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**TNO report**

## V9445 | 1

# Pilot "Kennisdelen Nano in de verfketen"

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| Copy no | - |
| No. of copies | - |
| Number of pages | 191 (incl. appendices) |
| Number of appendices | 9 |
| Sponsor | Ministerie van Infrastructuur en Milieu |
| Project name | Pilot "Kennisdelen Nano in de verfketen" |
| Project number | |

# Contents

# 1 Introduction

Several types of manufactured nano-objects (MNOs) are currently used in paint to improve its properties in terms of the resistance against scratches, dirt and/or the growth of bacteria. However, such use of MNOs can also pose potential risks as the effects of MNOs on human health and the environment are not fully understood.

The Ministry of Infrastructure and Environment (I&M) and the branch organization of paint and ink formulators (VVVF) initiated a pilot project to investigate the availability and subsequent gaps in current knowledge on hazard of, and exposure to MNOs used in the paint supply chain. This pilot project intends to facilitate the communication on potential risks for workers and the environment due to the use of MNOs or MNO-containing products and spread knowledge on this topic in the paint supply chain.

The project focuses on the substances Nano-$TiO_2$ and Nano-Ag that are produced and subsequently processed in coatings. Risks of Nano-$TiO_2$ and Nano-Ag for humans and the environment are assessed, from the production of both MNOs until the service life of products in which they are processed.

The first step of a risk assessment is setting the scope of the assessment. This scope can be visualized by a life cycle considering all stages of the MNO in the paint supply chain (i.e. manufacturing of the MNO, production of paint/coating using the MNO, application of paint/coating and service life of treated objects or surfaces). This life cycle and corresponding process descriptions of Nano-$TiO_2$ and Nano-Ag in the paint industry are described in chapter 4.

Chapter 5 provides guidance on the method used for evaluation of the current knowledge on human hazard and exposure to Nano-$TiO_2$ and Nano-Ag and its subsequent use for occupational and environmental risk assessment.
The consecutive occupational and environmental risk assessments are described in chapter 6 and 7 respectively.

One of the goals of this pilot project was collecting additional occupational exposure data by performing exposure measurements during manufacturing of Nano-$TiO_2$ and Nano-Silver, production of paint/coating using Nano-$TiO_2$ and Nano-Silver, and application of the paint/coating in which Nano-$TiO_2$ and Nano-Ag are processed. However, serious barriers were faced during selection of and cooperation with users of Nano-$TiO_2$ and Nano-Silver in the paint industry. Reasons are clarified in chapter 8.

Conclusions of this pilot project are drawn in chapter 9.

# 2 Summary

The Ministry of Infrastructure and Environment (I&M) and the branch organization of paint and ink formulators (VVVF) initiated a pilot project to investigate the availability and subsequent gaps in current knowledge on hazard of, and exposure to Manufactured Nano-Objects (MNOs) used in the paint supply chain. This pilot project intends to facilitate the communication on potential risks for workers and the environment due to the use of MNOs and spread knowledge on this topic in the paint supply chain.

The project focuses on the substances Nano-$TiO_2$ and Nano-Ag that are produced and subsequently processed in coatings. Risks of Nano-$TiO_2$ and Nano-Ag for humans and the environment are assessed based on available data, from the production of both MNOs until the service life of products in which these MNOs are processed.

*Main conclusions:*
For both occupational and environmental risk assessment good quality data are rarely available. Moreover, discussions about the appropriate method to perform occupational and environmental risk assessment are on going.

Despite the relatively high uncertainties in hazard and exposure assessment, an occupational risk assessment is performed for all stages from the paint supply chain. Quantitative occupational exposure data are not abundantly available; for only a few process steps a quantitative assessment could be performed. For all other process steps a qualitative assessment is done using a method (Stoffenmanager-Nano) with a low discriminating capacity which is actually still under development.
The results indicate that for certain process steps exposure may be at a level of concern. As a consequence of high uncertainties it is therefore recommended to control exposure to as low as reasonable achievable (ALARA) for all process steps.

An environmental assessment is performed based on best available but uncertain data in combination with many reasonable assumptions. Indicative risk quotients (PEC/PNEC ratios) were calculated, suggesting that there might indeed be reason of concern.
Acknowledging the high uncertainties and many unknowns on the environmental abundance, behavior, fate and toxicity of Nano-$TiO_2$ and Nano-Ag, the available data do show the urgency to take precautionary measures preventing emission of these MNO, but provide no hard proof for a direct environmental concern.

Efforts to generate good quality occupational exposure data, with the exception of two cases, failed for several reasons. Appropriate pilot sites could not be identified within the duration of the project. One of the main reasons is a lack of transparency and devoted communication about nanomaterials and their potential risks. It is therefore strongly recommended to try to improve this transparency and communication.

*Occupational risk assessment*

The scope of the occupational exposure assessment is determined by defining a life cycle considering all stages of the MNO in the paint supply chain (e.g. manufacturing of the MNO, Production of MNO containing paints, application of coating and the final service life stage of treated articles.)

A tiered approach was used for the occupational risk assessment of MNOs in all life cycle stages. Most value has been attributed to a risk assessment based on MNO-specific data for both hazard and exposure. However, since specific (quantitative) data on hazard and/or exposure are often not available, data obtained with analogous MNOs or analogue exposure scenarios may also serve as starting points. Data were obtained from literature; in addition exposure measurements were performed at two company sites. When a quantitative approach, based either on specific or analogous data, was not possible, a qualitative approach using Stoffenmanager Nano was applied.

Compared to other MNOs, relatively much hazard data are available for Nano-$TiO_2$ and Nano-Ag. For both Nano-$TiO_2$ and Nano-Ag, human health hazard data were found on all levels in the above described hierarchy. For Nano-$TiO_2$ either the derived DNEL of 830.000 #/$cm^3$ or the Stoffenmanager Nano hazard band of D is used for risk assessment. Regarding Nano-Ag, the DNEL of 4000 #/$cm^3$ or the Stoffenmanager Nano hazard band D is used.

It must be noted that the derived DNELs are based on currently available toxicity data. The authors of the publication (Christensen *et al*. 2010) state that these DNELs should not be used for regulatory purposes as the toxicity information is actually insufficient; there is still a lack of scientific consensus on how to obtain good quality hazard data and how to interpret the obtained data correctly. As a consequence the data are accompanied by high levels of uncertainty. Hence, one should always keep in mind which threshold value is used and which uncertainties are thereby introduced.

Worker exposure datasets are very scarce for scenarios from the paint supply chain and in most cases little or no contextual information is given. Besides that, information is often lacking about the type of data presented (e.g. AM, GM, 90-percentile, maximum). A harmonized measurement strategy, taking into account the difficulties related to activity and background exposure is currently not available, hampering straight forward interpretation of exposure data. Nevertheless, a relatively large number of exposure datasets is found for the stage of ‘manufacturing of MNO’ of differing quality. Only very few datasets are found for the stage of ‘production of paint’, ‘application of paint’ and ‘service life’ and the quality of the data is often disputable. In general, more data are found for Nano-$TiO_2$ compared to Nano-Ag. In all cases occupational exposure data on MNOs are, like hazard data, accompanied by many uncertainties.

Where more than one exposure data set was available for a process step, a worst case dataset has been selected based on defined criteria to be used for risk assessment to account for the precautionary principle.

For this risk assessment, quantitative exposure data are compared to corresponding DNELs, whereas exposure bands are combined with hazard bands to derive a risk (priority) band. A prerequisite for such a comparison is the similarity between the MNOs encountered at the workplace and the MNO used to obtain the toxicity data and threshold value. In this study it is known that hazard and exposure data concern Nano-$TiO_2$ and Nano-Ag respectively, however, the MNO are not thoroughly enough characterized to ascertain that the MNO used for hazard and exposure assessment are in fact identical substances. This is an important factor of uncertainty in the final risk assessment.

In the risk assessment, process steps are indicated with risk depending on the comparison between hazard and exposure values. Due to the high uncertainties in hazard, exposure and risk assessment, no conclusions on health risks or control of health risks can be drawn from this risk assessment. However, if the exposure value exceeds the threshold value, the process step can be prioritized for control measures.

When comparing quantitative task based exposure values to threshold values, the following process steps are prioritized: manufacturing and cleaning in the manufacturing stage of Nano-Ag and loading and waste treatment in the paint production stage of Nano-$TiO_2$. This indicates that a risk is expected from performing only these tasks for the whole working day. When compensating for task durations and assuming that the task is the only task performed with the nanomaterial during the day, none of these tasks exceeds the DNELs any longer. In reality however, a worker will perform several tasks with certain duration consecutively during the day. As a consequence of the different methods used (qualitatively vs. quantitatively) it was not possible to calculate the realistic exposure resulting from the combination of tasks.

Using Stoffenmanager Nano, additional tasks are prioritized for control measures: bagging during the manufacturing of Nano-Ag and waste treatment in both the manufacturing stage of Nano-$TiO_2$ and Nano-Ag. The task of storage, loading and waste treatment are prioritized during the paint production stage of Nano-Ag. Although not prioritized, it is worthwhile mentioning that also other process steps leave room for improvement. It should be noted however that this risk banding tool is still under development and therefore can only be used as indicative.

Given the current knowledge, no additional risk of exposure to the nano particles caused by fracturing/abrasion of surfaces treated with nanocoatings is assumed. The current hypothesis is that the nano particles are embedded in the solid matrix and nano particles are not released as “free” primary particles. However, this hypothesis is uncertain and future research will further clarify this.

Due to the high uncertainty in the risk assessment performed, it is advised to persist on the precautionary principle (minimization of exposure) until more data are available. Besides that, it is recommended to gather more data in practice in order to fill in the gaps in current knowledge on hazard of, and exposure to MNOs used in the paint supply chain. Acquiring knowledge on hazard of and exposure to MNOs in the paint supply chain enables a reliable and representative occupational risk assessment in the future.

*Environmental risk assessment*

Central in the debate on the use of nanomaterials and nanoproducts is the environmetal fate of these materials and their possible adverse effects on the environment. The two cases (1) a Nano-$TiO_2$ containing paint and (2) a Nano-Ag containing paint are used to sketch qualitatively what is currently known on the life cycle of these nano particles used in paints, their emissions from the “paint-chain” to the environment and their possible environmental fate, addressing the mass flow of these MNOs, their predicted environmental concentrations and toxicity, their environmental behavior and fate and the relative contribution of paints to the total emission of these MNOs predicted.

Analysis of the available environmental data on Nano-$TiO_2$ and Nano-Ag does show that both these MNOs may cause adverse effects to environmental organisms. However, the sincerity of these effects has been observed to strongly depend on the actual environmental conditions and large gaps remain with respect to a more thorough understanding on the behavior, fate and toxicity profile of these MNOs. Risk quotients (PEC/PNEC; predicted environmental concentration/predicted no effect concentration) derived in scientific literature and first environmental abundance studies nevertheless do suggest that there might indeed be reason of concern regarding the possible environmental concentrations of both Nano-$TiO_2$ and Nano-Ag that deserves further attention.

To date, there are no studies describing MNO emissions per phase in the life cycle of a paint system. Combination of the data available for the different life phases however do suggest that for Nano-$TiO_2$ emissions may be of the same order of magnitude during manufacturing, paint production, application, service life and the end-of-life phase but depends strongly on the actual handling of the individual worker. For Nano-Ag, the service-life appears the prominent phase for emissions to the environment. Because of the high uncertainty on the actual uses and market volumes of products containing Nano-$TiO_2$ or Nano-Ag one can only speculate about the relative contribution of paints to the total emission of these MNO to the environment. The preliminary data available suggest that for Nano-$TiO_2$, about 4% of all Nano-$TiO_2$ produced may enter the water environment as a consequence of its use in paints, which is about 9% of all Nano-$TiO_2$ emissions to water. The major fraction of Nano-$TiO_2$ emitted to water is suggested to originate from its use in cosmetics. For Nano-Ag, the relative contribution by paints to the total silver emission from Nano-Ag containing products seems higher than for Nano-$TiO_2$ as a consequence of dissolution from the paint matrix during the paint’s functional life. However, this derivation is based on one model only, aimed at following a worst case approach, but focused on the Swiss situation and not on the Dutch one.

Acknowledging the high uncertainties and many unknowns on the environmental abundance, behavior, fate and toxicity of Nano-$TiO_2$ and Nano-Ag, the available data do show the urgency to take precautionary measures preventing emission of these MNO, but provide no hard proof for a direct environmental concern.

However, despite the current lack of a complete toxicity profile, for Nano-Ag there is another reason to motivate not to use Nano-Ag in paints but safe it for very specific applications. One of the most essential applications of Nano-Ag used to be, and still is, for medical treatment of highly sensitive wounds, bacterial infections or as a disinfectant for bacterial strains that are very persistent and/or have become resistant towards other antibiotics. However, despite this valuable application, abundant use may contribute to the development of bacterial resistance to silver.

Various studies do point this out and moreover indicate that once developed, this resistance is in principle transferable to other bacterial strains as well. In this light, the current development of “silver-products” (e.g. food packaging, consumer products, sports gear, clothing, washing machines, silver coated kitchen surfaces, silver coated walls) should be considered carefully.

*Pilot companies*

This project aimed at measuring occupational exposure at 8 pilot company sites. It turned out to be rather difficult to identify pilot companies and obtain cooperation. Encouraged barriers were inventoried and reported.

The main barrier identified is the low transparency; there is little knowledge about nanomaterials (what are nanomaterials?) amongst employers, employees and HSE management. It is often unknown whether or not paints contain nano-materials. In addition, it is almost never known whether or not coated objects to be repaired contain nanomaterials. This situation is caused by a relatively small information stream down the supply chain, but also enhanced by the negative image of nanomaterials and the highly confidential character of the new products.

Practical barriers lay in the fact that a relatively low number of Dutch companies work with nanoproducts and the frequency of these activities appear to be incidental.

It is advised to try to enlarge the transparency around nanomaterials and intensify the communication on exposure to and dispersion of nanomaterials and their comprising potential risks along the paint supply chain.

# 3 Samenvatting

Het Ministerie van Infrastructuur en Milieu (I&M) en de branche organisatie van verf- en drukinkt fabrikanten (VVVF) hebben het initiatief genomen om de beschikbare gegevens op het gebied van gevaar, blootstelling en risico voor de verfketen te inventariseren en de hiaten in kennis te signaleren. Dit pilot project is bedoeld om de communicatie over potentiele risico's voor werkers en milieu ten gevolge van het gebruik van MNOs (manufactured NanoObjects) binnen de verfketen te verbeteren.

Het project richt zich op Nano-$TiO_2$ en Nano-Ag. Deze nanodeeltjes worden geproduceerd en vervolgens verwerkt in coatings. De potentiele risico's die hierdoor ontstaan voor mens en milieu zijn beoordeeld op basis van beschikbare gegevens voor alle fasen uit de verfketen: productie van de MNO, productie van verf, applicatie van verf, en de levensduur van gecoate objecten.

*Belangrijkste conclusies:*
Zowel voor werker risicobeoordelingen als voor milieu risicobeoordelingen zijn data van goede kwaliteit schaars. Daarnaast is de discussie omtrent de methoden die moeten worden toegepast om goede risicobeoordelingen uit te voeren nog in volle gang.

