

REINFORCING FILLERS IN THE RUBBER INDUSTRY

Assessment as potential nanomaterials with a focus on tyres

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Executive Summary

Amorphous silica and carbon black have been used as reinforcing fillers in the rubber industry for decades. Their presence in rubber is essential to achieve longer-wearing products, increased tyre strength and longevity and, especially for silica, decreased greenhouse gas emissions of the vehicles using these tyres. Despite a long history of safe use in the rubber and tyre industry, these fillers are being associated with man-made nanomaterials, which are being intensely studied for their potential adverse health effects and are the subject of pending regulatory controls. This paper provides information regarding the industry's use of these fillers, differentiates the filler materials used by the industry according to their particle sizes, and summarizes the state of knowledge with respect to the toxicological properties of amorphous silica and carbon black fillers.

In rubber industry applications, amorphous silica and carbon black are used in a form that exceeds all proposed size dimensions for nanomaterials. Although both amorphous silica and carbon black have primary particle sizes in the nanoscale, the particles to which workers may be exposed during raw materials handling are in the micrometer size range as a result of aggregation and agglomeration.

Aggregates and agglomerates are difficult or nearly impossible to dissociate under standard handling conditions. Furthermore, both amorphous silica and carbon black are used in the tyre industry in forms that are designed to reduce dustiness of the material, including pellets and micropearls. As a result, the exposure of workers to nanoscale particles when handling these materials in the tyre industry is expected to be negligible. Work is ongoing in the tyre industry to verify this conclusion.

In addition to what is known about the physical characteristics of amorphous silica and carbon black as they are used in the tyre industry, it is also well established that, from a toxicological perspective, neither are likely to represent a health risk. Although animal studies on some forms of amorphous silica and carbon black, particularly those evaluated for their nanoscale properties, indicate adverse effects may occur with exposure, numerous studies have indicated that there is no evidence of human health risks related to carbon black or amorphous silica as used in the rubber industry when air concentrations are below the established occupational exposure limits.

Based on physical characteristics, exposure to amorphous silica and carbon black used in the rubber and tyre industry is not likely to result in exposure to nanoscale particles, primarily due to aggregation and agglomeration of the particles. Furthermore, from a toxicological perspective, it appears that existing regulations on amorphous silica and carbon black are sufficiently health protective. Accordingly, additional or different regulation is not necessary to ensure continued safe use of these materials in the rubber and tyre industry.

1. INTRODUCTION

With the rapid emergence of the field of nanotechnology, regulations specific to nanomaterials are under development. One of the key issues hindering regulation is a lack of agreement on the definition of what constitutes a nanomaterial. Currently, the most comprehensive and internationally recognized definition of nanomaterials is presented by the International Standards Organization (ISO). The ISO definition distinguishes between two subgroups, nano-objects and nanostructured materials, and defines them as follows: [1]

- **Nano-objects** are materials that exist in defined singular form that have at least one dimension in the nano-scale, < 100 nm. These include nano-particles (3 dimensions in nano-scale), nanofibres (2 dimensions) and nano-plates (one dimension).
- **Nanostructured materials** are materials that have structural features on the nano-scale but whose particle size is typically greater than 100 nm. Examples of these are materials that primarily exist in aggregated and/or agglomerated forms.

A recently published paper by the European Commission Joint Research Centre (JRC) suggests the use of the more specific term “particulate nanomaterials” to identify materials which are in a particulate form at the nanoscale and are mobile in their immediate environment, and thus might raise health and safety concerns [2]. The JRC acknowledges that composite materials such as the rubber compounds used in tyres have been on the market for a long time already, have never been considered as a special technology due to “nano” ingredients and would not qualify as products of nanotechnology under this definition.

Recently, health concerns have been raised with regards to nano-objects, because their exceptionally small size may cause them to act and move differently in the human body than the same substances in larger sizes. Therefore, in evaluating whether a substance should be regarded as a nanomaterial requiring special precautions, it is important to consider its properties with respect to aggregation and agglomeration, ultimate particle size, and toxicity.

