

Chapter 5

Environment, health and safety: Development of a risk management framework

This chapter attempts to develop a risk management framework for nanomaterial used as an additive in any nano-enabled tyre. It provides a first insight into a methodology for evaluating the potential human health and environmental concerns associated with the entire life cycle of nanomaterials used in tyres, focusing on tyre manufacturing operations. It gives examples of how to use this methodology using two new nanomaterials that have potential real-world application in nano-enabled tyres: high-dispersion, high surface area (HD-HS) silica and nanoclays.

Whilst the potential benefits of the development of new nanomaterials in tyres could be very significant on a global scale, there is a need to ensure that any nanomaterial used in tyres is safe for humans and the environment across the tyre life cycle and value chain. Even if more generic environment, health and safety (EHS) good practice guidance may serve as a good starting point for the tyre industry, there is a recognised gap, which was highlighted in the first chapters of this report, concerning the lack of sector-specific guidance for dealing with new nanomaterials in tyre production.

This chapter aims to develop a risk management framework for any nanomaterial used as an additive in any nano-enabled tyre. The chapter aims to:

- Provide industry stakeholders with a first insight into a method for evaluating the potential human health and environmental concerns associated with the entire life cycle of nanomaterials used in tyres, focusing on tyre manufacturing operations. This general methodology has been developed as guidance for stakeholders to minimise proactively potential concerns for any nanomaterial of interest that is under development or retroactively for any existing processes to identify and mitigate unreasonable risk.
- Provide examples of how to use this methodology using two case studies of new nanomaterials that have potential real-world application in nano-enabled tyres: high-dispersion, high-surface area (HD-HS) silica and nanoclays.

Introduction to the risk management framework

This framework provides guidance that can be used to develop site- or company-specific risk assessments or risk management strategies for using nanomaterials as additives in tyres. This framework follows the risk-based decision-making framework discussed in the OECD's "Important issues on risk assessment of manufactured nanomaterials" (OECD, 2012a). The OECD adapted its framework from the National Research Council's (NRC) *Science and Decisions: Advancing Risk Assessment* (NRC, 2009).

Guidance can change as research reveals new findings and experts reach consensus on methods and protocols. Therefore, this framework specifically includes steps for continual revision and improvement based on future site-specific and/or general evaluations that improve the state-of-the-science and knowledge pertaining to nanomaterial use.

Further, the framework focuses on a qualitative approach to assessing and managing risk in occupational settings called the risk/control banding approach. For non-occupational settings, the framework recommends an exposure pathway evaluation. The risk/control banding approach follows the guidance presented in the International Organization for Standardization (ISO) document "Nanotechnologies – Guidelines for Occupational Risk Management Applied to Engineered Nanomaterials – Part 2: The Use of the Control Banding Approach in Occupational Risk Management" (ISO, 2012).¹ In general, ISO (2012) provides guidelines that follow these steps:

1. assign a hazard band ranking based on quantitative toxicological data or qualitative health hazard indicators (which are based on toxicity data)
2. assign an exposure band based on a description of processes and physical forms of the nanomaterials.

For proactive risk assessments, the hazard band and exposure band rankings are fed into a control banding matrix. The control banding matrix provides guidance on the proper selection of control strategies to manage risk. For retroactive risk assessments, the hazard band and exposure band rankings are fed into a risk-banding matrix to provide a qualitative assessment of the risk of a given process.

The qualitative risk/control-banding approach of ISO/TS 12901-2 focuses on industrial settings. Therefore, the framework developed in this report expands beyond the risk/control-banding approach in order to cover all life-cycle stages. The general approach proposed is as follows:

1. use of the risk/control-banding approach to assess or manage human health risks due to nanomaterials in occupational settings, particularly the manufacture of nanomaterials and processing of these materials for the manufacture of tyres
2. evaluate the general population and ecological endpoint exposure pathways over all life-cycle stages to assess the potential risk nanomaterials pose to these endpoints.

A risk management approach (i.e. similar to the risk/control-banding approach) is not presented because a generally accepted approach does not currently exist. However, the exposure pathway evaluation guidance can be used to critically evaluate the exposure potential over the entire product life cycle. In the absence of toxicological data for these endpoints, and fate and transport data for the nanomaterial, it is suggested that conservative control methodologies that aim to entirely eliminate exposures be applied.

Although this framework focuses on qualitative risk/control-banding, it also addresses topics of a quantitative risk assessment. If adequate data are available, a quantitative risk assessment can be used to assess risk over the entire life cycle of the use of nanomaterials in tyres. However, this framework is not intended to provide guidance on quantitative risk assessments. Risk-assessor expertise should be sought if a quantitative risk assessment is desired.

As with other recently published guidance, this framework presents the steps to perform a risk assessment following three phases (OECD, 2012a):

1. Phase I – Problem formulation and scoping
2. Phase II – Planning and conducting the risk assessment
3. Phase III – Risk management.

Figure 5.1 illustrates the organisation and flow of this framework.

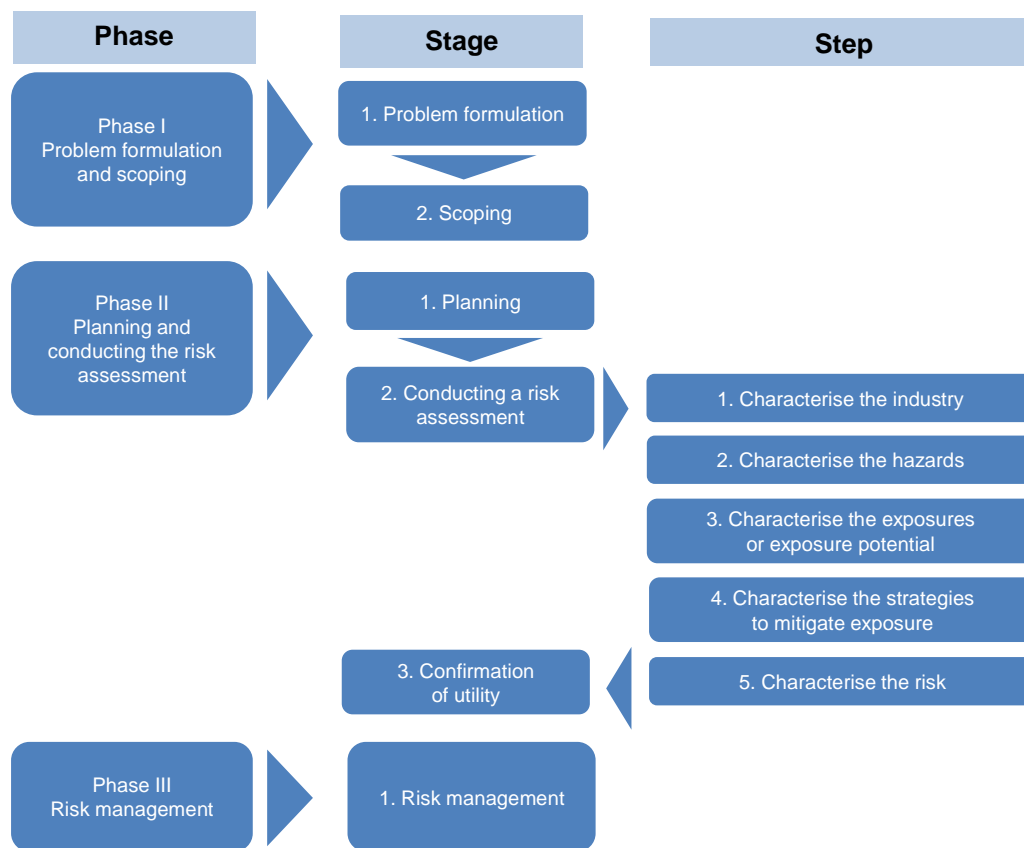
Phase I – Problem formulation and scoping

Problem formulation

Problem formulation should begin by considering the following questions:

1. Who is potentially at risk?
2. What are they at risk from?
3. Will this be a retroactive risk assessment or a proactive risk management strategy?
4. What risk assessment output types are desired?

Figure 5.1. Organisation and flow of this risk management framework



This risk management framework is specific to the use of nanomaterials in tyres. Therefore, this framework answers the first two questions above:

1. Question: Who is potentially at risk?
 - workers who manufacture the nanomaterial of interest
 - workers who mount, repair and/or balance nano-enabled tyres on vehicles
 - workers involved with nano-enabled tyre recycling and/or disposal
 - consumers who mount nano-enabled tyres on vehicles
 - the general population
 - key ecological endpoints.
2. Question: What are they at risk from?
 - Hazards associated with nanomaterials used in tyres.

The remaining two questions (questions 3 and 4) are left to the user of this framework to answer. The user should decide if this framework will be used to conduct a retroactive risk assessment for an existing facility or operation or, alternatively, to develop a proactive risk management strategy.

The user should also decide what risk assessment outputs are desired. For example, are quantitative results desired? If quantitative results are desired, will they be deterministic or probabilistic? Deterministic risk assessments provide a single point estimate of risk at a site of concern, while probabilistic risk assessment methods generate a range of values from probability distribution functions. Alternatively, is a qualitative risk-banding approach desired?

Problem scoping

The proposed risk management framework is specific to the following scope: the life cycle of a nanomaterial of interest used in tyres. For the purposes of this framework, the scope includes:

- manufacture of the nanomaterial being evaluated
- manufacture of tyres containing the nanomaterial
- use of the nano-enabled tyres
- end-of-life of the nano-enabled tyres.

The reader is referred to Chapter 4 for a detailed discussion of the life cycle along with guidance for completing a life-cycle assessment.

Phase II – Planning and conducting the risk assessment

Phase II consists of planning and then conducting the risk assessment. This phase is divided into three stages:

- Stage 1 – Planning for the risk assessment
- Stage 2 – Conducting the risk assessment
- Stage 3 – Confirmation of the utility of the risk assessment.

Although these stages are presented in a linear fashion, risk assessments should allow for refinement and continual improvement. Stage 3 – Confirmation of the utility of the risk assessment – should be performed to evaluate whether the risk assessment results meet the requirements set forth during Phase I – Problem formulation and scoping. Uncertainty associated with the risk assessment results should be characterised, and judgment should be used to determine if the results can be meaningfully interpreted for the purposes of risk management and decision making given the uncertainties. If the risk assessment results do not meet the goals set forth during Phase I, or are not adequate for risk management or decision making, then Phase II, Stage 1 should be revisited to design a new approach for the risk assessment. Additionally, the planning stage should be revisited if new data or techniques become available that will enhance and improve the risk assessment. Allowing feedback loops for continual improvement is particularly important for nanomaterials, since information regarding toxicity, fate and transport, and exposures is limited and significant research to increase the general scientific knowledge base is ongoing.

Phase II, Stage 1 – Planning for the risk assessment

Planning for the risk assessment should begin by answering the following questions.

- What data are needed?
- What data are available?

Data needs

The following information is important when conducting a risk assessment of a nanomaterial:

- characterisation and physical/chemical properties data
- toxicological data
- exposure data and information.

Each of these points is explained further below.

Characterisation and physical/chemical properties data

Because of their unique properties (even compared to their macro-scale counterparts), an adequate set of specific data is required to identify and characterise the nanomaterials. This includes data that characterises the different materials both at the macro- and nano-scale. For example, not all types of silica are equivalent. One may need to specify, as a minimum, the morphology (amorphous or crystalline); production method (precipitation or pyrogenic); particle size distribution; aggregation and agglomeration characteristics (e.g. sizes of primary particles, aggregates and agglomerates); and specific surface area to be able to distinguish between different types of silica. Properties of importance include, but are not necessarily limited to, the following:

- Data to identify the nanomaterial:
 - nanomaterial name
 - CAS number
 - structural formula and molecular structure
 - composition of nanomaterial
 - basic morphology
 - description of surface chemistry
 - method of production.
- Physical and chemical characteristics of the nanomaterial:
 - melting point
 - relative density
 - flammability
 - solubility (in water or other biologically relevant fluids)
 - dispersibility (in water or other biologically relevant fluids)
 - other relevant dispersibility data (e.g. zeta potential, isoelectric point)
 - partition coefficient (n-octanol/water)
 - physical state at standard conditions
 - crystalline phase
 - crystallite size
 - dustiness

- representative transmission electron microscopy (TEM) images
- aggregation and agglomeration potential
- particle size distribution
- specific surface area
- surface chemistry
- catalytic or photocatalytic activity
- pour density
- porosity
- reduction/oxidation potential
- radical formation potential.

Toxicological data

The following types of toxicological data should ideally be collected for the risk assessment:

- pharmacokinetics (absorption, distribution, metabolism, elimination)
- acute toxicity
- repeated dose toxicity
- chronic toxicity
- reproductive toxicity
- developmental toxicity
- genetic toxicity
- dose-response data
- experience with human exposure
- epidemiological data
- environmental fate and transport data
- environmental persistence data
- bioaccumulation data.

Exposure data and information

The following data elements should ideally be collected for each life-cycle stage to characterise exposure for the risk assessment.