Ondanks de grote onzekerheden in data en methoden, zijn zowel voor werker als voor milieu risicobeoordelingen uitgevoerd gebaseerd op de best beschikbare gegevens. Kwantitatieve blootstellingsdata zijn zeer beperkt voorhanden. Hierdoor kon slechts voor enkele processtappen een kwantitatieve risicobeoordeling worden uitgevoerd. Voor de resterende processtappen is een kwalitatieve risicobeoordeling uitgevoerd met een methode (Stoffenmanager-Nano) met een laag onderscheidend vermogen; er wordt momenteel nog aan de methode gewerkt om het onderscheidend vermogen te vergroten.
De resultaten laten zien dat er processtappen zijn waarbij de blootstelling tot een niveau kan komen dat rond of boven de afgeleide grenswaarde ligt. Vanwege het feit dat de risicobeoordelingen slechts op best beschikbare data is uitgevoerd, wordt geadviseerd voor alle processtappen het voorzorgsprincipe te hanteren door de blootstelling te minimaliseren.

Ook de milieu risicobeoordeling is gebaseerd op best beschikbare gegevens gecombineerd met aannames. Uit de berekende indicatieve risico quotiënten (PEC/NEC ratio's), komt naar voren dat er reden tot zorg zou kunnen zijn en dus reden om voorzorgsmaatregelen te treffen. Er wordt op basis van de gebruikte gegevens echter geen hard bewijs geleverd dat er echt sprake is van milieurisico's.

Er is getracht aanvullende blootstellingsdata voor werkers te genereren. Dit is deels gelukt, maar het vinden van pilot bedrijven bleek echter moeilijk. Het feit dat het voor bedrijven vaak onduidelijk is of ze met nanomaterialen werken lijkt hiervoor een belangrijke reden te zijn. Daarnaast is de (keten)communicatie over nanomaterialen en hun veronderstelde risico's momenteel marginaal. Het wordt daarom zeer aanbevolen om de transparantie en (keten)communicatie rond nanomaterialen te intensiveren.

*Werker risicobeoordeling*

Er is een risicobeoordeling uitgevoerd voor alle fasen van de levenscyclus van nano-coatings: de productie van de MNOs, productie van de verf, applicatie van de verf en de levensduur van de bewerkte objecten.

De risicobeoordeling is uitgevoerd volgens een getrapte aanpak, waarbij eerst gekeken is of er specifieke kwantitatieve data beschikbaar waren, vervolgens of er analoge data waren en als beide ontbraken is een kwalitatieve beoordeling uitgevoerd. Blootstellingsdata zijn verzameld uit literatuur en bij twee bedrijven is blootstelling gemeten. In principe geldt dat als er specifieke kwantitatieve data voorhanden zijn, er niet verder gekeken hoeft te worden. Omdat dit project echter een inventariserend karakter had, zijn data verzameld voor alle niveaus van de hiërarchie.

Er zijn relatief veel gevaar data beschikbaar voor Nano-$TiO_2$ en Nano-Ag. Voor beide nanodeeltjes zijn op alle niveaus gegevens gevonden. Voor de risicobeoordelingen voor Nano-$TiO_2$ is gebruik gemaakt van de afgeleide DNEL van 830.000 #/$cm^3$ voor de kwantitatieve beoordelingen of van de gevaarsklasse D voor de kwalitatieve beoordelingen. Voor Nano-Ag was de afgeleide DNEL 4000 #/$cm^3$ en is ook de gevaarsklasse D toegekend.

Blootstellingsdatasets voor werkers zijn niet veel voorhanden voor de verfketen en bovendien mist doorgaans informatie m.b.t. de blootstellingsbepalende determinanten (omstandigheden en toegepaste beheersmaatregelen). Ook wordt vaak niet gegeven welk soort data gepresenteerd wordt (AM, GM, 90-percentiel of maximum). En doordat er momenteel nog geen geharmoniseerde meetstrategie is, verschillen de data zo veel van elkaar dat interpretatie ervan niet eenvoudig is.
Desondanks zijn voor de levenscyclusfase ‘productie van MNO’ redelijk wat data gevonden van wisselende kwaliteit. Slechts enkele datasets waren beschikbaar voor de fase ‘productie van verf’, ‘applicatie van verf’ en ‘levensduur van gecoate objecten’. Over het algemeen zijn meer data gevonden voor Nano-$TiO_2$ dan voor Nano-Ag. Voor alle datasets geldt dat de onzekerheid rond de data vrij groot is.

Voor de risicobeoordeling zijn kwantitatieve blootstellingsdata vergeleken met de DNEL en voor de kwalitatieve risicobeoordeling zijn blootstellingsklassen vergeleken met de gevarenklasse. Een voorwaarde voor een goede risicobeoordeling is dat de blootstellingsmetingen betrekking hebben op hetzelfde deeltje als waar de toxiciteitstesten mee zijn verricht op basis waarvan de DNEL is afgeleid. In deze studie is wel bekend dat zowel het gevaar als de blootstelling is beoordeeld voor Nano-$TiO_2$ en Nano-Ag, echter het is niet bekend of de deeltjes precies dezelfde karakteristieken hadden (deeltjesgrootte, vorm, coating of functionalisering). Dit is een van de voornaamste onzekerheden in de risicobeoordeling.

Indien de blootstelling voor processtappen boven de DNEL werd ingeschat, is de processtap geprioriteerd voor beheersing. Doordat de risicobeoordeling is uitgevoerd met best beschikbare gegevens (en daarmee gepaard gaan met onzekerheden) kan op basis van de risicobeoordeling echter niet met zekerheid worden gesteld dat risico’s voldoende zijn beheerst.

De volgende processtappen zijn geprioriteerd op basis van kwantitatieve risicobeoordeling: productie en schoonmaakwerkzaamheden in de levenscyclus fase ‘productie van Nano-Ag’ en storten en afvalverwerking in de levenscyclusfase ‘productie van Nano-$TiO_2$ . Hierbij is ervan uitgegaan dat een werker deze taken de hele dag uitvoert. Indien gecompenseerd wordt voor de taakduur en aangenomen wordt dat de werker geen andere taken uitvoert met de MNO, dan komt de blootstelling van deze taken niet boven de DNEL uit. In werkelijkheid zullen werkers combinaties van taken achter elkaar uitvoeren. Doordat niet voor alle taken een kwantitatieve risicobeoordeling kon worden uitgevoerd is het echter niet mogelijk om voor deze combinaties van taken aan te geven of de blootstelling boven de DNEL uit komt of niet.

Uit de kwalitatieve risicobeoordeling worden de volgende processtappen geprioriteerd: Afzakken en afvalverwerking in de levenscyclusfase ‘productie van Nano-Ag’ en afvalverwerking in de levenscyclusfase ‘productie van Nano-$TiO_2$’. Daarnaast opslag, storten en afvalverwerking in de levenscyclusfase ‘productie van Nano-Ag houdende verf’. Het verdient vermelding dat, hoewel niet geprioriteerd, andere processtappen ook ruimte voor verbetering laten zien.

Op basis van de bestaande kennis wordt geen additioneel risico verwacht ten opzicht van niet-nanocoatings voor de zogenaamde verspanende werkzaamheden (o.a. schuren). De huidige mening is dat de nanodeeltjes ingekapseld zijn in een matrix en dat er geen vrije nanodeeltjes ontstaan. Dit is echter niet bewezen en verder onderzoek moet uitsluitsel geven.

Er wordt geadviseerd het voorzorgsprincipe (minimalisatie van blootstelling) toe te passen tot er meer data van betere kwaliteit beschikbaar komen. Daarnaast wordt geadviseerd specifieke data te genereren om de hiaten in kennis te kunnen vullen. Kennis vergaren op het gebied van zowel het gevaar van deeltjes als de blootstelling aan deeltjes kan het in de toekomst mogelijk maken betrouwbare en representatieve werker risicobeoordelingen uit te voeren.

*Milieu risicobeoordeling*
Centraal in het debat rond het gebruik van nanomaterialen en nanoproducten staat het lot (fate) van de deeltjes in het milieu en hun mogelijke effecten op het milieu. The twee cases, verf met Nano-$TiO_2$ en verf met Nano-Ag, zijn gebruikt om kwalitatief te demonstreren wat momenteel bekend is m.b.t. de levenscyclus van dit type verf, de emissie van de nanodeeltjes uit de verfketen naar het milieu en hun mogelijke lot in het milieu. Hierbij worden de massastroom van deze MNOs, hun voorspelde milieu concentraties (PEC), hun gedrag en lot in het milieu en de relatieve bijdrage van verven op de totale emissie van deze MNOs geschat.

Analyse van de beschikbare data laat zien dat beide MNOs nadelige effecten kunnen hebben op milieu organismen. Echter, de ernst van deze effecten hangt af van actuele milieucondities en er zijn grote hiaten in kennis op het gebied van gedrag, lot en toxiciteit van de MNO resulterend in grote onzekerheid omtrent de uitkomsten van de analyse. Risico quotiënten (PEC/NEC; predicted environmental concentration/predicted no effect concentration) gebaseerd op de best beschikbare data bevestigen dat er sprake kan zijn van zorg omtrent de mogelijke milieuconcentratie van beide MNOs, Nano-$TiO_2$ en Nano-Ag.

Er zijn momenteel geen studies beschikbaar waarin emissies per levenscyclus fase worden beschreven. Combinatie van beschikbare data voor de verschillende fasen laten zien dat de emissie van Nano-$TiO_2$ ongeveer vergelijkbaar is voor de fasen 'productie van MNO', 'productie van verf', 'applicatie van verf', 'levensduur van behandeld object' en 'afvalfase', maar ook dat deze erg afhankelijk is van de wijze van werken van individuele werkers. Voor Nano-Ag lijkt de levensduur van behandelde objecten vooral van belang. Gezien de onzekerheden in de gebruikte data, kan slechts een schatting worden gegeven m.b.t. de relatieve bijdragen van verf aan de totale emissie van deze MNOs naar het milieu. Op basis van de beschikbare data wordt geschat dat ongeveer 4% van alle geproduceerde Nano-$TiO_2$ in het waterig milieu terecht komt via verf. Dit is ongeveer 9% van alle Nano-$TiO_2$ die naar het water geëmitteerd wordt. Het grootste deel van de emissie van Nano-$TiO_2$ naar water lijkt van cosmetica te komen. Voor Nano-Ag lijkt de relatieve bijdrage aan de emissie naar water hoger te zijn dan voor Nano-$TiO_2$, doordat het uit de matrix lijkt te lekken in de levensduur fase van gecoate objecten. Deze conclusies zijn echter gebaseerd op slechts één model waarmee een worst case situatie in Zwitserland is berekend en het is maar de vraag in hoeverre dat ook representatief is voor Nederland.

Alle onzekerheden en aannames in ogenschouw nemende, laten deze data zien dat er reden is om voorzorgsmaatregelen te treffen, maar ze leveren echter geen hard bewijs dat er reden is tot zorg.

Ondanks het gebrek aan goede data en daarmee het ontbreken van een goed toxiciteitsprofiel, is er voor Nano-Ag nog een extra reden om voorzichtig te zijn met emissies naar het milieu. Nano-Ag wordt toegepast als antibioticum in delicate gevallen en tegen bacteriestammen die resistent zijn tegen andere antibiotica. Brede toepassing van nano-Ag en de daarmee gepaard gaande emissie naar het milieu kan ervoor zorgen dat deze bacteria ook resistent worden tegen Nano-Ag. Studies hebben aangetoond dat eenmaal ontwikkeld deze resistentie ook overgenomen kan worden door andere bacteria. Het is daarom belangrijk goed na te denken over het belang van Nano-Ag in potentiële toepassingen.

*Pilot bedrijven*

Eén van de doelen van dit project was het uitvoeren van blootstellingsmetingen bij 8 bedrijven. Het is echter moeizaam gebleken pilot bedrijven te vinden. Gesignaleerde knelpunten zijn gerapporteerd.

Het belangrijkste knelpunt ligt in de transparantie rond nanodeeltjes. Er is relatief weinig kennis rond nanomaterialen bij werkgevers, werknemers en arbo- en milieumedewerkers. Bedrijven weten niet altijd of ze met nanoproducten werken; het is vrijwel nooit bekend of een eerder aangebrachte coating nanodeeltjes bevat of niet. Deze situatie is een gevolg van het feit dat er zeer beperkt informatie en kennis langs de productketen verspreid wordt. Daarnaast heeft 'nano' momenteel een vrij negatief imago en willen bedrijven liever niet als 'nano'-bedrijf te boek staan. Om dit compleet te maken zijn bedrijven ook nog eens zeer terughoudend in het communiceren over hun nanoproducten door het innovatieve karakter ervan.

Praktische knelpunten worden gevormd door het feit dat maar weinig bedrijven in Nederland nanodeeltjes gebruiken en dat de werkzaamheden een incidenteel karakter kennen.

Het wordt geadviseerd om de transparantie rond nanomaterialen te vergroten en de communicatie rond blootstelling en verspreiding van nanomaterialen, en de potentiele risico's die daardoor ontstaan voor werker en milieu, te intensiveren.

# 4 Life cycle and process descriptions of Nano-$TiO_2$ and Nano-Ag in the paint industry

## 4.1 Introduction

This section describes the product chain of Nano-$TiO_2$ and Nano-Ag containing coatings. It explains the different life cycle stages and describes process steps with respect to possible deviations of work activities or exposure control measures from “common practice” related to the manufacturing of Nano-$TiO_2$ and Nano-Ag, the production of industrial and automotive paints and the application of these paints by professional end-users have been reviewed.

The life cycle of Nano-$TiO_2$ and Nano-Ag coatings consists of the following stages: manufacturing of Nano-$TiO_2$ and Nano-Ag, production of paint/coating using Nano-$TiO_2$ and Nano-Ag, application of paint/coating and service life of treated objects or surfaces. Waste phases are considered as part of these stages.

## 4.2 Manufacturing of Nano-$TiO_2$

Nano-$TiO_2$ is being manufactured by a large diversity of manufacturing processes (Robichaud *et al.* 2009) such as an undisclosed plasma process, physical vapor synthesis, laser pyrolysis, mechanical milling, a sol-gel process (Yun *et al.* 2008) or a hydrochloride process combined with spray hydrolysis, calcinations, milling and surface coating (described in detail by Verhulst *et al*. 2003). Alternatively Nano-$TiO_2$ is being produced via wet chemistry which include the sol–gel process.

$TiO_2$ as a nanomaterial (ultrafine $TiO_2$) is engineered to have primary particles less than 100 nm in order to optimize properties for non-pigmentary applications e.g. catalyst supports (De-$NO_X$ stationary and automotive), UV-absorbers (Cosmetics) and photo-catalysts. Due to their smaller size nano particle-containing products can be made transparent. Pigment grade $TiO_2$ on the other hand is manufactured to optimize the scattering of visible light and the consequently white opacity. This requires a primary particle size of approximately half the wavelength of the light to be scattered, which is half of 400 - 700nm for visible light.