The purpose of this report is to provide information regarding the industry’s use of amorphous silica and carbon black as reinforcing fillers, clearly establish the physical characteristics of the filler materials, particularly as they relate to particle size during handling in the tyre manufacturing setting, and summarize the state of knowledge with respect to the toxicological properties of the amorphous silica and carbon black fillers.

2. TYPES OF REINFORCING FILLERS IN THE TYRE INDUSTRY AND THEIR ROLE IN TYRE PERFORMANCE

The primary reinforcing fillers used for the production of rubber articles are precipitated amorphous silica and carbon black. These materials are delivered in bulk via rail cars, trucks, or large sacks (supersacks). On arrival they are transferred to and stored in silos. These silos feed the “internal mixers” that are used to manufacture tyre compounds via a system of pipes and weigh-scales. The mixer is a large vessel equipped with two rotating paddles (or rotors) connected to a motor of very strong power (more than 1200 KW).

The compound production is a batch process where the rubber and the reinforcing filler are introduced into the internal mixer and the rotation of the paddles causes high energy shearing inside the mixer between the rubber, filler and other chemicals. This shearing causes an intimate mixing (or dispersion) to occur of the fillers and chemicals into the rubber matrix. Figure 1 below shows a typical distribution of reinforcing filler in a rubber compound after mixing in the internal mixer (Internal Tyre Company Documents). A discussion of the reinforcing fillers and the characteristics of these materials from their manufacture to use in the tyre industry can be found in section 3.

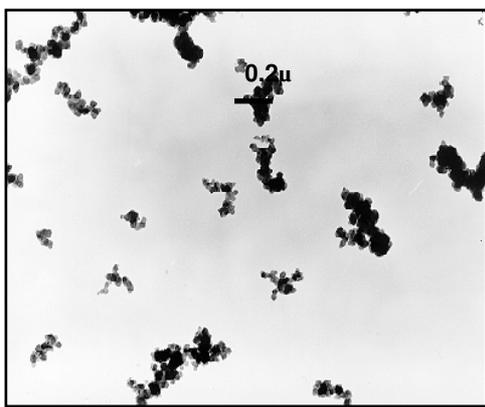


Figure 2. Reinforcing filler in rubber after mixing in internal mixer

Tyres have a wide range of performance requirements. They must carry the load of the vehicle, have sufficient grip on the road, transmit steering forces to guide the vehicle, provide dampening between the road and the vehicle, have durability that enables their use at high speeds and over long time periods, and have as low as possible impact on fuel consumption. As shown in Figure 2, tyres are complex composites made of mixtures of rubber with metal and textile reinforcements [3].