- physical form of the nanomaterial
- amount of nanomaterial handled or processed
- description of how the nanomaterial is handled or processed
- duration (time per day) and frequency (occurrences per year) workers or members of the general population are potentially exposed to nanomaterials

- determination of the potential for dust generation during the processes and worker activities
- description of worker activities
- actual exposure measurement data
- identification of potential release sources
- amount of nanomaterial released into the environment (per event or period such as per day or per year, and the frequency of release events such as per year).

Data availability

The planning stage should also include a step to identify and obtain all potentially applicable data for use in the risk assessment (including a literature search). It is recommended that search criteria and results be documented for future reference and refinement of the evaluation. After obtaining the data, planning should also include a data gap analysis to determine what data needs remain. Then, planning should include the development of approaches to satisfy the identified data gaps. Consider the following questions:

- Will testing be performed to satisfy data gaps (e.g. physical or chemical testing, toxicity testing, exposure monitoring)?
- In lieu of data for the nanomaterial being evaluated, is it appropriate to use surrogate data? Are surrogate data available? How will the surrogate data be used? What are the uncertainties associated with use of the surrogate data? For example, will the risk assessment use toxicity or exposure data of the bulk (macro-scale) version of the nanomaterial? Will the risk assessment use toxicity or exposure data of a similar nanomaterial? If surrogate data are used, how will they be evaluated to determine their appropriateness for the nanomaterial of interest?
- In lieu of data for this nanomaterial, is it appropriate to use extrapolation or modelling techniques to characterise hazards or exposures?
- How will the risk assessment results be evaluated to account for uncertainties introduced by the use of surrogate data or extrapolation or modelling techniques?

Phase II, Stage 2 – Conducting the risk assessment

A risk assessment typically follows five key steps:

- Step 1 – Characterise the industry
- Step 2 – Characterise the hazards
- Step 3 – Characterise the exposures or exposure potential
- Step 4 – Characterise the strategies or techniques to mitigate exposure
- Step 5 – Characterise the risk.

Phase II, Stage 2, Step 1 – Characterise the industry

The first step is to characterise the industry within the scope of the risk assessment. The industry characterisation is important to help understand the processes, equipment and worker activities involved in the industry. This information is used to identify

potential sources of exposure and environmental releases as well as work practices, engineering controls and personal protective equipment (PPE) that may mitigate or minimise exposures and releases.

The scope of this effort is the entire life cycle of a nanomaterial used in tyres. Therefore, industry characterisation includes all life-cycle stages. This section begins with a detailed characterisation of the tyre industry, which comprises process descriptions and potential sources of releases and exposures. Since this framework is applicable to any nanomaterial for use in tyres, guidance is presented for the user of this framework to characterise the manufacturing industry of a nanomaterial of interest once selected by the user.

For the purposes of this framework, the tyre industry is defined as the manufacture of tyres, mounting tyres on vehicles, the use of tyres on vehicles and the end-of-life of tyres. Information presented here on the characterisation of the tyre industry, particularly tyre manufacturing, was obtained from multiple interviews with industry stakeholders and a site visit to a US tyre manufacturing plant.

Tyre manufacturing

Tyre manufacturers receive raw materials from suppliers, typically in bulk containers. Raw materials include: elastomers (natural or synthetic rubber); fillers (including silica, carbon black and nanomaterials such as next generation HD-HS silica and nanoclays); plasticisers (e.g. oil); and chemical additives (e.g. vulcanisers, accelerators and antioxidants). Silica and carbon black can be transported via rail car or tank truck. Solid chemical additives can be transported in one-tonne flexible intermediate bulk containers (FIBCs).

Silica and carbon black are typically unloaded into silos prior to blending. Transfer of silica can include pneumatic transfer in pressurised piping. Transfer of carbon black can also include pneumatic transfer, as well as mechanical conveyer systems. From the silos, silica and carbon black are blown through lines into a high-temperature mixer, such as a Banbury mixer. Elastomers are added to the mixer as shredded rubber blocks. Chemical additives (except for vulcanisers and accelerators) are also added to the mixer.

From the high-temperature mixer, the compounded rubber masterbatch is rolled into sheets to cool and then added to a low-temperature mixer for further milling. Here, rubber blocks containing vulcanisers and accelerators are added. The milled, final rubber mix is rolled, flattened, coated with an anti-stick solution, dried and folded for tyre fabrication.

Each ply, or layer, is made and reinforcements (such as textiles and metals) are added. The tyre is then built and cured (vulcanised).

Worker exposure to nanomaterials will depend on the manner in which the nanomaterials are handled. For example, industry stakeholders indicate next generation HD-HS silica would replace currently used silica, essentially as a drop-in replacement using the same process steps. Therefore, exposures associated with handling a solid powder in bulk can be expected. Workers can be exposed to HD-HS silica when connecting and disconnecting transfer lines for unloading the silica from rail cars or tank trucks. If the silica is transported via pressurised, pneumatic lines, then workers could also be exposed to dusts and spills generated from leaks in the transfer lines. Workers can further be exposed to silica dusts in the air that are not captured by a ventilation system.

Other nanomaterial additives may be needed in smaller amounts (and/or for other purposes). Therefore, their processing may be similar to other solid chemical additives currently used in tyres. For example, if nanoclay is to be used at a small loading per tyre, then it may be shipped in one-tonne FIBCs. If the nanoclay is poured directly into the Banbury mixer by a worker, inhalation exposure to dusts can be expected. There is also the potential for inhalation and contact exposure if small manual blending operations are conducted and controls must be carefully evaluated for this work. Worker exposures in these situations could be minimised by using an automated filling system to use the FIBCs to load smaller (such as 25 kg size) plastic bags with the proper quantity of nanoclay as well as each chemical additive. A hopper and mechanical conveyer system could be used to load each bag. The plastic bag can be sealed and then dumped directly into the Banbury mixer without requiring workers to open the bag. In such a system, workers can be exposed to nanoclay dusts generated from the mechanical conveyer at the point in which it dumps the nanoclay into the plastic bag. Local exhaust ventilation can be used to capture generated dusts.

Another potential method for processing smaller quantity nanomaterials that was identified is the lab-scale formulation of nanomaterials into the rubber blocks that are added to the low-temperature mixer. Here, exposures to nanomaterials can be further minimised through the use of laboratory controls such as chemical fume hoods.

Once the nanomaterials are blended with the elastomers, inhalation and dermal exposures are expected to be less likely because the nanomaterials are bound within a polymer matrix. Once the tyre is built and vulcanised, nanomaterials are not expected to migrate from (or diffuse out of) the polymer matrix because of its cross-linked chemical structure.

Nanomaterial additives can be released to the environment from these industrial operations due to the disposal of nanomaterial-containing wastes. These wastes can be generated from cleaning rail cars or tank trucks, pipes/hoses and process vessels; cleaning spills; disposing scrap blended rubber; disposing spent FIBCs; and disposing filter bags and collected blow-down dust from dust collectors. Nanomaterial particulates can also be released to the environment from fugitive dusts generated inside the plant, captured by local or general ventilation, and released to ambient air through a stack due to filter bag or other removal inefficiencies. Accidental spills or releases at tank truck or rail car unloading stations can also be sources of the release of nanomaterials directly into the environment if unloading occurs outdoors.

The site-specific potential for worker exposures and environmental releases from these sources should be considered during the exposure pathway evaluation as discussed in Phase II, Stage 2, Step 3 of this framework. The mitigation strategies to reduce worker exposures and environmental releases should be considered as discussed in Phase II, Stage 2, Step 4.

Mounting tyres on vehicles

Tyres are mounted onto vehicles by workers (at original equipment manufacturers [OEMs] and mechanic shops) and by consumers in do-it-yourself (DIY) applications. Exposures and releases are less likely during these operations as the nanomaterials are bound within a cross-linked polymer matrix.

Use of tyres on vehicles

Tyres are used during the driving of automobiles and trucks. Nanomaterials could potentially be released to the environment from rubber particles wearing off or from blowouts. According to BLIC (2001), car tyres in Europe were observed to lose 10-20% of their weight by wear during use, due to abrasion from friction.

Chapter 4 includes more detailed data on tyre wear, which are reproduced in Table 5.1. These data represent the mass of tread loss per 40 000 km travelled per tyre for each of the reference passenger tyres studied in the life-cycle assessment of Chapter 4. Table 5.1 also summarises the market-weighted average life span for each reference tyre. The tread loss and life-span data can be used together to estimate the mass of tyre lost over its life span. Combined with data on the content of nanomaterials in a tyre, the user can calculate the release of rubber containing nanomaterials.

These mechanisms release vulcanised rubber containing nanomaterials. The subsequent release of nanomaterials from the rubber would depend on the properties of the nanomaterial and the degradation potential of the rubber in the environment.

Table 5.1. **Passenger tyre tread loss and life span for the reference tyres studied in the life-cycle analysis***

Reference passenger tyres from the life-cycle analysis*	Tread loss (kg per 40 000 km traveled)			Market-weighted average tyre life-span (km)		
	United States	Europe	China	United States	Europe	China
Baseline tyres	0.88	1.21	0.75	61 667	38 333	56 000
High dispersion silica-enabled tyres	0.73	1.01	0.62	74 006	46 169	67 446
MMT enabled tyres	0.86	1.18	0.72	62 906	39 483	57 977

Note: * See Chapter 4.

End-of-life of tyres

A tyre at its end-of-life is referred to as an end-of-life tyre (ELT). ELTs are recovered for reuse, material or energy recovery, or disposal. Material recovery includes using whole or shredded tyres in a variety of civil engineering projects such as embankments, backfill for walls, road insulation, field drains, erosion control/rainwater runoff barriers, wetlands and marsh establishment, crash barriers and jetty bumpers. ELTs can also be converted into ground or crumb rubber that can then be used for rubber-modified asphalt (resulting in reduced traffic noise), running tracks, sports fields, ground cover under playgrounds, molded rubber products and mulch in landscape applications. Ground rubber is produced either by ambient grinding or cryogenic (freeze) grinding, the latter producing finer particles by using liquid nitrogen to cool the tyres before processing (WBCSD, 2008). Energy recovery of tyres is the use of tyre-derived fuel (TDF) in applications such as cement kilns, thermal power stations, pulp and paper mills, steel mills and industrial boilers (WBCSD, 2008).

The percentage of tyres sent to each disposition varies among the major global tyre markets. Table 5.2 summarises the disposition of tyres in the major global markets: China, Europe and the United States (also see discussion in Chapter 4). The end-of-life evaluation includes landfilling and incineration, material recycling, energy recovery, re-treading, and reuse and export.

Potential exposures and releases vary depending on the disposition method. Re-treading, reuse and material recycling scenarios can lead to potential exposures to workers who handle the tyres. Releases can result from scrap rubber generated from the re-treading and material recycling process. Workers who handle tyres in transit to landfilling, incineration and energy recovery scenarios are less likely to be exposed because the nanomaterials are bound within a cross-linked polymer matrix. However, releases of nanomaterials are anticipated during these scenarios. Releases from landfilled tyres could result from the rubber, depending on the properties of the nanomaterial that may allow migration over time, and the degradation potential of the rubber itself in the landfill. Releases of nanomaterials are also anticipated from incineration and energy recovery. The incineration process completely combusts the rubber, potentially releasing nanomaterials even from cross-linked rubber. Releases of the nanomaterial will depend on the chemistry of the nanomaterial in the combustion chamber and the air pollution control technologies used by the incinerator or energy recovery system.

Table 5.2. **Disposition of tyres at their end-of-life for major global markets**

Region	Total volume		% of tyres for each end-of-life disposition method					Source
	Millions of tonnes	Millions of end-of-life tyres	Landfilling	Material recycling	Energy recovery	Re-treading	Reuse and export	
United States	4.60	184	15%	34%	40%	7.2%	3.0%	US Environmental Protection Agency MSW (2012)
Europe	3.30	132	4.0%	40%	38%	8.0%	10%	European Tyre and Rubber Manufacturers Association (2012)
China	5.00	200	83%	10%	0%	6.8%	0%	WBCSD (2012); Yang (2010)

This framework is applicable to any nanomaterial for use in tyres. Therefore, a characterisation of the nanomaterial manufacturing industry is not presented herein since the processes can vary greatly from one nanomaterial to another. Instead, the user of this framework should characterise the manufacture of the nanomaterial of interest once one has been selected for risk assessment and management. The following data elements should be included:

- process description
- identification of sources of occupational exposures to nanomaterials (note: exposure pathways are discussed in more detail under Phase II, Stage 2, Step 3)
- identification of sources of nanomaterial releases to the environment
- practices and technologies used to mitigate exposures and releases.

Phase II, Stage 2, Step 2 – Characterise the hazards

During the planning stage (Phase II, Stage 1), the user of this framework should have determined if toxicological data will be collected from the literature, obtained through toxicity testing or both. Whether reviewing toxicology studies in the literature or planning and conducting toxicity testing, the user should pay attention to key issues that affect the applicability and characterisation of test results:

- sample preparation

- dosing
- physical/chemical characterisation
- nanomaterial identification (CAS#)
- composition of nanomaterial being tested
- basic morphology
- method of production
- epidemiological data, if available.

