

Carbon Black User's Guide

Safety, Health, & Environmental Information

Purpose

This guide summarizes essential health, safety, and environmental information for operational design, maintenance, training, emergency response, and handling practices that may be associated with the use of carbon black. The information contained herein is provided to supplement the knowledge of trained and qualified users of carbon black.

This publication represents the current knowledge of the International Carbon Black Association (ICBA) members as of the date of publication. Users should remain informed on new developments and information about carbon black properties, handling technology and regulatory requirements that occur following the publication date. Any questions should be addressed to your carbon black supplier.

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General Information

What is Carbon Black?

Carbon black [C.A.S. NO. 1333-86-4] is virtually pure elemental carbon in the form of colloidal particles that are produced by partial combustion or thermal decomposition of gaseous or liquid hydrocarbons under controlled conditions. Its physical appearance is that of a black, finely divided pellet or powder. Its use in tires, rubber and plastic products, printing inks and coatings is related to properties of specific surface area, particle size and structure, conductivity and color. *Tables 1* provides general information on carbon black. Worldwide production in 2012 was about 24 billion pounds [11 million metric tons]. Approximately 90% of carbon black is used in rubber applications, with the remainder used as an essential ingredient in hundreds of diverse applications, such as plastics, pigments, and coatings.

Modern carbon black products are direct descendants of early “lamp blacks” first produced by the Chinese over 3,500 years ago. These early lamp blacks were not very pure and differed greatly in their chemical composition from current carbon blacks. Since the middle of the 20th century, most carbon black has been produced by the oil furnace process, which is most often referred to as furnace black.

How Is It Produced?

Two carbon black manufacturing processes (furnace black and thermal black) produce nearly all of the world's carbon blacks, with the furnace black process being the most common.

The furnace black process uses heavy aromatic oils as feedstock. The production furnace uses atomizing nozzles in a closed reactor to pyrolyze the feedstock oil under carefully controlled conditions (primarily temperature and pressure). The feedstock is introduced into a hot gas stream where the feedstock vaporizes and then pyrolyzes to form microscopic carbon particles. In most furnace reactors, the reaction rate is controlled by steam or water sprays. The carbon black flows from the reactor, through heat exchangers and is cooled and collected in bag filters in a continuous process. The exiting carbon black may be further processed to remove impurities. After the bag filters, the carbon black is pelletized, dried, screened, and prepared for shipment. Residual gas, or tail gas, from a furnace reactor includes a variety of gases such as carbon monoxide and hydrogen. Most furnace black plants use a portion of this residual gas to produce heat, steam, or electric power. *Figure 1a*, a typical furnace black process.

The thermal black process uses natural gas, consisting primarily of methane, as feedstock material. The process uses a pair of furnaces that alternate approximately every five minutes between preheating and carbon black production. The natural gas is injected into the hot refractory-lined furnace and, in the absence of air, the heat from the refractory material decomposes the natural gas into carbon black and hydrogen. The aerosol

material stream is quenched with water sprays and filtered in a bag house. The exiting carbon black may be further processed to remove impurities, to be pelletized, screened, and then packaged for shipment. The hydrogen off-gas is burned in air to preheat the second furnace. Residual heat can be used to generate electric power. See *Figure 1b*, a thermal black process.

Carbon Black, Soot, and Black Carbon

Carbon black is not soot or black carbon. “Soot” and “black carbon” are the two most common names applied to emissions from fires and incomplete combustion of carbon-containing fuels (e.g., waste oil, fuel oil, gasoline fuel, diesel fuel, coal, coal-tar pitch, oil shale, wood, paper, rubber, plastics, and resins). Such emissions contain some elemental carbon but also significant quantities of organics and other compounds. “Soot” refers to carbon-rich primary particles produced by a variety of different combustion processes, with diesel exhaust being a major source of urban soot. “Black carbon” is a term used to describe airborne urban or environmental, carbonaceous particulate that has been measured in many recent studies of ambient and indoor particulate matter. While carbon black consists almost exclusively of pure elemental carbon (>97%), “soot” is a heterogeneous substance that consists of less than 60% elemental carbon and large portions of inorganic impurities (ash and metals) and organic carbon species. Carbon black generally consists of <1% extractable organic compounds, including polycyclic aromatic hydrocarbons (PAHs). On the contrary, soot particles can consist of over 50% organic species and may include high concentrations of metals and PAHs, depending on the source material. For example, diesel exhaust soot particles typically consist of an elemental carbon core coated by nitrogen-containing organic matter and PAHs.

In the case of commercial carbon blacks, organic contaminants such as PAHs can only be extracted under very rigorous laboratory analytical procedures, using aggressive organic solvents and high temperatures. Water and body fluids are ineffective in removing PAHs from the surface of carbon black; therefore, PAHs are not considered to be biologically available when adsorbed onto carbon black.

Two other commercial carbonaceous products often confused with carbon black are activated carbon and bone black. Each is produced by processes different from carbon black and each possesses unique physical and chemical properties.

Particle structure – morphology

ASTM D3053-13a, *Standard Terminology Relating to Carbon Black*, provides the following definitional discussion related to carbon black morphology:

“Carbon black exhibits a hierarchy of morphological features: particles (that is, primary particles), aggregates, and agglomerates. While the fundamental building block of carbon black is the primary particle, they almost never exist in isolation, but are strongly fused by covalent bonds into aggregates.^[1] The primary particles are conceptual in nature, in that once the aggregate is formed the primary particle no longer exists, they are no longer discrete and have no physical boundaries

amongst them. Once produced, individual aggregates join together by van der Waals forces to form agglomerates. Agglomerates do not break down into smaller components unless adequate force is applied (e.g., shear force). Primary particle and aggregate sizes are distributional properties and vary depending on the carbon black grade. Transmission electron micrographs demonstrate that while primary particle and aggregate sizes vary greatly within a given grade of carbon black, the primary particle size is essentially uniform within an individual aggregate.^[1]”

[1] “The one exception to this general characteristic of manufactured carbon black is thermal black, in which primary particles may exist in isolation and the primary particle sizes within an aggregate are not necessarily uniform.”

Following the ASTM D3053 definition and applying the terminology of the International Organization for Standardization’s (ISO) Technical Specification 80004-1 of 2010, carbon black is considered a nanostructured material (a material having internal or surface structure in the nanoscale).

The size of the conceptual primary particle is in the nanoscale range. However, typically primary particles do not exist in isolation in Carbon Black powder. As primary particles are fused/covalently bonded together, the primary particle size distribution is not relevant to Carbon Black. As described above, the spheroidal primary particles strongly bond or fuse together to form discrete entities called aggregates (Figure 2). Aggregates are robust structures, able to withstand shear forces; they are the smallest dispersible units measuring ~80 to ~800 nm. Agglomerates are difficult to measure as they break apart when shear forces are applied. Figure 3 depicts the sequence of structure development. Typically, Carbon Black is shipped and placed on the market in the form of pellets (i.e., compressed agglomerates) to facilitate the ease of handling and to reduce the creation of dust (Figure 4). The size of pellets generally falls between 0.1 and several micrometers.

Safety

Combustible¹/Explosible Dust Hazard

According to the various international test methods (e.g. ASTM 1226, EN 14034, VDI 2263), carbon black is an explosible dust under laboratory test conditions (Hazard Class ST-1, weak explosion). All explosible dusts are combustible; however, not all combustible dusts are explosible. Carbon black is both combustible and explosible.

The **minimum explosible concentration (MEC)** for carbon black dusts suspended in air is $> 50 \text{ g/m}^3$. This concentration is much greater than current occupational exposure limits.

A main difference between carbon black and other explosible dusts is the high ignition energy of carbon black which is necessary to initiate a dust explosion. The dust of most carbon blacks suspended in air in sufficient quantities ($>50 \text{ g/m}^3$) have a **minimum**

ignition energy (MIE) greater than > 1kJ according to international test methods (e.g. ASTM 2019, EN 13821, VDI 2263).

The MEC and the MIE are dependent on particle size and moisture content. These parameters may vary when carbon black is mixed with other substance(s), especially if the substance carbon black is being mixed with is combustible or flammable. Therefore, testing of the specific mixture is recommended to determine the explosibility parameters.

Smoldering carbon black can release carbon monoxide (CO), which when combined with carbon black can form explosible mixtures with air. Depending on the composition of the hybrid mixture (CO/carbon black) explosibility parameters (e.g. lower flammable limit, MEC and MIE) may change.

Carbon black dust may contribute to secondary dust explosions (the blast waves of a small primary explosion create a carbon black dust cloud which is then ignited by the primary explosion).

Good engineering practices, good housekeeping practices, and effective dust removal systems are necessary to minimize carbon black emissions and resultant build-up on horizontal and some vertical surfaces. Fugitive carbon black emissions should be minimized and housekeeping activities performed periodically, see NFPA 654, Table A.6.7.

¹ Combustible Dust is defined as finely divided solid particles that present a dust fire or dust explosion hazard when dispersed and ignited in air. (NFPA, 654, 2013)

Fire Hazard

Carbon blacks in fluffy powder or pellet form are combustible as they burn slowly (smolder) and sustain combustion that may not be visible as flames or smoke. In the event of a fire, note that direct water spray or stream may spread the fire due to smoldering carbon black powder floating on the water. A fog spray is recommended when water is used as an extinguishing agent. Also, foam is an acceptable extinguishing agent. Nitrogen or CO₂ gases can be used as an extinguishing agent for smoldering carbon black in silos or confined areas. Carbon black that has been on fire (or suspected of being on fire) should be observed for at least 48 hours to ensure that smoldering has ceased. Combustion gases generated during smoldering include carbon monoxide (CO), carbon dioxide (CO₂) and oxides of sulfur.