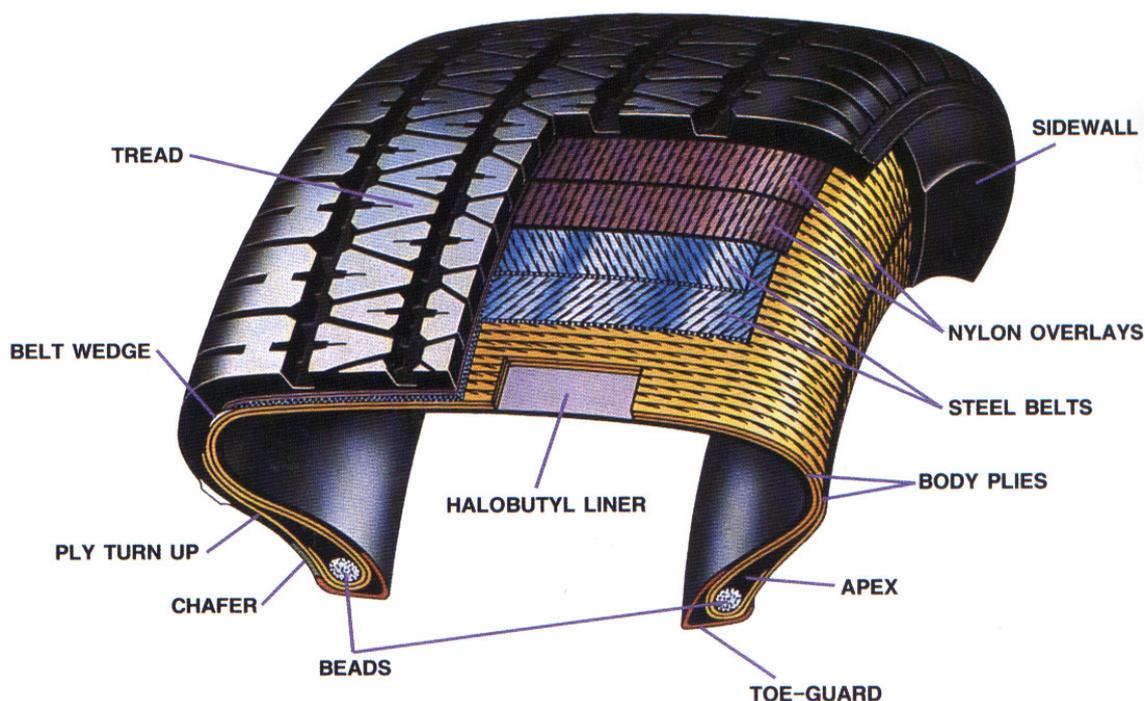


Figure 2. An example of a tyre construction [3]

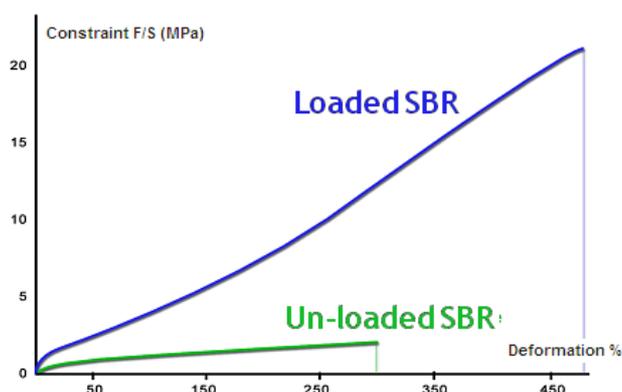
The rubber mixtures or compounds are, at a basic level, composed of polymers, reinforcing fillers, oils, and numerous chemicals used to crosslink or “cure” the compounds. Different rubber compounds exist for the various parts of a tyre, each with a specific combination of materials to provide the performance attributes for that part. For example, the compound used for the inner liner is specifically designed for minimizing air loss; the compound for the sidewall is designed for flex resistance and to protect from

weathering; and the tread compound is designed to provide traction and resistance to wear, while minimizing the impact on the vehicles fuel consumption.

The reinforcing fillers used in tyre compounding are critical to achieving the performance requirements. This is especially true for the tread compound with its large number of requirements and emphasis on wear resistance. The fillers provide a large degree of strengthening of the rubber network, resulting in a substantial increase in stiffness, tensile strength, and resistance to abrasion [4]. The reinforcing fillers achieve this via a high level of chemical links with the polymer network.

The use of reinforcing fillers in tyres improves both the strength and stiffness characteristics of the rubber polymer. Filled rubber polymer has significantly higher stiffness than unfilled rubber polymer at the same degree of deformation. Furthermore, filled rubber polymer has as well as considerably higher strength and deformation to break than unfilled rubber polymer [5].

The primary result of this strength improvement is the longevity of the tyres, in terms of overall load bearing, durability, and tread wear performance [6-9]. A tyre manufactured without the use of reinforcing fillers would not be strong enough to carry the load or handle the forces required by the vehicles of today. Without reinforcing fillers, tyres would need to be replaced considerably more often, resulting in an increased burden on end-of-life-tyre (ELT) management and an increase in tyre manufacturing energy requirements and greenhouse gas emissions per vehicle kilometer driven.



Another benefit of the compound strength is its ability to transmit forces through the tread area (or footprint) of the tyre. The most important aspect of this is improving traction and reducing stopping distance for the vehicle [4, 6]. Without well adapted reinforcing fillers, vehicles would not be able to stop as quickly as they currently can, causing safety concerns for drivers.