In order to obtain better insight in the dominant routes and practices for the manufacturing of Nano-$TiO_2$ in Europe, the TDMA (Titanium Dioxide Manufacturers Association) was consulted for more information on:

1. Manufacturing processes
2. Manufacturing volumes

### 4.2.1 *Manufacturing processes*

The chloride process accounts for a majority of pigment grade $TiO_2$ manufactured globally and within the U.S. the chloride process is preferred over the sulfate process (the second most common process) due to economic and environmental concerns. Large volume manufacturing of Nano-$TiO_2$ also takes place via the chloride (Pyrogenic) or the sulphate process (Klaessig, 2010). A third process, the sol-gel process, is used to manufacture exclusively Nano-$TiO_2$, and has been described in particular for the manufacturing of amorphous Nano-$TiO_2$. Since this process is only applied at small scale, it has not further been described here. The sol-gel process is only applied All these processes are reviewed in more detail by US EPA. In the chloride process the following process steps are defined:

- Ti-ore converted to volatile $TiCl_4$;
- $TiCl_4$ vaporized in an oxygen rich environment;
- $TiO_2$ particles captured from gas stream;
- Post treatment by fluid-bed or slurry system.

In their response, the TDMA states that "*common precursors for the manufacturing of ultrafine* $TiO_2$ *are intermediates of the pigmentary production process e.g. titanium tetrachloride – mainly converted to titanium oxychloride (chloride technology) - and titanium oxysulfate and titanium oxyhydrate (sulfate technology). These intermediates are further processed by precipitation, thermal hydrolysis or flame hydrolysis. Secondary steps are milling, coating and then milling again. It is unknown to what extent organometallic precursors like Titanium alcoholates are used in an industrial scale. Nearly all of these processes are proprietary knowledge and patent protected and not commercially available.*"

According to US EPA the chloride process is a fully closed process, up to the point where the end product (Nano-$TiO_2$) is being bagged or cans are filled.

The process step of manufacturing using the sulphate process is also fully closed and contains the following reaction steps:

- Ti-ore dissolved in sulphuric acid;
- Precipitation of methatitanic acid ($TiO_2.0.7H_2$);
- Filtering methatitanic acid, calcinating and milling;
- Post treatment in slurry system.

### 4.2.2 *Manufacturing volumes*

The TDMA anticipates that in 2011 the European manufacturing of pigmentary $TiO_2$ will exceed 1.000.000 tons per year (t/y). In 2007, the European manufacturing of $TiO_2$ accounted for 37% of the world-wide $TiO_2$ market. At present there are no statistics available on the manufacturing volume of Nano-$TiO_2$, however the TDMA estimates that the manufacturing of ultrafine $TiO_2$ equates to about 1% of the pigmentary production level (which then is ca. 10.000 tons). Major applications of this ultrafine $TiO_2$ are found as catalyst supports in various materials and in cosmetic applications (especially sunscreens). Consequently the amount of ultrafine $TiO_2$ used in coating applications e.g. as a UV absorber in wood coatings will only be a small proportion of this 1%, the TDMA estimate is only 100 to 200 t/y for these applications.

## 4.3 Manufacturing of Nano-Ag

Nano-Ag is being manufactured via wet chemistry (sol–gel process, Park and Kim 2008). The different manufacturing steps and corresponding occupational exposures to Nano-Ag were studied in detail by Park *et al.* (2009) for a large manufacturing facility in Korea. Manufacturing takes place in four steps:

1. A batch reaction process, based on wet chemical methods;
2. Filtering of the reaction product;
3. Drying of the reaction product;
4. Grinding of the reaction product.

In the batch reactor coarse silver is synthesized by the liquid-phase reaction of silver nitrate ($AgNO_3$) with nitric acid. A colloidal suspension of silver is produced by the reduction of $AgNO_3$ in the presence of a dispersing agent. A vent hood is installed approximately 1 m above the reactor. The Ag colloidal suspension is then transferred (probably open transfer) via an outlet from the reactor to a filtering device. Filtering and drying of the colloid suspension in a dryer (to remove volatile organic materials and water) generate the Ag nano particles. These are further grinded (probably open transfer) and packaged.

A positive exposure to nano particles could be detected during:

1. Opening of the Hatch of the Reactor;
2. Opening of the door of the Dryer;
3. Opening of the Hatch of the Grinder.

## 4.4 Production of paint using Nano-$TiO_2$ or Nano-Ag

Within the context of the REACH regulation CEPE has made an overview of the manufacturing and uses of paints and inks. Typically, traditional paint and ink manufacturing takes place in batch processes. Types, volumes, frequencies and manufacturing or application sites may differ though the general outline of the processes can be summarized in the two generic flow diagrams below.

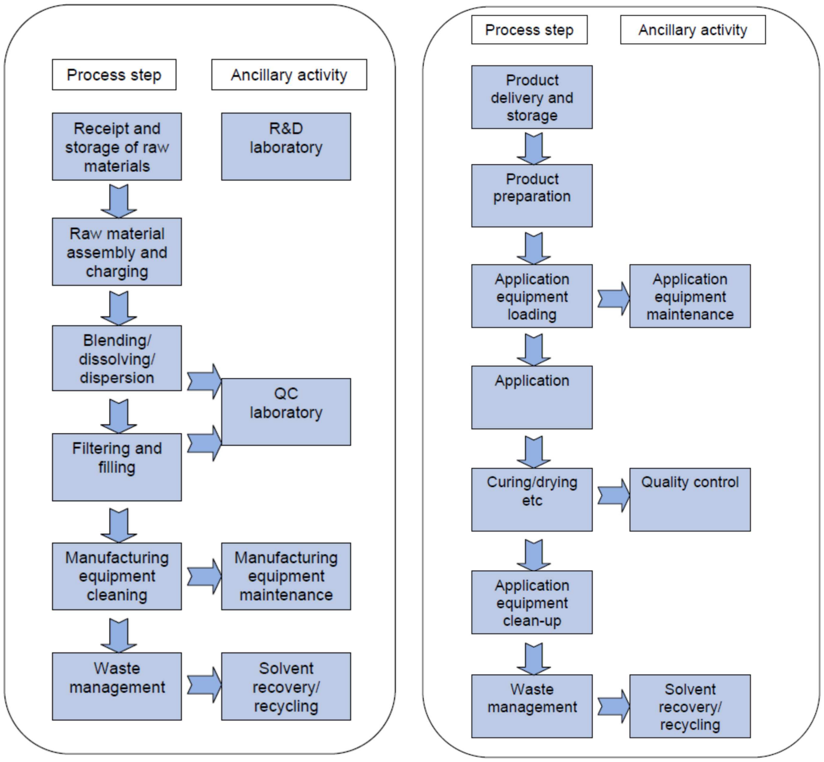

Figure 4.1 Schematic flow diagram of the production (left) and the application (right) of paints and inks. Source: Reach, Descriptors of use, coatings and inks manufacture and application

A more detailed description of each individual step in the process can be found in a report from the CEPE BAT-group (2001).

Compared to “traditional” paints and inks, the large difference for the production and application of Nano-$TiO_2$ and Nano-Ag paints is the frequency and volume of the batches. Because of the fact that these nanoproducts are still niche market, frequencies of batch preparation range typically between 1 – 10 times a year, producing smaller volumes than is normal for traditional paints.

Production of a nanopaint may take place in the “traditional” production line. However, because of the often small scale production, it may also be that the production of the nanopaint is organized on an “R&D” production test-line. In both situations, the production line may not be specifically equipped to manage possible exposures to MNOs.

In Annex 1, some examples describe in more detail where production of nanopaints may differ from the conventional production of (non-nano) paints. These examples are obtained from the workplace visits and occupational exposure measurements undertaken in the context of this project.

## 4.5 Application of paints containing Nano-$TiO_2$ or Nano-Ag

The Application of Nano-$TiO_2$ and Nano-Ag industrial and automotive paints typically occurs in a similar fashion with similar gears and similar protective measures as the application of standard non-MNO paints. A select group of end-users that are aware of the uncertainty around possible adverse occupational health effects do use specific protective clothing (non-woven plastic fabric, nytril gloves), respiration mask (equipped with a P3 or HEPA filter) and local exhaust ventilation (also equipped with a HEPA filter). However, depending on the paint characteristics the actual activities are slightly adjusted, for example to anticipate on a changed paint viscosity. This especially applies to the automotive sector but is again no different from normal practice.

## 4.6 Service life of articles with Nano-$TiO_2$ and Nano-Ag

Service and maintenance of Nano-$TiO_2$ and Nano-Ag paints in the sense of abrading, flexing or otherwise restoring the surface is expected to be similar to traditional non-MNO painted surfaces. However, it should be noted here that MNOs are typically applied to the paint to adjust the surface properties of the paint system, for example to enhance scratch resistance, introduce a hydrophobic effect or add anti-bacterial or self-cleaning properties. In case of an extra strong surface one may expect abrasion to become a much more elaborative process. In many paint applications MNOs are claimed to reduce the service and maintenance normally required. Potential moments at which occupational exposure to MNOs may occur are those where:

- dust or aerosols of MNO are being generated (fracturing, abrasion, sanding, abrading, sawing);

No specific protective measures are being described for use.

## 4.7 Life cycle and process steps of Nano-TiO2 and Nano-Ag in the paint industry

The information described in this chapter is used to build the following life cycle and corresponding process steps of Nano-$TiO_2$ and Nano-Ag use in the paint industry.

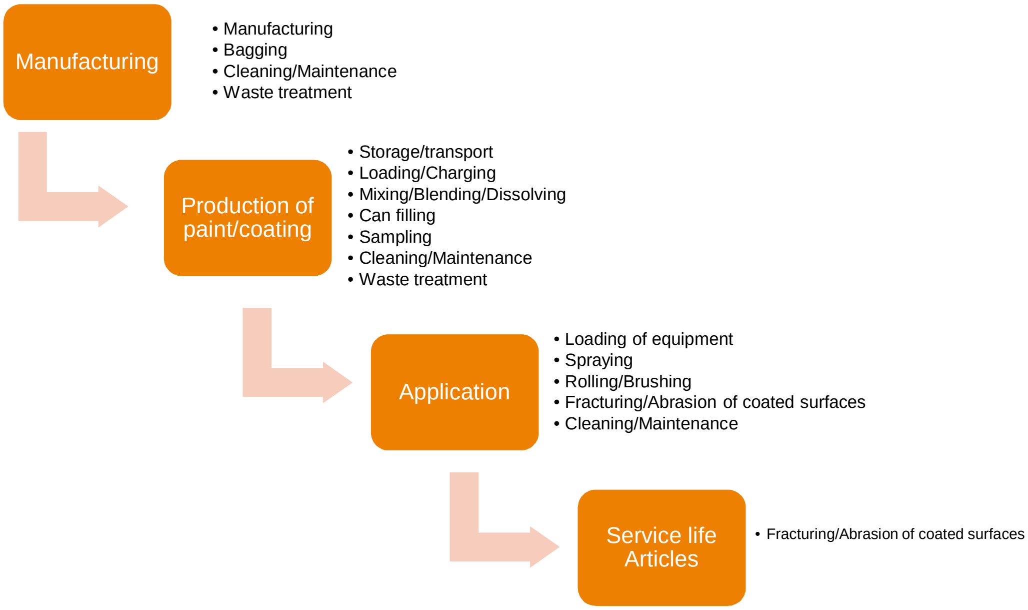

Fig. 4.2 Life cycle and process steps of Nano-$TiO_2$ and Nano-Ag in the paint industry.

# 5 Risk assessment framework

## 5.1 Human Risk Assessment framework

This framework focuses on the inhalation exposure route only as the inhalation route is anticipated to be the most relevant route of exposure to MNOs.
A risk assessment of workers exposed to MNOs combines the potential hazard of the MNO with the likelihood of exposure to the MNO. Currently, a tiered approach is proposed for the risk assessment of MNOs.
Traditionally, most value has been attributed to risk assessment based MNO-specific data. Since specific (quantitative) data on both hazard and exposure is currently lacking for most MNOs, data obtained with analogous MNOs can serve as starting point. When a quantitative approach, based either on specific or analogous data, is not possible, qualitative approaches such as control banding strategies can be considered. This tiered risk assessment approach is represented in the following figure, and will be explained in the next sections.

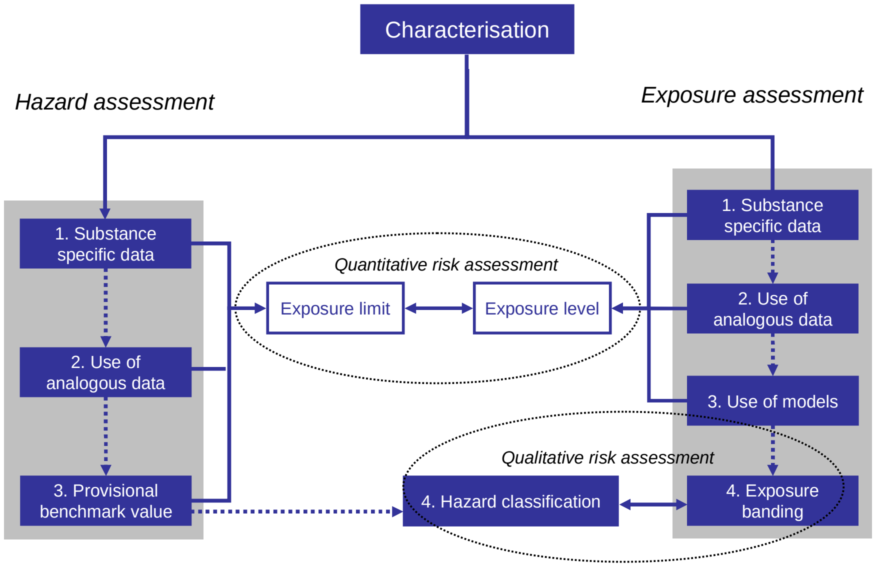

Fig.5.1 Tiered approach for the risk assessment of MNOs.

### 5.1.1 *Characterization of MNOs present in paint*

Before the specific risk of MNOs in paints can be assessed, it should be determined whether in fact MNOs are present in paints used in the supply chain.
At the start of the project, no univocal definition of an MNO was available and the definition as proposed by Van Duuren *et al*. (2010) was used:

- The particle should be intentionally produced or manufactured;
- Primary particle size should be smaller than 100 nm, and / or the specific surface area should be larger than 60 $m^2/g$ (SCENIHR, 2010);
- Manufactured nano objects may be present as single objects, but may also be present as agglomerates/aggregates.

On 18 October 2011 the European Commission adopted the Recommendation on the definition of a nanomaterial. According to this Recommendation a "Nanomaterial" means: A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm.

Both definitions are not contradictory but differ at some points. The definition of van Duuren *et al.* (2010) focuses on manufactured particles whereas the European Commission includes natural and incidental particles as well. Besides that, the European Commission introduces criteria on the size distribution of the particles. This criterion was not explicitly used by van Duuren *et al.* (2010); however all nano particles included in the definition by van Duuren are also included in the recommendation by the European Commision.

A proper physico-chemical characterisation is critical for a specific risk assessment of MNOs used in paints. Relevant characteristics of MNOs include the chemical composition, shape, primary particle size, solubility, surface area, mass density and crystallinity. Information on this characteristics can be provided by the manufacturer, product information and/or MSDS sheets. However, little information on those characteristics is dispersed into the supply chain in practice.
First, information on physico-chemical properties is needed to determine the level of similarity between MNOs described in literature and MNOs that might be present in paints. This similarity partially determines the uncertainty associated with the use of the data. Secondly, certain physico-chemical properties directly affect the biological behaviour of MNOs after exposure and are therefore highly relevant for the hazard assessment when no specific hazard data are available. It should be noted that physico-chemical characteristics are dependent on the situation in which they are measured. Normally, the characteristics reported are related to the MNOs as they are produced, as these characteristics are usually not available in later stages (*e.g.* during exposure conditions).