The OECD's "Guidance on sample preparation and dosimetry for the safety testing of manufactured nanomaterials" (OECD, 2012b) can be referenced for preliminary guidance on sample preparation and dosimetry during toxicity testing. An important aspect of dosimetry to which the user should pay attention is dose metrics. Toxicity tests of non-nanomaterials use mass-based metrics to describe dose-response relationships. However, mass-based metrics alone may not be sufficient for nanomaterials – additional metrics, such as number of particles or particle surface area, may need to be considered. Another important consideration of toxicity testing is the use of models developed for non-nanomaterials. For example, models can be used for interspecies extrapolation of toxic effects (e.g. extrapolating the toxic effects on rats to humans) and for predicting bioaccumulation from partition coefficients. Careful consideration should be given prior to applying such models to nanomaterials, and their use should be accompanied with adequate discussion of the limitations or uncertainties of the results.

Please note that guidance may change as additional research reveals new findings and as experts reach consensus on methods and protocols. For example, new occupational exposure limits may be determined and published as toxicological properties of nanomaterials become better understood.

The following subsection of this framework provides a summary of recommendations utilising the hazard banding approach as discussed in ISO (2012). This approach can use either quantitative toxicological data or qualitative health hazard indicators to assign the hazard band ranking.

Human health

The planning stage of the risk assessment (Phase II, Stage 1) identifies the categories of toxicological data needed for the risk assessment. These toxicological data can be used to describe the following human health hazard indicators as identified in ISO (2012):

- acute toxicity (Acute Tox.)
- skin irritation/corrosion (Skin Irrit./Skin Corr.)
- serious eye damage/eye irritation (Eye Dam./Eye Irrit.)
- respiratory or skin sensitisation (Resp. or Skin Sens.)
- mutations in germ cells (Muta.)
- cancer (Carc.)
- reproductive toxicity (Repr.)
- experience with human exposure

- epidemiological data
- Systemic Target Organ Toxicity – Single Exposure (STOT-SE)
- Systemic Target Organ Toxicity – Repeated Exposure (STOT-RE)
- aspiration hazard (Asp. Tox.).

The toxicological data and hazard indicators can be used to assign a human health hazard category to the nanomaterial of interest. Table 5.3 displays the human health hazard category allocation criteria for use in the control banding approach.

Ecotoxicity

Currently, ISO (2012) does not incorporate ecotoxicity into the control banding approach. The control banding approach is only meant for addressing human health concerns in occupational settings. However, some of the human toxicological data elements are also applicable for ecotoxicity (e.g. acute (LD50) and chronic toxicity data for terrestrial organisms, LC50 data for aquatic organisms). Ecotoxicity studies typically require fate, transport and bioaccumulation data to provide a complete picture of ecological effects. Toxic effects on single species should be evaluated in the context of entire community and ecosystem effects. For example, if a nanomaterial is toxic to a prey terrestrial organism and causes a decline in its population, this effect can cause a decline in a predator population by reducing the predators' food source.

The following list provides key environmental fate, transport and bioaccumulation topics to be considered when evaluating ecotoxicity of nanomaterials. This list is not comprehensive and is not meant to replace toxicological data. Rather, these data elements should be evaluated along with ecotoxicological data:

- environmental transport data (e.g. how the nanomaterial partitions between water and sediment media or between groundwater and soil media)
- environmental fate data, which comprises:
 - transformations (e.g. surface chemistry changes; aggregation/agglomeration or disaggregation)
 - biodegradation
 - abiotic degradation (e.g. hydrolysis, reduction, oxidation)
 - bioaccumulation (i.e. the transfer of nanomaterial between trophic levels in the food chain).

Phase II, Stage 2, Step 3 – Characterise the exposures or exposure potential

Given the level of uncertainty in work-related potential health risks from nanomaterials, control banding can be particularly useful for the risk assessment and management of nanomaterials for occupational settings. It can be used for risk control management in both a proactive and retroactive manner. In a proactive manner, potential risks are evaluated without the consideration of control measures. A risk management plan can then be implemented and control measures can be selected. In a retroactive manner, the risk of a current process is assessed with consideration of existing control measures. The risk assessment can be used to evaluate the adequacy of the existing control measures.

Table 5.3. Health hazard category allocation

Toxicological result or health hazard indicator	Category A	Category B	Category C	Category D	Category E
OEL dust (mg/m ³) (8-hr TWA)	1-10	0.1-1	0.01-0.1	< 0.01	--
Acute toxicity	Low	Acute tox 4	Acute tox 3	Acute tox 1-2	--
LD50 oral route (mg/kg)	> 2 000	300-2 000	50-300	< 50	--
LD50 dermal route (mg/kg)	> 2 000	1 000-2 000	200-1 000	< 200	--
LC50 inhalation 4H (mg/L) aerosols/particles	> 5	1-5	0.5-1	< 0.5	--
Severity of acute (life-threatening) effects	--	STOT SE 2-3 Asp. Tox 1	STOT SE 1	--	--
Adverse effects per oral route (mg/kg) (single exposure)	--	Adverse effects seen ≤ 2 000	Adverse effects seen ≤ 300	--	--
Adverse effects per dermal route (mg/kg) (single exposure)	--	Adverse effects seen ≤ 2 000	Adverse effects seen ≤ 1 000	--	--
Sensitisation	Negative	Slight cutaneous allergic reactions	Moderate/strong cutaneous allergic reactions Skin sens. 1	--	Prevalent moderate to strong respiratory allergic reactions Resp. Sens. 1
Mutagenicity/genotoxicity	Negative	Negative	Negative	Negative	Mutagenic in most relevant <i>in vivo</i> and <i>in vitro</i> assays Muta 2 Muta 1A – 1B
Irritant/corrosiveness	None to irritant Eye Irrit. 2; Skin Irrit. 2 EUH 066	--	Severe irritant to skin/eyes Irritant to respiratory tract STOT SE 3 Eye Dam. 1 Corrosive Skin Cor. 1A – 1B	--	--
Carcinogenicity	Negative	Negative	Some evidence in animals Carc. 2	--	Confirmed in animals or humans Carc. 1A – 1B
Developmental/reproductive toxicity	Negative	Negative	Negative	Reprotoxic defects in animals and/or suspected or proven in humans Repr. 1A, 1B, 2	--

Table 5.3. **Health hazard category allocation** (*cont.*)

Toxicological result or health hazard indicator	Category A	Category B	Category C	Category D	Category E
Likelihood of chronic effects (e.g. systemic)	Unlikely	Unlikely	Possible STOT RE 2	Probable STOT RE 2	--
Adverse effects per oral route (mg/kg-day) (90-day chronic study)	--	--	Adverse effects seen \leq 100	Adverse effects seen \leq 10	--
Adverse effects per dermal route (mg/kg-day) (90-day chronic study)	--	--	Adverse effects seen \leq 200	Adverse effects seen \leq 20	--
IH/occupational health experience	No evidence of adverse health effects	Low evidence of adverse health effects	Probably evidence of adverse health effects	High evidence of adverse health effects	High evidence of severe adverse health effects

Source: International Organization for Standardization (ISO) (2012), *Nanotechnologies – Guidelines for Occupational Risk Management Applied to Engineered Nanomaterials – Part 2: The Use of the Control Banding Approach in Occupational Risk Management*, ISO TC 229/SC N.

If a retroactive occupational risk assessment is being conducted, the existing exposures should be characterised. The exposure characterisation should include information on the efficacy of any existing exposure mitigation controls. However, the use of personal protection equipment (PPE) should not be included – exposures should be assessed as if no PPE is used. The use of PPE can then be taken into account after characterising the risk as part of an evaluation of an existing risk management strategy.

If a proactive occupational risk management strategy is being developed, the exposure potential should be characterised. As described above, the exposure potential should not account for any exposure mitigation controls, such as ventilation, enclosures or containment. However, the exposure potential should account for the physical form and process technologies that will be used. The results of the risk assessment will be used to help select appropriate control measures as part of the risk management strategy. PPE requirements should be determined after the consideration of work practices and control measures.

For non-occupational settings and receptor populations, control banding cannot be used. Here, exposure potential should be characterised considering existing controls (such as incinerator air pollution controls) and the fate and transport of nanomaterials along their exposure pathway.

Exposures or exposure potential should be characterised for complete exposure pathways. The United States Agency for Toxic Substances & Disease Registry (ATSDR) defines an exposure pathway as:

The route a substance takes from its source (where it began) to its end point (where it ends), and how people can come into contact with (or get exposed to) it. An exposure pathway has five parts: a source of contamination (such as an abandoned business); an environmental media and transport mechanism (such as movement through groundwater); a point of exposure (such as a private well); a route of exposure (eating, drinking, breathing or touching), and a receptor population (people potentially or actually exposed). When all five parts are present, the exposure pathway is termed a completed exposure pathway. (ATSDR, 2009)

Exposure pathways should be characterised for each receptor population, as defined during problem formulation, for each life-cycle stage:

- workers who manufacture the nanomaterial of interest
- workers who mount, repair and/or balance nano-enabled tyres on vehicles
- workers involved with nano-enabled tyre recycling and/or disposal
- consumers who mount nano-enabled tyres on vehicles
- the general population
- key ecological endpoints.

An evaluation can be made to determine which receptor populations are appropriate for each life-cycle stage during exposure characterisation. For example, exposure pathways for the general population and key ecological endpoints should be evaluated for all life-cycle stages. However, exposure pathways for the OEM and shop workers and the do-it-yourself (DIY) consumers who mount tyres need not be evaluated during nanomaterial and tyre manufacturing.

This framework presents guidance below on determining the exposure potential of nanomaterials without the use of controls (i.e. for a proactive approach) during the industrial operations: nanomaterial and tyre manufacturing. This framework uses the exposure banding approach (as part of the control banding approach) as described in ISO (2012). The exposure banding approach assigns an exposure band (EB) ranking based on a qualitative assessment of exposure potential without the consideration of controls.

If performing a retroactive risk assessment, the exposure can be characterised in the same manner as for a proactive risk assessment. An exposure band ranking can be assigned based on the exposure potential without consideration of the exposure mitigation controls in place. The risk assessment can proceed similarly as for a proactive risk assessment. Then, the control banding approach can be used to determine the recommended control strategy, which can be compared to the existing controls in place to evaluate the current risk management strategies. The use of the control banding approach is described below under Phase II, Stage 2, Step 5 – Characterise the Risk.

Note that the control banding approach is currently only applicable for assessing exposure potential for workers who directly handle the nanomaterials or nano-enabled tyres in occupational settings. The control banding approach is not applicable for assessing exposure potential for consumers, the general population or ecological endpoints. However, future editions or future versions of ISO (2012) may expand the exposure banding approach to qualitatively assess exposures during other (e.g. consumer) scenarios. Because of this limitation in ISO (2012), this framework presents additional guidance on identifying the five parts of an exposure pathway for each life-cycle stage.

With regard to quantitative exposure data, actual exposure measurements, when feasible, typically represent the best information for the selection of the appropriate exposure band. Therefore, their use should be encouraged. However, it should be understood that exposure measurement data can be misinterpreted, not used correctly or even be unnecessary in certain circumstances. Therefore, when measurement data are used, they must be carefully applied and scrutinised. When both personal sampling and area measurements are available, the preference should be given to personal exposure measurements, if appropriate. The results should be taken into account when determining the corresponding exposure band. ISO/TS 12901-1 provides information on available measurement equipment, possible measurement strategies and results interpretations (ISO, 2012).

Nanomaterial manufacturing: Exposure potential

This section of the framework presents guidance on identifying exposure pathways and exposure band rankings of nanomaterials during their manufacture.

Since this framework is intended to provide guidance for any nanomaterial used as an additive in tyres, the exact exposure pathways are not described herein. Rather, this framework provides guidance on identifying exposure pathways once the nanomaterial is chosen and its method of manufacture determined. Table 5.4 summarises some guidance and key points to consider when identifying exposure pathways during nanomaterial manufacturing.

Exposure band rankings for worker exposures should be assigned for nanomaterial manufacturing based on the production technology type used. ISO (2012) assigns the exposure bands for the listed production technology types in Table 5.5.