3. PHYSICAL CHARACTERISTICS OF REINFORCING FILLERS USED IN THE RUBBER INDUSTRY

Based on the ISO definitions of nanomaterials, it is important to make a distinction between nanostructured materials and nano-objects. For many nanostructured materials, aggregation and agglomeration results in particle sizes outside of the nanoscale and thus extyrepasures in occupational settings are not to true nanoparticles, but rather to larger particles that may not behave like or have the toxicity associated with some nanoparticles. The following section evaluates the characteristics of precipitated amorphous silica and carbon black as they are used in the tyre industry with respect to the ISO definition of nanomaterials in an effort to understand if these materials have the potential for initiating the adverse effects that have been reported with some nanoparticles.

3.1. AMORPHOUS SILICA

Amorphous precipitated silica, defined by a specific CAS number, is used in many applications in addition to its use in the rubber and tyre industry, including cosmetics, paper and many other applications related to nutrition and health [10, 11]. The world production of amorphous precipitated silica is 1.3 million tons of which one-third is used in tyre production [11]. Silica has been used in the treads of tyres for more than twenty years in order to reduce the fuel consumption of vehicles, thus contributing to a reduction in vehicle emissions of greenhouse gases [7].

Amorphous precipitated silica is produced from vitreous silicate. The vitreous silicate is dissolved in water and transferred to a reactor in which, through acidification and under agitation, amorphous silica is precipitated out [9, 11]. During this precipitation there is an instantaneous formation of primary nanoscale particles (from approximately 2 to 40 nm) of a very short lifespan [11, 12]. These particles may be considered nano-objects according to the ISO definition. These particles, however, immediately cluster to form non-dissociable aggregates (from approximately 100 to 500 nm in size) based on covalent bonds [4, 12]. Because of the nature of these bonds, these aggregates cannot disaggregate under standard conditions [11]. The aggregates subsequently electrostatically bind together to form agglomerates from 1 to 40 μm [4]. Electrostatic bonds, while weaker than covalent bonds, cannot be broken from normal use; breaking these bonds requires the use of a dispersant [11]. Because of these aggregates and agglomerates, precipitated amorphous silica meets the ISO definition of a nanostructured material, but it does not meet the definition of a nano-object.

At the end of the precipitation process, after drying and washing, the precipitated amorphous silica is mechanically processed into micro pearls or granules (dimension of 1/10 mm to a few mm) to ease shipping, handling and use. It is this form that is used by the tyre industry. The formation of these micro pearls and granules reduces the dustiness of the precipitated silica, and therefore reduces the potential for worker exposure to particles of amorphous silica during handling. During rubber compounding, due to the high energy involved, the granules or micropearls of the precipitated silica are broken down, transforming back to the aforementioned agglomerates with dimensions between 1 and 40 microns. Because of the strong mechanical energy applied to the rubber, agglomerates may be broken down and transformed into aggregates (see Figure 1), some of which are of nanometric size (their dimension ranges between 100 to 500 nanometers). However, it is crucial to understand that these aggregates are chemically bound to the rubber matrix by strong chemical links that result from the manufacturing process [13]. Furthermore, the physical mixing process itself does not create enough energy to break down the strong covalent forces that exist between the individual particles that form these aggregates [13].