### 5.1.2 *Hazard Assessment*

#### *5.1.2.1 Use of specific data for hazard assessment*

Hazard characterization should preferably be based on MNO specific (*in vivo*) data. Traditionally, a recommended exposure level (*e.g.* a health-based recommended occupational exposure limit, derived no-effect level) is derived from a no observed adverse effect level (NOAEL) obtained in a repeated dose (inhalation) toxicity study. For risk assessment, additional assessment factors (AF) are applied to take into account factors such as differences between species and exposure conditions (*e.g.* exposure duration). Hazard characterization based on specific data provides a (close to) substance-specific threshold value for adverse effects based on what is currently in the accepted approach by authorities for the derivation of human threshold values for conventional substances.

#### *5.1.2.2 Use of analogous data for hazard assessment*

Alternatively, hazard data of related particles can be used to derive a recommended exposure limit (*i.e.* use of analogous; read-across). This can be MNOs which are structurally and chemically comparable with the MNO in question, but also the bulk form of a MNO. Again, a recommended exposure level can be derived. For risk assessment, additional assessment factors can be introduced to take into account differences in biological behavior between particles. However, no standardized and accepted method is available to date. Mechanistic data, for instance from *in vitro* assays, can be used to substantiate read-across. Hazard characterization based on analogous data provides a threshold value for adverse effects based on (repeated dose) in vivo toxicity data, which is traditionally preferred for risk assessment. However, additional data are required to substantiate the use of alternative data (e.g. physico-chemical similarity, mode of action), which are currently lacking.

#### *5.1.2.3 Use of benchmark values*

When no hazard data are available, but exposure levels are known, benchmark values can be used to limit exposure to MNOs. Benchmark values however, are not health-based and therefore do not provide information on hazard.

Benchmark values can be used to prioritize exposure situations for MNOs for which no specific hazard data are available. In a report by the RIVM (2010), several benchmark values have been proposed for different types of MNOs. With the exclusion of nanofibers and soluble MNOs, benchmark values are attributed based on mass density. A reference value of 40,000 particles/cm$^3$ is specified for biopersistent granular nanomaterials with a primary particle size range of 1-100 nm and a mass density of < 6000 kg/m$^3$. This category includes metal oxides such as Nano-$TiO_2$. For biopersistent granular nanomaterials with a primary particle size range of 1-100 nm and a mass density of > 6000 kg/m$^3$, a reference value of 20,000 particles/cm$^3$ is specified. This category includes metals such as Nano-Ag.

#### *5.1.2.4 Control banding for hazard prioritisation*

When hazard data and analogous data are absent and benchmark values do not suffice, qualitative approaches can be applied to characterize hazard. Hazard banding strategies have been described by Stoffenmanager Nano (van Duuren *et al.*, 2011) and in ‘Handleiding veilig werken met nanomaterialen en –producten’ (Cornelissen *et al*. 2010). In general, both distinguish high and low hazard categories for nanofibers and soluble MNOs, respectively. In addition, Stoffenmanager Nano attributes the remaining MNOs in different hazard bands based on the classification and labelling of the parent materials (in the absence of nanospecific hazard data).

### 5.1.3 *Worker exposure assessment*

Apart from the hazardous properties of an MNO, the potential human health risk is related to the exposure to an MNO.
Worker exposure is determined by a high variety of factors including characteristics of the MNO, technical conditions of the work process, the type of equipment used, risk management measures available, housekeeping practices etc.
Hence, the assessment of workers exposed to MNOs in the paint supply chain requires a structured way of mapping information on all these factors.

#### *5.1.3.1 Life Cycle*

The first step of an exposure assessment of workers exposed to MNOs in the paint supply chain is setting the scope of the assessment. This scope can be visualised by a life cycle considering all stages of the MNO in the paint supply chain (e.g. manufacturing of the MNO, production of paint/coating using the MNO, application of paint/coating) as is done in chapter 4.

#### *5.1.3.2 Exposure scenarios*

Secondly, the life cycle is translated into different exposure scenarios describing the processes with corresponding operational conditions and risk management measures within each life cycle stage. In order to compose an exposure scenario, contextual information needs to be gathered on determinants that affect worker exposure levels.

#### *5.1.3.3 Use of specific data for exposure assessment*

For the assessment of worker exposure of a certain exposure scenario, the use of a reliable and representative set of occupational hygiene exposure data is preferred. Factors such as the measurement method, the extent and the information on operational conditions and risk management measures determine the reliability and representativeness of the exposure data. Currently, there is no online equipment available that is able to measure the MNO of interest specifically and it is difficult to distinguish the exposure of the activity from the exposure of other background sources. Hence, there is a lack of representative and reliable occupational hygiene data regarding worker exposure to MNOs. The state of the art measurement strategies consist of measurements of activity plus background sources to be corrected by background measurements which are biased either in time or in place.

#### *5.1.3.4 Use of analogous data for exposure assessment*

Alternatively, exposure data of analogue particles can be used to assess the worker exposure in a certain exposure scenario. In general, analogous data are either data based on similar operations, using the same substance or data based on the same operation, but for similar substances. Substances are considered similar if the exposure characteristics (e.g. dustiness) are comparable (REACH Guidance R14). Until now little is known about the exposure characteristics which are the basis for similarity of nanoproducts (e.g. dustiness, moisture content, agglomeration, aggregation). This hampers the identification and selection of analogous nanodata for exposure assessment.

#### *5.1.3.5 Use of quantitative exposure models for exposure assessment*

As an alternative for specific data, quantitative exposure models can be used to estimate worker exposure values due to exposure to a substance in a certain exposure scenario. However, a reliable and representative exposure model is underpinned with occupational hygiene exposure data. Due to a lack of measurement data regarding MNOs, such a model is not available yet.

#### *5.1.3.6 Control banding*

When both exposure data and quantitative exposure models are absent, qualitative approaches can be used to characterize exposure. In the Netherlands, Exposure banding strategies have been described by Stoffenmanager Nano and in ‘Handleiding veilig werken met nanomaterialen en –producten’ and are used to prioritize worker health risks by a qualitative, relative ranking.

### 5.1.4 *Risk characterization*

The risk characterization is the final step of the human risk assessment. Depending on the data available, a quantitative or qualitative risk assessment is performed. It consists of a comparison of the threshold value or hazard band defined by the hazard assessment with the exposure value or exposure band defined by the exposure assessment. In case of a quantitative approach, the risk of the substance is controlled if the estimated exposures for all exposure scenarios are below the threshold value. If exposure exceeds the threshold value, additional risk management measures need to be implemented. In case of a qualitative approach, risk characterization results in a relative ranking of risks in order to prioritize implementation of risk management measures.

## 5.2 Strategy for environmental risk assessment

In general, the steps to be taken to assess the environmental risks of Manufactured Nano Objects (MNOs) are very much comparable to traditional chemicals as should be conducted as described in the REACH Guidance on information requirements and chemical safety assessment**.** In practice though, the approach may differ as a consequence of current lack of knowledge on environmental behaviour and fate for MNOs. The environmental risk of MNOs will depend on (a non-exclusive list):

1. exposure (release into the environment): how much of the MNO (per unit of time) enters the environment during the relevant life-cycle stages? Including various forms of emission:
    a. direct emission
    b. emission from dissolution from the embedded material or product
    c. emission from wear/erosion / (bio-)degradation from the embedded material or product
2. form in which the MNO enters the environment:
    a. coarse particle being part of a matrix (covalently bound / electrostatic interaction / physically captured)
    b. primary particle /aggregate /agglomerate
3. environmental fate of the MNO:
    a. aggregation /agglomeration with similar materials or other materials
    b. adsorption on other materials (e.g. sediment)
    c. dissolution of the MNO in case of low soluble substances
    d. wear/erosion / (bio-)degradation of the MNO; i.e. coated MNOs
    e. bioavailability
    f. metabolism
    g. sedimentation / bioaccumulation
    h. transport phenomena trough water, air and soil
4. acute and chronic toxicity of the MNO
5. activity of the MNO as carrier of toxic material

In atmospheric chemistry, many works do study the behaviour and fate of Ultra Fine Particles (UFP), which will provide a first frame for behaviour and fate of MNO as well. For the environmental compartments water and soil though, information on environmental fate mechanisms and pathways is typically lacking for MNOs. With respect to the ecotoxicity, more and more information is becoming available. However, at present, the understanding of the mode of toxic action of MNOs is still limited in relation to their ‘traditional’ counterparts. Therefore, a preliminary environmental risk assessment is proposed here, mainly focusing on points 1 and 2. Points 3, 4 and 5 will be based on what is known from the limited amount of environmental research studies on MNOs and in a more generic manner about the behaviour of the 'traditional' chemicals and particles.

The environmental effect of a MNO will be influenced by points 1, 2 and 3, which together determine the amount of the material that might be bioavailable (the probability of exposure), and points 4 and 5, describing its hazardous nature.

In the absence of commonly agreed "nanospecific" environmental endpoints, the traditional PEC/PNEC ratio (Predicted Environmental Concentration / Predicted No Effect Concentration) will be used to assess the risk that Nano-$TiO_2$ and Nano-Ag may pose to the environment.

The PNEC will be obtained from literature. At present, there is limited information on acute and chronic effects of MNO. Consequently, the PNEC is typically obtained by using a default assessment factor of 1000 for the conversion of the derived NOECs[1] for the MNOs (= NOEC/1000), taking into account the current high uncertainty in the absolute numbers of the NOECs described (Gottschalk *et al.* 2010 and Aschberger *et al*. 2011).

The PEC will be obtained from the sum of all separate emissions of Nano-$TiO_2$ and Nano-Ag from the total value chain of coatings that are "released" into the environment (both intentionally and unintentionally).

### 5.2.1 *Exposure of environmental compartments*

The strategy to get to the data follows the order of decreasing specificity:

1. company specific information
2. branch specific information
3. specific scientific literature
4. literature on related subjects

Ideally, one should attempt to identify all possible emissions (*E*) of MNO at the separate life stages of the MNO in order to quantify emissions and prioritize emission control. The sections below do describe the possible strategies to do so. The emission flows to the different environmental compartments are defined as:

- $E_{air}$ *(= emission flow to air)*
- $E_{water}$ *(= emission flow to water)*
- $E_{soil}$ *(= emission flow to soil/ground)*

These flows can be a consequence of production (*P*), application (*A*) by brush or roller (*BR*) or spray (*S*), use (*U*), service and maintenance (*SM*), waste treatment (solid waste *SW*; liquid water *LW*) or transportation (*T*).

However, it may well be so that there is no information available related to emissions occurring at the various life stages. Then it is not useful to assess each separate chain individually. Instead, an absolute worst-case approach may be assumed "what goes in will come out". In that case the amount of MNO used is the amount of MNO that will be emitted to the environment.

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[1] No Observed Effect Concentrations

#### *5.2.1.1 Manufacturing of MNOs and the production of paint/coating*

Emissions of MNOs to the environment may occur during the manufacturing stage of the material and the production of the paint/coating. Either in the form of direct emissions to air, water and soil or from production of wastes, cleaning of the equipment and service- and maintenance activities. In the ideal situation, each of these emissions should be identified to quantify the total emission of MNOs from the manufacturing of the MNO and production of paint/coating.

In principle all before mentioned elements will be of importance for the assessment of any releases to the environment due to the manufacturing of MNOs and the production of paint/coating. However, under the assumption of indoor manufacturing processes and good housekeeping practices (including removal of waste water and solid waste as specific chemical waste) emission of MNOs through the exhaust ventilation system is likely to be the dominant environmental emission route during manufacturing. The concentration of MNOs in the exhaust gas could be expressed in mass/volume or in particles/volume, and it can be characterized in terms of volatility or dustiness. The removal efficiency of the risk management measures in place at the exhaust line should be indicated on the instrument specifications. Besides the emission to air, it might be so that production losses (sills) of MNO(-coating)-batches are being exposed off as landfill. In those cases this environmental exposure route should be taken into account and may dominate all other routes of exposure during the manufacturing stage of the MNO and nano based coatings.

#### *5.2.1.2 Strategy to determine the emission of MNOs to the environment*

In the ideal situation the Paint producer should keep records of any emission of MNOs (e.g. Nano-$TiO_2$ and Nano-Ag) that may enter the environment (via air, water or solid waste) per unit of end product (i.e. mass or volume of paint produced). The total release of MNOs into the environment from the Paint producer is the sum of the following releases:

- losses upon receiving the raw material
- losses upon internal transportation and storage
- losses (spills) upon adding the raw material to the liquid paint
- losses (spills) upon dosing the final formulation into its final package
- wastes occurring as a consequence of wrong batches
- wastes occurring as a consequence of service and maintenance of the equipment (including ventilation systems)
- wastes occurring as a consequence of “polluted” (used) personal protective measures (including respirator filters)
- wastes occurring as a consequence of cleaning activities of the workplace.

However, when this type of information is not available, a second acceptable approach could be followed, which is treating the manufacturing plant as a black box and determine the following:

1. mass of MNO that goes into the plant per volume or mass of end product
2. average percentage of MNO in the end product (mass percentage)
3. percentage product wastes that are properly destroyed (by i.e. chemical waste incineration)

The difference between the three aforementioned points is the amount of MNO-mass that will enter the environment in one way or another.

In the case of limited information where only information mentioned under point 1 and 2 are available and the information under point 3 is missing, the worst-case assumption can be made: emission = 1[2] - 2[3].

#### *5.2.1.3 Transportation*

The MNO and nano based coating have to be transported to the downstream users with the consequent risk of calamities. In the case of a major accident, spillage of relatively large amounts of the MNO or nano based coating will be released in the environment. Air, soil and surface water will be the main environmental systems exposed. To quantify this probability one should identify:

- transportation volume
- method of transportation (road / water / rail)
- chance of accidents

However, this emission will be a minor fraction of the total emission that will take place in the use stage of the coating. Therefore, general statistics can be adopted as an information source. For road and train transportation accidents emissions will be treated as emissions to soil and for water transportation accidents emissions will be treated as emissions to surface water.

#### *5.2.1.4 Application of nano based coatings*

In the application phase of a nano based coating, the coating is being prepared for use, applied to the object to be coated, the remaining coating material is disposed of and the instrumentation is cleaned. In practice, it may be difficult to distinguish between the corresponding different emissions.

When no detailed information can be obtained for the application phase, a typical percentage of 15% loss will be assumed for all activities involved in the application, in line with the default losses prescribed in the *Determination method Environmental Performance Buildings and Infrastructure and Water Works* of SBK (SBK, 2011).

The main part of this loss will leave the workplace as solid waste as it can be assumed that the paint is attached in dry form to e.g. used rollers, empty cans, protective clothing or wiping tissues. When this fraction is available, it will be assumed that this fraction of solid waste is incinerated. A smaller fraction might get flushed down the drain. When this fraction is known, this will be treated as emissions to the waste water treatment plant. When no information can be obtained for the separate emission flows a worst-case approach will be followed assuming all emissions go to surface water.

