). Since the introduction of the oil furnace process in the 1940s the industry has emphasized the development of new and improved grades to meet customer requirements, and process improvements to increase yields and capacities. Carbon black yields have almost doubled, and reactor capacities have increased about tenfold from 1950 to 1975. The carbon black industry is expected to devote more of its resources in the future to energy conservation, environmental problems, and health and safety aspects of its processes and products. Because of the increasing costs of new production capacity, plant production levels will be maintained closer to rated capacity of existing facilities. The following trends in carbon black manufacture can be expected: increasing use of by-product pyrolysis tars from ethylene manufacture for feedstocks; replacement of natural gas by liquid hydrocarbons for the primary heat source; increased sensible heat recovery from the combustion stream; increased use of tail gas for its heating value; use of higher sulfur content feedstocks; and increasing use of automatic computer control.

Economic Aspects

Carbon black consumption by the rubber industry has grown steadily from the time of the discovery of its outstanding reinforcing properties by S. C. Motte in Great Britain about 1912 (38). The average annual growth rate since 1925 has been about 5.8% in the United States. Figure 12 shows United States consumption from 1887 to 1975 in six distinct growth periods on a semilogarithmic plot.

Outside the United States carbon black consumption has followed a similar pattern with a few notable differences. From 1962–1974, consumption grew at 7.6% for Western Europe and 6.1% for the United States. The United States consumed more carbon black than the rest of the world combined for the period 1915–1965. By 1975 United States consumption accounted for about 42% of world consumption.

The pigment use of carbon black was the only important market until the discovery of rubber reinforcement. The United States market distribution from 1910 to the present is shown in Figure 13 (39). About 75% of the total market depends on motor vehicle applications including tires and automotive products (40). Carbon black prices depend mainly on costs of raw materials, plant equipment, labor, and utilities. Advances in technology and improved process economics had kept prices stable from 1950–1973 but in recent years the cost of feedstock has increased more than fourfold, causing about a twofold increase in the price of the large-volume rubber grades. The bulk price range in the United States for the major rubber grade carbon blacks in 1977 was 28–35¢/kg. Special pigment grades had a very wide price range from 31.4¢/kg for the least expensive low color SRF grades to $4.41/kg for the fluffy high color lacquer and enamel grades. The HAF (N300 series) grade is the most important and now accounts for almost one half the total market. This grade is divided into a number of subgrades with different structure levels. The next important grade is GPF (N660) which was introduced in the late fifties.

Health and Safety Aspects

Carbon is a relatively stable, unreactive element, insoluble in organic or other solvents. Carbon in the form of char has been used in the pharmaceutical industry for many years. Recently, vitreous and pyrolytic carbons have been found to be biocompatible and useful for artificial heart valves, and other medical applications (see Prosthetic and biomedical devices). There is no evidence of carbon black toxicity in humans, despite the fact that it contains trace amounts of some polynuclear aromatic compounds known to be carcinogenic.

During the first years of the carbon black industry, when major production was

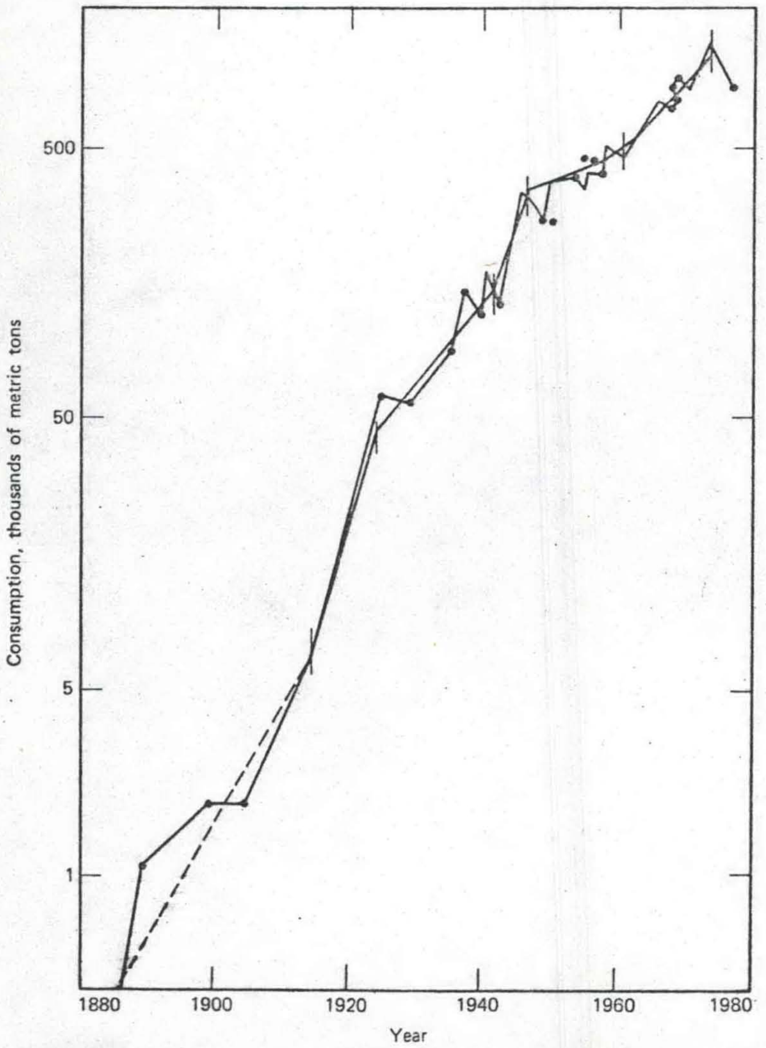

Figure 12. Carbon black consumption in the United States. Growth: 1915–1925, 16%; 1926–1942, 5.2%; 1943–1946, 17%; 1947–1961, 3.3%; 1962–1974, 5.9%.

by the channel black process, workers in the plants were exposed to an atmosphere containing carbon black. Channel black plants in the United States have been replaced by furnace process plants. Because carbon black is fine, light, easily carried by air currents, and jet black, special housekeeping procedures must be used during production and use. In order to reduce dustiness, the carbon black industry supplies its products either in loose compacted forms, or in more highly compacted pelletized forms.

The ingestion, skin contact, subcutaneous injection, and inhalation of channel, furnace, and thermal blacks by various animals causes no significant physiological changes (41–46). Although trace amounts of carcinogens were present, they were at too low a level, or were too inactive in their adsorbed state to cause a health hazard.

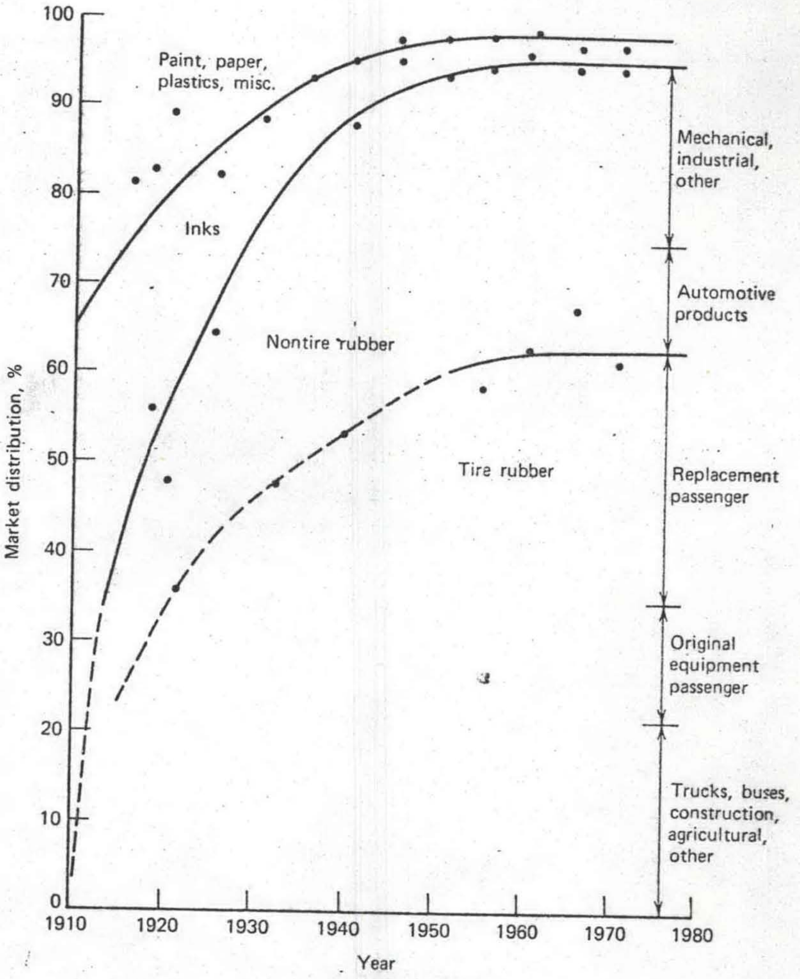

Figure 13. Carbon black market distribution.

Surveys of the health histories of carbon black workers published in 1950 and 1961 (47–48) showed their morbidity rate and observed death rate from cancer to be equal to or lower than those of comparable groups of industrial workers and the general population. Inhalation of high concentrations of carbon black over prolonged periods produced lung changes in animals due primarily to carbon black deposition with minimal or no fibrous tissue proliferation (44).

Carbon black is difficult to ignite, does not undergo spontaneous combustion, and does not produce dust explosions. When ignition does occur from contact with flames, glowing metal, sparks, or lighted cigarettes, it continues slowly with a dull glow. Due to the low conductivity of carbon black, storage fires may go undetected for some time. Fires may be controlled by purging with carbon dioxide. When this is done respirators must be used to avoid breathing carbon monoxide. Even in the absence of a fire, an air line or adequate respirator should be used when entering any confined carbon black storage facilities to avoid breathing possible toxic gases or a low oxygen atmosphere.

The level of toxic substances associated with carbon black is very low. Analytical values for a typical rubber grade semireinforcing carbon black (N774) showed 0.6 ppm phenols, 2.7 ppm lead, less than 0.05 ppm for cyanides, and less than 0.5 ppm for all other heavy metals (49). The metals have their origin in the petroleum feedstocks which have undergone various treatments and catalytic processes. The inorganic content of carbon black also includes such salts as sodium, potassium, calcium, and magnesium sulfates, chlorides, carbonates, and silicates which are contained in the water used for quenching and for wet pelletization.

The combustion of fuels can cause serious problems of atmospheric pollution from the emission of particulate material, sulfur compounds, nitric oxides, hydrocarbons, and other gases. Because of the intense blackness of carbon black it cannot be allowed to escape to the atmosphere even in minute quantities (50). Huge bag filters for complete recovery were put in operation over 30 years ago (see Air pollution control methods).

In the furnace process, tail gas burning to convert CO and H_2S to less noxious CO_2 and SO_2 has been practiced in some plants since 1950. This trend is increasing, stimulated by the necessity to recover the energy content of the tail gases. Not all the sulfur contained in carbon black feedstocks is converted to gases. One third to one half of the sulfur content is incorporated as nonextractable sulfur in the products.

Uses

Rubber. Table 11 lists the major grades used by the rubber industry, the general mechanical properties they contribute to rubber, and some examples of typical uses. A review of carbon black compounding and the types used in rubber products has been published (51) (see Rubber compounding).