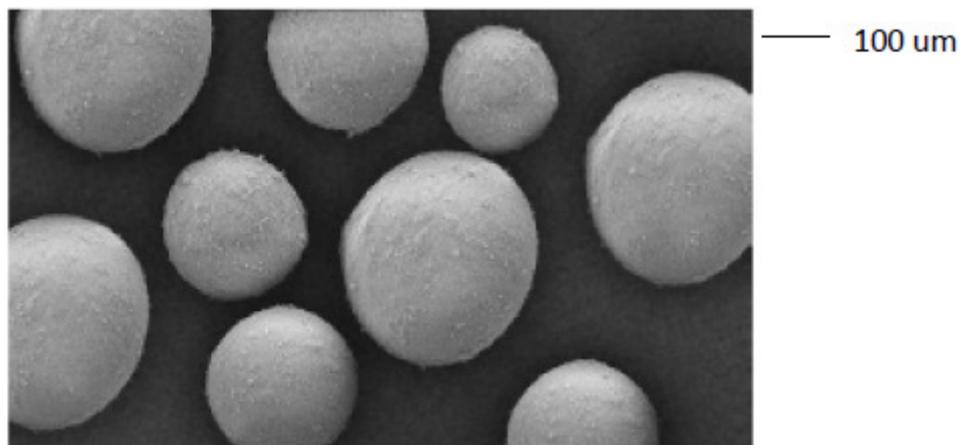


Figure 3. Silica micro pearls

Based on the physical characteristics, commercially available precipitated amorphous silica does not meet the criteria to be identified as a nano-object, although it does contain primary particles in the nanoscale. Under the use conditions in rubber manufacturing, these primary particles will not likely be released from the agglomerates and aggregates that are found in the precipitated amorphous silica. Therefore, precipitated amorphous silica used as a raw material in the tyre industry does not require special regulation or consideration as a nanomaterial.

3.2. CARBON BLACK

Carbon black, defined by a specific CAS number, is produced by incomplete combustion of oil under specific conditions and has a long history of safe production and use. Approximately 65% of the world's 8 million tons per year of carbon black are used in tyre production [11]. Several parameters are controlled in the process in order to achieve the specific characteristics of the finished carbon black products. Specifically, the oil ("feedstock") is injected at high speed into a reactor where it is pyrolyzed at high temperature (approximately 1200-1900°C) [11]. The combustion reaction is controlled by quenching with water such that the oxidation remains incomplete and the end-product carbon black is formed [11].

During the first split second of the combustion reaction, carbon nodules are formed with dimensions from approximately 5 to 100 nm, depending on the grade of carbon black to be produced [14]. On the basis of the proposed definitions for nanomaterials, these nodules may be considered nano-objects. However, the lifespan of these nodules is very short as they immediately cluster together to form aggregates of sizes between approximately 70 and 500 nm [14]. Because aggregation involves the formation of covalent bonds between primary particles, these bonds are not typically broken by physical means. In addition to aggregation, the aggregates are then subsequently combined together to form agglomerates after a few short seconds. The resulting agglomerates typically measure between 10 and 100 µm [15]. The bonds formed between the agglomerates are electrostatic, and therefore cannot be broken under normal handling conditions. Because this aggregation and agglomeration results in particle sizes well above the nanoscale, carbon black used as a raw material meets the definition of a nanostructured material, but does not meet the definition of a nano-object.

Furthermore, in order to produce the material used by the tyre industry, the carbon black passes through a pelletizer to compact the carbon black into a pellet form of millimeter dimension [11, 15]. This is done to facilitate the shipping and handling of carbon black for use by the rubber industry. The formation of a pellet decreases the dustiness of the carbon black, and thus decreases exposure to particle-form carbon black in workers in the rubber industry. Similar to what occurs with precipitated amorphous silica when it is introduced into the mixer, pellets of carbon black are broken down during mixing, transforming the

carbon black back into the agglomerated state. The shear forces applied during mixing may break apart the agglomerates resulting in reversion to the aggregated state, which includes particles ranging from 70 to 500 nm. As with precipitated amorphous silica, these aggregates become incorporated and chemically and/or physically bound to the rubber matrix, rendering them unavailable for release [13].



Figure 4. Carbon black pellets

Based on these characteristics, carbon black does not meet the criteria to be identified as a nano-object, although it does contain primary particles in the nanoscale. Under the use conditions in rubber manufacturing, these primary particles will not likely be released from the agglomerates and aggregates that are found in the carbon black. Therefore, carbon black, as used as a raw material in the tyre industry does not require special regulation or consideration as a nanomaterial.