#### *5.2.1.5 Preparation of nano based coatings*

Industrial coatings may consist of a one or a two component system. When the ready-for-use coating consists of two components, these are to be mixed on site. During mixing there is a potential exposure as a consequence of:

- vaporisation
- spillage
- cleaning of the instrumentation (emission to e.g. solid waste, on-site landfill, municipal waste or waste water treatment plant)

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[2] mass MNO per mass of endproduct

[3] mass percentage MNO in the endproduct

In order to make a worst-case risk assessment one has to estimate the average volume of spillage, the vapor density of the nanomaterial in the coating and the amount of remaining product (residue) on the instrumentation. For this, one can make use of the Technical Guidance Documents available for the coating industry. Information on the amount of losses and waste during preparation can also be obtained by interviewing the actual workers involved in the workplace exposure measurements. In the absence of detailed information an approach as described above, assuming 15% loss for the application phase, can be followed.

#### *5.2.1.6 Brush or roller application*

This type of application will be involved in only a small fraction of all coating applied.Significant emissions can be expected through spillage and cleaning during and after coating activities. Minor emissions might be expected from evaporation of the nano based coating. When no specific information is available on emissions occurring as a consequence of the roller/brush application process, the higher tiered approach described above, assuming 15% loss for the application phase, can be followed.

#### *5.2.1.7 Spray application*

Significant emissions can be expected through spillage and cleaning activities during and after coating activities. As a rough estimate one can assume that the spraying efficiency is a direct estimate of the fraction of the coating that might be released to the environment. This environmental exposure route is likely to dominate the emission during application in exterior workplaces. Minor emissions might be expected from evaporation of the nano based coating.

For indoor activities main exposure routes can be expected from the disposal of solid and liquid waste to landfill (construction area) or to the municipal waste water treatment plant. If not stated otherwise, the emissions involved are included in the 15% loss assumed for the total emissions occurring in the application phase.

For outdoor application an additional 50% default will be assumed for the emission to ground as a consequence of the average efficiency of spraying equipment (of that 50%, 10% is can be inhaled by non-protected workers[4]). This fraction is originally airborne, but will quickly deposit onto the soil. Given the typical “urban area”, this fraction will therefore be treated as emission to soil.

#### *5.2.1.8 User phase*

Any coated object enters the so-called service life (the use of an article containing the substance over a period of more than one year). During this time, the MNO might leak from the matrix of the nano based coating (depending on interaction of the nanomaterial with this matrix). Also, the coating erodes resulting in a emission of MNO-matrix entities, or the coating might undergo maintenance or repair, in which case sanding or sand blasting, stripping or burning might lead to a release of the MNO to the environment. Information on the total emission of MNOs will be obtained from literature, for example from the emission scenarios described for

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[4] Agreed as a default value by the technical committee of the AWARE-pilot project (2008): *The AWARE code, Adequate Warning and Air Requirement, code for risk assessment of, and hazard communication on products containing volatile organic compounds*, H Krop, P van Broekhuizen and F van Broekhuizen

antifouling paints and from scientific literature studying the erosion of specific Nano-$TiO_2$ and Nano-Ag façade coatings.

However, in the case of indoor use, environmental exposure from leaching is not to be expected, except i.e. as a consequence of washing of a coated surface through the emission of waste water. Another environmental exposure scenario that might occur is the emission of household-dust (e.g. the erosion of the indoor wall coating). Either through the air or via the “garbage” route of the vacuum cleaner bags some emission could occur. A third route is maintenance and repair via which liquid or solid waste may be emitted to the environment.
When active cleaning of walls which are treated with nano based coatings is foreseen releases to the environment might occur when the MNO is able to migrate from the matrix or dissolves (in the case of Nano-Ag). An emission scenario has been described for disinfectants during the cleaning of hospital walls, which may be used to provide first insights to the possible emission from indoor applications. Given further the expectation that emission from exterior facades will be significantly larger than any route from indoor use, this indoor emission will not be taken into account at this moment.

Nano specific knowledge is available on the erosion of Nano-$TiO_2$ and Nano-Ag painted exterior facades, which will be used to semi-quantify the possible emission of these MNOs to the environment for the two cases studied in the context of the present project. All emissions will be treated as emissions to surface water.

#### *5.2.1.9 The end of life*

The end of life stage of the coating is not subject of the current study. However, in order to assess possible emissions of MNO to the environment a similar strategy can be followed as is described for the other life stages. Generated wastes may get emitted to air, water or soil. The dominant fraction of the wastes generated will be exposed of as solid waste or liquid waste that will be transported to a waste treatment facility.

#### *5.2.1.10 Emission inventory*

The emissions of MNO to the environment that may occur during the different life stages of the coating described above are summarised in the emission inventory matrix shown below.

| Emission Inventory | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Emissions of MNO to the environment -->** | | **E (air)** | **E (water)** | **E (soil)** | **E (SW[5])** | **E (LW[6])** | **E (LF[7])** |
| **Life stage** | **Activity** | | | | | | |
| **Manufacturing** | | | | | | | |
| | delivery and storage | | | | | | |
| | manufacturing | | | | | | |
| | packing | | | | | | |
| | service and maintenance (equipment) | | | | | | |
| **Transport** | | | | | | | |
| **Application** | | | | | | | |
| | preparation | | | | | | |
| | application brush/roller/spray | | | | | | |
| | service and maintenance (equipment) | | | | | | |
| **Use** | | | | | | | |
| | service and maintenance (coated surface) | | | | | | |
| **End of life** | | | | | | | |
| | removal of the coating | | | | | | |
| | service and maintenance (equipment) | | | | | | |
| | | | | | | | |
| **Total emissions to the environment** | | **E (Total; to air)** | **E (Total; to water)** | **E (Total; to soil + LF[8])** | | | |

In order to assess the possible impact of MNO on the environment, this matrix should be completed to the best of knowledge. All emissions to a waste treatment facility are assumed to not impact on the environment as “nano particle”.

Emissions to air, water or soil include both intended and unintended emissions, e.g. all MNO material that is not explicitly transported to a waste treatment facility. Emissions to solid or liquid waste may include wrong batches and production wastes, wastes from service and maintenance, but also polluted disposable equipment, filter material or personal protective clothing. Emissions to landfill do also involve all kind of solid wastes. However, as the MNO material is not destroyed but stored, the possibility of leaching remains. Consequently, following a worst case approach this emission is summed to the total to soil. Emission to surface water is another possibility and will depend on the actual dumpsite.

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[5] SW = solid waste treatment facility

[6] LW = liquid waste treatment facility

[7] LF = landfill

[8] Assuming the MNO disposed of as landfill may leach to soil eventually. However, if landfill is guaranteed to occur in an enclosed area, leaching might be prevented for and $E_{LF}$ doesn’t have to be summed to the total.

### 5.2.2 *Strategy for assessing the emission of MNO to the environment*

To assess the emission of MNO to the environment during the various life stages described above the following strategy is to be followed:

1. the emission of MNO to the environmental compartments air, water and ground should be quantified (as much as reasonably possible);
2. these emissions should be compared to the corresponding PNEC.

Discussion is ongoing on the appropriate metric to describe MNO behaviour, i.e. by mass, by particle concentration or by its specific surface area (SSA). According to current understanding, the SSA or the particle size distribution are better indicators of the MNO's reactivity (and toxic behaviour) then mass is. However, at this moment in time, assessing the (MNO) particle emissions on site in a production facility or at the construction site for emissions of MNO to the environment is an elaborative task, which most companies are not yet equipped for. It is therefore proposed here to maintain the unit of mass to quantify emissions of MNO to the environment until prescribed otherwise. Still, when a company does have information on emissions in terms if particle numbers, size distribution or SSA, it is advisable to monitor both these and mass. It is expected that more knowledge on the environmental fate of MNOs will become available in the near future that might allow for the interpretation of size specific information in relation to the environmental impact of specific MNOs.

Depending on the information available on the emissions during the different life stages one should either:

A. determine;
B. derive or;
C. approximate.

the emissions to air, water (incl. waste water) and ground (incl. solid waste). Concrete actions corresponding to A – C are:

A. Measure the mass flows. For example by weighing the amount of MNO left in the package after “dumping” it in the coating, or by weighing the solid waste of MNO production;
B. Derive the emission by using the mass percentage of MNO present. For example, during the application of a coating some rest product remains on the roller or brush or in the package. Say this is 100ml (or ~120g) and the MNO accounts of 5% of the product, than the emission to solid waste is about 6g of MNO;
C. Approximating the emission by using a black box approach stating *what goes in must come out*. For example, for coating 100m$^2$ of a façade with a specific layer thickness 1,2 times the applied volume is required because about 20% get “spilled” along the road of the application. Assuming worst case this 20% is emitted to the environment. If there is more information available, for example that of this 20% 15% is removed as solid waste, then only 5% is emitted to the environment.

The resulting assessment of the possible adverse effects of the MNO on the environment is summarized in the matrix below, ideally leading to a PEC for the different nano additives.

| **Total emissions to the environment** | **Air** | **Water** | **Soil** |
|---|---|---|---|
| **PEC (based on sum of all *E*'s)** | | | |
| **PNEC** | | | |
| **PEC/PNEC** | | | |

Derivation of the PEC for the different environmental compartments is described in detail in the Technical Guidance Document on Risk Assessment of the European Chemicals Bureau Directive 98/8/EC Part II (2003) and should be approached accordingly. However, given the complexity of a detailed PEC modelling and fact that the environmental fate on MNO is still largely unknown, it is beyond the scope of the present study to derive the PECs for Nano-$TiO_2$ and Nano-Ag from the use of coatings.

# 6 Occupational risk assessment

Chapter 5 presents a tiered approach for the occupational risk assessment of MNOs. This approach presents an hierarchy of data gathering and use for risk assessment. If quantitative hazard and exposure data are available, a quantitative risk assessment is performed. In that case, it is not necessary to pay attention to a qualitative risk assessment. However, one of the aims of this pilot project is investigation of the availability and subsequent gaps in current knowledge was hazard of, and exposure to MNOs used in the paint supply chain. Hence, this chapter presents the availability and subsequent gaps of data on all levels of the hierarchy.

## 6.1 Hazard Assessment

### 6.1.1 *Use of specific data for hazard assessment*

Compared to other MNOs, relatively much hazard data are available for Nano-$TiO_2$ and Nano-Ag. The public literature on Nano-$TiO_2$ as well as Nano-Ag toxicity has been reviewed by Christensen *et al.* (2010) and serves as basis for derivation of a specific occupational exposure limit. It should be noted that the authors state that their risk assessment approach is of an exploratory nature and should not be used for regulatory purposes, as not all required toxicological end points are as thoroughly explored.

For Nano-$TiO_2$ a No Observed Adverse Effect Level (NOAEL) of 0.5 mg/m$^3$ derived in a 13-week inhalation study in rats was used as a starting point (Christensen *et al.*, 2010; Bermudez *et al.*, 2004). Rats were exposed to 0.5, 2 or 10 mg/m$^3$ 21 nm $TiO_2$ particles (anatase/rutile 80/20) for 6 hours/day for 5 days/week. This NOAEL was derived from the pulmonary response, observed at the two higher doses up to 52 weeks post exposure, consisting of an increased number of macrophages and neutrophils and an increased concentration of soluble markers in bronchoalveolar lavage fluid (Bermudez *et al*., 2004).

For Nano-Ag a Lowest Observed Adverse Effect Level (LOAEL) of 49 µg/m3 derived in a 13-week inhalation study (exposure for 6 hours/day, 5 days/week) with SD rats was used as a starting point (Sung *et al.*, 2008; 2009). Rats were exposed to Nano-Ag (18–19 nm), at low (49 µg/m$^3$, equivalent to 0.6 x 10$^6$ particles/cm$^3$ and 1.08 x 109 nm$^2$/cm$^3$), medium (133 mg/m$^3$, equivalent to, 1.4 x 10$^6$ particles/cm$^3$ and 2.39 x 109 nm$^2$/cm$^3$) and high (515 mg/m$^3$, equivalent to 3.0 x 10$^6$ particles/cm$^3$ and 6.78 x 109 nm$^2$/cm$^3$) concentrations. The main targets of accumulation and toxicity were the lungs and liver. All treated males showed elevated differential cell counts, where as females only exhibited inflammation at the highest concentration. All treated animals had decreased values for markers of lung function such as tidal volume, minute volume and peak inflammatory flow. Prolonged exposure to Nano-Ag seemed to elicit an inflammatory response within the lung, and induced alterations in lung function parameters at all particle concentrations indicating that the lowest concentrations was a LOAEL.

A DNEL is derived in multiple steps. First, the starting point (i.e. the NOAEL or LOAEL[9] observed in the inhalation study) is modified, mainly for correcting for differences between human and experimental exposure conditions. Secondly, assessment factors are applied to take into account factors such as intra- and interspecies differences. For details on DNEL derivation see Chapter 8 of the Guidance on information requirements and chemical safety assessment (ECHA, 2008) and Christensen *et al.* (2010).

For Nano-$TiO_2$ a chronic $DNEL_{inhalation}$ of 17 µg/$m^3$ (equivalent to 8.3 x $10^5$ particles/cm3 (RIVM, 2010)) has been proposed based on the results obtained by Bermudez *et al.*, (Christensen *et al.*, 2010). This chronic $DNEL_{inhalation}$ is also considered sufficient to cover acute inhalation effects as acute effects generally occur at higher exposure levels.

Recently also NIOSH has derived a threshold value for ultrafine $TiO_2$ (April 2011). They derived a value of 0,3 mg/$m^3$ 10h TWA based on lung cancer and 4 µg/$m^3$ for inflammation. Since lung cancer appear to be induced only after inflammation responses, the threshold for inflammation is further used. The difference between the NIOSH and Christensen threshold values may be explained by the method used; NIOSH used a dose response method, while Christensen used the DNEL method. We choose to follow the DNEL method as this is a highly accepted method within the REACH regulated countries. However, it is still unknown whether this method will be fully accepted for nano particles.

For Nano-Ag a chronic $DNEL_{inhalation}$ of 0.33 µg/$m^3$ (equivalent to 4000 particles/$cm^3$ and 7.2 x 106 $nm^2$/$cm^3$) has been proposed based on the results obtained by Sung *et al.* (2008; 2009) (Christensen *et al.*, 2010).
Again, this chronic $DNEL_{inhalation}$ is also considered sufficient to cover acute inhalation effects as acute effects generally occur at higher exposure levels.

### 6.1.2 *Use of analogues data*

In general, two types of analogues data can be distinguished. First, a MNO that is physico-chemically related to the MNO in question and is expected to behave biologically in a comparable way. Another source is the bulk form of a MNO. As it is currently not known which physico-chemical characteristics determine whether MNOs have the same biological behaviour, in this case study we only focus on the bulk form as a source for toxicity data.