Classification. The classification of carbon black grades for rubber was originally based on various performance or property characteristics, including: (*1*) levels of abrasion resistance—high abrasion furnace (HAF), intermediate super abrasion furnace (ISAF), and super abrasion furnace (SAF); (*2*) level of reinforcement—semireinforcing furnace (SRF); (*3*) a vulcanizate property—high modulus furnace (HMF); (*4*) a rubber processing property—fast extrusion furnace (FEF); (*5*) utility—general purpose furnace (GPF) and all-purpose furnace (APF); (*6*) particle size—fine furnace (FF), and large particle size furnace (LPF), fine thermal (FT), and medium thermal (MT); and (7) electrically conductive properties (XCF). Within some of these grades there were a variety of subgrades having different aggregate levels, eg, HAF with a high aggregate subgrade (HAF-HS), and a low aggregate subgrade (HAF-LS). The obvious inadequacies of this unwieldy classification procedure led ASTM Committee D-24 on carbon black to establish a letter and number system, shown in Table 3. In the ASTM system the N-series numbers increase as iodine adsorption values or surface areas decrease. The SAF grades have designated numbers from N100 to N199; the ISAF grades, N200 to N299; the HAF grades, N300 to N399; the FF and XCF (with this grade surface areas may be out of order with respect to the ASTM number) grades, N400 to N499; the FEF grades, 500 to N599; the HMF, GPF, and APF grades, N600 to N699; the SRF grades, N700 to N799; fine thermal (FT) has been designated as N880, medium thermal (MT) N990, and nonstaining medium thermal (MT-NS), N907. Aggregate levels or other quality variations within a grade are given arbitrary numbers. Table 3 lists a selected group of carbon black grades, their ASTM number,

Table 11. Applications of Major Rubber Grade Carbon Blacks

ASTM N-Type	Designation	General rubber properties	Typical uses
N990	medium thermal (MT)	low reinforcement, modulus, hardness, hysteresis, tensile strength; high loading capacity and high elongation	wire insulation and jackets, mechanical goods, footwear, belts, hose, packings, gaskets, O-rings, mountings, tire innerliners
N880	fine thermal (FT)	low reinforcement, modulus, hardness, hysteresis, tensile strength; high elongation, tear strength, and flex resistance	mechanical goods, gloves, bladders, tubes, footwear uppers
N700 Series	semireinforcing (SRF)	medium reinforcement, high elongation, high resilience, low compression set	mechanical goods, footwear, inner tubes, floor mats
N660	general purpose (GPF)	medium reinforcement, medium modulus, good flex and fatigue resistance, low heat buildup	standard tire carcass black; tire innerliners and widewalls; sealing rings, cable jackets, hose, soling, and extruded goods; EPDM compounds
N650	general purpose–high structure (GPF–HS)	medium reinforcement, high modulus and hardness, low die swell, smooth extrusion	tire innerliners, carcass, radial belt and sidewall compounds; extruded goods and hose
N550	fast extrusion (FEF)	medium-high reinforcement; high modulus and hardness; low die swell and smooth extrusion	tire innerliners, carcass, and sidewall compounds; innertubes, hose and extruded goods
N326	high abrasion–low structure (HAF–LS)	medium-high reinforcement; low modulus, high elongation, good fatigue resistance, flex resistance, and tear strength	tire belt, carcass, and sidewall compounds
N330	high abrasion (HAF)	medium-high reinforcement; moderate modulus, good processing	tire belt, sidewall, and carcass compounds; retread compounds, mechanical and extruded goods
N339, N347, N375	high abrasion–high structure (HAF–HS)	high reinforcement, modulus, and hardness; excellent processing	standard tire tread blacks
N220	intermediate super abrasion (ISAF)	high reinforcement, tear resistance; good processing	passenger and off-the-road tire treads; special service tires
N110	super abrasion (SAF)	high reinforcement	special tire treads, airplane, off-the-road, racing tires; products for highly abrasive service

their category, and typical analytical properties. Table 12 is a breakdown of the United States carbon black market according to consumption by type in 1975. Almost 80% of the market consisted of three types, HAF, GPF, and FEF.

Figure 14 is a chart of the carbon black product spectrum illustrating performance differences due to surface area, as assessed by iodine absorption, and aggregation or structure, as assessed by DBP absorption.

Properties of Carbon Black–Rubber Compounds. The general effects of different carbon blacks on rubber properties are dominated mainly by surface area and aggregation or structure. High surface area and small particle size impart higher levels of reinforcement as reflected in tensile strength, tear resistance, and resistance to abrasive wear with resulting higher hysteresis and poorer dynamic performance. Higher aggregation gives improved extrusion behavior, higher stock viscosities, improved green strength, and higher modulus values. A summary of the effects of carbon black structure and particle size on rubber processing and vulcanizate properties appears in Table 13.

Table 12. United States Carbon Black Distribution, 1975

Carbon black grade	Market, %
HAF (N300 series)	46.1
GPF (N600 series	20.3
FEF (N550)	11.5
SRF (N700 series)	8.8
ISAF (N200 series)	8.0
thermal (N800–N900 series)	4.4
SAF (N110)	0.9

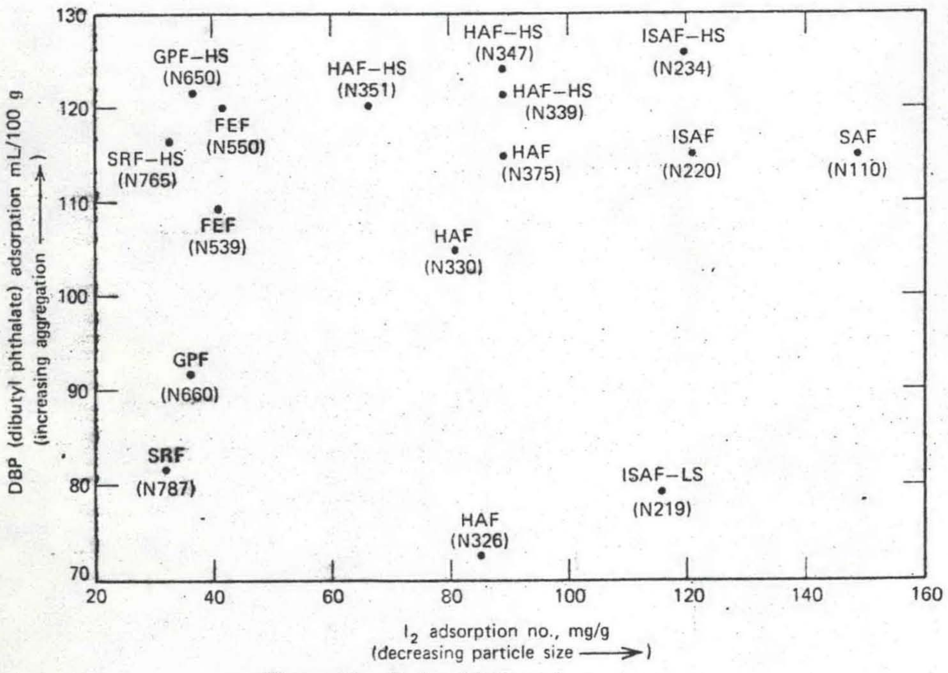

Figure 14. Carbon black grade spectrum.

Table 13. Effect of Carbon Black Colloidal Characteristics on Rubber Processing and Physical Properties

Property	Colloidal characteristics: Decreasing particle size	Colloidal characteristics: Increasing aggregation
	increasing surface area increasing iodine number increasing tinting strength	increasing aggregate size increasing DBP absorption decreasing bulk density
Rubber processing property		
loading capacity	decreases	decreases
mixing incorporation time	increases	increases
Mooney viscosity	increases	increases
dimension stability (green)	increases	increases
extrusion shrinkage	not significant	decreases
Rubber physical property		
tensile strength	increases	variable
modulus	not significant	increases
elongation	not significant	decreases
hardness	increases	increases
impact resilience	decreases	not significant
abrasion resistance	increases	variable

Rubber property changes produced by carbon black addition depend on loading. Tensile strength and abrasion resistance increase with increased loading to an optimum and then decrease. The optimum is normally in the range of 40–60 phr (parts per hundred of rubber). Increasing the loading level to 35–80 phr produces linear increases in hardness and modulus. The magnitude of these changes increases with structure. These effects are shown in Figure 15 for a group of carbon black grades including HAF (N330) used in tire treads, GPF (N660) and APF (N683) used in tire carcasses, and a medium thermal (MT) (N990) used in mechanical goods. Testing was done in a standard SBR-1500 recipe containing 12 parts of processing oil (52).

Special Carbon Blacks. About 6–7% of the total carbon black production consists of special industrial carbon grades for nonrubber applications (special blacks). Although some of the basic grades produced for the rubber market can be used for special black applications, most of these products are manufactured by methods developed to meet specific use requirements. They sell for a higher average price than the rubber grades. The growth of these markets over the last two decades has been about 4% annually. Of increasing importance in recent years have been applications in plastics where special carbon blacks are required to improve weathering resistance, or to impart antistatic and electrically conductive properties (see Antistatic agents).

About 40% of the special blacks are used in printing inks, 10% in paints and lacquers, 36% in plastics, 2% in paper, and 12% in miscellaneous applications. News inks account for most of the printing ink market. For this use special N300 series (HAF) grades containing 6% mineral oil are made to give rapid dispersion. Medium and high color blacks, the most expensive grades, are used in enamels, lacquers and plastics for their intense jetness. Carbon black grades for these applications are listed in Table 14.

Although the applications for special blacks have not changed greatly from 1965 to 1975, there were major changes in the product line and production technology. During this period the medium and high color grades, which were formerly made by the channel process, were replaced by furnace process grades.

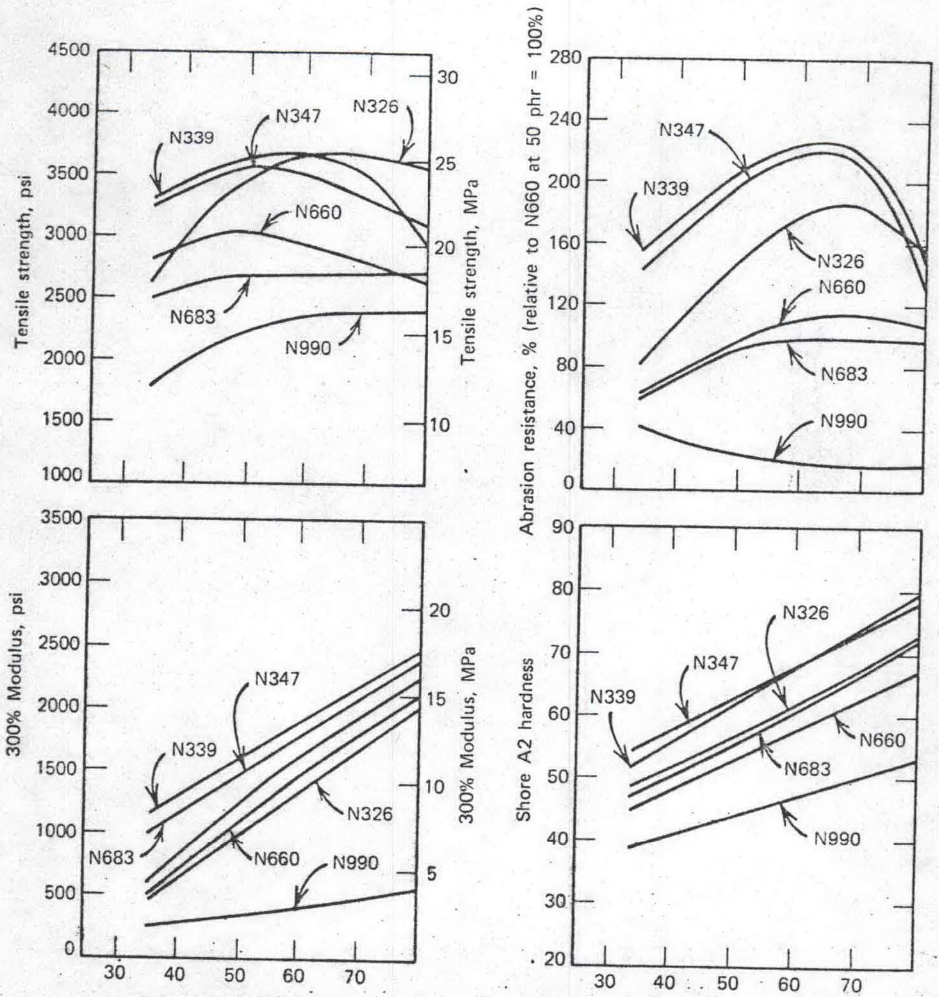

Figure 15. Properties in SBR of N339 (HAF-HS), N347 (HAF-HS), N326 (HAF-LS), N660 (GPF), N683 (APF), N990 (MT). phr = parts per hundred of rubber.