Housekeeping and Safe Work Practices

Spill clean-up and general housekeeping are very important for controlling carbon black exposures. Carbon black dust spreads easily in air through virtually any air current or movement. Additionally, carbon black may stain exposed surfaces. Housekeeping procedures that avoid the production of dust or generation of fugitive emissions in the process are highly recommended. Dry vacuuming, with appropriate filtration, is the preferred method for removing surface dust and cleaning spills. Dry sweeping or use of

compressed air should be avoided. Bulk carbon black should always be covered or contained. Care should be taken to avoid generating conditions that may result in unnecessary exposure.

Carbon black dust may be small enough to penetrate electrical boxes and other electrical devices, possibly creating electrical hazards resulting in equipment failure. Electrical devices that may be exposed to carbon black dust should be tightly sealed or purged with clean air, periodically inspected, and cleaned, as required.

Some grades of carbon black may be less electrically conductive, permitting a build-up of static energy during handling. Grounding of equipment and conveying systems may be required under certain conditions. (Contact your carbon black supplier if there is a question concerning the properties of your specific grade of carbon black.) Safe work practices include the elimination of potential ignition sources in proximity to carbon black dust; good housekeeping to avoid accumulations of dust on all surfaces; appropriate exhaust ventilation design and maintenance to control airborne dust levels to below the applicable occupational exposure limit; avoidance of dry sweeping or pressurized air for cleanup; use of carbon black with incompatible materials (e.g. chlorates and nitrates), and appropriate employee hazard training.

Storage and Handling

Carbon black should be stored in a clean, dry, uncontaminated area away from exposure to high temperatures, open flame sources and strong oxidizers (e.g., chlorates, bromates, liquid or compressed oxygen, and nitrates). Since carbon black adsorbs moisture and chemical vapors, it should be stored in closed containers. Review manufacturer's or supplier's Safety Data Sheet for additional information.

Confined Space Entry

Entry into bins, silos, rail tank cars, tank trucks, or other confined spaces used to ship or store carbon black should only be done following proper confined space entry procedures. Some carbon black grades may have trace concentrations of carbon monoxide adsorbed onto its particle surfaces. Smoldering carbon black can produce harmful levels of carbon monoxide in a confined space or in areas with limited ventilation.

Health

Acute First Aid

There is no evidence to suggest that acute exposure to carbon black may result in life threatening injury or illness. Ingestion is an unlikely method of accidental exposure. Carbon black is not a respiratory irritant, and does not produce respiratory or dermal sensitization. Like many dusts, inhalation may initiate a bronchial response among individuals with pre-existing lung conditions.

Inhalation: Short-term exposures to elevated concentrations may produce temporary discomfort to the upper respiratory tract, which may result in coughing and wheezing. Removal from carbon black exposure is normally sufficient to cause symptoms to subside without lasting effects.

Skin: Carbon black dust or powder may cause drying of the skin with repeated and prolonged contact. Skin drying may also result from frequent washing of carbon black contaminated skin. Carbon black may be washed from the skin using mild soap and water along with gentle scrubbing action. Repeat washing may be necessary to remove carbon black. A protective barrier cream on exposed skin surfaces may also be an effective method for minimizing dermal exposure.

Ingestion: No adverse effects are expected from carbon black ingestion. Do not induce vomiting.

Eye: Carbon black is not a chemical irritant. Treat symptomatically for mechanical irritation. Rinse eyes thoroughly with water to remove dust. If irritation persists or symptoms develop, seek medical attention.

Human Studies

Overview

Carbon black has been the subject of extensive scientific health studies during the past several decades, as well as four comprehensive reviews published by the International Agency for Research on Cancer (IARC) in 1984, 1987, 1996 and 2006. Although carbon black has been classified by IARC as a *Group 2B* carcinogen (*possibly carcinogenic to humans*) this is based on a finding of “*sufficient evidence* in experimental animals”, but there is “*inadequate evidence* in humans for the carcinogenicity of carbon black”. Scientific evidence indicates that the laboratory rat is a uniquely sensitive species in its pulmonary responses to persistent high doses of inhaled low solubility particles <1.0 micrometer in diameter. The pulmonary effects observed in rats, including inflammatory and fibrotic responses, eventually leading to lung tumor formation, have not been observed in other rodent species, such as mice and hamsters. Mortality studies of carbon black manufacturing workers do not show an association between carbon black exposure and elevated lung cancer rates.

Studies have demonstrated, however, that regular exposure to carbon black and other poorly soluble particles may play a role in declining lung capacity over long periods of time, as measured by forced expiratory volume in one second (FEV1). Good occupational hygiene practices should be followed to maintain worker exposures below the occupational exposure limit. (See Occupational Hygiene section and Appendix B.)

Mortality studies

A study on carbon black production workers in the UK (Sorahan, 2001) found an increased risk of lung cancer in two of the five plants studied; however, the increase was not related to the dose of carbon black. Thus, the authors did not consider the increased risk in lung cancer to be due to carbon black exposure. A German study of carbon black workers at one plant (Morfeld, 2006; Buechte, 2006) found a similar increase in lung cancer risk but, like the Sorahan, 2001 (UK study), found no association with carbon black exposure. A large US study of 18 plants showed a reduction in lung cancer risk in carbon black production workers (Dell, 2006). Based upon these studies, the February 2006 Working Group at the International Agency for Research on Cancer (IARC) concluded that the human evidence for carcinogenicity was *inadequate* (IARC, 2010).

Since the IARC evaluation of carbon black, Sorahan and Harrington (2007) have re-analyzed the UK study data using an alternative exposure hypothesis and found a positive association with carbon black exposure in two of the five plants. The same exposure hypothesis was applied by Morfeld and McCunney (2009) to the German cohort; in contrast, they found no association between carbon black exposure and lung cancer risk and, thus, no support for the alternative exposure hypothesis used by Sorahan and Harrington.

Overall, as a result of these detailed investigations, no causative link between carbon black exposure and cancer risk in humans has been demonstrated.

Morbidity studies

Results of epidemiological studies of carbon black production workers suggest that cumulative exposure to carbon black may result in small, non-clinical decrements in lung function. A U.S. respiratory morbidity study suggested a 27 ml decline in FEV₁ from a 1 mg/m³ 8-hour TWA daily (inhalable fraction) exposure over a 40-year period (Harber, 2003). An earlier European investigation suggested that exposure to 1 mg/m³ (inhalable fraction) of carbon black over a 40-year working lifetime would result in a 48 ml decline in FEV₁ (Gardiner, 2001). However, the estimates from both studies were only of borderline statistical significance. Normal age-related decline over a similar period of time would be approximately 1200 ml.

In the U.S. study, 9% of the highest non-smokers exposure group (in contrast to 5% of the unexposed group) reported symptoms consistent with chronic bronchitis. In the European study, methodological limitations in the administration of the questionnaire limit the conclusions that can be drawn about reported symptoms. This study, however, indicated a link between carbon black and small opacities on chest films, with negligible effects on lung function.

See Appendix A for more detailed information on these human studies.

Animal Studies

Long-term inhalation studies, up to two years, have resulted in chronic inflammation, lung fibrosis, and lung tumors in some rats experimentally exposed to excessive concentrations of carbon black. Tumors have not been observed in other animal species under similar study conditions. These same effects are observed when rats have been exposed to several other poorly soluble dust particles. Many researchers conducting rat inhalation studies believe the observed effects result from the massive accumulation of small dust particles in the rat lung after exposure to excessive concentrations. These accumulations overwhelm the natural lung clearance mechanisms of the rat and produce a phenomenon that is described as “lung overload.” The effects are not the result of a specific toxic effect of the dust particle in the lung. Many inhalation toxicologists believe the tumor response observed in the above referenced rat studies is species-specific and does not correlate to human exposure.

Carcinogenicity

The International Agency for Research on Cancer (IARC) evaluation (Monographs 65 & 93; 1996 & 2010 publications respectively) concluded, “There is *sufficient evidence* in experimental animals for the carcinogenicity of carbon black.” This categorization was based upon IARC's guidelines, which require such a classification if one species exhibits carcinogenicity in two or more studies. However, IARC found that there was *inadequate evidence* in humans for the carcinogenicity of carbon black. IARC's overall evaluation was that carbon black is *possibly carcinogenic to humans (Group 2B)*.

The position of other authoritative bodies, research, or regulatory organizations regarding the classification of carbon black as a carcinogen is noted below:

- The American Conference of Governmental Industrial Hygienists (ACGIH, 2010) classifies carbon black as A3, *Confirmed Animal Carcinogen with Unknown Relevance to Humans*;
- The U.S. National Toxicology Program (NTP) has not listed carbon black as a carcinogen;
- The U.S. Occupational Safety and Health Administration (US OSHA) has not listed carbon black as a carcinogen;
- The U.S. National Institute for Occupational Safety and Health (NIOSH) criteria document (1978) on carbon black recommends only carbon blacks with polycyclic aromatic hydrocarbon contamination levels greater than 0.1% (1,000 parts per million) be considered suspect carcinogens;
- The Office of Environmental Health Hazard Assessment (OEHHA) of the California Environmental Protection Agency added “carbon black (airborne, unbound particles of respirable size)” (CAS No. 1333-86-4) to the Proposition 65 substances list on February 21, 2003. This listing, triggered by the “authoritative body” mechanism in the California Code of Regulations, was based solely on IARC's 1996 classification of carbon black as a Group 2B carcinogen.
- The German MAK Commission has classified carbon black as a suspect carcinogen, category 3B;

- The Japan Ministry of Labor, Health and Welfare “recommends” a classification on carbon black as a carcinogen, category 2; Target organ systemic toxicity following repeat exposure, category 1; Taiwan Council of Labour Affairs “recommends” a classification on carbon black as a carcinogen, category 2; Target organ systemic toxicity following repeat exposure, category 3;
- The Korean Occupational Health and Safety “recommends” a classification on carbon black as a carcinogen, category 2; Target organ systemic toxicity following repeat exposure, category 1; Self-heating substances and mixtures: category 1
- Under the UN-Global Harmonized System (GHS) framework adopted by OSHA’s 2012 HazCom Standard, the International Carbon Black Association has determined that carbon black does not meet the criteria for classification as a human carcinogen. The epidemiological evidence from well-conducted investigations has shown no causative link between carbon black exposure and the risk of non-malignant respiratory or malignant disease in humans.