4. TOXICOLOGY OF REINFORCING FILLERS USED IN THE RUBBER INDUSTRY

From a chemical substance standpoint, carbon black and amorphous precipitated silica are relatively inert and stable materials, and have been subject of substantial health studies over the past decades [10, 16-21]. Recently, both substances have been REACH registered by several major manufacturers, without any hazard classification [22, 23].

The purpose of this section is to provide a basic review of the human health toxicity studies evaluating carbon black and amorphous silica. In particular, it reviews toxicity specific to the materials as they are used in the tyre industry (commercially available materials used in industry), in comparison to other forms of amorphous silica and carbon black that are being evaluated for their specific characteristics as nanomaterials (e.g. ultrafine carbon black and mesoporous silicas). Ultrafine carbon black is often used as a surrogate to understand adverse effects associated with exposure to ultrafine particles in the ambient air, where amorphous silicas are being developed for use as nanomaterial-based drug delivery systems, as well as a number of other uses. Because results of these studies can differ, it is important to make a distinction between effects seen with the material used in the tyre industry and those seen in studies that have been conducted to investigate amorphous silica and carbon black as nanomaterials.

4.1. AMORPHOUS SILICA

Precipitated amorphous silica and other commercially available synthetic amorphous silicas have been studied by a variety of researchers and results of toxicity studies summarized by national and international agencies including the U.S. Environmental Protection Agency (U.S. EPA) and the Organization for Economic Cooperation and Development (OECD). The results of animal-based toxicity studies with synthetic amorphous silicas including precipitated silica are remarkably consistent; the effects of amorphous silica are transient and include an initial inflammatory response that occurs with exposure to particles, and resolution of these effects with cessation of exposure [10, 24].

Epidemiological studies of workers exposed to synthetic amorphous silicas do not find any adverse pathological effects in the lung, indicating that routine exposure in the workplace is not likely to lead to even the transient effects seen in animal models [10, 18, 25, 26]. Based on both epidemiology and animal studies, precipitated amorphous silica is of low toxicity. While it is clear from the literature that precipitated amorphous silica is of low toxicity, newly emerging studies on other kinds of nano-sized amorphous silicas, such as those being developed for use in drug delivery systems, may cause some to erroneously draw conclusions about the hazards of precipitated amorphous silica. These materials, while chemically identical to precipitated amorphous silica (e.g. SiO₂), are manufactured using different methods, maintain different physical properties, and may have different toxicities as a result, in the same way that crystalline silica differs from all amorphous silicas. In particular, studies in a variety of cell models have found that exposure to nano-sized amorphous silicas result in an inflammatory reaction and cell damage [27-39]. While these studies may suggest that some nano-sized amorphous silicas are toxic: 1) they do not characterize the effects of precipitated amorphous silica, which has been deemed to be of low toxicity by a number of groups and 2) they were not conducted using an animal model. In fact, for most types of nano-sized amorphous silicas, studies in animal models are consistent with those effects seen with precipitated amorphous silicas [33, 34, 40- 43].

Therefore, when drawing conclusions about the safety from exposure to amorphous silica as it is used in the tyre industry, it is important to consider not only the type of material being investigated (e.g. precipitated amorphous silica versus nano-sized amorphous silicas designed for their nano-sized properties) but also the type of toxicity study (animal versus cell-based). Studies conducted in animal models are more representative of potential toxicity in humans and, in fact, are consistent across all types of amorphous silicas. Based on these considerations, it is clear that the amorphous silica as used in the tyre industry does not represent a health hazard, independent of particle size considerations.

4.2. CARBON BLACK

As with amorphous silica, carbon black has been analyzed by a number of national and international agencies for risks associated with human health, including Environment and Health Canada, OECD, and the International Agency for Research on Cancer (IARC) [21, 44, 45]. In animal models, carbon black was deemed to be of low acute toxicity following oral and inhalation exposure, with no inflammation observed in rat lung following exposure to fine carbon black (particle size = 200 nm) and only mild inflammation in rat lung with exposure to ultrafine carbon black (particle size = 20 nm) [21]. Repeated inhalation of carbon black in animal models also caused pulmonary inflammation [21, 45]. In two year carcinogenicity studies of carbon black in rats, lung tumors developed after prolonged exposure; however, most researchers believe this is a consequence of particle overload, an effect that results in tumors in animals that are not seen in humans [45].