Printing Inks. The printing ink industry uses about 40% of the special blacks production in the United States. The grade and concentration used depend on the type and quality of the ink, and are selected for such factors as degree of jetness, gloss, blueness of tone, viscosity, tack, and rheological properties. Carbon black surface area, structure, degree of surface oxidation, moisture content, and bulk density are the most important factors in performance. Over forty special black grades have been developed having a broad range of properties from 20 m^2/g surface area grades used for inexpensive inks and tinting to oxidized, porous low-aggregation grades of about 500 m^2/g used for high-color enamels and lacquers. The color and rheological properties of inks are influenced by both surface area and structure as shown in Table 15. The surface chemistry of carbon blacks affects their behavior in some types of ink. Special flow grades are made by a secondary oxidative aftertreatment process to increase their volatile content, a measure of the chemisorbed surface oxygen complexes. This

Table 14. Types and Applications of Special Carbon Blacks

Type	Surface area, m^2/g	DBP absorption, mL/100 g	Volatile content, %	Uses
high color	230–560	50–120	2–10	high jetness for alkyl and acrylic enamels, lacquers, and plastics
medium color	200–220	70–120	1–1.5	medium jetness and good dispersion for paints and plastics; ultraviolet and weathering protection for plastics
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 dispersibility
medium color, medium flow	96	70	2.5	used for gloss printing and carbon paper inks; excellent jetness, dispersibility, tinting strength, and gloss in paints
regular color	80–140	60–114	1–1.5	for general pigment applications in inks, paints, plastics, and paper; gives ultraviolet protection in plastics, and 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 blacks—blue tone; used for inks—gravure, one-time carbon paper inks; also for paints, sealants, plastics, and cements
thermal blacks	7–15	30–35	0.5–1.0	tinting—blue tone; plastics and utility paints
lamp blacks	20–95	100–160	0.4–9.0	paints for tinting—blue tone
conductive blacks	254	180	2.0	conductivity and antistatic applications in rubber and plastics
acetylene	65	250	0.3	conductive and antistatic applications, dry cells, tire curing bags

treatment improves wetting, dispersion, and prevents pigment reagglomeration. Inks made with flow carbon blacks have lower viscosities and a reduced tendency to body-up or thicken during storage. Another factor influencing ease of dispersion is bulk density. Pelleted products (250–500 g/L) are more difficult to disperse than lower density or fluffy products (100–300 g/L).

Different methods of printing require inks with specially designed rheological and drying properties. Table 16 lists the major types of printing inks, typical carbon black grades and concentrations, and the basic ink vehicle composition. Letterpress news inks normally contain from 9–14% carbon black in a petroleum oil. Such inks are relatively fluid, and dry by penetration of the oil into the fibers of the paper. Cost is a paramount factor in news ink production. Large circulation weekly publications printed on coated papers at very high speeds use inks containing solvent, resin, and 10–22% carbon black. Offset or lithographic gloss inks are used in high quality book printing, illustrations, and other material where excellence in detail and transfer are paramount. Such inks must possess maximum tinting strength and covering power. This is achieved by using carbon black concentrations of 15–22%. Gravure inks vary

Table 15. Surface Area and Aggregation Effects on Ink Performance

Ink property	High surface area	Low surface area
masstone color	darker	lighter
tone	browner	bluer
viscosity	higher	lower
tint strength	stronger	weaker
dispersion	more difficult	easier
wetting	more difficult	easier
Ink property	**Low aggregation**	**High aggregation**
dispersibility	harder	easier
gloss	higher	lower
wetting	faster	slower
viscosity	lower	higher
color	darker	lighter
undertone	browner	bluer
tint strength	higher	lower
thixotropy	lower	higher

Table 16. Types and Composition of Various Printing Inks

Ink	Grades of carbon black	Carbon black concentration, %	Vehicle composition
letterpress news ink	medium color, medium structure; oil pellets	9–14	mineral oil
letterpress gloss ink (nonheat-set, heat-set)	medium color, low structure, oxidized flow; oil pellets	16–22	nonheat-set or heat-set varnish
lithographic news ink	medium color, medium structure; oil pellets	18–20	mineral oil and varnish
lithographic gloss ink (nonheat-set, heat-set)	medium color, low structure, oxidized flow; oil pellets	15–22	nonheat-set or heat-set varnish
gravure (roto)	low-medium color, low structure	5–15	resins, polymers
flexographic	low to medium structure, oxidized flow grades	12–18	resins, polymers

widely in requirements and formulation because of their diversity of applications. These inks must have good strength, low viscosity, and good gloss. Low-to-medium color, low aggregation carbon blacks are used. Highly fluid flexographic inks designed for printing on nonporous surfaces, such as plastics metal foil, and special coated paper, must dry very rapidly. The most widely used carbon blacks for flexographic inks are the medium-to-long flow, medium color grades (see Inks; Printing processes).

Paints, Lacquers, Enamels, and Industrial Finishes. Carbon black pigments for paints, lacquers, enamels, and industrial finishes fall into three categories, classified as high, medium, and standard color (see also Coatings, industrial; Paints; Pigments). In these applications, jetness or masstone is of primary significance. The coating industry uses a wide range of furnace carbon blacks. High color carbon blacks provide exceptional jetness and gloss for automobile finishes and high grade enamels. Medium color carbon blacks are used in industrial enamels, and the standard grades are used in general utility and industrial paints. Large particle size furnace and thermal grades are used to a limited extent in paints and other coatings. Although they are deficient in jetness, they provide a desirable blue tone. Carbon black is sometimes supplied to the lacquer industry in the form of masterbatch chips. These chips consist of a high loading of carbon black dispersed in a resin.

Plastics. Medium and high color carbon blacks are used for tinting and also to provide jetness in plastics (see Plastics technology). Carbon black is used in polyolefins as a protective agent. Polyolefins without carbon black degrade rapidly on exposure to sunlight. Carbon black is an excellent black body, absorbing both ultraviolet and infrared (53). When dispersed in polyethylene it preferentially absorbs and dissipates the incident radiation (54). Since carbon black also appears to be effective in terminating free radicals it provides protection against thermal degradation (see Heat stabilizers). Clear polyethylene cable jackets become brittle after two years of outdoor exposure, but the same compound containing 2% black showed no change after twenty years' exposure (55) (see Insulation, electric). Medium color furnace blacks are preferred in this application as well as for the weathering protection of plastic pipe.

Polyethylene compounds containing up to 50 wt % of furnace or thermal blacks have been developed. The deterioration of physical properties and embrittlement that would normally accompany such high loadings of black is reduced substantially by cross-linking the compound either by radiation or addition of organic peroxides. This provides greatly increased strength, and makes possible strong, tough compounds for cable coatings or pipe (56–57). Electrically conductive compounds for the cable industry depend on the use of about 30% of electrically conductive grades of carbon black (see Polymers, conductive).

Paper. The paper industry employs carbon black to produce a variety of black papers, including album paper, leatherboard, wrapping and bag papers, opaque backing paper for photographic film, highly conducting and electrosensitive paper, and black tape for wrapping high voltage transmission cables. The use of carbon black is essential when a conducting paper is desired. The loading of black will vary with the application in the range of 2–8 wt % of pulp. To obtain adequate dispersion, the black is employed in the fluffy form and added directly to the beater in a dispersible paper bag to avoid dusting. It may also be added in the form of an aqueous slurry. Aqueous dispersions containing 35% of carbon black are available. Reference 58 is a review of the applications of carbon black in the paper industry (see Paper).

Other Applications. The low thermal conductivity of carbon black makes it an excellent high temperature insulating material. For high temperature insulation up to 3000°C (59), it must be maintained in an inert atmosphere to prevent oxidation. Thermal-grade carbon black has been most widely used.

Carbon black is a source of pure carbon both for ore reduction and carburizing. Carbon brushes and electrodes are fabricated from carbon black.

There are a number of other minor applications of carbon black. For example, it is used as a pigment in the cement industry, in linoleum, leather coatings, polishes, and plastic tile.

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ELI M. DANNENBERG
Cabot Corporation

DIAMOND, NATURAL

Diamond [*7782-40-3*], the high-pressure allotrope of carbon, changes to graphite, the high-temperature allotrope of carbon, when heated above 1500°C *in vacuo.* Diamond is metastable and chemically inert at moderate temperatures. Although diamond is the hardest known substance, it is quite brittle and is readily crushed to grit and powder, the form in which approximately 75% of all industrial diamond is used. These properties make diamond of ever-increasing importance in industry and technology as a fixed abrasive in saws, drills, and grinding wheels. In the form of single crystals (stones), it is used in turning and boring tools, wire dies, indenters, tools, to shape and dress conventional abrasive wheels, and in drill crowns.

The high refraction index (2.42) and high optical dispersion give gem diamond its brilliance and fire. Diamond is the most valued of all gems because of these properties and its durability, and also because of its scarcity: the ratio of rock or gravel processed per part of diamond recovered ranges from 10 million to 100 million. Value is dictated by scarcity, color, crystal perfection, and size. The cost may range from approximately $2 to as much as $10,000 per carat (0.2 g).

Diamond, as a natural mineral, ranges widely in purity, soundness, size, color, and shape. Thus, it is necessary to sort diamonds as mined into many categories according to potential uses. Those of near flawless quality having colors of blue, blue-white, water-white, pink, green, or a slight tinge of yellow are of greatest value as gems. Approximately 20% of mined diamonds are classified as gems. Other stones that are

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Occurrence and Geology

Historically, India and Borneo were the earliest sources of diamond, but their production is now very small. Diamonds were discovered in Brazil in 1670 and have been mined there since 1721.

Diamonds were first found near Kimberley, South Africa, in 1866. Mining was started at Dutoitspan in 1871 and at Wesselton in 1890. The Premier mine was discovered in 1902. Diamonds were found in South West Africa (Namibia) in 1908, near the mouth of the Orange River in 1925, and were discovered in Mwadui, Tanzania, in 1940.

At present, approximately 90% of the world's diamonds are from the continent of Africa and are produced in Angola, Botswana, Zaire, the Central African Republic, Ivory Coast, Ghana, Sierre Leone, South West Africa (Namibia), Tanzania, and the Republic of South Africa. Extensive deposits have been found in Siberia, and the U.S.S.R. has become an important producer. Other significant producers are Brazil, British Guiana, and Venezuela (1).