Table 5.4. **Guidance for identifying complete exposure pathways of nanomaterials during their manufacture**

Potential sources from common manufacturing operations	Expected environmental media and transport mechanism	Point of exposure	Route of exposure	Receptor population
Openings in process vessels (e.g. sample ports, leaks)	Indoor air and transport of aerosolised solid particles or mists of liquid dispersions	Workers' breathing zones	Inhalation	Workers
Loading of nanomaterial into containers	Indoor air and transport of aerosolised solid particles or mists of liquid dispersions	Workers' breathing zones	Inhalation	Workers
Loading of nanomaterial into containers	Contact of solids or liquid dispersions against skin	Workers' skin	Dermal	Workers
Cleaning up spilled nanomaterials	Indoor air and transport of aerosolised solid particles or mists of liquid dispersions	Workers' breathing zones	Inhalation	Workers
Cleaning up spilled nanomaterials	Contact of solids or liquid dispersions against skin	Workers' skin	Dermal	Workers
Spraying of nanomaterials	Indoor air and transport of aerosolised solid particles or mists of liquid dispersions	Workers' breathing zones	Inhalation	Workers
Spraying of nanomaterials	Contact of solids or liquid dispersions against skin	Workers' skin	Dermal	Workers
Blending small amounts of nanomaterials	Indoor air and transport of aerosolised solid particles or mists of liquid dispersions	Workers' breathing zones	Inhalation	Workers
Blending small amounts of nanomaterials	Contact of solids or liquid dispersions against skin	Workers' skin	Dermal	Workers
Packaging activities	Indoor air and transport of aerosolised solid particles or mists of liquid dispersions	Workers' breathing zones	Inhalation	Workers
Packaging activities	Contact of solids or liquid dispersions against skin	Workers' skin	Dermal	Workers
Maintenance activities	Indoor air and transport of aerosolised solid particles or mists of liquid dispersions	Workers' breathing zones	Inhalation	Workers
Maintenance activities	Contact of solids or liquid dispersions against skin	Workers' skin	Dermal	Workers
Dumping of nanomaterials	Indoor air and transport of aerosolised solid particles or mists of liquid dispersions	Workers' breathing zones	Inhalation	Workers
Dumping of nanomaterials	Contact of solids or liquid dispersions against skin	Workers' skin	Dermal	Workers
Dusts generated from solid powder nanomaterials	Collection via exhaust ventilation, passing through air pollution control device and emission from stack to air	Ambient air	Inhalation	General population
Collection of process aqueous waste, including rinsing process vessels with wash water, and their disposal down the drain or to on-site wastewater treatment	Nanomaterials passing through treatment system to surface water and nanomaterials subsequently passing through drinking water plant	Drinking water	Ingestion	General population
Collection of process solid or hazardous waste, including rinsing process vessels with solvent or wash water treated as solid or hazardous waste, and their disposal via incineration	Nanomaterials passing through incinerator and air pollution control device to ambient air	Ambient air	Inhalation	General population
Collection of process aqueous waste, including rinsing process vessels with wash water, and their disposal down the drain or to on-site wastewater treatment	Nanomaterials passing through treatment system to surface water, with nanomaterials dispersing in surface water or partitioning to sediment	Surface water or sediment	--	Aquatic ecological endpoints (e.g. pelagic species, benthic species)

Table 5.5. **Exposure band rankings for nanomaterial production technology types**

Production technology type		Exposure band
– Gas-phase synthesis – Flame pyrolysis – Laser ablation – Electrospraying		EB4
Mechanical reduction	Grinding	EB4
	Cutting	EB2
– Laser ablation in liquid – Sintering		EB3
Chemical vapour condensation		EB4
Wet chemistry	Introduced into solution	EB2
	Produced within solution	EB1

Source: International Organization for Standardization (ISO) (2012), *Nanotechnologies – Guidelines for Occupational Risk Management Applied to Engineered Nanomaterials – Part 2: The Use of the Control Banding Approach in Occupational Risk Management*, ISO TC 229/SC N.

Tyre manufacturing: Exposure potential

This section of the framework presents guidance on identifying exposure pathways and exposure band rankings of nanomaterials during their use in tyre manufacturing.

The exposure pathways of nanomaterials during their incorporation into tyres depend on the manner in which the nanomaterials are handled. Some nanomaterial handling procedures may be similar to procedures that are currently used for tyres that do not use nanomaterials. In other cases, nanomaterials may be incorporated into tyres using new procedures. Table 5.6 presents guidance for identifying complete exposure pathways of nanomaterials during their incorporation into tyres. This guidance is not meant to cover all possible methods that may be used to incorporate nanomaterials into tyres, since some methods may not yet be developed or implemented. Therefore, both industrial hygiene and environmental stewardship expertise should be sought when evaluating current or potential methods for incorporating nanomaterials into tyres.

This framework discusses guidance below on assigning exposure band rankings for nanomaterials used as additives in tyres following the exposure banding approach discussed in ISO (2012). This approach is only applicable for the workers within the tyre manufacturing plant. It is not applicable for other receptor populations. The guidance is presented for three different physical forms of nanomaterials. The appropriate ranking must be determined on a case-by-case basis for the applicable situation:

1. nanomaterials in solid powder form
2. nanomaterials in suspension in a liquid
3. nanomaterials dispersed in solid materials (solid matrix).

Table 5.7 summarises exposure band rankings for the nanomaterial physical forms and associated processes that could be encountered during the manufacture of tyres. Table 5.7 does not encompass all exposure band rankings of nanomaterials during processing and use – it does not reproduce the processes discussed in ISO (2012) that are unlikely to be encountered during tyre manufacturing. ISO (2012) should be consulted for a comprehensive discussion of all possible exposure band rankings. The subsequent subsections below discuss the physical forms and processes identified in Table 5.7.

Table 5.6. **Guidance for identifying complete exposure pathways of nanomaterials during their incorporation into tyres**

Potential sources from common processing operations	Expected environmental media and transport mechanism	Point of exposure	Route of exposure	Receptor population
Connecting and disconnecting transfer lines to rail cars and tank trucks	Indoor air and transport of aerosolised solid particles	Workers' breathing zones	Inhalation	Workers
Cleaning up spilled or leaked nanomaterials	Indoor air and transport of aerosolised solid particles	Workers' breathing zones	Inhalation	Workers
Cleaning up spilled or leaked nanomaterials	Contact of solids against skin	Workers' skin	Dermal	Workers
Dumping of nanomaterials into mixer	Indoor air and transport of aerosolised solid particles	Workers' breathing zones	Inhalation	Workers
Dumping of nanomaterials into mixer	Contact of solids against skin	Workers' skin	Dermal	Workers
Automatic charging of nanomaterials into small bags	Indoor air and transport of aerosolised solid particles	Workers' breathing zones	Inhalation	Workers
Blending small amounts of nanomaterials into rubber blocks	Indoor air and transport of aerosolised solid particles	Workers' breathing zones	Inhalation	Workers
Blending small amounts of nanomaterials into rubber blocks	Contact of solids against skin	Workers' skin	Dermal	Workers
Dusts generated from solid powder nanomaterials	Collection via exhaust ventilation, passing through air pollution control device and emission from stack to air	Ambient air	Inhalation	General population
Using water to rinse spilled solid nanomaterials from the floor, and disposing the rinse water down the drain or to on-site wastewater treatment	Nanomaterials passing through treatment system to surface water, and nanomaterials subsequently passing through drinking water plant	Drinking water	Ingestion	General population
Using water to rinse spilled solid nanomaterials from the floor, and disposing the rinse water down the drain or to on-site wastewater treatment	Nanomaterials passing through treatment system to surface water, with nanomaterials dispersing in surface water or partitioning to sediment	Surface water or sediment	x	Aquatic ecological endpoints (e.g. pelagic species, benthic species)
Collection of process solid or hazardous waste (including collected solid nanomaterials, scrap blended rubber and captured dust), and their disposal via incineration	Nanomaterials passing through incinerator and air pollution control device to ambient air	Ambient air	Inhalation	General population
Collection of process solid or hazardous waste (including collected solid nanomaterials, scrap blended rubber and captured dust), and their disposal via landfill	Degradation of rubber and leaching of nanomaterials through landfill liner and/or leachate collection system into soil and groundwater	Soil, groundwater	x	Terrestrial ecological endpoints (e.g. plants)
Nanomaterials in groundwater from above pathway	Nanomaterials passing through drinking water plant or getting into drinking water wells	Drinking water	Ingestion	General population

Note: x: not applicable.

If the nanomaterial is shipped to the tyre manufacturer in a solid powder form, then the exposure potential should be considered from the point of arrival at the site through blending operations. Once a nanomaterial is blended into molten elastomers (a viscous liquid), exposure banding should follow the guidance for nanomaterials in suspension in a liquid, presented below.

Table 5.7. **Exposure band rankings for processing nanomaterials during the manufacture of tyres**

Physical form	Process type	Exposure band
Solid powder (not deliberately aerosolised; > 1 kg)	High potential of dust generation	EB4
	Low potential of dust generation	EB3
Suspension in a liquid (not deliberately aerosolised; > 1 g of nanomaterial and > 1 L of liquid)	High potential of aerosol generation	EB3
	Low potential of aerosol generation	EB2
Dispersed in solid materials – unbound or weakly bound	High energy process	EB4
	Low energy process	EB3
Dispersed in solid materials – strongly bound	High energy process	EB2
	Low energy process	EB1

Source: International Organization for Standardization (ISO) (2012), *Nanotechnologies – Guidelines for Occupational Risk Management Applied to Engineered Nanomaterials – Part 2: The Use of the Control Banding Approach in Occupational Risk Management*, ISO TC 229/SC N.

According to the control banding approach (ISO, 2012), general guidance is such that the deliberate aerosolisation or spraying of powdered nanomaterials should be assigned an exposure potential of EB4. All other handling of solid powder nanomaterials is assigned an exposure band ranking depending on the amount of nanomaterial handled and whether there is a high or low potential for dust generation.

For tyre manufacturing, deliberate aerosolisation or spraying of the nanomaterials is not expected. Further, greater than 1 kg of nanomaterial per batch is likely to be handled. Therefore, according to the control banding approach, the exposure band ranking should be EB3 for a low potential of dust generation or EB4 for a high potential of dust generation. The determination of the level of potential dust generation should be made on a process-specific basis.

If the nanomaterial is shipped to the tyre manufacturer in a liquid suspension, then the exposure potential should be considered from the point of arrival at the site up until the point of curing (vulcanisation). Alternatively, if a nanomaterial is shipped to the tyre manufacturer as a solid powder (as described above), then exposure potential for nanomaterials in suspension in a liquid should be considered from the point of blending the nanomaterial with the elastomers up until the point of vulcanisation. Once the tyre is cured, the exposure banding should follow guidance for nanomaterials dispersed in solid materials, presented below.

According to the control banding approach (ISO, 2012), the deliberate aerosolisation or spraying of the liquid suspension should be assigned an exposure potential of EB4. All other handling of the liquid suspension is assigned an exposure band ranking depending on the amount of nanomaterial handled and whether there is a high or low potential for aerosol generation.

For tyre manufacturing, deliberate aerosolisation or spraying of the liquid suspension is not expected. Further, it is expected that greater than 1 gram of nanomaterial (or greater than 1 L of the liquid suspension) will be handled per batch during the manufacture of tyres. Therefore, according to the control banding approach, the exposure band ranking should be EB3 for a high potential of aerosol generation or EB2 for a low potential of aerosol generation. The determination of the level of potential aerosol generation should be made on a process-specific basis.

After the tyre is built, the elastomers are then cured (vulcanised). Once the tyre is vulcanised, the nanomaterials can be assessed as nanomaterials dispersed in solid materials (solid matrix).

According to the control banding approach (ISO, 2012), the exposure band ranking of a nanomaterial dispersed in solid materials depends on whether the nanomaterial is weakly bound or unbound to the solid matrix, or strongly bound to the solid matrix. Additional consideration is given and assigned depending on the level of mechanical or thermal energy associated with the processes involving the solid materials. For unbound or weakly bound nanomaterials, high energy processes or activities are assigned an exposure band ranking of EB4. Low energy processes or activities are assigned an exposure band ranking of EB3. For strongly bound nanomaterials, high energy processes or activities are assigned an exposure band ranking of EB2, while low energy processes or activities are assigned an exposure band ranking of EB1. The definitions of “high energy” and “low energy” processes are qualitative terms that are not defined in ISO (2012) and are instead left to the discretion of the user.

For tyre manufacturing, it is anticipated that processes or activities involving the vulcanised tyre can be considered low energy. However, the determination of how the nanomaterial is bound within the tyre should be made on a nanomaterial-specific basis. For example, silica, in the presence of silanes, becomes chemically bonded to emulsion-polymerised styrene-butadiene rubber (SBR) during blending. Nanomaterials chemically bonded to the rubber can be considered strongly bound. Note that chemical bonding alone should not be the sole consideration for determining whether there is a strongly bound situation. Non-chemically bonded nanomaterials can also be considered strongly bound based on the tyre’s cross-linking and the nanomaterial’s properties within the vulcanised tyre.

Worker and consumer mounting of tyres on vehicles

Tyres are mounted on vehicles by workers (both in the OEM and commercial aftermarket shops) and by consumers in DIY applications.

During the mounting of tyres, workers and consumers handle vulcanised tyres containing nanomaterials. The associated exposure pathways are expected to be limited to the dermal contact with nanomaterial-containing (nano-enabled) tyres by these workers and consumers.