Polycyclic aromatic hydrocarbons (PAH) are adhered strongly to carbon black. Concern has been expressed about the PAH (sometimes referred to as polynuclear aromatics (PNA) content of manufactured carbon blacks. In non-adsorbed forms, some PAHs have been found to be carcinogens in animal studies. In-vitro studies indicate that the PAHs contained in carbon black are not bioavailable. Scientific studies have demonstrated that once incorporated into a rubber matrix the PAHs originating from carbon black do not migrate from the rubber matrix.

Modern production and quality control procedures are generally able to maintain extractable PAH levels to less than 0.1% (<1000 ppm) in carbon black with PAHs regulated as carcinogens representing a smaller fraction of the extractables. Extractable PAH content depends on numerous factors including, but not limited to, the manufacturing process and the ability of the analytical procedure to identify and measure extractable PAHs. Specific questions concerning PAH content should be addressed to your carbon black supplier.

Mutagenicity

Carbon black is not suitable to be tested directly in bacterial (Ames test) and other *in vitro* systems because of its insolubility. However, when organic solvent extracts of carbon black have been tested, results showed no mutagenic effects. Organic solvent extracts of carbon black can contain traces of polycyclic aromatic hydrocarbons (PAHs). A study to examine the bioavailability of these PAHs showed that they are very tightly bound to carbon black and are not bioavailable (Borm, 2005).

In an *In vivo* experimental investigation, mutational changes in the *hprt* gene were reported in alveolar epithelial cells in the rat following inhalation exposure to carbon black (Driscoll, 1997). This observation is considered to be rat-specific and a consequence of “lung overload,” which leads to chronic inflammation and release of reactive oxygen species. This is considered to be a secondary genotoxic effect and, thus, carbon black itself would not be considered to be mutagenic.

Reproductive Effects

No effects on reproductive organs or fetal development have been reported in long-term repeated dose toxicity studies in animals.

Chronic Ingestion

No significant abnormalities were seen in rats or mice following feeding studies of up to two years.

Skin Contact

After application of a carbon black suspension to the skin of mice, rabbits, and rats, no skin tumors were reported. Dust may cause drying of the skin with repeated or prolonged contact.

Sensitization

Tests on the skin of Guinea pigs do not produce sensitization. No cases of sensitization have been reported in humans.

Animal Irritant Tests

Primary Eye Irritation (rabbit): Produced slight conjunctiva redness, which cleared within seven days. Primary Skin Irritation (rabbit): Very slight erythema (redness).

Occupational Hygiene

Overview

Occupational hygiene (also known as industrial hygiene) principles are used in the management of exposures in the work environment. These principles include efforts to anticipate and identify potential worker exposure conditions, measure worker exposures, and implement appropriate controls to reduce exposures to the lowest feasible levels. Although this section will focus on carbon black, industrial hygiene principles are applicable to all potential exposure agents and conditions present in a work environment.

Experience suggests that routine activities having the greatest potential for occupational exposure to airborne carbon black are those related to manual handling, packaging, bulk loading, and some maintenance activities. Non-routine activities related to maintenance operations and upset conditions also have potential for exposures to carbon black.

Each employer must conduct job-specific hazard assessments based on knowledge of their own work environment activities (routine, non-routine) and site-specific conditions.

Airborne Exposure Assessment

The most significant route of exposure is inhalation of airborne carbon black; therefore, the primary focus during the assessment should be on airborne exposures. Personal monitoring techniques are used to collect the air samples in the worker's breathing zone (mouth/nose area). Measurements performed in locations that are not representative of the worker breathing zone may either underestimate or overestimate airborne exposures.

Air sampling methods may vary by country and be dependent on the particle fraction/size range of the corresponding occupational exposure limit (OEL). The types of air sample collection devices and the air sampling flow rates are different depending on whether the air samples need to be total, inhalable, or respirable carbon black samples. Collection of air samples should be performed by a trained individual, such as an occupational/industrial hygienist. Publications on this subject are available from the American Industrial Hygiene Association (AIHA).

Results of airborne exposure assessments identify and quantify inhalation exposures and operations requiring exposure controls. These results also establish baseline data for evaluating the effectiveness of controls, determining compliance with regulatory and non-regulatory occupational exposure limits, and providing information useful in characterizing historical exposures. Additional information and guidance can be obtained from national or regional professional occupational hygiene associations.

Occupational Exposure Limits

Occupational exposure limits for airborne carbon black vary by country and are subject to change (See Appendix B). These limits are expressed as specific airborne particle fractions (total, inhalable, or respirable). Each particle fraction/size range requires that a different methodology be used when conducting the airborne exposure assessment.

Occupational exposure limits are usually expressed as average concentrations during a specific time period. Full-shift OELs are usually 8-hour time-weighted averages (TWA), and some countries have also specified short-term exposure limits (STEL), which are 15-minute averages.

Additional information and guidance can be obtained from national or regional professional occupational hygiene associations.

Particle Size Assessment

Studies conclude that carbon black manufacturing workers are not exposed to nanoscale (between 1 to 100 nanometers in diameter) carbon black particles. An ICBA-sponsored study conducted at carbon black plants in Europe and the US in 2000 found that there

were no exposures to carbon black particles less than 400 nanometers in diameter. The ICBA continues to support work in this area as measurement technologies advance.

Engineering Controls

If the results of airborne carbon black sampling indicate that worker exposures are above acceptable limits, then appropriate controls must be identified and implemented to reduce the exposures.

Engineering controls designed to eliminate or reduce occupational exposure to carbon black dust to the lowest feasible level are preferred to the use of respirators or other types of personal protective equipment. Engineering controls prevent or minimize contact with the hazard by removing the hazard or preventing the worker from being exposed to the hazard. The most cost-effective time to implement engineering controls is either at the planning and design stage of a new operation or during modifications to existing operations.

Engineering controls that have been used with success in the handling of carbon black include: (1) local exhaust ventilation (e.g., laboratory hoods) for controlling exposures to laboratory personnel engaged in handling samples; (2) source capture hoods for dusty operations, such as bagging, bag splitting, and bulk loading; and, (3) containment of powders and dusts within sealed mixing, processing, and conveying systems. Containment systems (e.g., an enclosed conveyor) are especially effective when operated under a slight negative pressure to minimize fugitive dust emissions and leaks.

Use of a dedicated central vacuum cleaning system instead of dry sweeping is a more effective method for cleaning spilled carbon black in areas where it is routinely used. Motors and air cleaners for the vacuum system should be placed outdoors, and exhausted away from occupied areas. Numerous vacuum connect ports that seal when not in use should be provided throughout areas where carbon black is transferred, handled or used. Sufficiently long vacuum hoses should be strategically located throughout the areas of potential use. To prevent the spread of carbon black dust, spills should be vacuumed immediately.

The local exhaust ventilation and vacuum systems mentioned above should be properly designed to maximize effectiveness and to avoid performance problems. Principles of good industrial ventilation design can be found in the most recent edition of the ACGIH publication, *Industrial Ventilation, A Manual of Recommended Practice*.

Respiratory Protection

When respiratory protection is required to minimize exposures to carbon black, programs should follow the requirements of the appropriate governing body for the country, province or state. Please consult the current version of the standard or regulation that may apply to your operations.

The selection of a correct respirator is based on the exposure concentration of carbon black against which protection is required, as well as the possible presence of other contaminants that may be released in the workplace. Representative exposure assessment measurements of contaminants that may be encountered must be conducted to ensure appropriate respirator selection.

Medical Surveillance

Employees who have job duties that involve exposure to carbon black dust may have questions about the health implications of exposure. These questions generally focus on understanding whether a more specialized medical examination is appropriate. It should be emphasized that based on the results of numerous worker studies a dose:response relationship between carbon black exposure and increased lung cancer rates does not exist.

In considering employee medical surveillance, the physician should understand that job duties vary considerably. The major medical issue the physician should address is whether individuals evaluated for certain jobs have a history of lung disorders, such as emphysema or asthma, and/or skin diseases. These conditions may be exacerbated by exposure to high dust levels of any type, including carbon black.

It is advisable for the physician to become familiar with the operations, working conditions, and potential exposure concentrations for the various job positions. Periodic tours of the operations by the occupational physician are recommended.

The determination of worker participation in a medical surveillance program should be based on working conditions, such as exposure concentration of carbon black and respirator use. It is desirable for the physician to develop a complete occupational history for each employee as part of any medical surveillance program to include, at a minimum, past medical history, prior working experience in other occupational settings, and personal lifestyle habits (e.g., smoking history, hobbies, etc.).

Environmental

Greenhouse Gas Emissions

The carbon black production process uses carbon-rich feedstock in combination with oxygen. The reaction process is quenched with water to minimize the oxidation of the carbon to carbon dioxide, and to maximize the recovery of the carbon black. Greenhouse gas emissions are reduced through process yield improvement activities and the use of combustion byproduct gases in the process and the creation of steam and/or electricity. As production processes vary based on the facility design and carbon black grades produced, information about greenhouse gas emissions and carbon footprint should be obtained from your supplier.