Diamonds are found in New South Wales, Australia, Colombia, Mexico, and British Columbia. In the United States diamonds have been found in Wisconsin, Indiana, Michigan, California, Georgia, North Carolina, and Arkansas. The most important find is near Murfreesboro, Arkansas, although it has not been commercially significant (2). Diamonds are also found in meteorites (3).

The genesis of diamond is not well established. One theory postulates that diamond was formed in plutonic reservoirs before eruption. The volcanic pipes were probably first filled with kimberlite magma, and while still in a plastic state, the deeper seated, more fluid magma carrying diamonds and other mineral crystals continued to rise up through it and become inhomogeneously mixed with the plastic magma. The resulting rock became the present kimberlite (4–6).

Diamonds are found in ancient volcanic pipes in relatively soft, dark, basic peridotite rock called blue ground or kimberlite. Although these are considered the primary sources, not all diamonds have remained in the pipes. Over geologic ages the pipes weathered and eroded, and their diamonds were deposited in the surrounding areas or transported by rivers and concentrated in alluvial gravels or on marine terraces by the action of the sea.

Forms of Natural Diamonds

In nature, diamonds occur in a wide range of shapes, sizes, and crystal perfection. They occur as near perfect single crystals, twins, dense agglomerates of crystallites, and crystals with foreign inclusions and ingrowths. Many of these forms and shapes have been found particularly useful in industrial applications. Seven of the main diamond forms are listed below.

The most perfectly formed diamond crystal habit is the octahedron, particularly in sizes of $\frac{1}{4}$ carat and smaller. In this habit, angles and faces (111) are well defined.

Commercially, the most frequent habit is called a dodecahedron, but nearly approaches a tetrahexahedron (24 sides). The (110) faces are seldom, if ever, flat. Crystals of this habit vary from symmetrical to elongated and flattened shapes.

The cube is the most infrequent habit for single crystals. Usually, cubes contain ingrowths and spinel twins or have a surface texture resembling cube sugar.

Macles, an industrially useful form, are triangular, flat, pillow-shaped stones, consisting of twin crystals. They are twinned on the (111) plane.

Carbonado (carbons) is a cryptocrystalline material composed of diamond crystallites, graphite, and other impurities. They are extremely strong and difficult to fracture and are used in drill crowns.

Ballas, a near spherical form, consists of a dense growth of randomly oriented crystallites. These crystallites may vary in size from a few micrometers upward. Because of this microstructure, the ballas does not exhibit cleavage and is thus tougher than a single crystal. The ballas finds its best use in the severe applications of dressing large, coarse-grained abrasive wheels (see Abrasives).

Boart usually refers to minutely crystalline gray-to-black pieces of diamond which are most useful when crushed to grit for grinding wheels. The term may also be used to designate all other diamonds of inferior quality.

Properties of Diamond

Structure. Diamond is composed of the single element carbon and has a cubic crystal structure of space group 0_h^7. The lattice constant, a_0, falls between 3.56683 ± 1×10^{-6} nm and 3.56725 ± 3×10^{-6} nm (25°C). The nearest neighbor distance is 1.54450 ± 0.00005×10^{-1} nm (25°C) (7–9). The carbon in diamond is covalently bonded (10).

Classification. Diamonds are classified into four groups based on their optical and electrical properties as types 1a, 1b, 11a, and 11b. Diamond may contain several impurities, some in substantial amounts. Diamond may have mineral inclusions. There have been twenty-two species identified (11). Types 1a and 1b are the most impure with up to 0.2% nitrogen being the major impurity. Other impurities such as silicon, magnesium, aluminum, calcium, iron, and copper are present, generally in amounts below 100 ppm (12–17).

Type 1a diamonds contain 0.1% nitrogen in the form of platelets in the crystal. Most natural diamonds are of this type.

Type 1b diamonds contain up to 0.2% nitrogen in dispersed form. Almost all synthetic diamonds are of this type.

Type 11a diamonds are effectively free of nitrogen. They are very rare and have enhanced optical and thermal properties.

Type 11b diamonds are very pure, are generally blue in color, and extremely rare in nature. They have semiconducting properties thought to be caused by boron atoms in the lattice, which may also be responsible for the blue color (18–22).

Typical Physical Properties. Typical physical properties of natural diamond are listed in Table 1.

Table 1. Physical Properties of Natural Diamond

Property	Value	Reference
density[a], g/cm^3, 25°C	3.51524 ± 0.00005	23
thermal conductivity, W/(cm·K), 20°C[b]		24
Type 1	9	
Type 11a	26	
maximum at 190°C		
Type 1	24	
Type 11a	120	
thermal expansion coefficient[c]		25–26
20°C	$0.8 \pm 0.1 \times 10^{-6}$	
−100°C	$0.4 \pm 0.1 \times 10^{-6}$	
100–900°C	$(1.5 - 4.8) \times 10^{-6}$	
specific heat (constant volume), J/(mol·K)[d], 20°C	6.184	27–29
refractive index, μm		30
546.1 nm (Hg green)	2.4237	
656.3 nm	2.4099	
226.5 nm	2.7151	
dielectric constant, 27°C, 0–3 kHz	5.58 ± 0.03	31–32
optical transparency		33
Type 11a diamond	225 nm to 2.5 μm > 6 μm	
Type 1 diamond	340 nm to 2.5 μm > 10 μm	
resistivity, 20°C, Ω·cm		34–35
Type 1 and most Type 11a	$>10^{16}$	
Type 11b	$10–10^3$	
hardness, Mohs' scale (scratch hardness)[e]	10	36
Knoop scale (indentation hardness)[f,g], kg/mm^2	5,700–10,400	37–41
compressive strength[g,h], kg/mm^2		
average (flawless octahedral diamond)	885	44
maximum	1685	44
modulus of elasticity[g,i], kg/mm^2	118.1×10^3	46
Young's modulus[j,k], MPa	1.16×10^6	46

[a] Average of 35 diamonds.

[b] For comparison at 20°C, copper has 4 W/(cm·K) conductivity.

[c] For comparison, fused silica at 0–30°C is 0.4×10^{-6}.

[d] To convert J to cal, divide by 4.184.

[e] For comparison, WC, W_2C, and VC have 9.5 and SiC and Al_2O_3 have 9 hardness.

[f] Values for SiC (42) and Al_2O_3 (43) are 2480 and 2100 kg/mm^2, respectively.

[g] To convert kg/mm^2 to psi, multiply by 1422.

[h] Values for SiC and Al_2O_3 are 57.6 and 300.2 kg/mm^2, respectively (45).

[i] Values for SiC (47) and Al_2O_3 (48) are 38.7×10^3 and 35.9×10^3 kg/mm^2, respectively.

[j] To convert MPa to psi, multiply by 145.

[k] Values for SiC (47) and Al_2O_3 (48) are 0.379 and 0.345 MPa, respectively.

Chemical Properties

Diamond is chemically inert and is not attacked by acids or other chemicals except those that act as oxidizing agents at high temperature. Diamond reacts readily with molten sodium carbonate and nitrate.

Graphitization. Graphitization is the transition of diamond to graphite without the aid of external agents. If diamond is heated in vacuum or an inert atmosphere, graphitization is detected at 1500°C and increases rapidly with increased temperature (49). The octahedral surface graphitizes with an activation energy of 1059 ± 75 kJ/mol (253 ± 18 kcal/mol) and the dodecahedral surface graphitizes more rapidly with an activation energy of 728 ± 50 kJ/mol (174 ± 12 kcal/mol). The activation volume of the graphitization process is about 10 cm^3/mol (49–51). Diamond will form a black surface when heated in air at temperatures as low as 600°C.

Investigation of diamond wear on glass suggests that graphitization of diamond in contact with the glass is the primary mechanism. There may also be some chemical reaction (52). Similar studies on wear of diamonds against metals indicates that wear is related to the melting point of the metal. The ability of metals to form carbides is also involved. Thus, it appears that the mechanism of wear is through graphitization and chemical action at high temperature (53).

Recovery

Pipe mines start as open-cast operations or open-pit mines. As the pits deepen, this method becomes impractical and underground methods are used.

Along the Atlantic Coast of South West Africa (Namibia) and near the mouth of the Orange River, marine terraces, covered with many meters of sand, are mined for diamonds. The most recent operation was the dredging of the shallow ocean floor for diamonds.

Production is also from alluvial deposits in ancient river beds, flood plains, and lake beds now covered with an overburden of soil, sand, gravel, or cemented agglomerates.

Recovery of diamond from blue ground or gravel concentrate is accomplished through progressive crushing, screening, and separation of gangue from diamond and heavy minerals by gravity methods (see Gravity concentration). Jigs and heavy media separators are used. The properties of diamonds that determine the method of final recovery are size, surface conditions, optical, dielectric, and x-ray luminescence.

Grease tables are used where the diamonds are clean or can be cleaned by attrition. A clean diamond surface is not wet by water but will adhere to grease. Some marine and alluvial diamonds have a film of mineral salts that is wettable and must be chemically treated or removed before recovery is practical on grease tables.

A process called skin-flotation is also used where the nonwet diamonds float and the wet gangue material sinks.

For diamonds finer than 0.84 mm (20 mesh), electrostatic separation can be used for separation when hand sorting and other methods are impractical.

A method of separation based upon x-ray luminescence is utilized where a column of single particles of concentrate is fed past an x-ray source. The diamond luminescence is detected by a photomultiplier, and through an associated apparatus, the diamond is deflected by a synchronized air jet from the normal path, and thus separated from other minerals. This method is used extensively for recovery and is superior to an earlier, similar optical method because it is more efficient in detecting dark and discolored industrial diamonds.

Final separation, sorting and classification of all diamond is by hand, utilizing an eye loop of 7 to 10 power.

Diamond Size. The largest gem recovered was the Cullinan, weighing 3106 carats or 621.2 g (5 carats per gram). This was found in the Premier mine in 1905. The average diamond size recovered varies greatly with the mine, and may range from as small as 10 stones per carat, to as large as 1.8 carats for deposits on the Orange River terraces (54–55).

Within one century (1870–1970) of diamond mining in South Africa, 2577 gem diamonds were recovered that were larger than 100 carats and three of which were over 1000 carats (56).

Because of their great value, every effort is made to avoid loss in processing diamond. The largest gem or the most valuable combination of gems is cut from a stone; for use in tools, stones are selected that require the minimum work and have just the required quality. The smallest fragments are converted to powder. Diamonds and powder are reclaimed from worn tools and reused.

Shaping Diamond

Although diamond is the hardest material known, it may be shaped precisely. The process by which the skilled craftsman turns a stone into a brilliant faceted gem or a precisely shaped tool may involve combinations of sawing, cleaving, bruting, grinding, polishing, and drilling. Diamond boart is converted industrially by crushing to carefully sized and shaped grit and powder.

The processes of cleaving, sawing, and grinding of diamonds depend upon the proper direction of force or abrasion. The craftsman can determine the appropriate direction by observing the surface details of a stone. The three prominent planes in diamond are referred to by diamond cutters as: cleavage or 3-point (111); cube or 4-point (100); and dodecahedral or 2-point (110). The abrasion resistance and mechanical properties of the diamond are systematically related to these planes (57).

Diamond exhibits a high degree of anisotropy in abrasion resistance, which is referred to as hardness. Abrasion resistance is systematically related to the crystal structure and corresponds to a similar pattern in the coefficient of friction. This property is frequently described as the hardness vector (see Hardness).

Figures 1 and 2 show diamond crystals referred to the crystallographic axis and indicating the cubic, octahedral, and dodecahedral faces. The arrows of Figures 1 and 2 indicate "hard" and "easy" work directions, respectively. For effective grinding, polishing, and sawing, the abrasion must approximate the easy directions. Slight angular deviations in direction radically change the ability to work the diamond.