As described under tyre manufacturing for vulcanised tyres, the bounding of nanomaterials in the tyres and the level of energy associated with processes and activities of the tyres are used to determine the exposure band ranking. The mounting of tyres on vehicles is a low energy process or activity. Therefore, following ISO (2012) for nanomaterials dispersed in solid materials, the exposure band ranking for tyre mounting should be considered EB3 for unbound or weakly bound nanomaterials or EB1 for strongly bound nanomaterials.

Use of tyres: Exposure potential

Since the use of tyres is a non-occupational setting, the exposure band ranking approach is not appropriate for this life-cycle stage. Because the ISO (2012) exposure band ranking does not apply, this subsection discusses guidance for the evaluation of the general population and ecological endpoint exposure pathways.

Nanomaterials can be released to the environment from rubber particles wearing off or from blowouts. These mechanisms release vulcanised rubber that contains nanomaterials. The release of nanomaterials from the rubber depends on the properties of the nanomaterial and the degradation potential of the rubber in the environment. Table 5.8 presents guidance for identifying exposure pathways of nanomaterials during the use of tyres.

Table 5.8. **Guidance for identifying exposure pathways of nanomaterials during the use of tyres**

Potential sources from tyre blowouts or worn-off particles	Expected environmental media and transport mechanism	Point of exposure	Route of exposure	Receptor population
Vulcanised rubber particles or pieces laying on the ground	Degradation of rubber and leaching of nanomaterials onto soil or into groundwater or captured in stormwater runoff to surface water and sediments	Soil, groundwater, surface water or sediment	–	– Terrestrial ecological endpoints (e.g. plants) – Aquatic ecological endpoints (e.g. pelagic species, benthic species)
Nanomaterials in groundwater or surface water from above pathway	Nanomaterials passing through drinking water plant or getting into drinking water wells	Drinking water	Ingestion	General population

End-of-life of tyres: Exposure potential

At their end-of-life, tyres are recovered for reuse, burned for energy recovery or disposed. The percentage of tyres sent to each disposition for each major global tyre market is summarised in Table 5.2.

To determine exposure pathways of nanomaterials associated with the end-of-life of tyres, each final disposition must be considered. Table 5.9 presents guidance on identifying complete exposure pathways for the major disposition of tyres: re-treading, material recovery, disposal and incineration (including energy recovery).

Key concepts to consider in analysing the exposure pathways of nanomaterials from tyres that are landfilled or shredded with the resulting product used as playground surfacing include, but are not limited to, the following:

- degradation (through biological or chemical mechanisms) of the rubber in the landfill or playground environment
- leaching of nanomaterials from rubber into the environment
- leaching of nanomaterials through soil or through landfill liners or leachate recovery systems.

Key concepts to consider in analysing the exposure pathways of nanomaterials from an incinerator or energy recovery system include, but are not limited to, the following:

- oxidation or other reactions that occur in the combustion chamber (e.g. a carbon-based nanomaterial that is fully or partially oxidised; a fully oxidised metal nanomaterial that cannot further oxidise)
- breakdown of larger, nanostructured, non-oxidisable nanomaterials into smaller particles
- transport of nanomaterials, or nanomaterial combustion by-products, through an air pollution control device.

Table 5.9. Guidance for identifying complete exposure pathways of nanomaterials during the end-of-life of tyres

Disposition method	Potential sources from common disposition methods	Expected environmental media and transport mechanism	Point of exposure	Route of exposure	Receptor population
Disposal and re-treading	Re-treading of tyres	Dust formation of rubber during re-treading	Workers' breathing zones	Inhalation	Workers
	Landfilling of disposed tyres or scrap generated during tyre re-treading	Degradation of rubber and leaching of nanomaterials through landfill liner and/or leachate collection system into soil and groundwater	Soil, groundwater	x	Terrestrial ecological endpoints (e.g. plants)
	Nanomaterials in groundwater from above pathway	Nanomaterials passing through drinking water plant or getting into drinking water wells	Drinking water	Ingestion	General population
Material recovery (e.g. shredded tyres used as playground surfacing)	Vulcanised rubber particles or pieces laying on the ground	Degradation of rubber and leaching of nanomaterials onto soil or into groundwater or captured in stormwater runoff to surface water and sediments	Soil, groundwater, surface water or sediment	x	– Terrestrial ecological endpoints (e.g. plants) – Aquatic ecological endpoints (e.g. pelagic species, benthic species)
	Nanomaterials in groundwater or surface water from above pathway	Nanomaterials passing through drinking water plant or getting into drinking water wells	Drinking water	Ingestion	General population
	Vulcanised rubber particles or pieces laying on the ground	Children eating small pieces of rubber	Oral	Ingestion	General population (children)
Incineration (including energy recovery)	Nanomaterials not or only partially oxidised in combustion chamber	Nanomaterials passing through air pollution control device to ambient air	Ambient air	Inhalation	General population
	Nanomaterials in ambient air from above pathway	Nanomaterials condensing or depositing into surface water, and subsequently passing through drinking water plant	Drinking water	Ingestion	General population
	Nanomaterials in ambient air from above pathway	Nanomaterials condensing or depositing onto soil and surface water	Soil, surface water or sediment	x	– Terrestrial ecological endpoints (e.g. plants) – Aquatic ecological endpoints (e.g. pelagic species, benthic species)
	Nanomaterials not or only partially oxidised in combustion chamber	Nanomaterials captured in wet scrubber, scrubber wash down sent to wastewater treatment, and nanomaterials subsequently passing through treatment system to surface water, with nanomaterials dispersing in surface water or partitioning to sediment	Surface water or sediment	x	Aquatic ecological endpoints (e.g. pelagic species, benthic species)
	Nanomaterials in surface water from above pathway	Nanomaterials passing through drinking water plant	Drinking water	Ingestion	General population

Table 5.9. **Guidance for identifying complete exposure pathways of nanomaterials during the end-of-life of tyres** (*cont.*)

Disposition method	Potential sources from common disposition methods	Expected environmental media and transport mechanism	Point of exposure	Route of exposure	Receptor population
Incineration (including energy recovery) (<i>cont.</i>)	Nanomaterials not or only partially oxidised in combustion chamber	Nanomaterials captured by dry system (filter bag, cyclone, electrostatic precipitator), and dust/ash sent to landfill, and subsequent leaching of nanomaterials through landfill liner and/or leachate collection system into soil and groundwater	Soil, groundwater	x	Terrestrial ecological endpoints (e.g. plants)
	Nanomaterials in groundwater from above pathway	Nanomaterials passing through drinking water plant or getting into drinking water wells	Drinking water	Ingestion	General population

Note: x: not applicable.

As described under tyre manufacturing for vulcanised tyres, the bounding of nanomaterials in the tyres and the level of energy associated with processes and activities of the tyres are used to determine the exposure band ranking. The re-treading and shredding of tyres is anticipated to be a low energy process or activity. Therefore, following ISO (2012) for nanomaterials dispersed in solid materials, the exposure band ranking for tyre re-treading and shredding should be considered EB3 for unbound or weakly bound nanomaterials or EB1 for strongly bound nanomaterials. However, unlike previous discussions, the potential for dust generation during tyre re-treading and shredding exists and should be evaluated. The associated potential health hazards, both for general dusts and dusts containing nanomaterials, should also be evaluated.

Phase II, Stage 2, Step 4 – Characterise the strategies or techniques to mitigate exposure

Exposure control measures that are, or can be, implemented in the workplace should be identified. They can lower exposures by reducing emission (the release of nanomaterials from a source), transmission (the transport of nanomaterials from an emission source to an endpoint) and immission (the introduction of nanomaterials into an endpoint, e.g. a worker). The reduction of nanomaterial emission from the source can be achieved through work practice controls such as handling nanomaterials in suspension into a liquid or dispersed into a paste or a solid matrix rather than in the form of dry powders. Handling nanomaterials in these physical forms is likely to reduce fugitive dust emissions. It is also recommended to avoid high thermal or mechanical energy processes or other activities that are likely to release nanomaterials from their matrix.

Engineering controls can also be very useful in reducing the transmission from the source to the worker. Two generic transmission control measures that may be applicable during tyre manufacturing operations are: *i*) local control, e.g. containment and/or local exhaust ventilation; and *ii*) general ventilation, e.g. natural or mechanical ventilation. The reduction of emission has three generic control measures: *i*) personal enclosure/separating the worker from the source, e.g. a ventilated cabin; *ii*) segregation of the source from the worker, i.e. isolation of sources from the work environment in a separate room without direct containment of the source itself; *iii*) use of PPE. Use of PPE is usually the last resort in exposure reduction (ISO, 2012).

Administrative and engineering controls can also be implemented to mitigate releases of nanomaterials into the environment. Administrative controls can include work practices such as handling all wastes that contain, or may potentially contain, nanomaterials as hazardous waste. Work practices can even include treating nanomaterial-containing wastewater as hazardous waste and avoiding the discharge of any nanomaterials to on-site or off-site wastewater treatment.

Engineering controls to prevent the release of nanomaterials into the environment can include air pollution control devices on stack air vents and incinerators that combust nanomaterial-containing wastes. Air pollution control devices for removing particulates from gaseous waste streams can include filter bags, wet and dry electrostatic precipitators, cyclones and scrubbers. These control technologies should be evaluated for their removal or capture efficiency of nanomaterials.

Phase II, Stage 2, Step 5 – Characterise the risk

This section discusses characterising the resulting risk for both occupational and non-occupational settings, both quantitatively and qualitatively.

Occupational human health risk assessment

This framework uses the risk/control banding approach to assess and manage occupational human health risks (i.e. during nanomaterial and tyre manufacturing).

The use of a quantitative risk assessment is briefly discussed for informative purposes only. The remainder of this subsection demonstrates the use of the risk/control banding approach following ISO (2012). As previously described, the best information to base the selection of the appropriate exposure band is typically exposure measurements. The determination as to what sampling/monitoring should be performed will depend on many variables, such as: the specific nanomaterial being measured; the tasks that workers are performing; whether area or personal sampling is preferable; the number of workers involved; what instrumentation/capabilities are available; and the intended use of the data. Preference should typically be given to individual exposure measurements as opposed to area monitoring results. The results should be taken into account when determining the corresponding exposure band. ISO/TS 12901-1 provides information on available measurement equipment, possible measurement strategies and interpreting the results (ISO, 2012).

As an alternative to the risk/control banding approach, quantitative exposure measurements can be used for a risk assessment. However, a quantitative risk assessment also requires quantitative toxicological data. If such quantitative data are available or are pursued, risk assessor expertise should be sought. This framework is not intended to provide guidance on quantitative risk assessments.

Qualitative risk assessments, both proactive and retroactive, can be made using ISO (2012), as summarised below.

Proactive risk assessments can use the control banding approach to provide guidance on the selection of control strategies to manage risk. After assigning hazard band and exposure band rankings, the control banding matrix in ISO (2012) (reproduced in Table 5.10) can be used to determine the recommended control band to manage the risk of the nanomaterial in an occupational setting.

Table 5.10. **Control banding matrix**

Hazard band	Exposure band			
	EB1	EB2	EB3	EB4
A	CB1	CB1	CB1	CB2
B	CB1	CB1	CB2	CB3
C	CB2	CB3	CB3	CB4
D	CB3	CB4	CB4	CB5
E	CB4	CB5	CB5	CB5

Source: International Organization for Standardization (ISO) (2012), *Nanotechnologies – Guidelines for Occupational Risk Management Applied to Engineered Nanomaterials – Part 2: The Use of the Control Banding Approach in Occupational Risk Management*, ISO TC 229/SC N.

The control bands are defined in ISO (2012) as correlating to specific control strategies as follows:

- CB1: natural or mechanical general ventilation
- CB2: local ventilation: extractor hood, slot hood, arm hood, table hood, etc.

- CB3: enclosed ventilation: ventilated booth, fume hood, closed reactor with regular opening
- CB4: full containment: glove box/bags, continuously closed systems
- CB5: full containment and review by a specialist: seek expert advice.

Retroactive risk assessments can use the risk banding approach to qualitatively characterise the risk of an existing occupational setting. After assigning hazard band and exposure band rankings, the risk or priority banding matrix in ISO (2012) (reproduced in Table 5.11) can be used to determine the qualitative assessment of risk for the nanomaterial in an existing occupational setting, accounting for existing controls in place.

Table 5.11. **Risk or priority banding matrix**

Hazard band	Exposure band			
	EB1	EB2	EB3	EB4
A	Low	Low	Low	Medium
B	Low	Low	Medium	High
C	Low	Medium	Medium	High
D	Medium	Medium	High	High
E	Medium	High	High	High

Source: International Organization for Standardization (ISO) (2012), *Nanotechnologies – Guidelines for Occupational Risk Management Applied to Engineered Nanomaterials – Part 2: The Use of the Control Banding Approach in Occupational Risk Management*, ISO TC 229/SC N.