Water Use

Water is used in the manufacture of carbon black to quench the production reaction and by some manufacturers to pelletize the carbon black. Process water recycling and rain water recovery are widely practiced within the industry. Production process water usage can vary widely by plant and grades produced. Contact your supplier for details.

Disposal

With the exception of chemically treated and water dispersible grades, carbon black is most often disposed of in landfills, provided those landfills meet all applicable regulations. Carbon black is non-toxic and will not leach or release any constituents to the groundwater from a landfill.

Carbon black can also be used as an alternative fuel for kilns or can be incinerated in municipal waste incinerators as non-hazardous waste. It has approximately the same heat value per pound as pulverized coal and will combust completely with low emissions and virtually no residual ash. Adequate residence time and oxygen content needs to be provided to assure that complete combustion occurs. These alternatives to landfill disposal are environmentally suitable disposal methods, provided they are in accordance with applicable regulations.

Carbon black has a high surface area and a strong adsorptive capacity. Organic materials that come in contact with carbon black can be adsorbed and are not easily liberated thereafter. As a result, disposal determinations should consider any chemical(s) that may be adsorbed onto the carbon black. Carbon black is not biodegradable. Care should always be taken with disposal actions to control dust emissions during the pick-up, transportation and subsequent depositing of waste material at the landfill site or during other disposal activities.

Air

Carbon black is not typically regulated under a substance-specific air pollution control or ambient air quality standard, but emissions of carbon black to the atmosphere are typically regulated as a component of a facility's particulate matter (PM) or dust emissions under other rules. Air regulations vary by region, generally differing based on the air quality in those regions. Employment of fabric filters and other PM capture and collection technologies to minimize PM emissions is commonplace throughout the industry and may be necessary to ensure compliance with applicable regulations. In some regions, particulate matter regulations are based on the size of the particulate being emitted, with regulations addressing particles of less than 2.5 microns; less than 10 microns and/or total particles mass.

Wastewater

Wastewater discharges containing carbon black must comply with applicable requirements. Carbon black is not soluble in water and has a specific gravity of 1.7 to 1.9

(water = 1). Gravity settling is effective and is the most common technique employed to remove carbon black from wastewater. Under some circumstances, settling may be inhibited because of the small particle size and/or high surface areas that may resist wetting. Various metallic salts, such as ferric or aluminum sulfate, and/or synthetic polymers, are effective as flocculating agents to enhance settling. The type of flocculent and optimum dosage rate can best be determined by bench scale or laboratory tests. Filtration may also be used as a technique for solids removal.

Leaks or Spills

Spills of carbon black should be cleaned immediately to prevent spread and dispersion. Dry vacuuming is the recommended method for collecting spilled carbon black. If a portable vacuum is used, care must be taken to ensure that filters are maintained. A central vacuum system should be considered for routine housekeeping and the clean-up of localized process leaks. The collector serving the central vacuum should be located outdoors and contain fabric filters. If it is necessary to clean a remote or small spill by dry sweeping, care should be taken not to disperse the carbon black into the air. Carbon black is not easily wetted and water may cause spilled material to disperse, so water sprays and wetting are not recommended for cleaning. Should this method be used, however, caution should be exercised since wet carbon black makes walking surfaces very slippery.

Shipping Containers

Reusable shipping containers should be returned to the manufacturer. Paper bags may be incinerated, recycled or disposed of in an appropriate landfill in accordance with national and local regulations.

Transportation

Commercial carbon black is not classified as a hazardous material by the following agencies:

- UN Recommendations on the Transport of Dangerous Goods
- European Agreement concerning the International Carriage of Dangerous Goods (ADR)
- Regulations concerning the International Carriage of Dangerous Goods by Rail (RID), part of the Convention concerning International Carriage by Rail
- European Agreement concerning the International Carriage of Dangerous Goods by Inland Waterways (AND)
- International Convention for the Safety of Life at Sea – International Maritime Dangerous Goods Code (IMDG Code)
- Convention on International Civil Aviation – Annex 18 – Safe Transport of Dangerous Goods by Air
- Canadian Transport of Dangerous Goods Regulations
- International Air Transport Association (IATA-DGR)
- MARPOL 73/78, Annex II

- IBC-Code
- United States Department of Transportation
- Canadian Transport of Dangerous Goods Regulation
- Australian Dangerous Goods Code

Specific questions regarding transport classification should be referred to your carbon black supplier.

Self-Heating

Carbon black has been tested in accordance with the UN method, Self-Heating Solids, and found to be “Not a self-heating substance of Division 4.2”. In addition, carbon black has been tested in accordance with the UN method, Readily Combustible Solids, and found to be “Not a readily combustible solid of Division 4.1”; under current UN Recommendations on the Transport of Dangerous Goods.

Carbon Black in Materials in Contact with Foodstuffs

Carbon black produced by certain processes has been approved under specific circumstances and for specific uses involving contact with foodstuffs. Contact your carbon black supplier for additional information.

National Registries and Other Applicable Regulations (not all inclusive)

Carbon black, CAS number 1333-86-4, is listed on the following inventories.

- Australia: Australian Inventory of Chemical Substances (AICS).
- Canada: Canadian Environmental Protection Act (CEPA), Domestic Substance List (DSL); Workplace Hazardous Material Identification System (WHMIS). Carbon black is listed as a D2A controlled substance.
- China: Inventory of Existing Chemical Substances in China (IECSC).
- European Union: European Inventory of Existing Commercial Chemical Substances (EINECS), 215-609-9.
- European Union: REACH Regulation (EC) No. 1907/2006: Company specific registration is required; contact your supplier for additional information.
- Japan: Existing and New Chemical Substances (ENCS), Industrial Safety and Health Law Inventory (ISHL).
- Korea: Toxic Chemical Control Law (TCCL), Korean Existing Chemicals Inventory (KECI).
- Philippines: Philippine Inventory of Chemicals and Chemical Substances (PICCS).
- Taiwan: Chemical Substance Nomination and Notification (CSNN).
- United States: Toxic Substances Control Act (TSCA) Inventory

Note: Readers are urged to review their national, provincial, state, local, and federal safety, health and environmental regulations, as well as their carbon black supplier's

safety data sheet (SDS). Specific questions should be addressed to your carbon black supplier.

This guide is not a substitute for the current product SDS. Please contact your carbon black supplier for the appropriate carbon black SDS.

Appendix A

Health Studies of workers in the carbon black, rubber and toner Industries

Epidemiology Studies of carbon black workers and risk of cancer

Different types of research studies have been conducted to evaluate carbon black's potential to cause cancer, lung disease, or any other adverse health effect from the manufacture or use of carbon black. What follows is a summary of the major epidemiology and toxicology studies that have addressed potential cancer and/or adverse respiratory effects from carbon black exposure

Epidemiology studies are commonly conducted to address potential health related risks among workers exposed to a particular product or who work in a designated industry. Mortality studies evaluate the risk of dying from certain types of diseases in the working group studied in comparison to the general population. They form the basis-along with toxicology and exposure assessments-of international carcinogen classification systems and exposure limits for workers.

Carbon black and its corresponding research studies, including epidemiological studies, have been the subject of a number of scientific reviews by the International Agency for Research on Cancer (IARC) of the World Health Organization (IARC, 1985; IARC, 1995 and IARC, 2006). The most recent comprehensive evaluation of cancer risks potentially due to carbon black exposure was performed by an IARC Working Group in February 2006 (IARC 2010). The Working Group noted the following key points: (1) lung cancer is the most important health endpoint to consider [regarding potential malignant effects] and (2) exposures of workers at carbon black production sites are the most relevant group for an evaluation of potential cancer risk. The IARC Working Group concluded that the human evidence for carcinogenicity was inadequate, which confirmed the 2B classification first noted at the IARC working group meeting of 1995 (IARC 2010). A 2B classification mean the scientific evidence for carcinogenicity is a "possible" human carcinogen based on results from animal studies. The human evidence on carcinogenicity was considered "inadequate" by the IARC working group.

Cohort Mortality Studies of Carbon Black Workers

IARC, in its 2006 working group meeting, reviewed three major epidemiological studies of carbon black worker cohorts in the United States, the United Kingdom and Germany. Each study investigated lung cancer mortality among workers in carbon black production plants. Summaries of the results of each cohort evaluation follow.

1. The world's largest cohort study of mortality risks of carbon black manufacturing includes 5,011 workers at 18 plants in the United States (2006 and 2014, completed manuscript). In 2006, a lower than expected lung cancer SMR* of 0.85 was observed, based on 127 cases; (95%-CI: 0.71, 1.00) (Dell *et al.* 2006). An update of this study with ascertainment of vital status through 2011 has recently been completed but not yet published at the time of preparation of this report (Dell *et al.* 2015). No excess in lung cancer or non-malignant respiratory disease was reported in the updated analysis.

2. A study of British carbon black workers was first published in 1985 and updated thereafter (Hodgson et al, 1985; Sorahan et al., 2001). A cohort of 1,147 at five manufacturing plants was shown to have an SMR of 1.73 (61 cases, 0.95-CI¹: 1.32, 2.22) (Sorahan *et al.* 2001). No trend across crudely assessed cumulative exposures, lagged up to 20 years, was noted. Elevated lung cancer SMRs were observed at two plants; the SMRs of the other three plants were unexceptionable.