Orientation of diamond permits the consistent manufacture of tools designed to best utilize its properties so that cleavage planes may be avoided at critical edges, and a uniform abrasion resistance may be presented to the work around the radius and flanks of shaped tools.

Cleaving is an efficient method of dividing a stone. The operation consists of identifying and marking the cleavage plane (111) which will part the stone into the desired portions. A kerf or notch is abraded into the stone at a point along the mark with a sharp fragment of diamond. A steel blade is inserted into the kerf and given

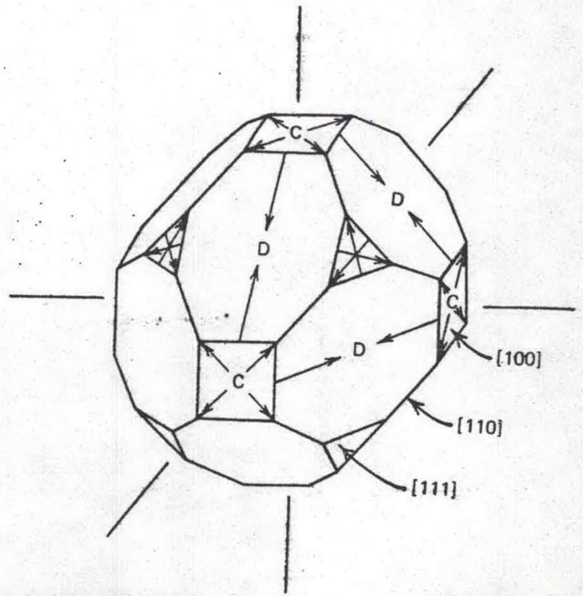

Figure 1. Arrows indicate "hard" directions of three major planes in diamond. Diamond is most resistant to abrasion in these directions.

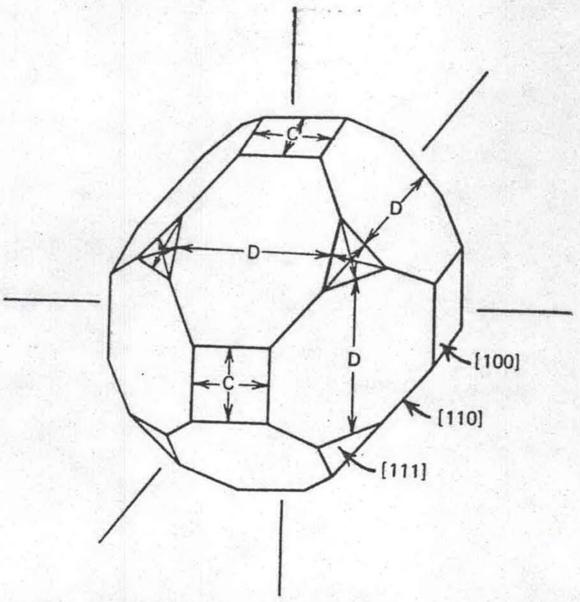

Figure 2. Arrows indicate "easy" direction of three major planes of diamond. Abrasion, sawing, and polishing are more easily accomplished in these directions.

a sharp rap with a mallet. If all steps are correct, the stone parts cleanly as planned.

Sawing is performed with thin disks of phosphor–bronze alloy of 0.076 to 0.127 mm thickness and from 7.6 to 12.7 cm diameter. These are impregnated with diamond powder. The disk is held between flanges and spins at high speed between pivots. The stone to be sawed is inspected and marked according to the desired position for parting and permissible directions of sawing. The stone is then mounted in the universally adjustable, gravity-operated saw mechanism.

A diamond can be sawed only along a plane parallel to one of the three crystallographic axes. The line of contact or abrasion of the blade must also be tangent to an axis.

Sawing of a clean stone, free of naats or cracks, proceeds quite rapidly. A stone of one carat is usually sawed in an hour or less. Since many stones contain naats, techniques of electrically-assisted abrasive sawing are used.

The same abrasion action is used in grinding and polishing, as in sawing. A diamond may be ground on a diamond-impregnated grinding wheel. Polishing is done on a high-speed cast iron lap or scaife, the surface of which is impregnated with diamond powder. The diamond is held securely in a dop that permits a wide range of angular adjustments so that the facet or radius being ground may be presented in the proper direction to the abrasive action of the wheel or scaife.

Bruting is used to round off corners and to create the girdle on gems and cylindrical, conical, or ball-shaped diamonds. The operation is similar to lathe turning. The turning tool is a piece of diamond, cemented to a hand-held holder which is brought to bear against the spinning diamond. The material removed is in the form of fine chips.

Diamonds are drilled for wire dies. The holes range in size from 0.01 to 3 mm, and are precisely shaped, sized, and polished with diamond powder. In the traditional method of drilling, the die stone is moved with a reciprocating motion against a thin steel needle rotating at high speed. A mixture of olive oil and fine diamond powder is applied to the work area. Diamond die stones are now pierced by laser (58). Traditional methods are used to shape and polish the rough laser-pierced hole (see Lasers).

Diamond powder is manufactured from boart and the lowest quality diamond. This material is progressively crushed, milled, and screened to produce the grit and powder of desired sizes. Every effort is made to produce the desired mesh sizes and shapes without producing excessive fines. Grit and powder down to 44 μm (325 mesh) are usually sized on wire mesh screens. Elutriation and sedimentation (qv) techniques are used to grade subsieve sizes.

World Production

Statistics, for 1971, on world production (in carats) of natural diamond were (59–60):

gem	11,682,000
industrial	37,877,000
total	*49,559,000*
for 1961	34,000,000
for 1950	15,517,344

Diamond Uses

High indexes of refraction, dispersion, rarity, and durability make diamond a highly prized gem.

Hardness and chemical stability make diamond a valuable and strategic industrial material. Its performance as an abrasive in shaping tungsten carbide, ceramics, and other hard materials is unsurpassed. As single crystals, it is used as wire dies and tools for turning, ruling, rock drilling, and abrasive trueing.

The thermal and electrical properties make diamond useful in solid-state applications, such as heat sinks and thermistors.

Every fragment of diamond is utilized and processed, recovered and reprocessed for applications as abrasives and lapping compounds.

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H. C. MILLER
Super-Cut, Inc.

DIAMOND, SYNTHETIC

Interest in the synthesis of diamond *[7782-40-3]* was first stimulated by Lavoisier's discovery that diamond was simply carbon; it was also observed that diamond, when heated at 1500–2000°C, converted into graphite. In 1880, the British scientist Hannay reported (1) that he made diamond from hydrocarbons, bone oil, and lithium, but no one has been able to repeat this feat (2). About the same time, Moissan believed (3) that he made diamond from hot molten mixtures of iron and carbon, but his experiments could not be repeated (4–5).

The graphite–diamond equilibrium line up to 1200 K was calculated in 1938 (6) by using the observed heat, compressibility, and thermal expansion data of the two components (see lower portion of Fig. 1). Subsequently, estimates of the diamond–graphite equilibrium line were refined and extended (7) and the extrapolation to higher temperatures fits the experimental data (8). It is evident that diamond is not thermodynamically stable below a pressure of about 1.6 GPa (16 kbar) and early investigators were using pressures in their experiments where diamond would have been unstable.

Reproducible Laboratory Diamond Synthesis

In 1955, a team of research workers at General Electric developed the necessary high-pressure equipment and discovered catalytic processes by which ordinary forms of carbon could be changed into diamond.

In the attempt at diamond synthesis (4), much unsuccessful effort was devoted to processes that deposited carbon at low, graphite-stable pressures. Many chemical reactions liberating free carbon were studied at pressures which were then available. New high-pressure apparatus was painstakingly built, tested, analyzed, rebuilt, and sometimes discarded. It was generally believed that diamond would be more likely to form at thermodynamically stable pressures. The refractory nature of carbon indicated that temperatures of about 2000 K and pressures of 5–10 GPa (50–100 kbar) might suffice. Months after operating pressures of ca 7 GPa (70 kbar) had been attained, a reproducible diamond synthesis was finally achieved which is termed the catalyzed diamond synthesis.

Catalyzed Synthesis

In this process, a mixture of carbon (eg, graphite) and catalyst metal is heated high enough to be melted while the system is at a pressure high enough for diamond to be stable. Graphite is then dissolved by the metal and diamond is produced from it. Effective catalysts are Cr, Mn, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, and Ta, and their alloys and compounds. If the metal is not molten, graphite is obtained instead of diamond even at pressures high enough to produce diamond. (The exception is tantalum which does not have to be molten to be effective.)

Generally the two requirements that the catalyst be molten and diamond be stable define a pressure–temperature area in which diamond may form with the aid of a particular catalyst system. This diamond-forming region is illustrated in Figure 2 for the nickel–carbon system. The shaded area in which diamond may form is bounded

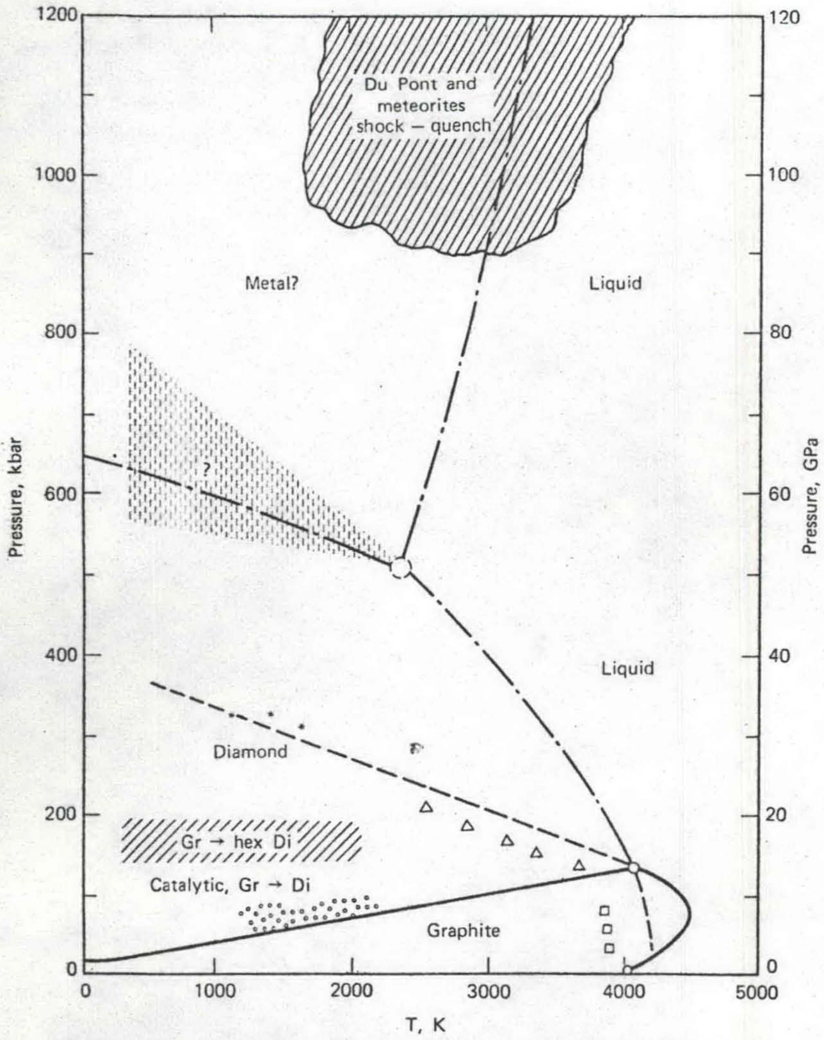

Figure 1. Carbon phase diagram (9). Gr = graphite; Di = diamond.

along the temperature axis by the nickel–carbon eutectic melting line and along the pressure axis by the graphite–diamond equilibrium line. Other catalyst metal systems define similarly shaped regions above the graphite–diamond equilibrium line. The region for platinum, for example, lies at higher pressures and temperatures than that of nickel because of the higher melting temperature of the Pt–C eutectic. Diamonds have been grown at temperatures as low as ca 1500 K and at a pressure of ca 5 GPa (50 kbar), using certain alloys of iron, nickel, and chromium as catalysts; the growth rate then is rather slow and the diamonds are heavily contaminated with metal, carbides, and graphite. Observation of the growth or disappearance of diamond has permitted a closer estimate of the course of the equilibrium line between graphite and diamond as indicated by the dashed line in Figure 2.