NIOSH derived recommended exposure limits for fine $TiO_2$ based on both cancer (lung tumor induction) and non-cancer (pulmonary inflammation) responses. Carcinogenicity data were derived from studies in rats, exposed for 2 years to fine (pigment-grade) $TiO_2$ (99.5% rutile) in a range of 5-250 mg/$m^3$ (Lee *et al.*, 1985; Muhle *et al.*, 1991). Lung tumor incidence was fitted to lung particle burden (expressed as surface area dose) using benchmark dose (BMD) models to derive a benchmark dose. Pulmonary inflammation data were derived from 2 sub-chronic inhalation studies (Tran *et al.*, 1999; Cullen *et al.*, 2002) and fitted with lung particle

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[9] In case a LOAEL is used as starting point an additional factor of 3 is used to compensate for the fact that a NOAEL could not be established. This is based on concentration rates normally used in toxicity tests, however, it is of course uncertain whether or not this factor is sufficient.

burden (expressed as surface area dose) with both linear and non-linear models, of which the latter was considered most realistic (NIOSH, 2005).
Subsequently, several human lung dosimetry models were used to calculate mean airborne concentration estimates associated with either an <1/1000 excess cancer risk (based on lung tumors) or a threshold estimate (based on pulmonary inflammation). An <1/1000 excess cancer risk was related to a working lifetime mean concentration of 1-5 mg/m$^3$ (8h-TWA), depending on the model used. Working lifetime mean concentration based on threshold estimates ranged from <2-10 mg/m$^3$. Subsequently, NIOSH considered a recommended exposure level not exceeding 1.5 mg/m$^3$ for fine $TiO_2$ reasonable.

With respect to the toxicity of Ag in bulk form, it is known that Ag compounds are relatively nontoxic, and that the main effect is accumulation of Ag in various organs, e.g. skin and eyes. In humans the latter results in argyria, in most cases without accompanying health problems. In animal studies with silver thiosulphate (STS), the main effect was visible pigmentation in the gastrointestinal tract, liver and kidneys. This also points to (undesirable) Ag accumulation. Except for this pigmentation, no other histological changes were observed in any tissue, including brain. Clinical effects were absent, as well as effects on neurotoxicological parameters (studied in a 90-day oral study with rats).
The Scientific Committee for Occupational Exposure Limits (SCOEL) has derived an OEL (8 hr TWA) of 0.1 mg/m$^3$ for metallic Ag and insoluble Ag compounds based on local argyrosis in the conjunctivae of the eyes observed in human studies (SCOEL, 1993).

The present case shows that the DNEL value for Nano-Ag (0.33 µg/m$^3$) is far below the OEL for metallic Ag and insoluble Ag-compounds as derived by the SCOEL. Therefore, we strongly suggest not to use a threshold value for bulk substances, unless it is known that the nano-and bulkform of the substance show comparable toxicity patterns[10].

### 6.1.3 *Benchmark values*

When no hazard data are available, but exposure levels are known, benchmark values can be used to limit exposure to MNOs.
In a report by the RIVM (2010), benchmark values have been discussed for different types of MNOs. Benchmark values are based on biopersistence, size and mass density, with the exclusion of carbon nano tubes displaying asbestos-like properties.

It is important to realize however, that these benchmark values are not based on toxicological data, and therefore in general do not provide any reassurance for save

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[10] Currently it is unknown to which extent the nano-silver becomes systemically available solely as ions or also as nano particles (and whether the size of the nano-silver influences the uptake mechanism(s)). Should the latter occur it is speculated to potentiate the nano-silver toxicity by delivering a silver-ion source close to sensitive tissues thereby by-passing the silver ion elimination mechanisms (precipitation with sulphide and chloride and binding to proteins) normally in place following exposure to non-nano-silver and silver compounds. This could clarify the lower threshold value for nano-silver compared to bulk silver.. Should silver uptake occur solely as ions, the already rich database for silver, could be applied to assess systemic nano-silver toxicity. For that exercise, consideration of whether and how the dramatically increased surface area of nano-silver could be taken into account. A threshold for bulk silver could be used as starting point.

use. Consequently, benchmark values can be used to prioritise exposure situations for MNOs for which no specific hazard data are available.
For $TiO_2$, a reference value of 40,000 particles/$cm^3$ is established as it is a metal oxide with a mass density < 6000 kg/m3 (RIVM, 2010). Comparison of this value to the derived DNEL of 8.3 x $10^5$ particles/$cm^3$ shows that for $TiO_2$ this reference value is indeed a conservative value, minimizing potential health risks.

For Nano-Ag, a reference value of 20,000 particles/$cm^3$ is established. Comparison of this value to the derived DNEL of 4000 particles/$cm^3$ shows that it cannot be generally assumed that the reference values are conservative, underpinning the remark that reference values can only be used to prioritise exposure situations for MNOs.

### 6.1.4 *Control banding for hazard prioritisation*

When hazard data and/or exposure data are absent, qualitative approaches can be applied to characterize hazard. Hazard banding strategies have been described by Stoffenmanager Nano and in ‘Handleiding veilig werken met nanomaterialen en – producten’. In general, both distinguish high and low hazard categories for nano fibers and soluble MNOs, respectively. In addition, Stoffenmanager Nano attributes the remaining MNOs in different hazard bands based on the C&L of the parent materials (Van Duuren *et al.,* 2010).

Stoffenmanager Nano is applicable to insoluble manufactured particles with a primary particle size range of 1-100 nm or powders with a specific surface area of > 60 $m^2$/g. Stoffenmanager Nano attributes MNOs in one of the 5 hazard bands (A to E) based on particle characteristics. Although not explicitly stated, it is assumed that the Nano-$TiO_2$ as well as Nano-Ag do not include nano fibers. For MNOs other than nano fibers, Stoffenmanager Nano proposes a hazard band based on data currently available for the nano form and its parent material. For $TiO_2$ as well as Nano-Ag, this leads to a classification into hazard band C or D, for particles > 50 nm or < 50 nm, respectively.

### 6.1.5 *Summary*

In table 6.1 the established threshold values are summarized.

Table 6.1: overview established threshold values for Nano $TiO_2$ and Nano-Ag

| **Nanoparticle** | **Specific data** | **Analogue data (bulk)** | **Reference value** | **Hazard class (Stoffenmanager Nano)** |
|---|---|---|---|---|
| Nano-$TiO_2$ | 17 ug/$m^3$<br>830.000 #/$cm^3$ | 1,5 mg/$m^3$ | 40.000 #/$cm^3$ | C or D |
| Nano-Ag | 0,33 ug/$m^3$<br>4000 #/$cm^3$<br>7.200.000 $nm^2$/$cm^3$ | 0,1 mg/$m^3$ | 20.000 #/$cm^3$ | C or D |

As described in Chapter 5, threshold values based on specific data are preferred over values based on analogue data, which are in turn preferred over reference values, and then over hazard classes. However, one should always keep in mind which value is used and which uncertainties are thereby included.

### 6.1.6 *Uncertainties in hazard data*

#### *6.1.6.1 Uncertainties in specific hazard data:*

Although specific data provide in principle a substance-specific threshold value for adverse effects, this method still includes major uncertainties:

- In most cases nano particles, either used for toxicity studies or exposure measurements, are insufficiently characterized to conclude that the exposure levels and DNELs refer to the same particle in the same condition. Among others, differences may relate to size (including agglomeration state), chemical composition (shell, coatings, functional groups) and shape (including crystallite size and structure).
- Traditionally, a DNEL expressed in mass/volume (mg/m$^3$) derived from an experimental study is used for risk assessment. However it is uncertain whether mass is the most appropriate unit for risk assessment for the prediction of health effects of nano particles in humans.

#### *6.1.6.2 Uncertainties is specific analogue hazard data*

Additional uncertainties are introduced with the use of analogue data:

- Bulk data: gives in a lot of cases access to a considerable amount of data However, clear knowledge regarding the comparability of the toxicity between the nano and bulk form of the substance is normally lacking.
- Analogue nanoparticle: additional data are required to substantiate the use of alternative data (e.g. physico-chemical similarity, mode of action).
- Due to limitations in characterisation and uncertainties related to similarity (related to both MNO and its analogue) it is unclear to what extent the effect level is relevant for the actual human exposure.

#### *6.1.6.3 Uncertainties in reference hazard values*

Again additional uncertainties are introduced as the reference values are no longer health effect based

- Although intended to be conservative, reference values are not in all cases lower than DNELs. It is not known in which cases the reference values are indeed conservative. Therefore, reference values may only be used as prioritization aid.

#### *6.1.6.4 Uncertainties in hazard banding*

Control banding tools are still under development. The discrimination functionality is currently low. Basically the method filters out very severe hazards and very low hazards, equally judging the majority (in most cases based on lack of data).

### 6.1.7 *Conclusions on Hazard Assessment*

Compared to other MNOs, relatively much hazard data are available for Nano-$TiO_2$ and Nano-Ag. For both Nano-$TiO_2$ and Nano-Ag, human health hazard data were found on all levels in the above described hierarchy.

For Nano-$TiO_2$ a specific DNEL was derived of 830.000 #/cm$^3$ , a threshold value of 1,5 mg/m$^3$ was based on analogous data, a reference value of 40.000 #/cm$^3$ was identified and the hazard assessment of Stoffenmanager Nano results in a hazard band of D.

For Nano-Ag a specific DNEL was derived of 4000 #/cm$^3$ , a threshold value of 0,1 mg/m$^3$ was based on analogous data, a reference value of 20.000 #/cm$^3$ was identified and the hazard assessment of Stoffenmanager Nano results in a hazard band of D.

Following the hierarchy in the tiered approach, the DNELs are used for quantitative assessments whereas the hazard bands are used for qualitative assessments.

The threshold values derived for Nano-Ag are low compared to Nano-$TiO_2$. Hence, stronger potential health hazard effects are expected from exposure to Nano-Ag compared to Nano-$TiO_2$.

Reference values could in principle be used for MNOs for which no specific hazard data are available. Comparison of the reference value to the derived DNEL shows that for $TiO_2$ this reference value is indeed a conservative value, minimizing potential health risks. Comparison of both values for Nano-Ag shows that it cannot be generally assumed that the reference values are conservative. This underpins that reference values can only be used to prioritize exposure situations for MNOs.

For $TiO_2$ as well as Nano-Ag, Stoffenmanager Nano leads to a classification into hazard band C or D, for particles > 50 nm or < 50 nm, respectively. Looking at the differences in DNEL and benchmark values, it is remarkable that both substances are categorized in the same Stoffenmanager hazard band. This illustrates the insufficiency in discrimination functionality of control banding methods.

There is still a lack of scientific consensus on how to obtain good quality hazard data and how to interpret the obtained data correctly. As a consequence the data are accompanied by high levels of uncertainty. Issues like the influence of medium used to perform toxicity tests and sameness of the particles used for different tests remain unclear.

## 6.2 Occupational exposure assessment

### 6.2.1 *Approach*

This study focuses on the nano particles Nano-$TiO_2$ and nano-silver in combination with processes and activities relevant for the supply chain of the paint industry.
A literature study is performed on worker exposure data concerning manufactured nano particles published until July 2011. Besides that, exposure data gathered in practice during this project were included.

#### *6.2.1.1 Life cycle and exposure scenarios*

First, the scope of the literature search was visualised by composing a life cycle considering all stages of the nanoparticle in the paint supply chain as described in chapter 5. This life cycle is reported in the column Life cycle stage of Table 1 ($TiO_2$) and table 2 (nano-silver) presented in Annex 2 respectively.
The life cycles show that similar activities are described in several different life cycle stages; bagging of nanopowders, loading/charging of nanopowders, cleaning and maintenance of equipment and waste treatment. The activity is similar, but the characteristics of the nanoproduct change in the different life cycle stages (e.g

physical state and or concentration nano in the product). This results in a different exposure patterns for different life cycle stages.
Waste treatment was considered relevant only for process steps in which powdered nanomaterial was used. No additional inhalation exposure is expected in case of the treatment of waste contaminated with liquid nanoproduct as this activity seems not to result in aerosol formation. Inhalation exposure to nano particles due to treatment of waste contaminated with nano particles embedded in a solid matrix is not considered likely as well.

#### *6.2.1.2 Specific and analogous exposure data*

Secondly, all relevant specific and/or analogous data were identified from literature for each life cycle stage. Annex 2 presents the results of Nano-$TiO_2$ and nano-silver in Table 1 and 2 respectively. Most of the data were provided with very little contextual information. The contextual information reported in the relevant literature sources is summarized in the column “Process Description of sources” of Annex 2 Table 1 and 2, and separately described in Annex 3.

A dataset was considered specific if Nano-$TiO_2$ or nano-silver was studied during processes/activities relevant for the paint industry (independent of actual OC/RMM). In general, analogous data are either data based on similar operations, using the same substance or data based on the same operation, but for similar substances. Substances are considered similar if the exposure characteristics (e.g. dustiness) are comparable (REACH Guidance R14). Until now little is known about the exposure characteristics which are the basis for similarity of nanoproducts (e.g. dustiness, moisture content, agglomeration, aggregation). Suscribing this uncertainty, in this study we consider other nanoforms of metaloxides to be analogous to Nano-$TiO_2$ and other nanoforms of metals to nano-silver. However, this choice is rather arbitrary.

Because of a lack of workplace data, the study includes some indicative data as well. These data are considered indicative due to a lack of information on the type of nano particle studied, poor quality of the contextual information and/or different measurement set up. This latter include laboratory simulation experiments. Indicative data are considered indicative for the release of particles due to a specific process, but are not representative for worker exposure in the paint industry. The indicative data are presented in the column analogous data of the tables presented in Annex 2.

Personal protective equipment is not described as risk management measure in the description of literature sources as exposure data are collected outside of this equipment. As a consequence, the exposure data are not corrected for the personal protective equipment used.
The task based exposure values presented in Annex 2 are time weighed for comparison with an 8 hour threshold value.

#### *6.2.1.3 Exposure banding*

Stoffenmanager Nano was used to assess the exposure band for each life cycle stage. Both the task based and the time weighed exposure bands are presented. The task based exposure band represents the exposure corresponding to the activity performed. In the time weighted exposure band, the activity exposure is corrected for the time duration of the activity each day, assuming that no other activities, or combination of activities with the MNOs are performed. Both exposure bands are presented because the task based exposure band corresponds better tot the task based measurement data, whereas the time weighed exposure band represents the actual exposure which is used for the final risk assessment. The Stoffenmanager exposure bands need to be interpreted as qualitative, relative ranking bands to be used for prioritizing worker health risks in relation to needs to control activities. Assumptions used for this assessments are described in Annex 5.

#### *6.2.1.4 Data selection for risk assessment*

For each life cycle stage and process step, data are selected for the final risk assessment. In principle, the following strategy was followed for selection;

- The use of specific data is preferred above analogous data. The use of analogous data is preferred above exposure bands.
- If different quantitative datasets are available, data that represent a worst case situation[11] are taken forward to the risk assessment.

The dataset is screened on the following quality criteria;

- The measurements are performed at the workplace
- The identity of the nano particle is clear
- Data include background measurements
- The way of presentation of data is clear (e.g. AM, GM, min-max)
- Data include basic information on operational conditions and risk management measures.

Due to scarcity of quantitative occupational exposure data, the quality criteria mentioned are used to judge the quality of the dataset, but are not used very strictly as almost no dataset would remain available for risk assessment.