Additionally, retroactive risk assessments can use the exposure banding approach in the same manner as a proactive risk assessment. The exposures can be characterised without considering the exposure mitigation controls in place, and an exposure band ranking can be assigned per ISO (2012). A control band can then be assigned as described for the proactive risk assessment approach above (using Table 5.10). The assigned control band can then be compared to the existing mitigation controls in place. This comparison can be used to evaluate the effectiveness of the current controls in place.

General population and ecological risk assessment

This framework includes guidance for the evaluation of the entire life cycle in the assessment and management of risk. Therefore, it is acknowledged that risks posed to the general population and ecological endpoints should be evaluated and incorporated into the overall assessment and site-specific risk management strategies. At this point in time, limited data are available regarding the fate and transport and toxicity of nanomaterials in general, and even less is available in public literature regarding those used in tyres. Therefore, it may be difficult to complete a quantitative risk assessment – especially for specific nanomaterials used in specific applications. Additionally, a qualitative risk/control banding approach (similar to that used for assessing and managing worker exposures) is not presented, as one does not currently exist.

However, the steps discussed in this framework can be used to form the basis for an appropriate evaluation and conservative risk management strategy until additional information becomes available. As new data and information are developed, the results should be fed back into the aforementioned steps and the strategy should be revised as needed. This feedback step should be a formal part of the overall strategy such that continual improvement is achieved and potential risks are truly identified and minimised.

Additional guidance for evaluating risk to general population and ecological endpoints is presented below.

Exposure measurements can be used in a quantitative risk assessment. However, a quantitative risk assessment also requires quantitative toxicological data. If such data are available or are pursued, risk assessor expertise should be sought. This framework is not intended to provide guidance on quantitative risk assessments.

In the absence of quantitative toxicological data, risk can be evaluated through a qualitative risk assessment. To most conservatively protect general population and ecological health, it can be assumed that a nanomaterial may pose a severe hazard. Then, a comprehensive evaluation of exposure pathways can be used to look for areas where chemistry, fate and transport data are needed to further characterise the exposure pathway. For example, further data may be needed to determine the fate of a nanomaterial in an incinerator (e.g. is it destroyed or is it liberated from a cross-linked product and subsequently released in exhaust gas as a product of incomplete combustion?).

A nanomaterial or tyre manufacturing company can use this guidance to evaluate all potential exposure pathways over the entire life cycle of the nanomaterial and develop a risk management strategy that extends beyond the company fence line. For example, a nanomaterial or tyre manufacturer could use the exposure pathway evaluation to improve the facility or company-wide environmental stewardship plan by avoiding any wastewater discharges of nanomaterials and evaluating the efficacy of dust collector systems associated with air streams potentially containing nanomaterials. Recognising that exposure pathways during the use and end-of-life of tyres may be outside the control of these companies, it may be appropriate to implement public awareness and hazard communication programmes that recommend safe handling and disposal methods.

A tyre manufacturer pursuing research and development of a particular nanomaterial could use this framework to evaluate where more data are needed to evaluate the risk posed to the general population and ecological endpoints. For example, risks could be evaluated from the release and disaggregation of nanomaterials from rubber due to chemical and physical degradation of tyre particles during use and on the side of a road, or due to incineration of tyres in energy recovery processes.

Regulatory bodies can also use the exposure pathway evaluations to inform decision makers when determining where further research funding is needed to assess the level of risk posed to the general population and ecological endpoints.

Phase II, Stage 3 – Confirmation of utility of risk assessment

To confirm the utility of a risk assessment, certain questions must be asked, including the following:

- Do the assessment results include the attributes called for in planning?
- Do the assessment results provide sufficient information to discriminate among risk management options?
- Has the assessment been satisfactorily reviewed by others?

If the utility of the risk assessment cannot be confirmed, then the planning stage must be re-visited to evaluate what is necessary to appropriately characterise the risks. The level of uncertainty and variability must also be re-evaluated to determine if the risk

results can be reported within an acceptable level of confidence. If confirmation of utility can be achieved, then Phase III of the framework (risk management) can begin.

Phase III – Risk management

The purpose of risk management is to reduce risks to an appropriate level and the process should follow the control hierarchy demonstrated by the STOP principle (as described in ISO [2012]) and the United States Occupational Safety and Health Administration's (OSHA) hazard prevention and control guidance (OSHA, 2013). The STOP principle (substitution, technical measures, organisational measures, and personal protective equipment) and OSHA's hazard prevention and control guidance both follow the same hierarchy of first attempting to remove a hazard through design or redesign of industrial processes; then trying to minimise exposure to a hazard through controls and management practices; and finally to protect workers against any remaining exposure to the hazard.

When incorporating nanomaterials into tyres, this control hierarchy should be incorporated into the company- and site-specific risk management plan. The following key points should be integrated into the risk management plan:

1. Substitution: if the nanomaterial presents hazard concerns, determine if it can be substituted with a less hazardous material.
2. Process design: design the process such that exposures are minimised (e.g. enclosed process, using automation in place of manual activities).
3. Engineering controls: implement engineering controls to minimise exposures (e.g. barriers, local ventilation).
4. Safe work practices: implement company- or site-specific workplace rules to ensure workers take necessary precautions to minimise exposures (e.g. respiratory protection standards, laboratory chemical hygiene standards, protocols for cleaning spilled nanomaterials and fixing leaks).
5. Personal protective equipment: require the use of proper PPE to minimise exposures that remain after all of the above considerations. Include proper PPE training.
6. Systems to track hazard correction: develop a hazard tracking system to track the original discovery of a hazard to its correction.
7. Preventive maintenance systems: implement good scheduling and documentation of maintenance activities. For example, good maintenance scheduling of pressurised pneumatic transfer lines can prevent leaks, instead of relying on visual inspection of leaks before maintenance occurs.
8. Medical programmes and industrial hygiene monitoring: implement industrial hygiene monitoring programmes to regularly monitor exposures. Implement a medical programme to record and document employee health complaints and injuries.

The above key points focus on worker health within occupational settings. However, risks posed to the general population and ecological endpoints can also be considered as part of a company- or site-specific environmental stewardship plan. This plan can include provisions such as:

1. Avoid any discharge of nanomaterials to wastewater.
2. Treat nanomaterials and any wastes potentially containing nanomaterials as hazardous waste.
3. Where possible, handle nanomaterials in small quantities in controlled, laboratory settings.
4. Where possible, handle nanomaterials incorporated into a solid matrix instead of as a solid powder. For example, the laboratory incorporation of nanomaterials into rubber blocks for subsequent addition to the low-temperature mixer during tyre manufacturing could be considered a good practice, not only to minimise worker exposures, but also to reduce fugitive dust releases.

Review of available information on HD-HS silica and nanoclays for use within the risk management framework

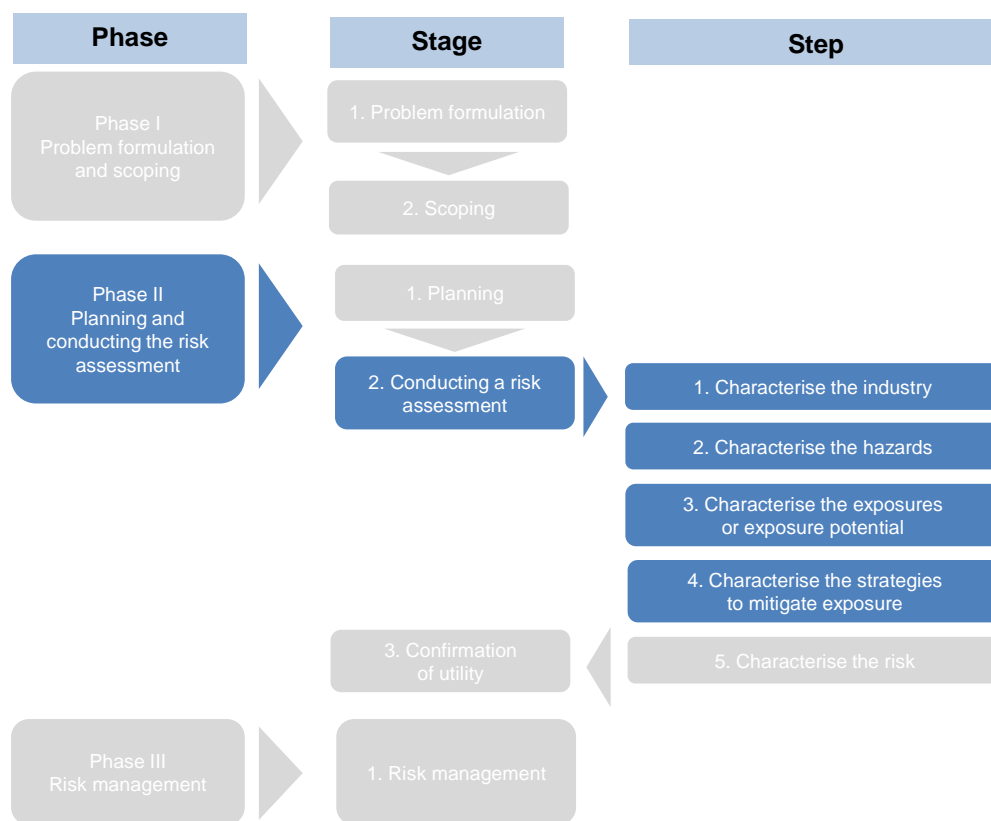
This section presents the information currently available for HD-HS silica and nanoclays that can be used within the risk management framework discussed in the previous sections. Multiple suppliers were contacted with requests for site-specific information that could be used to develop full case study examples. These contacts indicated the requested information was either not available (e.g. toxicity studies had not been conducted and industrial hygiene monitoring had not occurred) and/or information was considered to be confidential (e.g. detailed information pertaining to worker activities and process descriptions). Because information is not publicly available, there are numerous data gaps. Therefore, not enough information is available to complete a case study utilising the control banding (and other) approaches recommended in the framework. Nonetheless, publicly available information was gathered (and is presented below) such that it can be used in future evaluations along with company-specific, confidential data. The information presented below was obtained entirely from publicly available sources and interviews with tyre industry stakeholders.

The information search revealed that there is not enough publicly available information to characterise the risk of using HD-HS silica or nanoclays in tyres following the risk management framework. Therefore, this section instead presents a literature review of information obtained on HD-HS silica and nanoclays following the data elements required for risk assessment identified in Phase II, Stage 1 of the risk management framework. Since information specific to the use of these nanomaterials in tyres was not identified, this section focuses on characterising the industry, exposure potential and exposure mitigation strategies for nanomaterial manufacturing only. The risk management framework presented above already addresses these topics for nanomaterials in general for all other life-cycle stages. Figure 5.2 presents a flow diagram that illustrates the sections of the framework covered in this section for HD-HS silica and nanoclay. This section presents the information that is currently available and highlights the data gaps that must be addressed before the risks can be properly characterised.

HD-HS silica

The following subsections discuss the chemistry of HD-HS silica, the processes used to manufacture each nanomaterial, and potential sources of exposure or release, based on Phase II, Stages 1 and 2 of the risk management framework.

Figure 5.2. Phases and stages of the risk management framework covered in this section



Physical/chemical properties data

According to the Synthetic Amorphous Silica and Silicate Industry (SASSI) Association, there are two main polymorphs of synthetic amorphous silica: precipitated silica and pyrogenic silica (also known as fumed silica) (SASSI, 2008). Silicas used as reinforcing fillers are mainly obtained by precipitation (SASSI, 2008; Rodgers and Waddell, 2005). Precipitated silica is the most commonly produced synthetic amorphous silica and is widely used in Europe, with increasing demand in North America and Asia (Bergna and Roberts, 2006, as cited in SASSI, 2008). Pyrogenic silica does not appear to play a significant role in the tyre industry, based on west European consumption rates (European Commission, 2007).

Precipitated silicas can be grouped by dispersibility and surface area, as shown in Table 5.12. These groups include:

- conventional silica
- semi-high dispersion (semi-HD) silica
- high dispersion silica (HD) silica
- highly dispersible high surface area (HD-HS) silica.

Table 5.12 shows there is a correlation between surface area and application, where tyre casings incorporate silicas with low- to mid-range surface areas and tyre treads incorporate silicas with mid- to high-range surface areas. High-performance tyre treads are unique in that they only incorporate HD-HS silica.

Table 5.12. **Classification of silica groups used in rubber tyres**

Silica type	Surface area (m ² /g)		
	90-130	130-180	180-220
Conventional	Tyre casings	Tyre casings Tyre treads	Tyre treads
Semi-high dispersion	Tyre casings	Tyre casings Tyre treads	Tyre treads
High dispersion	Tyre casings Tyre treads	Tyre treads	--
Highly dispersible high surface area	--	--	High-performance tyre treads

Source: Rodgers, B. and W. Waddell (2005), “The science of rubber compounding”, In: *The Science and Technology of Rubber*, 3rd ed., Elsevier, Burlington, MA; interviews with industry stakeholders.

There do not appear to be widely accepted standard distinctions between the four silica types listed above. Based on a review of product specification data from silica manufacturer websites, as well as discussions with tyre manufacturers, the key distinctions include surface area, elementary particle diameter and aggregate mean diameter. Table 5.13 summarises characteristic values associated with each type.