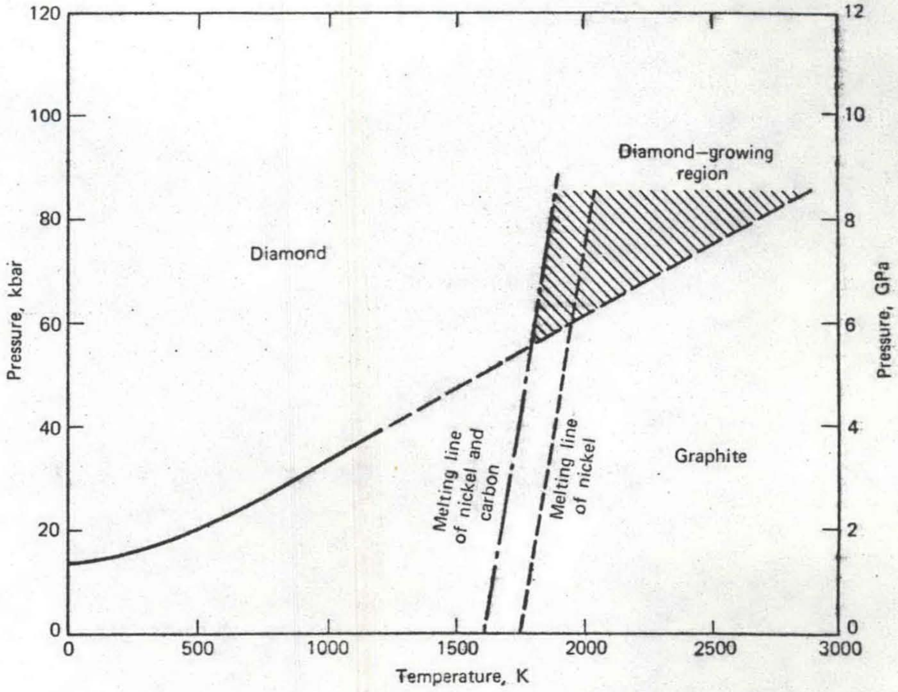

Figure 2. Diamond-forming region for the nickel–carbon system (3).

Apparatus. Many kinds of apparatus have been devised for simultaneously producing the high-pressures and temperatures necessary for diamond synthesis (9). An early, successful design is the belt apparatus (10), shown in cross section in Figure 3.

In the belt apparatus, two opposed, conical punches, made of cemented tungsten carbide and carried in strong steel binding rings, are driven into the ends of a short, tapered chamber which is also made of cemented tungsten carbide supported by strong steel rings. A compressible gasket, constructed in a sandwich-fashion of stone, usually pyrophyllite, and steel cones, seals the annular gap between punch and chamber, distributes stress, provides lateral support for the punch, and permits axial movement of the punches to compress the chamber contents. The reaction zone, usually a cylinder, is buried in pyrophyllite stone in the chamber. The pyrophyllite, a good thermal and electrical insulator, is easily machined and transmits pressure fairly well. The reaction zone is heated electrically with a heavy current.

The reaction zone temperature is measured by introducing thermocouple wires through the compressible gaskets, whereas the pressure is estimated by a calibration technique. A relationship is obtained between the force on the pistons and the pressure in the chamber by loading the reaction zone with certain metals in which abrupt changes of electrical resistance occur at certain pressures, and by noting the piston forces at which these changes occur. Typical pressure changes used are those occurring in bismuth at 2.5 and 7.5 GPa (25 and 75 kbar), in thallium at 3.7 GPa (37 kbar), and in barium at 5.3 GPa (53 kbar); such resistance changes usually coincide with changes of phase or structure in the metals at high pressure.

A belt apparatus is capable of holding pressures of 7 GPa (70 kbar) and temper-

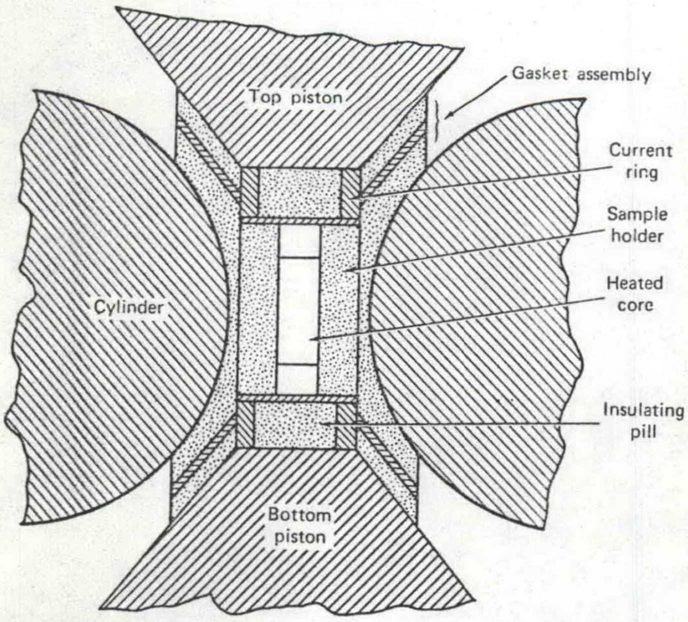

Figure 3. Cross section of belt high-pressure apparatus.

atures of up to 3300 K for periods of hours. The maximum steady-state temperatures are limited by melting of the refractory near the reaction zone (11).

Figure 4 shows an arrangement of carbon and catalyst metal. As the sample is heated at high pressure, the metal next to the graphite usually melts and diamond begins to form there. An exceedingly thin film of molten metal (at most a few thou-

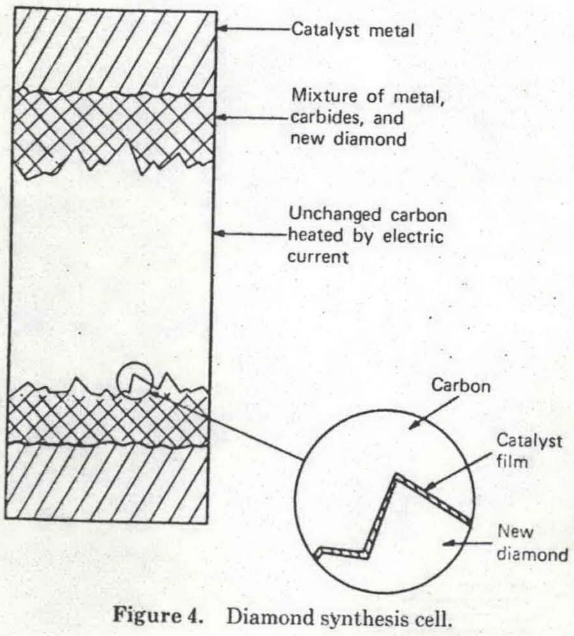

Figure 4. Diamond synthesis cell.

sandths of a cm thick) separates the newly formed diamond from the unchanged graphite. This film advances like a wave through the mass of graphite and transforms it to diamond. The speed at which this film travels depends only slightly upon the temperature but increases very rapidly to at least 1 mm/s as the pressure is increased above that necessary for diamond to be stable. Thus all graphite present in the sample, with the exception of carbon dissolved in the metal, may be transformed to diamond in time intervals of a few minutes to a few hours, depending upon the pressure, temperature, and catalyst system.

A mass of diamond crystals in a metallic matrix remains (see Fig. 5), where most of them are still covered by the catalyst metal film which is dissolved in acids to free the diamonds.

Comprehensive accounts of the methods and phenomena involved in diamond synthesis can be found in references 12 and 13.

Crystal Morphology. Size, shape, color, and impurities are dependent on the conditions of synthesis (12,14). Lower temperatures favor dark-colored, less pure crystals; higher temperatures promote paler, purer crystals. Low pressures (about 5 GPa or 50 kbar) favor the development of the cube faces, whereas higher pressures produce octahedral faces. Nucleation and growth rates increase rapidly as the process pressure is raised above the diamond–graphite equilibrium pressure.

The growing faces of diamond crystals are chemically active and tend to adsorb and incorporate certain impurities, particularly those which may be accommodated in the diamond without greatly straining the host lattice. Common contaminants are graphite, nitrogen, and certain catalyst metals, particularly nickel. The lattice dimensions of nickel and diamond are similar enough so that invisible clusters of nickel,

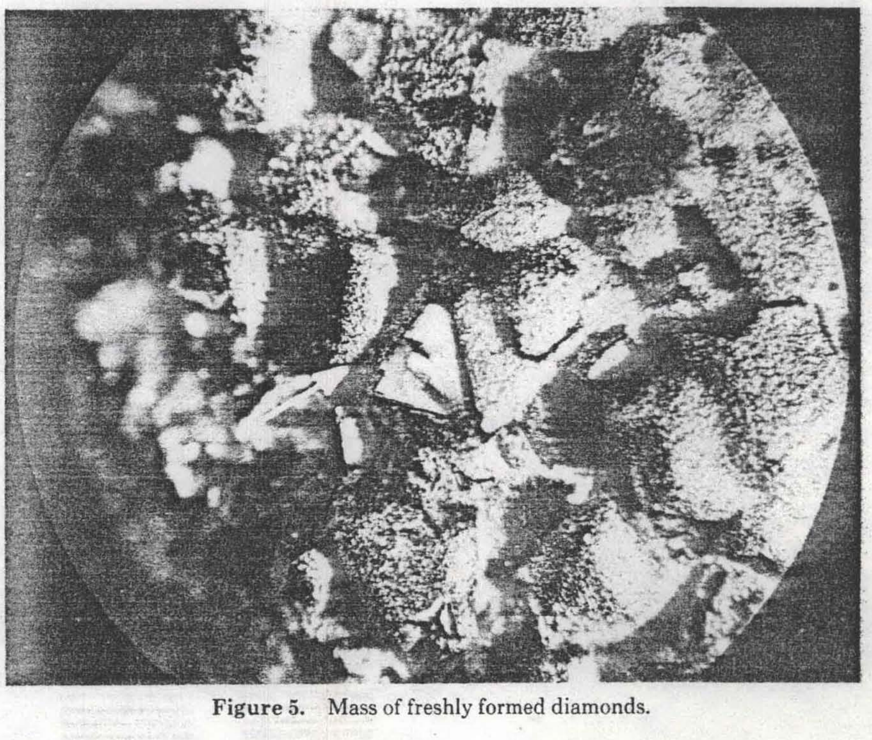

Figure 5. Mass of freshly formed diamonds.

at least several thousand atoms in diameter, may be included in diamond in an oriented sense. X-ray diffraction studies (12) show that these crystallites are oriented parallel to the diamond host lattice; the composite crystals, usually containing less than 1% of nickel, are ferromagnetic with approximately the same Curie temperature as massive nickel. It appears that even though synthetic diamonds are essentially the same as natural diamonds, there are enough differences between them, mainly in structure and impurity content, to permit an observer to distinguish between them.