3. A German cohort of carbon black workers from one specific plant in North Rhein Westphalia (NRW) was evaluated on a number of occasions (Wellmann *et al.* 2006, Morfeld *et al.* 2006, Buechte *et al.* 2006, Morfeld *et al.* 2006). The initial evaluation showed an SMR of 2.18 (CI: 1.61-2.87) for lung cancer based on 50 cases when national German rates were used as the reference population. The SMR for lung cancer was 1.83 (CI: 1.36-2.41); however, when the work group was compared to regional rates for the people of NRW, NRW had a higher background rate of lung cancer due to a higher prevalence of cigarette smokers in the general population. Like the UK study above, no positive trends with carbon black exposures were noted. The study identified smoking and prior exposures to known carcinogens as important risk factors that could explain the major part of the excess risk.

Research Studies since IARC 2006 Evaluation

Subsequent to the most recent IARC evaluation in 2006, further evaluations of the three major carbon black cohorts have been published. The authors of the UK mortality study conducted an extended follow-up of their cohort and applied a novel exposure metric, known as “lugging,” in an attempt to address the potential effect of recent exposures to carbon black on lung cancer risk (Sorahan and Harrington, 2007). In contrast to lagging, a “lugging” analysis focuses on the most recent exposures, in contrast to distant exposures. The authors hypothesized that carbon black may act as a late stage lung cancer carcinogen at the 2 of the 5 plants where elevated SMRs were noted in the 1985 and 2001 publications (Hodgson et al, 1985 and Sorahan et al, 2001). If the “lugging” hypothesis is true, that is, the most recent exposures confer the actual risk, the elevated SMRs should decrease progressively and substantially after cessation of exposure; positive associations would be expected with “lugged” cumulative carbon black exposure. For example, “lugging” the exposure by 15 years, means to count only exposures received during the last 15 years in the analysis of risk. The authors noted a “lugging” effect in two of the UK plants that had elevated lung cancer SMRs. In their publication, the authors suggested repetitions of their methodology in other cohorts.

The “lugging” hypothesis was then tested in the German carbon black cohort (Morfeld and McCunney, 2007, 2009). Neither a decreasing SMR, after cessation of exposure, nor a positive relationship with “lugged” cumulative carbon black exposure was noted, despite the fact the German cohort showed a clearly elevated lung cancer SMR. Thus, the German cohort, with the use of the same methodology, did not confirm the UK hypothesis on “lugging”. Another study of the German cohort employed a Bayesian bias analysis to explore all potential risk factors and confounders that may have contributed to the SMR results (Morfeld and McCunney 2011). These additional investigations did not support the “lugging” hypothesis.

¹ CI = confidence interval

Case-Control Studies

Case-control studies compare “cases” of a particular disease with people who are otherwise similar in demographic characteristic, such as age, gender, and occupation, among others. The purpose is to evaluate whether people with a certain disease, such as lung cancer, have had greater exposure to a potential hazard in comparison to unexposed people. These types of studies are helpful to assess risks of rare diseases and when a large number of cases can be assembled. Unfortunately, a major limiting factor to these types of studies is “recall bias”, in which subjects with a serious disease tend not to recall past events as accurately as they occurred. Nonetheless, by considering results of cohort mortality studies and case-control studies, one can form a reasonable assessment as to whether a significant hazard, such as a human carcinogen, may be present.

The relationship between workplace exposure to carbon black and lung cancer risk was examined in two large population-based case-control studies in Montreal, Canada (Parent *et al.*, 1996; Ramanakumar *et al.*, 2008). Interviews related to jobs and exposures for Study I were conducted in 1979–1986 (857 cases, 533 population controls, 1,349 cancer controls) and interviews for Study II were conducted in 1996–2001 (1,236 cases and 1,512 controls). Detailed lifetime job histories were elicited and a team of hygienists and chemists evaluated the evidence of exposure to a host of occupational substances, including carbon black. Lung cancer risk was analysed in relation to each exposure, adjusting for several potential confounders, including smoking. Subjects with occupational exposure to carbon black did not experience any detectable excess risk of lung cancer.

Cohort Morbidity Studies of Carbon Black Workers

Morbidity studies evaluate the risk of illness secondary to work place activities and exposure to potential hazards. Occupational exposure to carbon black has been assessed for its impact on non-cancerous conditions such as lung diseases for over 50 years. Morbidity studies assess the incidence and prevalence of illnesses among a worker population that may be attributable to exposure to a chemical or physical agent. Morbidity studies can be performed at one particular time (cross-sectional), based on a review of old records (retrospective), or into the future over time (longitudinal). Results from morbidity studies are often used as the scientific basis for establishing occupational exposure limits, such as Threshold Limit Values (TLVs) of the American Conference of Governmental Industrial Hygienists (ACGIH). In fact, a major morbidity study sponsored by the ICBA has served as the basis for the ACGIH TLV on carbon black (Harber *et al.*, 2003).

This section summarizes the major morbidity studies conducted on carbon black workers, who have participated in cross-sectional morbidity studies in Europe and in the U.S. Both studies addressed potential relationships between exposure (defined quantitatively and qualitatively) and designated health endpoints, such as abnormal chest films, declines in lung function, or increased rates of certain respiratory symptoms (See Gardiner *et al.*, 1995 for a review of morbidity studies conducted up to that time).

It is useful to consider results from different morbidity studies in understanding risk; although, comparisons among studies can be complicated by different methodologies used to assess exposure and health effects. For example, different carbon black exposure fractions (that is, inhalable, respirable, and “total” dust) have been measured via various types of sampling methods. Similarly, the number of readers used to review chest films, equipment standardization for assessing lung function, and the types of questionnaires used to collect information on symptoms have varied considerably among different studies. For example, a German study used whole body plethysmography to assess lung function; whereas, most other studies have used spirometry to assess lung function (Kuepper et al., 1996).

European Morbidity Studies of Carbon Black Workers

The first major European morbidity study of carbon black workers was published in 1986 (Crosbie et al, 1986). Among over 3,000 carbon black workers employed at 19 European plants with a mean work history of over ten years, weak associations were noted between exposure to carbon black (based on job titles) and chronic cough and sputum production (Crosbie, 1986). No data were available on dust levels, thus dose-response relationships could not be established. Minor exposure-associated declines in forced vital capacity (FVC) and forced expiratory volume in one second (FEV₁) were noted.

A further long-term morbidity study was initiated in 1988 and was designed to be conducted over a 10-year period with three distinct phases. The study included over 3,000 workers at 18 carbon black plants in 7 Western European countries (Gardiner et al., 1993). Data on exposure and health outcomes were collected on three separate occasions: Phase I (1987 - 1989), Phase II (1991 - 1992), and Phase III (1994 - 1995). The study is analogous to a prospective longitudinal study. Health outcome measures included pulmonary function, respiratory symptoms, and chest radiographs.

In Phase I, among 3,086 workers, a relationship between exposure to carbon black and certain symptoms (cough, sputum production) was noted. Average exposure to carbon black was 1.52 mg/m³ (inhalable fraction). The manner, in which the symptom information was collected, however, was the subject of an independent scientific review, conducted at the request of ACGIH's TLV® Committee. The review noted methodological problems with the manner in which symptom data were acquired from the investigators and independently analyzed. The review concluded that the questionnaire component of data from the European study could not be meaningfully interpreted. The authors acknowledge this limitation of the questionnaire data in their discussion of the results of the study (Gardiner et al, 2001.)

Among the worker cohort, lung function measurements averaged more than 100% of that predicted for a person's age, height and gender for all categories of exposure, except for cigarette smokers in the highest exposure group (98.3% of the predicted value). When all results were analyzed in aggregate form, however, a small, but statistically significant relationship was noted between exposure to carbon black and decrements in FVC and FEV₁. The authors described their findings as “consistent with a non-irritant effect on the airways” (Gardiner et al., 1993).

Among the 1,096 workers who underwent chest films, 9.9% showed readings of 1/0* (small opacities) or greater, the scoring system used by the International Labor Organization (ILO) for reading chest radiographs for pneumoconiosis. These results, however, were actually lower than the average background chest film readings of European populations (11.3%) unexposed to any type of dust (Meyer et al., 1997). Of the entire working group, three people had ratings of 2/2 or greater (increased profusion of small opacities).

Data from Phases II and III have also been published (Gardiner et al., 2001 and van Tongeren et al., 2002). In Phase II, 2,955 workers were evaluated. Approximately 48% of the group was cigarette smokers. The average exposure to carbon black was 0.81 mg/m³ (inhalable fraction), which is approximately 50% less than the results reported in Phase I of the study.

In Phase III, the participation rate was 95%, with 45% of the group being cigarette smokers. Average exposure to carbon black was 0.57 mg/m³ (inhalable fraction), a further decrease from Phase II. The average age of the carbon black workers was 41, with the average length of employment in the industry being 15 years.

The authors reported that carbon black exerted a significant effect on most respiratory symptoms and lung function, although they acknowledged shortcomings in the symptom data: "*respiratory symptom results may have been biased and care should be taken in the interpretation of these results*" (Gardiner et al., 2001). Although exposure related decrements in lung function were measured, the percentage of predicted lung function volumes, as noted above, exceeded 100% for FEV₁ and FVC, the key parameters for evaluating lung function. These results suggest that conclusions regarding the health implications of carbon black exposure were based on the statistical significance of the results rather than the clinical relevance.

In a cross-sectional study of a German carbon black manufacturing facility, 677 examinations were performed among exposed employees; no significant relationship was noted between bronchial hyper-reactivity (assessed by body plethysmography) and exposure to carbon black (Kuepper et al., 1996). Exposure to carbon black did not increase the risk of either lung related symptoms or lung function decrement in non-smokers or ex-smokers.