Table 5.13. **Characteristic properties of conventional, high dispersion and highly dispersible high surface area silica**

Physical property	Unit	Conventional silica	HD silica ¹	HD-HS silica ²
CTAB surface area	m ² /g	~110	160	200
BET surface area	m ² /g	~115	165	215
Diameter of elementary particles	nm	25	20	10
Mean diameter of aggregates	nm	95	50	55-60

Notes: CTAB: cetyltrimethylammonium bromide; BET: brunauer–emmett–teller. 1. Rhodia Zeosil 1165 is used as representative of HD silica. 2. Rhodia Zeosil Premium 200 MP is used as representative of HD-HS silica.

Source: Rhodia (2011), “Safety data sheet. Zeosil Premium 200MP”, Revision 4.00.

Previous work conducted in support of the Tyre Industry Project (TIP) indicates that precipitated amorphous silica meets the ISO definition of a nano-structured material. It does not meet the definition of a nano-object because the primary particles bind to form aggregates and agglomerates that are above the nanometre range. While the initial precipitation step yields primary particles that meet the ISO definition of nano-objects, they immediately bond covalently to form non-dissociable aggregates having diameters of approximately 100-500 nm. The aggregates then electrostatically bind together to form agglomerates with diameters ranging from 1-40 µm. The study notes that aggregate and agglomerate bonds are not broken during use (ChemRisk, 2011).

HD-HS silica manufacturing risk assessment

Phase II, Stage 2 of the risk management framework describes the assessment of risk per the characterisation of the following elements: the industry, hazards, exposures or exposure potential, and strategies or techniques to mitigate exposure. The following subsections characterise each of these elements for the manufacture of HD-HS silica. However, a risk assessment has not been completed at this time due to significant data

gaps. Additional research to fill these gaps may allow for development of a risk assessment in the future.

Process description

Solvay submitted a patent application for a production process of an HD-HS silica product which is similar to the generic precipitated silica manufacturing process. The difference in Solvay's HD-HS silica production method is a different method of reacting the silicate solution with the acidifying agent. The remaining steps (precipitation, filtration, washing, etc.) are identical to conventional precipitated silica manufacturing operations as discussed in further detail below. The patent application recommends the use of a filter press and spray dryer to perform the solid-liquid separation (Valero, 2005).

The manufacture of precipitated synthetic amorphous silicas usually comprises the following major unit operations: precipitation, filtering/washing, drying and granulation/milling (Luginland, 2002). Packaging of the final product occurs during granulation/milling, where the granulised product is packaged into product containers (European Commission, 2007). According to European Commission (2007), only batch precipitation processes have attained economic importance; however, continuous precipitation techniques can also be employed. The general precipitated silica manufacturing process is described below, followed by a brief discussion of key process differences for manufacturing HD-HS silica.

During the initial step (i.e. precipitation), an aqueous alkali metal silicate solution (e.g. waterglass) is mixed with either concentrated sulfuric, hydrochloric or carbonic acids (European Commission, 2007; SASSI, 2008). The raw materials needed to produce waterglass are sand, sodium carbonate, sodium hydroxide and water (European Commission, 2007; SASSI, 2008). The molar ratio of silicon dioxide to sodium dioxide is kept to a range of 2 to 4 (European Commission, 2007; Hewitt and Ciullo, 2007; SASSI, 2008).

According to SASSI (2008), precipitated silicas are manufactured under neutral to alkaline conditions and result in primary particle, aggregate and agglomerate size ranges of 5-100 nm, 0.1-1 µm, and 1-250 µm, respectively.

The precipitation reaction produces not only a hydrated silica slurry, but also residual salts such as sodium sulfate, sodium chloride or sodium carbonate (Hewitt and Ciullo, 2007). The residual salts content is reduced by 1% or 2% by passing the slurry through a counter-current decantation system or by filtering (Hewitt and Ciullo, 2007). Filtration units consist of filter presses, rotary filters and belt/drum driers, and produce a solid wet cake containing 15-25% silica (European Commission, 2007; Hewitt and Ciullo, 2007). Immediately after filtration, the wet cake is washed to remove residual salts. This washing step typically occurs within the filtration section (European Commission, 2007). The salt content remaining in the product will vary depending on the intended application of the final silica product (European Commission, 2007).

In industrial scale operations, the resulting wet cake is dried by belt, turbine, recycling, rotary drum and spray dryers (European Commission, 2007). The specific equipment that is employed will depend on the desired structure and properties of the final silica product (European Commission, 2007). Shorter drying times are typical of HD silica production while longer drying times are typical of conventional silica production (as cited in Mihara, 2009).

After drying, the final silica product contains about 6% water (Hewitt and Ciullo, 2007) and is an irregular granulate that requires milling (European Commission, 2007). Milling establishes the particle size distribution of the final product (European Commission, 2007; SASSI, 2008). Milling requires air or steam and is energy intensive (European Commission, 2007). Hammer and jet mills are most typically used (European Commission, 2007).

For certain applications, a dust-free product is required. To fulfill this requirement, the spray-dried or milled products must be granulated, which is normally carried out with drum granulation equipment. Granulators are used to increase the particle size of silica, mainly for improved handling and to reduce dusting. The final product is then packaged using automatic or manual filling machines, which load the silica into paper or plastic bags of 5-25 kg, big bags of 100-1 000 kg, or silo containers. Inputs and outputs to mills and granulators are often handled by airway systems equipped with bag houses for product recovery and dust extraction. To minimise particulate emissions, bagging machines are always equipped with their own dust extraction and control systems (European Commission, 2007).

Hazard characterisation

The material safety data sheet (MSDS) for an HD-HS silica product contains information about toxicity and potential human health effects, as listed in Table 5.14, although the majority of results are from unpublished studies. The MSDS also indicates that the HD-HS silica is not bioaccumulative, based on published data (Rhodia, 2011). No other HD-HS silica-specific studies were identified.

Exposure or exposure potential characterisation

HD-HS silica is expected to be handled primarily in solid particulate form. However, there were no specific data available to characterise the amount of nanomaterial handled, duration and frequency of exposure, or any other data elements to quantify potential exposures.

Potential occupational exposure pathways associated with silica production include packaging and shipping activities (European Centre for Ecotoxicology and Toxicology of Chemicals, 2006; SASSI, 2008). For each of these exposure sources, the generation of airborne dusts represents a potential inhalation exposure route for workers. Dermal exposures also may occur through incidental contact. Refer to Table 5.4 for specific occupational exposure pathways from handling solid particles.

The environmental release media associated with precipitated silica manufacturing are air, water and landfill (European Commission, 2007; SASSI, 2008). According to European Commission (2007), air and water make up the two major release sources. The specific sources of environmental release include:

- Air: fugitive dust releases occur during drying operations. The level of particulates generated depends on the drying technology used. Fast-drying processes (e.g. flash or spray dryers) are typically used for precipitated silicas and result in fewer dust emissions than slow, indirect drying processes. Slow-drying processes rely on large volumes of air and are used in the manufacture of other silica types (European Commission, 2007).

- Water: releases occur during silica washing. Wastewaters generated during silica washing pass through wastewater treatment plants prior to direct release to surface waters (European Commission, 2007).
- Landfill: releases occur as a result of product spills and wet sludge from on-site wastewater treatment (European Commission, 2007).

Table 5.14. Toxicological and ecological information for highly dispersible high surface area silica

Category	Information available	Source
Acute oral toxicity	LD50 : > 5 000 mg/kg – rat	Unpublished reports
Acute inhalation toxicity	Risk of physical blockage of the upper respiratory tract. By analogy, an LC50/inhalation/4h/rat could not be determined because no mortality of rats was observed at the maximum achievable concentration.	Unpublished reports
Acute dermal toxicity	LD50 : > 5 000 mg/kg – rabbit	Unpublished reports
Acute toxicity (other routes of administration)	No data available.	
Aspiration toxicity	Not applicable.	
Skin irritation	Repeated or prolonged contact may cause slight irritation to the skin.	Unpublished reports
Eye irritation	Mild eye irritant.	Unpublished reports
Sensitisation	Humans: no cutaneous sensitisation reaction observed.	Unpublished reports
Repeated dose toxicity	If inhaled: no irreversible effect or symptom of silicosis was observed during the inhalation toxicity tests.	Unpublished reports
	Oral exposure: no irreversible effects were observed during chronic oral toxicity tests.	Unpublished reports
STOT – single exposure	The substance or mixture is not classified as specific target organ toxicant, single exposure.	Not listed
STOT – repeated exposure	The substance or mixture is not classified as specific target organ toxicant, repeated exposure.	Not listed
Carcinogenicity	Rat, oral exposure: animal testing did not show any carcinogenic effects.	Unpublished reports
	Mouse, oral exposure: animal testing did not show any carcinogenic effects.	Unpublished reports
Genotoxicity <i>in vitro</i>	<i>In vitro</i> tests did not show mutagenic effects.	Unpublished reports
Genotoxicity <i>in vivo</i>	<i>In vivo</i> tests did not show mutagenic effects.	Unpublished reports
Reproductive toxicity	Fertility and developmental toxicity tests did not reveal any effect on reproduction.	Unpublished reports
Neurological effects	No neurotoxic effects observed.	Not listed
Experience with human exposure: Inhalation	Mild respiratory irritant.	Unpublished reports
Toxicity to fish	LC50 – 96 h : > 10 000 mg/l – <i>Danio rerio</i> (zebra fish)	Unpublished reports
Toxicity to daphnia and other aquatic invertebrates	EC50 – 24 h : > 1 000 mg/l – <i>Daphnia magna</i> (water flea)	Unpublished reports
Ecotoxicity assessment	The product does not have any known adverse effects on the aquatic organisms tested.	

Notes: LD50: lethal dose, 50%; the dose required to kill half the members of a tested population after a specified test duration. LC50: lethal concentration, 50%; the concentration of the surrounding medium required to kill half the members of a tested population after a specified test duration; STOT – Specific Target Organ Toxicity.

Source: Rhodia (2011), “Safety data sheet. Zeosil Premium 200MP”, Revision 4.00.

According to SASSI (2008), most non-occupational exposures are likely to be from the ingestion of silica dissolved in water, although an MSDS for an HD-HS silica product describes the silica as “practically insoluble” in water, with an estimated solubility of 0.1 g/L.

Refer to Table 5.4 for additional guidance on potential exposure pathways for the general population or aquatic ecological endpoints.

In terms of fate and transport, the Rhodia MSDS for an HD-HS silica product indicates the ultimate destination of the product is to soil or sediment (Rhodia, 2011). No other HD-HS silica-specific studies were identified.

Strategies or techniques to mitigate exposure

The Rhodia MSDS for an HD-HS silica indicates that specific PPE should be used, including safety glasses, and a respirator with an approved filter if a risk assessment indicates that it is necessary (Rhodia, 2011). No other information was found concerning current specific strategies practised by industry to mitigate nanomaterial (including HD-HS silica) release or exposure during nanosilica manufacturing. As mentioned previously for certain silica products, bagging machines are equipped with dust extraction and control systems (European Commission, 2007).

Nanoclays

The following subsections discuss the chemistry and processes used to manufacture nanoclays, and potential sources of exposure or release, based on Phase II, Stages 1 and 2 of the risk management framework.

Physical/chemical properties data

Clays are classified as a group of minerals in the phyllosilicate subclass (sheet-like structures) of the silicate class. Clay minerals may be divided into four major groups, mainly in terms of the variation in the layered structure. These include the kaolinite group, the montmorillonite (MMT)/smectite group, the illite group and the chlorite group (Uddin, 2008). This section focuses on MMT and kaolinite nanoclays, which have applications in the tyre manufacturing industry.

MMT and kaolinite are aluminosilicates, which have a sheet-like (layered) structure, and consist of silica SiO_4 tetrahedra bonded to alumina AlO_6 octahedra in a variety of ways. A 2:1 ratio of the tetrahedra to the octahedra results in smectite clays, the most common of which is MMT (Hay and Shaw, 2000). The MMT has a typical chemical description of $(\text{Ca},\text{Na})(\text{Al},\text{Mg})_2(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2$. Kaolinite has a 1:1 structure consisting of one tetrahedral sheet bonded to one octahedral sheet, giving a typical chemical description: $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. *In situ* additional mineral content is present in clay due to its geological formation. In most applications, these minerals are considered impurities and downstream processing is aimed toward removing the extraneous minerals setting the particle fineness (and distribution) (Uddin, 2008; Michelin, 2013).

Clay minerals used as fillers occur in two main varieties: non-expanding and expanding. Kaolin is a non-expanding mineral, which has a neutral surface and does not have any chemistry on the surface that promotes separation of platelets. The MMT is an expanding mineral, which has a negative surface charge that promotes easy dispersion in aqueous systems (Lopez, 2000).