Carbon black, like amorphous silica, also comes in different sizes, although the morphology remains similar across all types, unlike amorphous silica. There is a wealth of recent literature that has aimed to investigate the effects of ultrafine carbon black, particularly as those effects relate to particle size [46-53]. These results indicate that carbon black of smaller size is more potent at inducing inflammatory effects. Therefore, it is important to consider the size of the particle to which one is exposed when extrapolating the results of these studies to human exposure scenarios. Furthermore, many studies employ a liquid treatment medium, either in animal or cell-based studies. These liquid media may disperse the agglomerates of carbon black, resulting in exposures to particle sizes that are not relevant to human exposure via inhalation.

Epidemiology studies of workers that manufacture or use carbon black offer the most representative studies for understanding the potential health effects associated with carbon black. Such workers are exposed to carbon black as it is used in industrial settings, rather than in ways that are manipulated to facilitate exposure in animal or cell based models (e.g. dispersed in a liquid solution, forced aerosolized

under non-handling conditions, etc.). Epidemiology studies have evaluated both cancer and respiratory function as endpoints. Contrary to what occurs in rat models, carbon black workers do not develop cancers as a result of exposure to carbon black [16, 19, 20, 54, 55]. Supporting this negative finding are results of mutagenicity studies with carbon black that were generally negative [56]. However, small reductions in pulmonary function and other respiratory symptoms have been found in carbon black workers [21, 45], indicating that prolonged exposure to carbon black may result in adverse effects.

Environment and Health Canada and the OECD have determined that carbon black does not pose a significant health risk and/or is of low priority for further investigation. IARC has deemed carbon black “possibly carcinogenic to humans” but has concluded that there is limited evidence for carcinogenicity from carbon black based on studies in humans; these conclusions are based solely on animal studies utilizing very high exposure concentrations [44]. Based on the literature summarized above and what is known about the aggregation and agglomeration that occurs with carbon black under normal handling conditions, one can conclude that carbon black, as it is used in the rubber and tyre industry, is not likely to cause appreciable adverse effects in workers. Care should be taken in extrapolating results from studies in ultrafine carbon black in animal and cell models to human exposure scenarios as particle size, and method of administration (e.g. use of liquid media) may have an impact on the toxic potency of the particle.

5. CONCLUSIONS

Based on the manufacturing and use of carbon black and silica, it is evident that the points at which these materials exist in nano-object form are limited to either short-lived intermediates during synthesis or to polymer-bound small aggregates. Due to the strength of the bonding forces between individual particles in an aggregate, and between the polymer and filler in rubber compounds, it is not physically or chemically possible to obtain individual nano-object forms during rubber article life cycle. As a result, there is no likely human or environmental exposure to nano-object forms of carbon black or amorphous precipitated silica used as fillers to reinforce rubber.

Based on the existing assessments of the toxicity of carbon black and precipitated amorphous silica, in the forms used in the tyre industry, it is not expected that adverse health effects would occur from exposure to these materials. Effects of these materials, particularly for amorphous silica, can differ from the nanoscale forms of the same material (e.g. mesoporous silica). Those forms used in the tyre industry have always been supplied in the form of aggregates and agglomerates, and hence have only existed as nanostructured materials. Thus all historical risk assessments on the use of these materials in the rubber and tyre industry have already, de facto, addressed the potential effects of nano forms of these materials.

Based on both the physical characteristics and what is known about the toxicity of these materials, additional regulation on amorphous silica and carbon black based on their classification as a nanostructured material is unnecessary. To the extent that the tyre industry may develop and introduce new nanomaterials in the future, any health, safety and environmental impacts will be assessed in accordance with all relevant chemical substance regulations. The need for risk management measures will be reviewed with the competent authorities and, if appropriate, introduced across the industry to ensure safe use.

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