In a 1975 study in the former Yugoslavia, respirable dust concentrations of carbon black were 7.2 mg/m³ and 7.9 mg/m³ (Valic, 1975). Among 35 workers, a minor reduction in FEV₁ was noted among smokers. No relationship was noted among the non-smoking control group. Based on the recent particle size characterization studies conducted in Western European and North American carbon black plants (Kerr, 2001; Kuhlbusch, 2004), the magnitude of these respirable dust concentrations reported in Yugoslavia in 1975 suggest extremely high exposure levels to "total" and inhalable dust.

United States Studies of Carbon Black Workers

Morbidity studies of U.S. carbon black workers have been performed for over 50 years. The most recent study evaluated over 1,000 North American carbon black workers to assess relationships between exposure to carbon black and corresponding lung related symptoms and lung function (Harber et al., 2003). Results of this study had a major impact on the recently

established ACGIH TLV for carbon black. Workers (1,175) from 22 North American manufacturing facilities underwent a pulmonary function test and completed a health questionnaire. Analyses showed links between cumulative exposure and small reductions in lung function (FEV₁). Recent exposures showed no effect on symptoms or lung function measurements. Results indicated that exposure to carbon black at 1.0 mg/m³, over a 40-year career, could result in a 27 ml decrement in FEV₁ in addition to normal age related decline of ~ 30 ml per year or 1200 ml.

Prior to the recent USA morbidity study, a case-control morbidity study was conducted on U.S. employees in seven carbon black plants (Robertson and Ingalls, 1989). Workers, who submitted health insurance claims with diagnoses of certain types of illnesses, in particular, respiratory and circulatory ailments, were evaluated in relation to exposure to carbon black. Based on estimates of cumulative dust exposures, no significant relationship was noted between carbon black and the designated diseases.

In addition to health indices of pulmonary function, symptoms, and fibrotic disease, the U.S. carbon black workforce was also evaluated for cancer morbidity, that is, malignancies diagnosed, but which had not led to death (Ingalls, 1950; Ingalls and Risquez-Iribarren, 1961; Robertson and Ingalls, 1989). The incidence of cancer among carbon black workers was compared both to unexposed carbon black workers and to cancer rates compiled in various states. No increase in cancer morbidity was noted in these investigations.

A nested case control study was also performed on this same cohort (Robertson and Ingalls, 1989). A case was defined as a member of the study population who filed a health insurance claim with a diagnosis of either a malignancy or a disorder of the circulatory or respiratory system. Two controls were matched to each worker and cumulative exposure to carbon black was estimated by relating measured concentrations of carbon black to specific job categories. No statistically significant increase in the risk of any malignancy was noted.

Case Report of carbon black exposure

Although case reports have limited value in occupational health, they can be used to highlight unusual occurrences. A report in 2012 described a *“44-year-old man who had intense exposure to carbon black when his crane ran into a truck with a trailer filled with carbon black.”* (Halemariam, 2012) *A week thereafter, he developed shortness of breath and cough...Pulmonary function tests revealed a mild obstruction. The patient responded to treatment with fluticasone and salmeterol with a reduction in symptoms and improvement in his spirometry to a normal range.”*

The authors concluded: *“acute exposure to carbon black can cause respiratory symptoms and an obstructive ventilatory defect”*.

This unfortunate and rare event fortunately had a favorable outcome. Nonetheless, the report underscores the importance of dust control and that virtually any dust, despite how inert it may be, can overwhelm customary pulmonary defense mechanisms and lead to symptoms if the exposure is high enough and no respiratory protection is provided.

Summary of Human Studies on Carbon Black Workers

Mortality studies have evaluated the risk of death from illness, including cancer, non-malignant respiratory disease, and cardiovascular disease. These studies do not link any increase in either overall mortality or lung cancer deaths to carbon black exposure.

Morbidity studies have addressed whether carbon black causes increases respiratory symptoms, decrements in lung function, or abnormalities on a chest film. Long-term exposure to carbon black in the manufacturing industry may lead to minor decrements in FEV₁ (27 – 48 ml) an additional loss over a 40-year working lifetime in addition to the 1200 ml age related decline. Small changes have also been noted in the chest radiographs. Chest film opacities observed in carbon black workers tend to resemble opacities found in populations unexposed to dust, although slight increases have been noted in some carbon black workers. The studies do not delineate whether such effects are specific to carbon black or reflect effects that may be seen with other relatively inert, poorly soluble, inorganic dusts.

Acute exposure to carbon black does not pose any significant risk to health, beyond what might be expected from exposure to any poorly soluble dust in extremely high concentrations, such as described in the case report earlier. In occupational settings, airborne carbon black consists of large-sized agglomerates that can deposit in the upper respiratory tract. As a result, in high concentrations, cough and irritation to the eyes may occur at high levels in some settings. Such effects are expected to be transitory and not to result in any long-term effect on lung function. Consisting almost entirely of carbon, carbon black is not metabolized in the body and remains inert.

On-going Research Studies of Carbon Black Workers

USA Mortality Study Update

Two epidemiological studies of workers currently and previously involved in the manufacture of carbon black are underway at the time of preparation of this report. In the USA, an update of the cohort mortality study reviewed by IARC in 2006 has been completed and published (Dell et al., 2015). The updated cohort includes vital status assessment through 2011; the earlier version addressed vital status through 2003. Individual cumulative dose-response exposure assessments were conducted on cohort members. This metric was based on quantitative exposure data, and a comprehensive review of job descriptions, duties and production process changes. Published exposure data related to the manufacture of carbon black date back to 1979, which provided nearly 30 years of quantitative data for the dose response assessment. A similar “lugging” analysis as done in the British and German cohorts was also performed.

Meta-analysis of risk of Heart Disease

Recent position papers, including a comprehensive review by The American Heart Association, have called attention to the potential role of particles in causing or aggravating cardiac disease (Brook et al, 2010). To address this potential health risk among carbon black manufacturing workers, single and combined analyses (meta regression) of the three cohorts in the USA,

Germany and UK are underway. Extended SMR and Cox regression will be performed, including an update of the mortality follow-up in the UK. Due to privacy laws in Germany, the earlier records of the cohort evaluation were destroyed and as a result no further updates of this cohort are feasible.

Carbon Black User Industry Studies

Carbon black is used primarily in the rubber industry; other less common uses include printing inks and toner manufacturing. Highlights of recent mortality and morbidity studies from these industries follow. The focus of the review was primarily to address any role carbon black might have played in the results of the various studies, not to comprehensively assess risk of cancer or morbidity in these respective industries.

Rubber Industry Mortality Studies

One of the major uses of carbon black is in the manufacture of rubber products, most notably tires for cars, trucks, and other transportation applications, among others. Numerous epidemiological studies have been conducted in the rubber industry, which, in addition to carbon black, uses other materials including accelerators and solvents. Earlier mortality studies in the rubber industry were confounded by the presence of asbestos in the manufacturing plant. Working in the rubber and rubber product manufacturing industry has been classified by the International Agency for Research on Cancer (IARC) as carcinogenic (Category 1) but no specific substance was highlighted as the causative agent (IARC, 1982; IARC, 1987).

A review article in 1998 summarized the studies of rubber industry workers conducted since IARC reviewed the industry in 1982 and 1987 (Kogevinas et al, 1998). The authors concluded that there was: “*excess risks of bladder cancer, lung cancer and leukemia*” in the rubber industry based on their review of 12 cohort studies in 9 countries and a variety of nested case control and community based studies. Excess risks of lung cancer were noted in four cohort studies with SMRs ranging from 1.7-3.3. No excess was noted in the other cohort studies. The authors concluded that there was no information associating specific exposures, such as carbon black, with cancer risk.

Subsequently, a study of nearly 9,000 German rubber workers evaluated the risk of cancer associated with the use of specific agents in the rubber industry (Straif et al, 2000). The authors claimed their report was the first to examine exposure specific data in terms of cancer risks in the rubber industry. In this study of over 8,000 workers, no causative link between carbon black and cancer risk was observed. To the contrary, the authors speculated that the lung cancer risk observed in the rubber industry workers was likely due to asbestos and talc exposure.

A mortality study of a cohort of over 17,000 rubber tire workers in Poland showed no excess in lung cancer (Wilczynska et al, 2001). Finally, a study of a large USA rubber manufacturing facility that included over 3400 workers showed no excess in lung cancer (Beall et al, 2007).

The rubber industry has been the subject of more recent studies conducted since the IARC assessments of the rubber industry in the 1980s. Technical changes in the manufacturing process

and control of exposure to hazardous materials have improved over the past decades and there is interest in assessing whether the contemporary rubber industry has the same risk of cancer as earlier processes and time periods. Discussions of these recent studies follow.

A mortality and cancer incidence survey among relatively recently hired employees (1982-1991) in the British rubber industry showed no increase in mortality from lung cancer (Dost et al, 2007). The authors suggested “*elevated SMRs for stomach and lung cancers reported for historical cohorts of UK rubber workers will not be present in more recent cohorts.*” A similar study among recent German rubber industry entrants showed no statistically significant excess in cancer. The authors cautioned, however, that the cohort was “*still too young to provide conclusive evidence*” (Taeger et al, 2007).

A cohort mortality study of workers in an Italian tire manufacturing plant, 1962–2004, has recently been published (Mirabelli et al, 2012). Mortality rates of 9,501 workers first hired between 1962, when the plant started operations, and 2000 showed SMRs significantly reduced for all causes, all cancers, (including lung cancer), cardiovascular, and ischemic heart diseases. This cohort is relatively young; < 10 % have died. There was, thus, limited power to detect small increases in risk at rare cancer sites. Further epidemiological surveillance of this cohort is planned. Mortality among 6,246 workers of an Italian rubber tire factory employed between 1954 and 2008 was significantly lower than expected for all cancers (SMR = 79) and all causes (SMR = 85) (Pira et al, 2012). This study showed no excess cancer risk among male rubber tire workers employed after 1954.