### 6.2.2 *Results*

#### *6.2.2.1 Manufacturing stage*

The stage of manufacturing is subdivided in four process steps;

- Manufacturing by specific industrial processes (including monitoring, sampling and harvesting of product)
- Bagging manufactured particles
- Cleaning and maintenance of equipment used in the manufacturing process
- Treatment of waste contaminated with powdered nanomaterial

Compared to the other life cycle stages, a large number of workplace exposure data is available on manufacturing of Nano-$TiO_2$ and nano-silver. Four literature sources were considered applicable in the stage of manufacturing Nano-$TiO_2$. Regarding Nano-Ag, four literature sources were identified for manufacturing as well. For Nano-$TiO_2$ the process step of manufacturing, bagging and cleaning are covered by the data available. For nano-silver, the step of manufacturing and cleaning are covered with exposure data. No data were identified for bagging of Nano-Ag and for waste treatment of both Nano-$TiO_2$ and nano-silver during the stage of manufacturing.

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[11] Worst case situation refers to the workplace with least exposure control measures. This is not necessarily the workplace with the highest exposure levels.

No exposure data are generated during this project. Therefore, the risk assessment is based on the worst case data presented in literature. These data are selected from Annex 2 and presented in Table 6.2. For a description of the literature source, the task and occupational conditions and risk management is referred to Annex 2 and 3. For the process of data selection is referred to section 6.2.1.4. For process steps for which no data were identified, the risk assessment is based on exposure bands derived with Stoffenmanager Nano.

Table 6.2 Worst case data for risk assessment Manufacturing stage

| | **Nano-$TiO_2$** | **Nano-silver** |
|---|---|---|
| **Manufacturing** | Source no 10<br>Task measurement (312-350 min)<br>Location 2<br>Mass concentration data<br>(max van N=7)<br>0.89 mg/m3<br>SMPS data<br>(background corrected)<br>54695 #/cm3 | Source no 10<br>Task measurement (9.6-223 min)<br>Location 2<br>Mass concentration data<br>(max van N=2)<br>0.00102 mg/m3<br>SMPS data<br>(background corrected)<br>6122.4 #/cm3 |
| **Bagging** | Source no 1<br>Task measurement (337 min)<br>Bag filling<br>SMPS data(AM)<br>(NP<100 and >100 nm, background corrected)<br>9432 #/cm3 | Source no 18<br>Task based exposure class 3<br>Time weighed exposure class 3 |
| **Cleaning & Maintenance** | Source no 9<br>Task measurement<br>(Time unknown)<br>CPC data<br>(background corrected)<br>144800 #/cm3 | Source no 9<br>Task measurement<br>(Time unknown)<br>CPC data without LEV<br>(background corrected)<br>6100 #/cm3 |
| **Waste treatment** | Source no 18<br>Task based exposure class 3<br>Time weighed exposure class 2 | Source no 18<br>Task based exposure class 3<br>Time weighed exposure class 2 |

###### *6.2.2.1.1 Reflection on exposure data from the stage of manufacturing*

According to US EPA manufacturing by the chloride process is a fully closed process, up to the point where the end product (Nano-$TiO_2$) is being bagged. In the whole manufacturing of the raw nanomaterial, this bagging of the Nano-$TiO_2$ at the manufacturer and loading/charging at the customer are indicated as the moments that may lead to possible exposure to Nano-$TiO_2$. However, even a fully closed process needs to be serviced or cleaned once in a while and one may suggest that during such events exposure of residual Nano-$TiO_2$ may occur. Information on actual nanospecific activities, measures for exposure control and details on possible exposure levels are nevertheless missing to further support this suggestion.

Multiple sources identified bagging of the Nano-$TiO_2$ as being a relevant activity leading to exposure to Nano-$TiO_2$. These packaging options include solids sold in 10-kg and 20-kg bags, 55-gallon drums, and totes; and liquid-based dispersions sold in 60-kg containers, 220-kg drums, and 1,000-kg intermediate bulk containers (IBCs) *(US EPA, STREAMS).

According to the TDMA, "*Workers at ultrafine $TiO_2$ manufacturing plants can be exposed to $TiO_2$ dust. Protection measures including engineering controls and personal protective equipment are applied for exposure control and worker risk mitigation in accordance with existing regulations*." This suggests no additional measures are normally taken just because of the nanoprocess. However, according to TDMA, workers are being protected against exposure to ultrafine dust in general.

Considering the step of manufacturing by specific industrial processes, it is known that manufacturing of nano particles involve specific processes. For specific processes used for the manufacturing of the pilot substances is referred to section 4. The type of manufacturing process used influences the likelihood and intensity of exposure to nano particles (van Duuren *et al.* 2011). Generally, the sources studied did not include information on the specific process used for manufacturing. Hence, it is not clear whether all the relevant manufacturing processes are represented by the exposure data found.

In some references the manufacturing process is subdivided in different activities (e.g. controlling the process, harvesting, sampling). From these references it is clear that sampling and harvesting result in relatively high exposures at the manufacturing stage: source no 10 presents a maximum mass concentration of 4.99 mg/m3 during TiO2 collection and source no 6 presents SMPS data of 120.000 #/cm3 for sampling of nano-silver.
In other references, this subdivision was not made. Consequently, it is not known if the activities such as sampling and harvesting are included.

###### *6.2.2.1.2 Selection of manufacturing data for risk assessment*

Regarding the process step of Manufacturing by specific industrial processes, specific data are available for both pilot substances. Looking at Nano-$TiO_2$, both data from source number 9 and 10 meet most of the quality criteria. Data from source no 10, location 2 are taken forward to the risk assessment as the production amount is relatively high, the measurement includes activities with high exposure potential (e.g. sampling and collection) in the presence of little risk management measures.
The highest value of the mass concentration data together with background corrected SMPS data are taken forward to the risk assessment.

Both source no 6, 9 and 10 meet most of the quality criteria for nano-silver. At first glance, data from source no 9 represent a worst case situation the best as the measurement includes activities with high exposure potential (e.g. opening the reactor) and no control measures are present. However, it is not clear if it is normal practice to open the reactor during the manufacturing process. Source no 10 is considered a reasonable worst case alternative with a production amount of 5 kg and little risk management measures present. In this study, the minimum value is considered the background value. The highest value of the mass concentration data together with background corrected SMPS data are taken forward to the risk assessment.

Two specific datasets are available for the process step of Bagging manufactured Nano-$TiO_2$ particles. However, the quality of data from source no 2 is considered to be low as it is not clear if background measurements are included and little contextual information is available on the operational conditions and risk management measures. Therefore, data from source no 1 are taken forward to the risk characterization. The sum of particles < and > 100 nm measured by SMPS corrected for the non-activity periods are presented in Table 6.2. No quantitative data are available for bagging manufactured nano-silver. As an alternative, a qualitative risk assessment will be performed based on the Stoffenmanager Nano Exposure bands.

For the process step of Cleaning and maintenance of equipment used in the manufacturing process one quantitative, specific dataset is available for Nano-$TiO_2$ and one for nano-silver. Both datasets meet most of the quality criteria. Risk assessment will be based on those data. In case of nano-silver, data are presented from cleaning with and without the use of LEV. Data without the use of LEV are considered worst case and presented in Table 6.2.

No quantitative data are available for the process step of Treatment of waste contaminated with powdered Nano-$TiO_2$ and/or nano-silver. As an alternative, a qualitative risk assessment is performed based on the Stoffenmanager Nano Exposure bands. For a description of the task and occupational conditions and risk management assumed in for the Stoffenmanager Nano exposure estimations is referred to Annex 5.

#### *6.2.2.2 Production of paint/coating using MNOs*

The stage of production of paint/coating using MNOs is subdivided in seven process steps;

- Receipt, storage and transport of closed bags with nano product
- Opening of bags, Loading/Charging of powdered Nano product
- Mixing/Blending/Dissolving
- Filling cans with liquid coating
- Sampling of liquid coating
- Cleaning and maintenance of equipment
- Treatment of waste contaminated with powdered nano material

Considering the stage of production of paint/coating using MNOs, quantitative exposure data are available from literature for the process step of loading/charging of powdered Nano-$TiO_2$ only. One specific, and 2 analogous datasets were identified. The specific data meet the quality criteria. Within this project, exposure data were collected during storage/transport, loading/charging and waste treatment of Nano-$TiO_2$ as well.
The final risk assessment is based on exposure values collected in practice as it is considered that these data represent the worker exposure in the dutch paint industry the best. The process step of loading/charging was measured at two

different locations. The highest measurement values are used for the risk assessment for this process step in order to represent a worst case situation.
For a description of the task, occupational conditions and risk management measures during the practical measurements is referred to Source no 19 in Annex 2 and 3.

The process steps of mixing/blending, filling cans, sampling, cleaning and maintenance of Nano-$TiO_2$ are not covered with quantitative data. Hence, a qualitative exposure assessment is performed for those process steps.
Regarding nano-silver, no quantitative data were identified or collected on the stage of production of paint/coating. Hence, a qualitative exposure assessment is performed for those process steps. For a description of the task and occupational conditions and risk management assumed in for the Stoffenmanager Nano exposure estimations is referred to Annex 5. It should be noted that, as a worst case assumption, production of paint using powdered nano material is assumed for the qualitative exposure assessments.

Table 6.3 Data for risk assessment regarding the production of paint/coating

| | **Nano-$TiO_2$** | **Nano-silver** |
|---|---|---|
| **Storage/ Transport** | Source no 19<br>Data company 2<br>Task measurement (3:12 min)<br>Philips Aerasense data (background corrected)<br>24580 #/cm3 | Source no 18<br>Task based exposure class 3<br>Time weighed exposure class 2 |
| **Loading/ Charging** | Source no 19<br>Data company 1<br>Task measurement (12:32 min)<br>Philips Aerasense data (Background corrected)<br>875333 #/cm3 | Source no 18<br>Task based exposure class 3<br>Time weighed exposure class 2 |
| **Mixing/ Blending** | Source no 18<br>Task based exposure class 1<br>Time weighed exposure class 1 | Source no 18<br>Task based exposure class 1<br>Time weighed exposure class 1 |
| **Filling cans** | Source no 18<br>Task based exposure class 1<br>Time weighed exposure class 1 | Source no 18<br>Task based exposure class 1<br>Time weighed exposure class 1 |
| **Sampling** | Source no 18<br>Task based exposure class 1<br>Time weighed exposure class 1 | Source no 18<br>Task based exposure class 1<br>Time weighed exposure class 1 |
| **Cleaning & Maintenance** | Source no 18<br>Task based exposure class 1<br>Time weighed exposure class 1 | Source no 18<br>Task based exposure class 1<br>Time weighed exposure class 1 |
| **Waste treatment** | Source no 19<br>Data company 1<br>Task measurement (4:43 min)<br>Philips Aerasense data (Background corrected)<br>1300336 #/cm3 | Source no 18<br>Task based exposure class 3<br>Time weighed exposure class 2 |

###### *6.2.2.2.1 Reflection on exposure data from the stage of paint production*

Paint production may involve a manual or an automatic process that may be closed, partially closed, or open. The MNO added may be in a powder or liquid form and may be “dumped” in the coating by simply cutting a bag open with a Stanley knife above the mixed fluid of the coating, “sucked-in” by a vacuum lance (vacuum dissolver), poured in or added by an automatic feeder system. At most work places, these activities do not differ from conventional paint production. However, one does find that in the companies visited in the context of this project (local) exhaust ventilation systems are applied when nano-powders are handled and a higher personal protection is prescribed than for handling more coarse powders: e.g. respiration masks with P3 filter, protective clothing and gloves.

Generally speaking, working with powdery MNO will involve a higher risk for occupational inhalation exposure during production of the paint/coating than working with liquid forms of MNO. This, because of the dispersive nature of dry powders in contrast to powders that are pre-dispersed in fluids or in pastas. Similarly, when the production process takes place in an automatic enclosed system risks of occupational exposure are expected to be less than when processes take place in an open system. Storage and (internal) transportation of the MNO, as far as it concerns packaged MNOs, are not identified as high risk activities for possible exposure.

#### *6.2.2.3 Application stage*

The stage of application is subdivided in five process steps;

- Loading of application equipment with coating
- Application of coating by spraying
- Application of coating by rolling/brushing
- Cleaning/Maintenance of equipment used in the stage of application
- Fracturing/Abrasion of coated surfaces (see 6.2.2.4)

No quantitative exposure data are available for the process steps loading of equipment and cleaning & maintenance.
Indicative data are available for the process steps of spraying and rolling/brushing. These measurements are considered indicative for the release of particles due to a specific process, but are not representative for worker exposure in the paint industry. For a description of those indicative data, the task and occupational conditions and risk management is referred to Annex 2 and 3.

Due to a lack of workplace exposure data of enough quality in combination with the absence of companies to gather exposure data, a qualitative risk assessment is performed based on the Stoffenmanager Nano Exposure bands. For a description of the task and occupational conditions and risk management assumed in for the Stoffenmanager Nano exposure estimations is referred to Annex 5.

Table 6.4 Data for risk assessment Application stage

| | **Nano-$TiO_2$** | **Nano-silver** |
|---|---|---|
| **Loading of equipment** | Source no 18<br>Task based exposure class 2<br>Time weighed exposure class 1 | Source no 18<br>Task based exposure class 2<br>Time weighed exposure class 1 |
| **Spraying** | Source no 18<br>Task based exposure class 2<br>Time weighed exposure class 2<br>Source no 8<br>Task measurement<br>Philips Aerasense<br>No background correction<br>Mean 39000 #/cm3<br>Peak 1100 000 #/cm3 | Source no 18<br>Task based exposure class 2<br>Time weighed exposure class 2<br>Source no 8<br>Task measurement<br>Philips Aerasense<br>No background correction |
| **Rolling/ Brushing** | Source no 18<br>Task based exposure class 1<br>Time weighed exposure class 1 | Source no 18<br>Task based exposure class 1<br>Time weighed exposure class 1<br>Source no 7<br>Task measurement<br>Nano Tracer<br>(Background corrected)<br>0 |
| **Cleaning & Maintenance** | Source no 18<br>Task based exposure class 1<br>Time weighed exposure class 1 | Source no 18<br>Task based exposure class 1<br>Time weighed exposure class 1 |

###### *6.2.2.3.1 Reflection on exposure data from the application stage*

Both rolling/brushing and spraying are wet processes. During wet processes, exposure to nano particles can take place through uptake of aerosols with dispersed nano particles.

Occupational hygienists assume that rolling/brushing results in release of larger droplets rather than fine aerosols. The likelihood of uptake of those larger droplets is considered to be low as they deposit rapidly under the influence of gravity. This theory is illustrated by the workplace measurement of rolling/brushing presented by source no 7 in Annex 2. During this measurement, no difference was observed in background concentration and activity concentration. It is not clear if this measurement is representative for the paint industry as the task duration was short and the treated surface area small. Therefore, this dataset is only used as illustration of the qualitative risk assessment.

Occupational hygienists consider exposure to nano particles due to spraying a complex process influenced by factors like the spray technique used (nozzle and pressure) the evaporation rate of the solvent and the air temperature and humidity.