The thickness of the MMT and kaolinite layers are similar: an MMT layer is approximately 1 nm (Lopez, 2000) while the thickness of a kaolinite layer is approximately 0.7 nm (Marquis et al., 2011). However, aspect ratios differ greatly. The MMT plates have aspect ratios (width to thickness) from 50 to over 1 000, while water-washed kaolins have ratios of 10-30. The size and shape of montmorillonite gives a surface area of approximately 800 m²/gram (Lopez, 2000).

In terms of classification, each layer of the MMT and kaolinite can be considered a nanoplate. However, nanoclays normally exist as agglomerated bundles, consisting of thousands of platelets held together by van der Waals forces (Kang, 2010). Therefore, nanoclays primarily exist on their own as nanostructured materials.

In order to optimise the use of nanoclays in rubbers and plastics, the individual layers must be partially or fully separated (exfoliated) and dispersed into the polymer matrix (Kang, 2010). nanoclay, sheets primarily remain bound together and can be separated within a nanocomposite to form three main types of nanocomposite structures (Sengupta, 2007):

- conventional: nanostructured material is dispersed within the matrix
- intercalated: nanoplates are separated by polymer fillers
- exfoliated: nanoplates are completely dispersed within the polymer matrix.

Nanoclay manufacturing risk assessment

Phase II, Stage 2 of the risk management framework describes the assessment of risk per the characterisation of the following elements: the industry (process description), hazards, exposures or exposure potential, and strategies or techniques to mitigate exposure. The following subsections characterise each of these elements for the manufacture of nanoclays. However, a risk assessment has not been completed at this time due to significant data gaps. Additional research to fill these gaps may allow for development of a risk assessment in the future.

Process description

Clay processing is divided into two major groupings: dry state processing or wet. Clay from the dry process is used where purity and appearance characteristics are not critical to the end use. Alternatively, wet processing is conducted to allow further improvement of the clay properties, referred to as “beneficiation” (Michelin, 2013; USEPA, 1995).

Note that no specific information was found specifically concerning the manufacture of nanoclays. However, information from Brell (2000) of Rockwood additives and Tellaetxe et al. (2004) points to a wet processing method.

The wet process for “high grade kaolin products” is assumed to also be applicable to MMT processing until further information is obtained. Wet processing of kaolin begins with blunging to produce a slurry, which then is fractionated into coarse and fine fractions using centrifuges, hydrocyclones or hydroseparators. At this step in the process, various chemical methods, such as bleaching, and physical and magnetic methods, may be used to refine the material. Chemical processing includes leaching with sulfuric acid, followed by the addition of a strong reducing agent such as hydrosulfite. Before drying, the slurry is filtered and dewatered by means of a filter press, centrifuge, rotary vacuum filter or tube filter. The filtered dewatered slurry material may be shipped or further processed by drying in apron, rotary or spray dryers (USEPA, 1995).

Further beneficiation may include chemical treatments, delamination and calcination, depending on application requirements. Chemical treatments such as mercapto-silane coupling agents may be applied to the clay offer more functionality. Resulting rubber products exhibit improved compression set, permanent set and reduced heat build-up (Michelin, 2013).

Delamination is the process of separating the nanoclay stacks into finer platy particles by attrition grinding of slurries using sand or other media to facilitate the process. Such products can add benefit to certain rubber applications where products need higher stiffness, modulus, less die swell or reduced gas permeability (Michelin, 2013).

Hazard characterisation

Martin et al. (2008) found that there are very limited toxicological data available for nanoclays, with only acute (mostly *in vitro*) studies performed, which is consistent with the results of the literature search, as summarised in Table 5.15. Studies that examined ecotoxicity were not identified.

Table 5.15. Nanoclay toxicity studies

Source	Summary
Totuska et al. (2009)	Analysed <i>in vitro</i> genotoxic effects of kaolin microparticles on human cancer cell line (A549) cells. Results revealed increased micronuclei (MN) frequencies after treatment. Additionally, kaolin nanoparticles induced lung DNA damage and mutagenicity in mice (<i>in vivo</i>).
Lordan et al. (2010)	Evaluated the cytotoxicity of unmodified nanoclay, Cloisite® Na ⁺ and the organically modified nanoclay, Cloisite 93A® in human hepatoma HepG2 cells. Data demonstrated nanoclays are highly cytotoxic and as a result pose a possible risk to human health.
Li et al. (2010)	Evaluated toxicity for nanosilicate platelets (NSP) derived from natural montmorillonite clay. The material had been previously shown to be effective for antimicrobial properties and tendency for adhering onto the biomaterial surface based on observations by a scanning electron microscope. Overall, the study demonstrated the safety of the NSP for potential uses in biomedical areas.
Sharma et al. (2010)	Investigated natural clay mineral montmorillonite (Cloisite) Na ⁺ and an organo-modified montmorillonite (Cloisite 30B) for genotoxic potential as crude suspensions and as suspensions filtrated through a 0.2-micron pore-size filter to remove particles above the nanometre range. Filtered and unfiltered water suspensions of both clays did not induce mutations using the tests in the study, but both the filtered and the unfiltered samples of Cloisite 30B induced DNA strand-breaks in a concentration-dependent manner. Further study suggested that the genotoxicity of organo-modified montmorillonite was caused by the organo-modifier. The detected organo-modifier mixture was synthesised and comet-assay results showed that the genotoxic potency of this synthesised organo-modifier was in the same order of magnitude at equimolar concentrations of organo-modifier in filtrated Cloisite) 30B suspensions, and could therefore at least partly explain the genotoxic effect of Cloisite 30B.
Verma et al. (2012)	Investigated cytotoxic effects of platelet and tubular type nanoclays on cultured human lung epithelial cells A549. A low, but significant, level of cytotoxicity was observed at 25 µg/mL of platelet type nanoclays. Results indicate potential hazard of nanoclay-containing products at significantly higher concentrations.
Smirnova et al. (2012)	Analysed intragastric administration of nanoclay to rats. Exposure over 28 days led to reductions in the relative weight of the liver, the activity of its conjugating enzymes, the antagonistic activity of bifidoflora, and the hyperproduction of colonic yeast microflora. The findings lead to the conclusion that nanoclays that may be present in foods must be the object of sanitary regulation.
Lordan et al. (2012)	Investigated the effect of the commonly used growth supplement, fetal calf serum (FCS), concentration on the cytotoxic behaviour of the unmodified nanoclay, Cloisite® Na ⁺ (<i>in vitro</i>). Human monocytic U937 cells in medium supplemented with 5% FCS, 2.5% FCS or serum-free medium were treated with 1 mg/mL Cloisite Na ⁺ . Cell growth in 2.5% FCS was significantly inhibited by Cloisite Na ⁺ within 48 h, whereas little effect was seen with a supplement of 5% FCS. Without serum, cell growth was inhibited and Cloisite Na ⁺ had a detrimental effect on these cells. In media supplemented with FCS, the nanoclays agglomerated together to form large bundles, whereas they were evenly dispersed throughout the medium in the absence of serum. Clay particles, therefore, have cytotoxic properties that may be linked to their dispersion pattern. These adverse effects seem to be masked by 5% FCS. Serum supplementation is an important consideration in the toxicological assessments of nanomaterials on cells, which needs to be addressed in the standardization of <i>in vitro</i> testing methods.

Exposure or exposure potential characterisation

Nanoclays such as MMT and kaolinite are expected to be handled primarily in solid particulate form. However, there were no specific data available to characterise the amount of nanomaterial handled, duration and frequency of exposure, or any other data elements to quantify potential exposures as discussed in the risk management framework.

No information was found concerning specific exposure points associated with nanoclay manufacturing. Particulate matter is emitted from all dry mechanical processes, such as crushing, screening, grinding, and materials handling and transfer operations (USEPA, 1995). Potential occupational exposure pathways associated with the wet production process for “high grade” nanoclay products include inhalation and dermal exposures from dry handling and transfer of clay particles. Specific activities may include, but are not limited to: loading/packaging, spill clean-up and maintenance. Additional exposure pathways listed in Table 5.4 involving solid particles may also be applicable.

Fugitive particulate emissions are potentially emitted from all dry mechanical processes; therefore, the main environmental release media is to air (USEPA, 1995). It is unclear whether there are significant water releases from dewatering operations. Exposure pathways for the general population or aquatic ecological endpoints are dependent on pollution control technologies or waste disposal methods, as illustrated in Table 5.4.

No specific information on nanoclays was found concerning fate and transport of nanoclays.

Strategies or techniques to mitigate exposure

No information was found concerning mitigation specifically for nanoclays. For most clay processing operations, cyclones, wet scrubbers and fabric filters are the most commonly used devices to control particulate emissions. Cyclones often are used for product recovery from mechanical processes. In such cases, the cyclones are not considered to be an air pollution control device. Electrostatic precipitators also are used at some facilities to control PM emissions (USEPA, 1995).

Concluding remarks

Phase II, Stage 1 of the risk management framework (Planning for the Risk Assessment) discusses the need to identify what data are needed and what data are available in order to conduct a risk assessment. There is a general lack of publicly available information pertaining to the hazard potential and the exposure potential associated with the nanomaterials of interest. In an attempt to acquire corporate industrial hygiene, human health, and fate and transport information, input was solicited from industrial stakeholders that manufacture HD-HS silica and nanoclays as well as tyre manufacturers that may use these and other nanomaterials in the future. These stakeholders provided information that was readily available and not considered confidential. However, after assessing the information, it was determined that too many information gaps remain to complete a full risk management plan, even as a case study. Therefore, rather than providing complete case studies, this report presents information that was identified such that it can be used by interested parties as a first step. This information can be used and supplemented by additional data as it becomes available to provide a detailed evaluation.

There are ongoing efforts by industrial stakeholders, academic entities and government organisations to characterise the risk associated with these and other nanomaterials. For example, tyre manufacturing stakeholders are actively trying to identify data that are needed to inform corporate decision makers for their internal product stewardship programmes. Also, some governments are in the process of developing regulations that require testing of certain nanomaterials. Table 5.16 summarises several key risk assessment data gaps that were identified (organised by life-cycle stage). Industrial, government and academic stakeholder decision makers can use this as a guide to help prioritise future research efforts. These could include industrial hygiene studies at nanomaterial manufacturing and tyre manufacturing facilities, toxicological and ecotoxicological studies by industry or academic institutions, and fate and transport studies.

Table 5.16. Summary of key risk assessment data gaps for nanomaterial use in each life-cycle stage of the tyre industry

Data required for risk assessment	Data availability
Nanomaterial manufacturing	
Characterisation and physical/chemical properties data	Basic chemical information is available to identify each nanomaterial, such as molecular structure and basic morphology, but there are not well-defined differences to be able to distinguish between certain types of silica, or even nanoclays. Data on physical and chemical properties for each compound at the nanoscale is practically non-existent.
Toxicological data	Only a few published studies have been performed to evaluate toxicological properties of nanosilica and nanoclay. More studies will need to be completed before a full risk assessment is possible.
Exposure data and information	Industrial manufacturing processes of bulk (macro- and microscale) silicas and clays are well characterised; however, information on manufacturing the nanoscale versions is limited. General process descriptions and unit operations can be deduced from literature, but detailed process operation, release and exposure data are not publicly available. Several of these data gaps could be filled with additional information from industry.
Tyre manufacturing	
Exposure data and information	Nanomaterial fillers have not yet been widely implemented for use in tyre manufacturing. Therefore, no specific exposure data are available. Some industry stakeholders expect that nanosilica will be a drop-in replacement for currently used silica (and use the same handling methods), while the method of handling nanoclays will be chosen based on the results of an exposure assessment.
Mounting of tyres on vehicles	
Exposure data and information	Potential exposures to and releases of the nanomaterials are expected to be less likely due to being bound in the polymer matrix. However, no specific studies were identified to verify this assumption.
Use of tyres on vehicles	
Exposure data and information	Tyre wear or blowouts may result in potential nanomaterial releases to the environment. However, no data were found on the release of nanomaterials from the vulcanised rubber and subsequent fate and transport in the environment.
End-of-life tyres	
Exposure data and information	End-of-life tyres may be recovered for reuse, material or energy recovery, or disposal. Therefore, potential exposures and releases will vary depending on the disposition method. No data were found on the exposure to or release of nanomaterials from the vulcanised rubber for any disposition method.
Fate and transport data	Studies to investigate potential leaching of nanomaterials from rubber under end-of-life scenarios (e.g. incineration, landfill) were not identified. Further, data on the fate and transport of nanomaterials after their release from the rubber under end-of-life scenarios is very limited (this data gap is also discussed under the section entitled "Use of tyres").

Notes

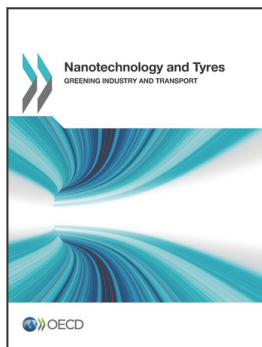
1. At the time of writing, the ISO document was still under development – the latest version available at the time (September 2012) was used.

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