Paget-Bailly analyzed 99 publications and noted significantly increased meta-relative risks (meta-RRs) for laryngeal cancer for workers in the rubber industry (meta-RR 1.39; 95% CI 1.13 to 1.71) (Paget-Bailly et al, 2012). Carbon black was not implicated as a potential contributor to the excesses in laryngeal cancer reported.

A follow-up of a cohort of over 12,000 German rubber industry workers demonstrated significantly elevated standardized mortality ratios (SMRs) for cancer of the lung and pleura in men (Vlaaderen et al, 2013). Lung cancer was statistically significantly elevated with an SMR of 1.23 (95% CI: 1.12-1.35); cancer of the pleura was also statistically significantly increased with an SMR of 2.57 (95% CI: 1.59-3.93). Women also had an elevated SMR for lung cancer. Carbon black was not implicated in the results.

Although the rubber industry has been associated with increases in some types of cancer, no study has implicated carbon black exposure as an explanation for these findings including the risk of lung cancer reported in earlier studies.

Current activities underway in Europe regarding potential health issues in the rubber industry include a follow up of the UK rubber industry cohort (McElvenny, 2014). A large retrospective cohort study of 40,000+ workers is being conducted. Dose-response relationships will be assessed for suspected carcinogens using quantitative exposure modeling based on available measurement data from the EXASRUB project (dust, fumes, solvents, and n-Nitrosamines). This is the largest and statistically most powerful cohort of its type and will have an exhaustive, quantitative exposure assessment.

Rubber Industry Morbidity Studies

In light of the extensive scientific work directed toward cancer risks and mortality risks in the rubber industry and the numerous studies published, it is surprising that there are relatively few morbidity studies that have been performed in the industry. One such morbidity study was reported from an Iranian Rubber Plant (Neghab et al, 2011). A cross sectional morbidity assessment was designed to assess and characterize pulmonary reactions, if any, associated with occupational exposure to carbon black, among a group of rubber workers.

Participants included 72 workers from the warehouse, loading, and Banbury areas and 69 controls of the plant. Symptoms were assessed by a questionnaire and pulmonary function tests. Exposure assessment included inhalable and respirable fractions. Cough and wheezing were higher in the exposed group (23.6% vs. 1.44% and 25% vs. 1.44, respectively).

In this study, the exposure assessment methodology is unclear, as no details of basic sampling strategy (area, personal, production conditions, etc.) were provided. Nonetheless, the exposures were excessive. Reported concentrations were 5-6 times higher than current North American inhalable exposures in the carbon black industry. Thus, results from high exposure to any type of dust, whether reactive or inert, would likely cause these results. In this study, (1) exposures were significantly above past and current OELs; (2) there was an absence of engineering controls, maintenance, work practices, employee training, industrial hygiene activities; and (3) there was no respiratory protection.

Conclusions about mortality risks in the rubber industry

A 2009 IARC evaluation of the rubber industry concluded that there was sufficient evidence in humans for elevated risk of cancers of the lung, bladder, and stomach, in addition to higher risks of leukemia and lymphoma. There is no mention about carbon black use in the rubber industry contributing to these excesses in cancer (IARC, 2012).

Toner Industry Mortality Studies

Another common use of carbon black is in the production of toner. Some laser printers and photocopiers use toner, which commonly contains carbon black mixed with a heat sensitive polymer. These products are ubiquitous in businesses and homes all over the world. The purpose of this part of the report is to summarize studies of the toner industry in which carbon black exposure was measured, assessed, or discussed.

A large retrospective study of mortality risks of 33,671, employees occupationally exposed to toner was conducted (Abraham et al, 2010). The exposed group included employees involved in the manufacturing of toner and customer service engineers who serviced copiers in the field. All cause SMRs for toner-exposed populations were 0.65 and 0.84 for white men and women respectively. SMRs for all cancers including lung cancer were lower than 1.0. There was no evidence that toner exposure increased the risk of all-cause mortality or cause-specific mortality for the 23 categories of death analyzed.

Toner Industry Morbidity Studies

A study of 1,504, male workers in a Japanese toner and photocopier manufacturing company, demonstrated no evidence of adverse effects on pulmonary function or chest x-rays (Kitamura et al., 2014 a,b,c). Means of personal 8-hour respirable dust concentrations spanned from 0.012 mg/m³ in toner manufacturing to 0.989 mg/m³ in toner and photocopier recycling. The authors noted significantly higher prevalence of breathlessness for the toner-handling group as compared to the never-toner-handling group. No association was observed with breathlessness and pulmonary function decrements or fibrotic changes on the chest X-rays. The authors noted that asthma morbidity was higher compared to the Japanese population in both the toner-handling group and the never-toner handling group (Kitamura et al., 2014, a, b, c)

Occupational Exposure Limits for Carbon Black: ACGIH TLV

On February 1, 2011, the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLV) Committee announced adoption of a new health-based guideline (TLV®) for carbon black of 3 mg/m³, measured as the inhalable dust fraction of an 8-hour Time-Weighted Average (TWA) (ACGIH, 2011). The Carbon Black REACH Consortium calculated a DNEL for carbon black for occupational environments of 2 mg/m³, measured as the inhalable dust fraction of an 8-hour TWA. The DNEL was included with the carbon black registration dossier, which passed ECHA's completeness check on January 26, 2009.

The TLV® and DNEL values were both derived from the same US carbon black worker exposure study (Harber et al, 2003). ACGIH (2011) stated that *"Symptoms of bronchitis are the human health effect most sensitive to exposure to CB; therefore, the recommended TLV-TWA is intended to prevent CB-related bronchitis."* The organization also noted "a statistically significant but slight increase in bronchitis (from 5% to 9%) only in non-smokers whose mean exposures were ≥ 137.9 mg-year/m³, equivalent to 3.44 mg/m³ over a 40-year period." The TLV® of 3 mg/m³ (inhalable) is meant to be protective of bronchitis symptoms.

1. Although the increase in bronchitis symptoms for non-smokers in the cumulative exposure group was statistically significant, the increase is slight (10% or 9% in the 4th and 5th pentiles, respectively, compared to 5% in the lowest exposure pentile).
2. Recent exposures based on 2000-2001 industrial hygiene data showed no increase in bronchitis symptoms even at the highest exposure pentile of 3.8 mg/m³.
3. At exposures > 3.5 mg/m³, there were decreases in FEV₁; however, the decreases are within the normal mean FEV₁. ACGIH (2011) stated: *"these changes in pulmonary function values at these exposure levels are not used as a basis for, but support the recommendation of the TLV-TWA."* The measured lung function data do not show significant adverse effects above normal age-related declines in lung function.

Derivation of DNEL

The derivation of the DNEL is described in the Chemical Safety Report of the REACH dossier for carbon black developed by the Carbon Black REACH Consortium. This report states that Harber et al. (2003) described elevated prevalence of symptoms (chronic bronchitis) in the highest exposure pentile, which is comparable to an exposure to inhalable dust of 138 mg-years/m³ or to an average concentration over 40 years of exposure of 3.5 mg/ m³ (138 mg-years/m³)/(40 years). However, the DNEL derivation also recognizes that an increase in bronchitis symptoms was also seen in the 4th pentile representing cumulative exposure. Therefore, it was necessary to identify an adverse effects threshold based on data showing that no increased symptoms were detected up to the 3rd pentile of cumulative exposure (Table 6 of Harber et al. (2003)).

The study authors did not age-adjust the data; therefore, it is possible that workers in the 5th pentile were older, and hence more susceptible to disease. The threshold level was estimated at $(3/5) * 3.5 \text{ mg/ m}^3 = 2 \text{ mg/ m}^3$ (inhalable), which corresponds to a DNEL in humans of 2 mg/m³ (inhalable dust fraction). The factor of 3/5 was used to account for the adverse effects threshold being somewhere between the 3rd and 5th pentiles, with the consideration that age adjustment was not conducted. As the third pentile did not show adverse effects, this threshold was approximated on a continuous exposure scale by multiplying the value of the fifth pentile with the factor 3/5.

Appendix B

Selected Occupational Exposure Limits for Carbon Black*

| <u>Country</u> | <u>Concentration, mg/m³</u> |
|--------------------|---|
| Argentina | 3.5, TWA |
| Australia | 3.0, TWA, inhalable |
| Belgium | 3.6, TWA |
| Brazil | 3.5, TWA |
| Canada (Ontario) | 3.0 TWA, inhalable |
| China | 4.0, TWA 8.0, TWA, STEL (15 min) |
| Colombia | 3.0, TWA, inhalable |
| Czech Republic | 2.0, TWA |
| Egypt | 3.5, TWA |
| Finland | 3.5, TWA; 7.0, STEL |
| France – INRS | 3.5, TWA/VME inhalable |
| Germany – MAK | 0.3 x GBP density in g/cm ³ , TWA, respirable; 4.0, TWA, inhalable |
| Germany – TRGS 900 | 0.5 x GBP density in g/cm ³ , TWA, respirable; 10, TWA, inhalable |
| Germany – BeKGS527 | 0.2 x nano-GBP density in g/cm ³ , TWA, respirable - if no other relevant information is available |
| Hong Kong | 3.5, TWA |
| Indonesia | 3.5, TWA/NABs |
| Ireland | 3.5, TWA; 7.0, STEL |
| Italy | 3.5, TWA, inhalable |
| Japan – MHLW | 3.0 |
| Japan – SOH | 4.0, TWA; 1.0, TWA, respirable |
| Korea | 3.5, TWA |
| Malaysia | 3.5, TWA |
| Mexico | 3.5, TWA |
| Russia | 4.0, TWA |
| Spain | 3.5, TWA (VLA-ED) |
| Sweden | 3.0, TWA |
| United Kingdom | 3.5, TWA, inhalable; 7.0, STEL, inhalable |
| EU REACH DNEL | 2.0 (inhalable) |
| United States | 3.5, TWA, OSHA-PEL 3.0, TWA, ACGIH-TLV®, inhalable 3.5, TWA, NIOSH-REL |