Crystal Growth. If diamond seed crystals are placed in the active diamond growing zone of a typical graphite–catalyst metal apparatus, new diamond usually forms on the seed crystals. However, the new growth tends to be uneven in thickness and quality, with gaps or inclusions of foreign material. Such defects probably appear because the main driving force for the nucleation and growth under these conditions is the Gibbs free energy difference between diamond and graphite, which is a function of pressure, temperature, and composition; none of these variables can be sufficiently controlled. However, excellent growth can be obtained if pressure and composition are held relatively constant while the change of composition with temperature is employed as a driving force. In practice, small diamonds are used as the source of carbon in a hotter portion of a molten catalyst metal bath at about 1500°C and 5.5 GPa (55 kbar). Diamond seed crystals are placed in a cooler portion of the bath and the difference in solubility resulting from the difference in temperature causes diamond to recrystallize on the seed crystals in a slow, controlled fashion (15). Growth periods up to a week are used for the larger crystals of about 5 mm or 1 carat (0.2 gram). The process is not commercially feasible, but the control of growth conditions and bath compositions permits the formation of various types of high-quality diamond crystals for property studies (16–17). A few parts-per-million of boron impart a blue color and make the diamonds semiconducting (see Semiconductors). A few dozen parts-per-million of nitrogen give a yellow color. Colorless crystals of outstanding purity, crystal perfection, and thermal conductivity have been made (see Fig. 6).

Direct Graphite-to-Diamond Process

In this process, diamond forms from graphite without a catalyst. The refractory nature of carbon demands a fairly high temperature (2500–3000 K) for sufficient atomic mobility for the transformation, and the high temperature in turn demands a high pressure (above 12 GPa; 120 kbar) for diamond stability. The combination of high temperature and pressure may be achieved statically or dynamically. During the course of experimentation on this process a new form of diamond with a hexagonal (wurtzitic) structure was discovered (18).

Shock Synthesis. When graphite is strongly compressed and heated by the shock produced by an explosive charge, some (up to 10%) diamond may form (19–20). These crystallite diamonds are small (on the order of 1 μm) and appear as a black powder. The peak pressures and temperatures, which are maintained for a few microseconds, are estimated to be about 30 GPa (300 kbar) and 1000 K. It is believed that the diamonds found in certain meteorites were produced by similar shock compression processes which occurred upon impact (5).

Some diamond powder is produced commercially by shock-wave methods. The DuPont process (21), exposes small, well-crystallized graphite lumps in nodular cast iron to the brief, intense pressure generated by a suitable charge of high explosive.

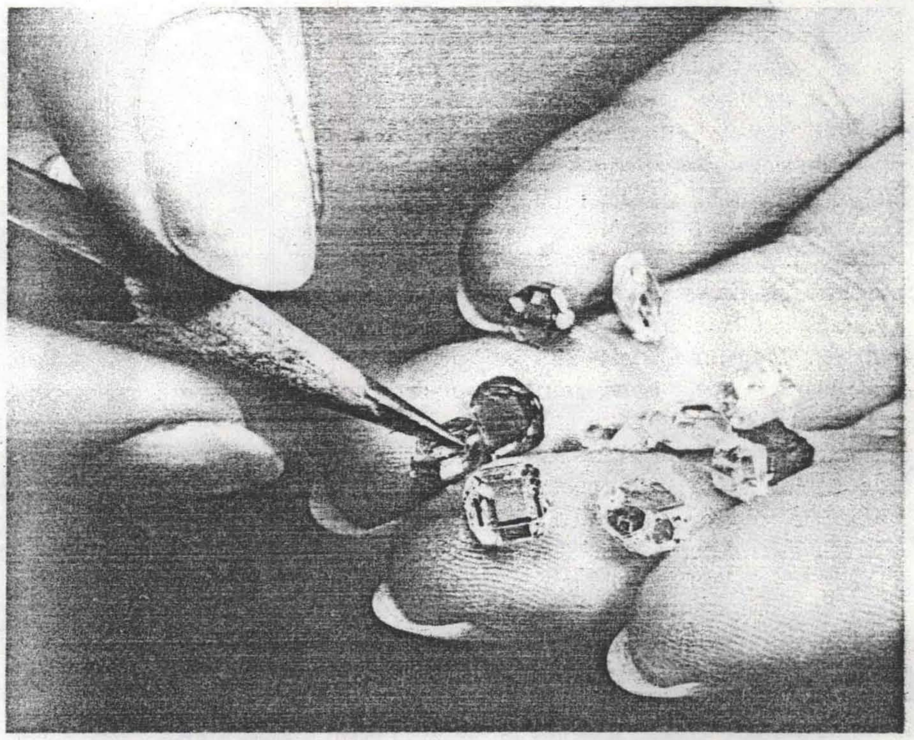

Figure 6. Synthesized high-quality single crystal diamonds.

The graphite lumps are more compressible and reach much higher temperatures than the surrounding iron at the peak pressures, which last for a few microseconds, and part of the graphite turns into diamond. The carbon is cooled rapidly by the iron environment and the new diamond is thereby preserved. After recovery of the mass, the iron is dissolved and the diamond is separated by controlled oxidation of the graphite. The final product is a gray powder with particles ranging in size up to 30 μm.

The annual production of diamond by this process is only a small fraction of total industrial diamond consumption.

Static Pressure Synthesis. Diamond can form directly from graphite at pressures of about 13 GPa (130 kbar) and higher at temperatures of about 3300–4300 K (22). No catalyst is needed. The transformation is carried out in a static high-pressure apparatus in which the sample is heated by the discharge current from a capacitor. Diamond forms in a few milliseconds and is recovered in the form of polycrystalline lumps. From this work the triple point of diamond, graphite, and molten carbon is estimated to lie at about 13 GPa and 4200 K (12,22).

At pressures of 13 GPa many carbonaceous materials decompose when heated and the carbon eventually turns into diamond. The molecular structure of the starting material strongly affects this process. Thus condensed aromatic molecules, such as naphthalene or anthracene, first form graphite even through diamond is the stable form. On the other hand, aliphatic substances such as camphor, paraffin wax, or polyethylene lose hydrogen and condense to diamond via soft, white, solid intermediates with a rudimentary diamond structure (23).

Crystal Structure. A diamond prepared by the direct conversion of well-crystallized graphite, at pressures of about 13 GPa (130 kbar), shows certain unusual reflections in the x-ray-diffraction patterns (18). They could be explained by assuming a hexagonal diamond structure (related to wurtzite) with $a = 0.252$ and $c = 0.412$ nm, space group $P6_3/mmc - D^4_{6h}$ with 4 atoms per unit cell. The calculated density would be 3.51 g/cm^3, the same as for ordinary cubic diamond, and the distances between nearest neighbor carbon atoms would be the same in both hexagonal and cubic diamond, 0.154 nm.

Figure 7 shows the crystal structures of graphite, ordinary cubic diamond, and hexagonal diamond. The layers of carbon atoms lie in flat sheets in graphite, but in diamond the sheets are more wrinkled and lie closer together. Taken separately, the sheets are similar but they may be stacked in various lateral positions and still have bonding between them.

In cubic diamond (zinc-blende structure) the wrinkled sheets lie in the (111) or octahedral face planes of the crystal and are stacked in an ABCABC sequence. In real crystals, this ABCABC sequence continues indefinitely, but deviations do occur. For example, two crystals may grow face-to-face as mirror images; the mirror is called a

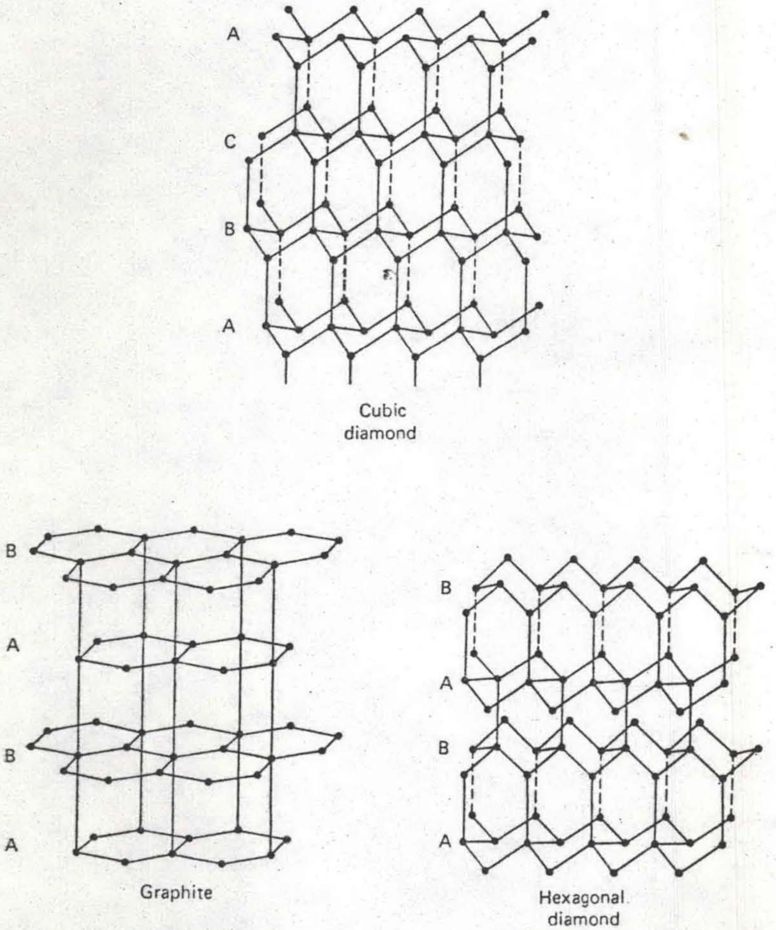

Figure 7. Crystal structures of graphite, ordinary cubic diamond, and hexagonal diamond; A, B, and C are the lateral positions.

twinning plane and the sequence of sheets crossing the mirror runs: ABCABCCBACBA. Many unusual sequences may exist in real crystals, but they are not easy to study.

In hexagonal diamond (wurtzite structure) the wrinkled sheets are stacked in an ABABAB sequence, as shown in the Figure 7. Looking down on the stack from above, hexagonal holes can be seen formed by the six-membered carbon rings. The crystal has hexagonal symmetry about this axis, hence the name hexagonal diamond.

The sequence of sheets in graphite is also ABAB; however, an examination of the atomic positions shows that they are not simply related to those in either kind of diamond. Thus the simple compression of graphite should not be expected to yield diamond. However, well-crystallized graphite, in which the ABAB sequence extends for at least hundreds of layers, tends to form hexagonal diamond more easily than cubic diamond.

In spite of the close relationship between the two structures, some reshuffling of the atoms is necessary to complete the transformation of graphite into hexagonal diamond crystals of a large enough size to detect. The necessary atomic motions can be provided by heating to about 1500 K, much lower than the 2300–3300 K required to make cubic diamond from ordinary graphite without a catalyst. Even so, various departures from ideality make it difficult to prepare entirely hexagonal diamond material, even when the best graphite is used. The products obtained so far always contain some ordinary diamond as well as some remnant graphite, parts of which are compressed by the nearby diamond regions. Hence many physical properties of hexagonal diamond are not very well known, including its stability relative to cubic diamond.