*Please consult the current version of the standard or regulation that may apply to your operations.

| | |
|-------------------|--|
| ACGIH® | American Conference of Governmental Industrial Hygienists |
| mg/m ³ | milligrams per cubic meter |
| DNEL | Derived no-effect level |
| GBP | Granular biopersistent particles without known specific toxicity (carbon black is not listed in TRGS 900) |
| Nano-GBP | Dust of biopersistent nanomaterials without specific toxicological properties and without fibrous structures (carbon black is listed in BeKGS 527) |
| NIOSH | National Institute for Occupational Safety and Health |
| OES | occupational exposure standard |
| OSHA | Occupational Safety and Health Administration |
| PEL | permissible exposure limit |
| REL | recommended exposure limit |
| STEL | short-term exposure limit |
| TLV | threshold limit value |
| TRGS | Technische Regeln für Gefahrstoffe (Technical Rules for Hazardous Substances) |
| TWA | time weighted average, eight (8) hours unless otherwise specified |

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The International Carbon Black Association attempts to maintain a complete and current bibliography of occupational and environmental health related literature for carbon black. Contact your carbon black supplier for additional information.

Tables and Figures - User's Guide

Table 1. General information and physical-chemical properties

| | |
|------------------------------|--|
| Chemical Name | Carbon Black |
| Synonyms | Acetylene Black, Channel Black, Furnace Black, Gas Black, Lampblack, Thermal Black |
| CAS Name | Carbon Black |
| CAS Registry Number | 1333-86-4 |
| Chemical (Molecular) Formula | C |
| Formula weight | 12 (as carbon) |
| Physical state | Solid: powder or pellet |
| Solubility | Water: insoluble Solvents: insoluble |
| Color | Black |

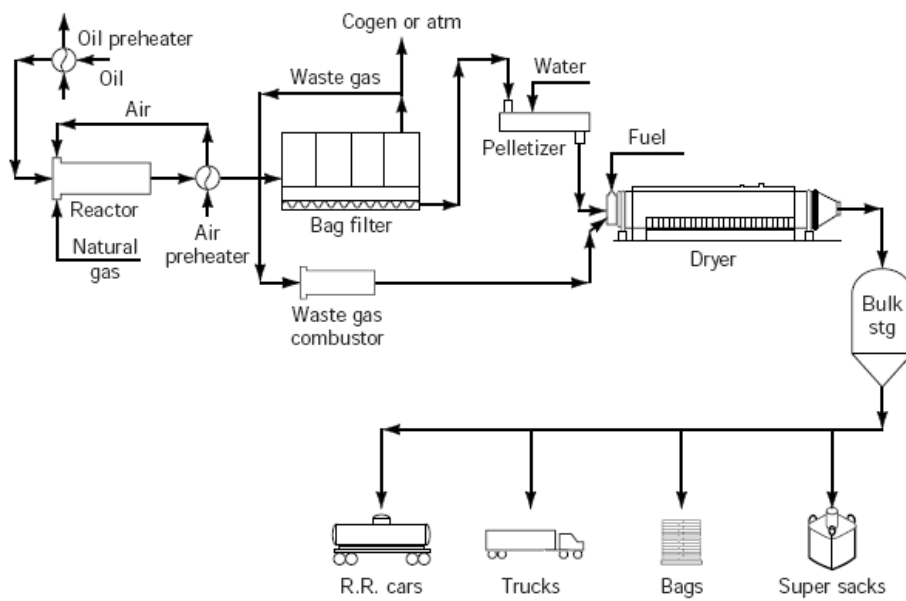


Figure 1a. Furnace black production process.

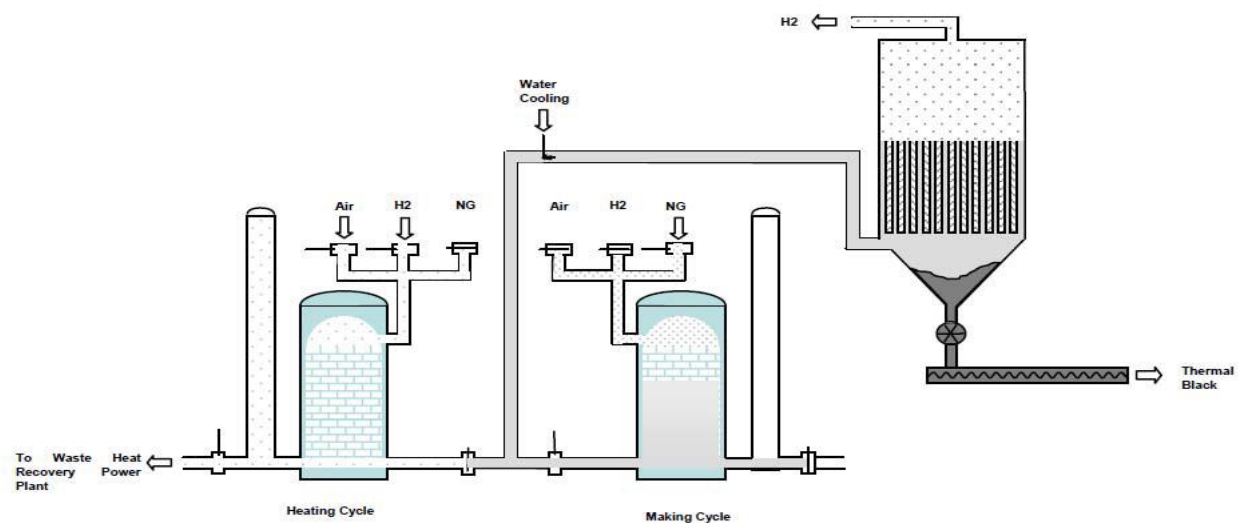


Figure 1b. Thermal black production process.

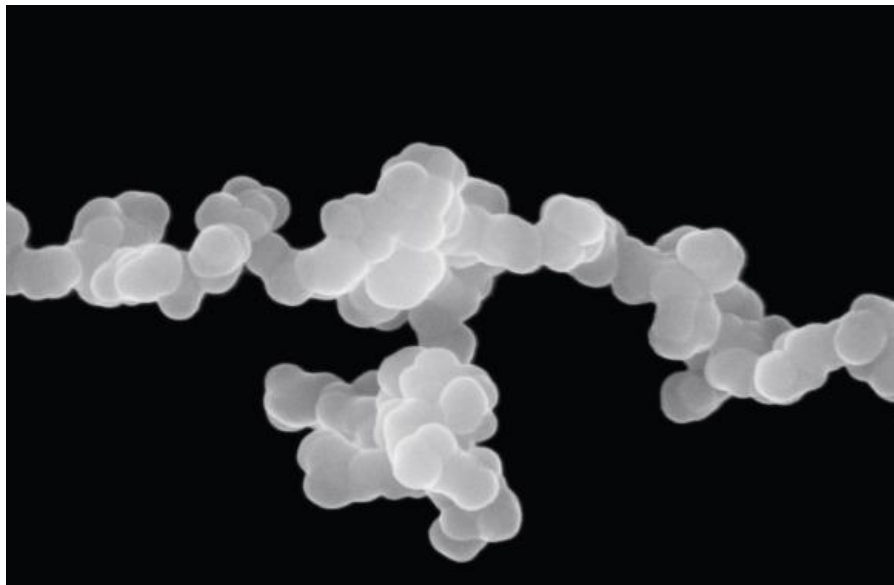


Figure 2. Scanning electron microscope view of a typical carbon black aggregate consisting of fused primary particles (120,000x).

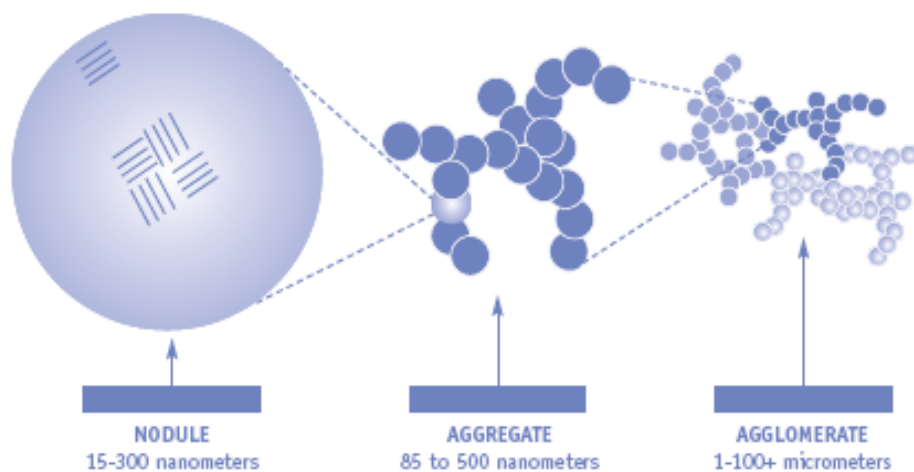


Figure 3. Sequence of carbon black structure development. The spheroidal nodule (primary particle) is the fundamental building block of carbon black, strongly fusing into aggregates of colloidal dimension forming an aciniform (grape-like) morphology. Strong electrical forces maintain the integrity of the aggregate and promote the formation of agglomerates.



Figure 4. Carbon black as typically placed on market.