The same general kinds of effects described here for carbon have also been noted in the direct conversion of hexagonal boron nitride to the denser forms (24) (see Boron compounds, refractory boron compounds).

Hexagonal diamond was found in the Canyon Diablo meteorite and in the shock-made diamond from DuPont, but not in the diamond from Allied Chemical nor in regular abrasive synthetic diamond (25). This new mineral form of natural carbon has been named Lonsdaleite.

Metastable Vapor Phase Deposition

Metastable growth of diamond takes place at low pressures where graphite is thermodynamically stable. The subject has a long history, and work in the United States and the Soviet Union indicates that diamond may form at moderate pressures during decomposition of gases such as methane. In a patented process (26–28), batches of clean diamond powder were alternately exposed to methane at about 1320 K and 10 kPa (0.1 atm) for a few hours followed by hydrogen at 1300 K and 5050 kPa (50 atm). The hydrogen treatment removed graphite. After several such cycles the diamond masses gained in weight by several percent and contained only diamond.

In a similar process for growth of diamond whiskers, a single crystal diamond is heated by radiation during observation under a microscope. The mean growth rate was about 10 μm/h and crystals of 400 by 20 by 20 μm were grown. So far this general method of diamond growth is not used commercially.

The Synthetic Diamond Industry

Soon after the first successful diamond syntheses by the catalyst process, small batches of crystals were prepared in the laboratory. When mounted in abrasive wheels, these first synthetic diamonds performed better than comparable natural diamonds for shaping of ceramics and cemented tungsten carbide. A pilot plant for producing synthetic diamond was established, the efficiency of the operation was increased, production costs declined, and product performance was improved. Today the price of General Electric man-made diamond is competitive with natural diamond prices.

Several kinds of diamonds can be produced, depending upon synthesis conditions, with each kind especially suited for particular uses. For example, the shaping of cemented tungsten carbide is an operation that consumes a large fraction of industrial diamond grit, and friable crystals with many sharp edges and corners, such as shown in Figure 8, mounted in a free-cutting resinoid or vitrified wheel matrix, are the most suitable for this task. The excellent abrasive properties seem to be caused by a better bond between diamonds and wheel matrix, and a greater number of constantly renewed sharp cutting edges per abrasive grain.

When the diamond grit is carried in a sintered, metal matrix in the abrasive tool, tougher, more coherent, block-shaped crystals, as shown in Figure 9, are preferred. The combination of more severe operating conditions and the strong metallic matrix imposes high loads upon each abrasive grain and the grains must be strong enough to resist these high cutting forces without crumbling (see Abrasives).

As of 1977, the bulk of synthetic industrial diamond production consists of the

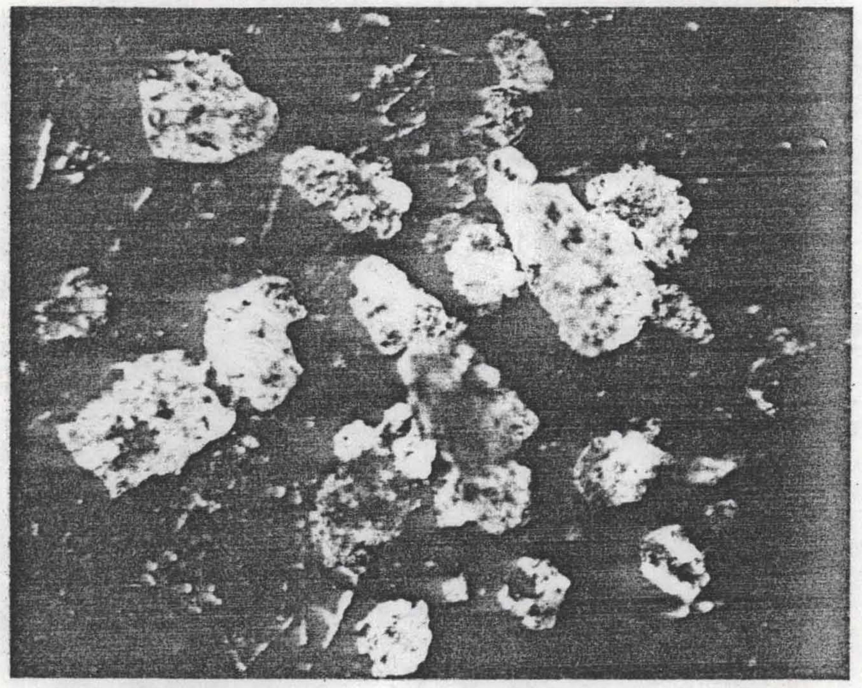

Figure 8. Synthetic diamond grit for resinoid or vitreous bond (free-cutting) abrasive wheels.

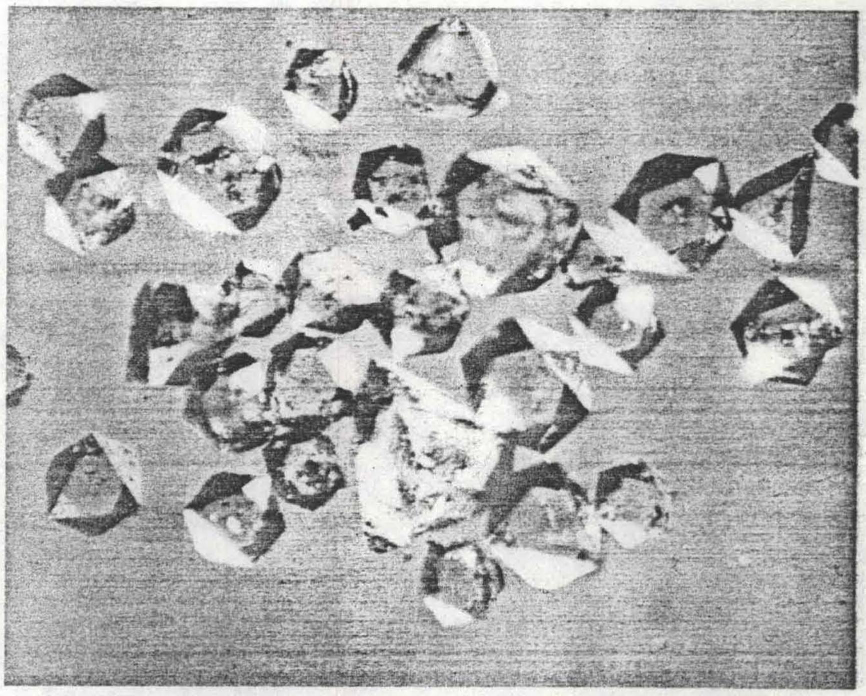

Figure 9. Synthetic diamond grit for metal bond abrasive wheels.

smaller crystal sizes up to about 25 mesh (0.7 mm) particle size. This size range has wide utility in industry, and a significant fraction of the world's need for diamond abrasive grit is now met by synthetic production (hundreds of kilograms per year). Because the raw materials are plentiful, synthetic production could, if necessary, supply the world demand for diamond abrasive. Development work continues in order to improve size and utility of the manufactured product and to realize the full potential of diamonds at minimum cost. An appreciable increase in performance has been obtained by coating the diamonds with a thin layer of nickel or copper, before incorporating them into wheels. The thin layer of metal apparently improves adhesion and heat transfer. The General Electric Company is the major producer of synthetic industrial diamonds. DeBeers Consolidated Mines in South Africa (which has a large stake in natural diamonds), and the Soviet Union have recently begun manufacture of synthetic diamonds. DeBeers currently produces synthetic diamond grit in plants in Shannon, Ireland, as well as in South Africa and Sweden. Synthetic, industrial diamond is also made in Japan and in the People's Republic of China.

Semiconducting Diamonds. With the exception of the rare, natural type IIb, diamond is normally a good electric insulator. However, semiconducting diamonds are prepared by adding small amounts of boron, beryllium, or aluminum to the growing mixture, or by diffusing boron into the crystals at high pressures and temperatures. Such diamonds are *p*-type, with activation energies for conduction usually ranging between 0.1 and 0.35 eV. Addition of boron gives the diamonds a blue color. Some of these crystals have been used as thermistors with a very wide, stable operating temperature range, −200 to 500°C having nominal resistance of 4,000–40,000 ohms (29).

Sintered Diamond Masses. Some natural diamonds known as carbonado or ballas occur as tough, polycrystalline masses. The production of synthetic sintered diamond masses of comparable excellent mechanical properties has only been achieved recently (30). The essential feature is the presence of direct diamond-to-diamond bonding without dependence on any intermediate bonding material between the diamond grains, since no extraneous bonding material can match the stiffness, thermal conductivity, and hardness of diamond. Formidable inherent obstacles are encountered when the sintering of small diamond crystals is attempted (13), and the process must be conducted at high pressure to keep the diamonds from changing into graphite.

Since these masses of polycrystalline diamond possess extensive diamond-to-diamond bonding, they have, in contrast to single-crystal diamond, excellent crack resistance since any crack that begins in one crystal on an easy cracking plane (parallel to an octahedral face), is halted by neighboring crystals that are unfavorably oriented for their propagation.

Natural single diamond crystals and carbonado can now be replaced in many industrial uses by sintered diamond tool blanks. Such tool blanks are available in disks and cores. The disks (or sectors of disks) consist of a thin (0.5–1.5 mm) layer of sintered diamond up to about 13 mm diameter on a cemented tungsten carbide-base block about 3 mm thick. Using diamond abrasive, such blanks can be formed into cutting tools of various shapes. Typical tool blanks are shown in Figure 10. The core blanks have diamond cores up to 6 mm in diameter and 6 mm in length which are encased in a cemented tungsten carbide sleeve up to 13 mm in diameter.

These disks enjoy wide usage as cutting or shaping tools for a variety of hard, abrasive materials such as fiber-reinforced composites, ceramics, rock, silicon-rich aluminum alloys, etc (30). Their toughness, shock resistance, ready availability, and uniform reliable properties have greatly enlarged the use, scope, and durability of diamond cutting tools over that of natural single crystals. They are not suitable for use on ferrous or nickel-base alloys because of the reactivity of diamond with these metals when hot (for such metals, sintered cubic boron nitride tools are useful; see Boron compounds). They show considerable promise as well-drilling bits. The diamond core pieces are commonly pierced and used as wire-drawing dies (31). The uniform polycrystalline character and resistance to bursting of such dies give them improved performance and utility as compared to single crystal diamond dies, and the larger

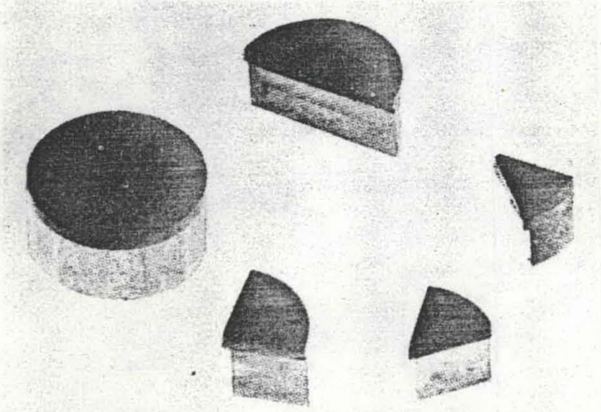

Figure 10. Sintered polycrystalline diamond cutting tool blanks.

sizes cost less. Some of them have drawn over 160,000 km of copper wire before repolishing was needed.

A few special high pressure pistons with sintered diamond working faces have been made for laboratory experiments. Although the sample volume is very small, pressures of 50 GPa (500 kbar) at temperatures of up to 500°C have been reached with such an apparatus (32).

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R. H. WENTORF, JR.
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