Besides this, the interpretation of exposure measurements from spray activities is more difficult as a consequence of the fact that the measurement equipment currently available does not differentiate between wet and solid particles in the nano

range. Hence, spray data presented in Annex2 include both wet aerosols in the nano range and solid nano particles dispersed in those aerosols.
The literature studied confirms that the spray technique influences the likelihood of exposure. Hagendorfer et al, 2009 studied nanoparticle release due to spraying of a consumer product containing nano-silver particles using both pump and gas propellant spray techniques. The pump spray shows no measurable particle release, whereas in case of the gas spray, a significant release of nano-silver particles was observed. Besides this, the literature confirms that spraying using high pressure results in aerosols in the nanorange. The availability of solid nano particles in those aerosols was confirmed by filter analysis. These findings show that there is a high likelihood of release of aerosols including nano particles due to spray activities using high pressure. For a detailed description of literature on spray activities using nanoproducts is referred to Annex 3.
One set of workplace measurement data on spray activities was identified and reported by source no 8. The quality of this dataset is poor; no background measurements were included and the identity of the nano particles is not clear. This dataset can however be used as illustration of the qualitative risk assessment.

#### *6.2.2.4 Service Life stage*

The stage of service life is expressed in the process of fracturing/abrasion of surfaces coated with nanocoatings.

No specific exposure data are available for the process of fracturing/abrasion of surfaces coated with nanocoatings. Indicative workplace measurements and/or simulation experiments performed in a laboratory setting are available for this process. Those measurements are considered indicative for the release of particles due to a specific process, but are not representative for worker exposure in the paint industry.

At this moment it is considered that the risk of workers performing sanding activities of surfaces treated with nanocoatings is not different from sanding activities of surfaces treated with non-nanocoatings. The current hypothesis is that the nano particles are embedded in the solid matrix and nano particles are not released as “free” primary particles. However, this hypothesis is uncertain and future research will further clarify this. Given the current knowledge, no additional risk of exposure to the nano particles caused by fracturing/abrasion of surfaces treated with nanocoatings is assumed. Hence, this process step is excluded from the final risk assessment until further research will indicate otherwise.

##### *6.2.2.4.1 Reflection on exposure data from the service life stage*

Available data show that the abrasion technique influences the likelihood of exposure; low energy abrasion does not result in significant particles release < 100 nm (Vorbau et al, 2009) whereas machine sanding does (Gohler et al, 2010 and Koponen et al, 2010) The process of machine sanding results in exposure to particles < 100 nm. However, no significant difference could be observed between coatings containing and not containing nanoparticle additives. Besides this, Koponen identified the motor from the sanding machine to be the dominant source of particles < 100 nm. SEM and TEM analysis demonstrate that the particles generated by machine sanding are made up from matrix material which contains the embedded nanoparticle additives. No free nano particles could be collected or

additionally counted. From the data available, it can be concluded that sanding/abrasion of treated surfaces results in exposure to ultrafine dust composed of matrix material with embedded nano particles. Exposure to the free synthetic nano particles is not considered likely as decomposition of the ultrafine dust into free nano particles in the body is not likely to occur.
For a detailed description of literature on fracturing/abrasion activities using nanoproducts is referred to Annex 3.

### 6.2.3 *Uncertainties in occupational exposure data*

#### *6.2.3.1 Uncertainties in specific exposure data:*

For the assessment of worker exposure, the use of a reliable and representative set of exposure measurements is preferred (Guidance on information requirements and Chemical Safety Assessment R14, 2008). Workplace measurements for assessing occupational exposure to engineered nano particles are performed for only a few years. Hence, worker exposure datasets are very scarce on use of nanomaterials.

In literature, occupational exposure data on use of nanomaterials are provided with little contextual information on the characteristics of the nanomaterial used, the operational conditions and risk management measures. This makes it difficult to judge whether a dataset is representative for the exposure situation to assess. This introduces uncertainty in the final risk assessment.

Until now, no harmonized measurement strategy for workplace measurements is available. One of the reasons is that there is no consensus about the metric in which the concentration of particles should be expressed. In case of regular chemicals, exposure is expressed in mass concentration. For nano particles number concentration and surface area concentration are relevant as well. Hence, exposure data show a wide variety in experimental set-up, devices and metrics to express occupational exposure. All this differences make it very hard to compare the occupational exposure data on nanomaterials.

Besides that, the presentation of occupational data on nanomaterials varies; both arithmetic mean values, peak values and data ranges are presented. Exposure data can be presented as geometric mean value as well. The most suitable parameter for risk assessment depends on the specific situation, but it is important to know which parameter is used. However, these parameters are not specified in several cases. This makes a dataset less suitable for risk assessment as it is difficult to interpret the result of a risk assessment performed with such a dataset. A risk assessment based on the aritmic mean value, maximum or peak value is worst case compared to a risk assessment based on the geometric mean value.

The measurement equipment currently available does not differentiate between different sources of nano particles; both nano particles from the work process and other natural or incidental sources are measured. The equipment takes both the wet and solid particles in the nano range into account in case of wet processes. Hence, occupational exposure measurements represent potential exposure to nanomaterials, they cannot be interpret as actual exposure values to nanomaterials. This introduces uncertainty in the final risk assessment.

#### *6.2.3.2 Uncertainties in analogous exposure data:*

In general, analogous exposure data are either data based on similar operations, using the same substance or data based on the same operation, but for similar substances. Substances are considered similar if the exposure characteristics (e.g. vapor pressure, dustiness) are comparable (REACH Guidance R14). Until now little is known about the exposure characteristics which are the basis for similarity of nanoproducts (e.g. dustiness, moisture content, agglomeration, aggregation). This makes it difficult to select a suitable set of analogous exposure data

#### *6.2.3.3 Uncertainties in exposure banding:*

Control banding tools are still under development. The discrimination functionality is currently low. Basically the method filters out situations with a very high or very low exposure potential, equally judging the majority (in most cases based on lack of data).

### 6.2.4 *Conclusions on occupational exposure assessment*

Worker exposure datasets are very scarce for scenarios from the paint supply chain. Nevertheless, a relatively large number of exposure datasets is found for the stage of manufacturing of differing quality. Only very few datasets are found for the stage of paint production, end use and service life. In general, more exposure data are found for Nano-$TiO_2$ compared to Nano-Ag. The quality of the data is often disputable.

Compared to the other life cycle stages, a large number of workplace exposure data is available on manufacturing of Nano-$TiO_2$ and Nano-Ag. The type of manufacturing process used, influences the likelihood and intensity of exposure to nano particles (van Duuren *et al.* 2011).

The stage of manufacturing is subdivided in the process step of manufacturing, bagging, cleaning/maintenance and waste treatment. The process of bagging is expected to have the highest exposure potential. However, the available quantitative data show that the activity of cleaning/maintenance can be responsible for high exposure values as well. These data learn us that risk management measures should not be focused on the process of bagging only.

The stage of paint production is subdivided in the process step of storage/transport, loading/charging, mixing/blending, sampling, cleaning/maintenance, waste treatment and fracturing/abrasion of coated surfaces. Based on the quantitative data, the task of waste treatment seem to result in a higher exposure compared to the task of storage/transport and loading/charging. This is remarkable as the process of loading is expected to have the highest exposure potential. Again, these data learn us that risk management measures should not be applied for the process of loading/charging only as waste treatment can be responsible for high exposure values as well.

During this project, the process step of loading/charging was measured at two different companies. A big difference in exposure levels was observed between both companies. The main observed differences were in the amount of nanomaterial used and the work behavior. Although exposure is a result of many factors, it is emphasized that work behavior, as for exposure to other substances, plays an important role.

The qualitative exposure assessment performed for the production of paint/containing Nano-Ag provides insight in the difference in exposure potential of wet and dry processes during the stage of paint production. During the task of storage/transport, loading/charging and waste treatment, the worker is exposed to pure, powdered nano-powder. During the process of mixing, filling cans, sampling and cleaning, the worker is exposed to liquid paint formulated with a limited percentage of nanomaterial. The exposure potential of activities performed with pure powdered nano product exceeds the exposure potential of activities performed with liquid paint production. This explains the lower risk priority corresponding to the wet process tasks compared to the dry process tasks.

The stage of application is subdivided in the process step of loading of equipment, spraying, rolling/brushing, fracturing/abrasion and cleaning/maintenance of coated surfaces. The qualitative exposure assessment with Stoffenmanager Nano indicates a higher exposure class for spraying compared to rolling/brushing. This finding corresponds to the trend found in indicative measurements on spraying and rolling/brushing.

The stage of service life is expressed in the process of fracturing/abrasion of surfaces coated with nanocoatings. The current hypothesis is that the nano particles are embedded in the solid matrix and nano particles are not released as “free” primary particles. However, this hypothesis is uncertain and future research will further clarify this.

In all cases occupational exposure data on MNOs are accompanied by many uncertainties. An important factor in this uncertainty is the lack of contextual information provided with the data. Besides that, information is often lacking about the type of data presented (e.g. AM, GM, 90-percentile, maximum). A harmonized measurement strategy, taking into account the difficulties related to activity and background exposure is currently not available, hampering straight forward interpretation of exposure data.

## 6.3 Risk Assessment

### 6.3.1 *Approach*

For a risk assessment either quantitative or qualitative data may be used, in this preferred order. The Hazard Assessment described in section 6.1 presents a DNEL of 17 µg/m$^3$, equivalent to 8.3 x 10$^5$ particles/cm$^3$ for Nano-TiO$_2$ (Christensen et al. (2010). For Nano-Ag a DNEL of 0.33 µg/m$^3$ (equivalent to 4000 particles/cm$^3$ and 7.2 x 10$^6$ nm$^2$/cm$^3$) was presented (Christensen et al. (2010). Since specific hazard data are available, a quantitative risk assessment is performed if quantitative exposure levels are available as well (See sections 6.2, Annex 2).

This risk assessment provides a risk indication for each process step in a life cycle stage based on available data. Most exposure data on use of nanomaterials are reported as task based measurements representing exposure during the period of a specific task. The threshold value represents the maximum exposure for each 8 hour working day independent from the task performed. A risk indication is provided for two scenarios;

- Task exposure; Task exposure values are directly compared with the threshold value. This result provides insight in the risk of performing a specific task on nanomaterials assuming a duration of 8 hours a day.
- Day exposure; Task exposure values are corrected for the actual time of exposure during a working day. This result provides insight in the risk of performing a task on nanomaterials for a certain period a day assuming that no other tasks with nanomaterials are performed on that day.

In practice, the actual health risk is caused by the exposure from all different tasks performed with nanomaterials on each working day. Due to a lack of quantitative exposure data, the exposure assessment of all process steps in a life cycle stage includes both quantitative and qualitative methods. This makes it impossible to judge the actual health risk to nanomaterials in case of the performing different tasks with nanomaterials during one working day.

Table 6.5 till 6.10 provide the risk indication of use of Nano-$TiO_2$ and Nano-Ag in the paint supply chain. The risk indication for the different process steps of the life cycle stage is based on a quantitative or qualitative risk assessment depending on available data. It is possible to compare the results of a quantitative risk assessment with each other. It is also possible to compare the results of a qualitative risk assessment with each other. However, it is not possible to compare the results based on a quantitative risk assessment with the results derived by a qualitative risk assessment as both methods are not comparable.
The metric particle number/$cm^3$ (#/$cm^3$) is used for the quantitative risk assessment as this metric was available for all exposure data identified.

In the absence of quantitative exposure data, a qualitative risk assessment is presented based on Stoffenmanager Nano. In that case the risk assessment is based on hazard band D corresponding to particles < 50 nm for both nano-$TiO_2$ as Nano-Ag. This choice is explained in section 6.1.4, 6.3.2.1 and 6.3.3.1. The qualitative risk assessment is based on exposure bands based on the assumptions described in Annex 5.
As the qualitative hazard assessment with Stoffenmanager Nano results in band D (highly hazardous), the final risk prioritization result consists of a High or Medium priority for the implementation of risk management measures. This can be considered as a conservative result.

The risk assessment is based on current scientific insights combined with pragmatic choices. Due to the current lack of scientific consensus and data on the potential human health hazard and exposure pathways the risk assessment includes major uncertainties. These uncertainties are summarized in the sections 6.1.6 en 6.2.3.

### 6.3.2 *Risk assessment for the use of nano-$TiO_2$ in the paint industry*

#### *6.3.2.1 Characterization of nano-$TiO_2$*

For the risk assessment it is important that the exposure data and the DNEL are based on the same substance. Therefore characterization data such as primary particle size, chemical composition, surface area and mass density are very relevant.

The characterization data of the $TiO_2$ nano particles used to derive the DNEL is limited to a primary size of 21 nm. For the crystallinity, an anatase/rutile proportion of 80/20 is reported. Exposure data reported in literature are generally provided with electron micrographs giving insight in the shape, primary particle size and agglomeration state of the nanomaterial measured at the workplace. Data from literature source no 1, 9 and 10 are used for the risk assessment during the stage of manufacturing. No information on the primary particle size and crystallinity was reported by source no 1. Source no 9 reports a primary particle size of 40 nm, and no information on the crystallinity. Source no 10 shows an electron micrograph with clumped $TiO_2$ structures. No individual particles are shown and no primary particle size is reported. This source provides no information on the crystallinity of the material. The risk assessment during the stage of paint production, is based on the data gathered in practice. The product information provided by the pilot companies report a primary particle size of <10 and 30 nm respectively. The crystallinity is described as anatase for one of the products. This characteristic is not specified for the other product.

The available data provide little characterization data which makes it difficult to compare the substances used for the toxicology and exposure studies. This improves the uncertainty of the final risk assessment.

However, the available data underpin the choice of hazard band D corresponding to particles < 50 nm in case of a qualitative risk assessment with Stoffenmanager Nano.

#### *6.3.2.2 Risk assessment during manufacturing of Nano-$TiO_2$*

A quantitative risk assessment is performed for the process steps of manufacturing, bagging and cleaning. The process step of waste treatment is qualitatively assessed using Stoffenmanager Nano. Results are summarized in table 6.5.

Table 6.5 Risk assessment manufacturing of Nano-$TiO_2$ [1]

| Manufacturing | | | | | |
|---|---|---|---|---|---|
| Process step | Threshold value | Task exposure | Day exposure | Risk indication (Task) | Risk indication (Day) |
| Manufacturing | 830,000 #/cm3 | 54,695 #/cm3 (350 min) | 39,882 #/cm3 (480 min) | No | No |
| Bagging | 830,000 #/cm3 | 9432 #/cm3 (337 min) | 6622 #/cm3 (480 min) | No | No |
| Cleaning | 830,000 #/cm3 | 144,800 #/cm3 (30 min[2]) | 9050 #/cm3 (480 min) | No | No |
| Waste | Band D | Class 3 (1-30 min) | Class 2 (4-8 hours) | High | Medium |

[1] Results of a quantitative risk assessment (manufacturing, bagging, cleaning) are not comparable with the results of a qualitative risk assessment (waste treatment) as both methods are not comparable.

[2] Exposure time is assumed to be 30 min as this parameter is not provided in literature.

Looking at this set of quantitative exposure data, the task of cleaning seems to results in the highest exposure potential. Due to differences in the task duration, the process step of manufacturing provides the highest contribution to exposure over the working day. Both task and day exposure values are below the threshold value.

This indicates that no risk is expected from performing only the task of manufacturing or bagging or cleaning for the whole working day or for the specified period that day. In practice, the actual health risk is caused by the exposure from all different tasks performed with nanomaterials on each working day. Due to the absence of quantitative exposure data covering the process step of waste treatment, it impossible to judge the actual health risk due to exposure to Nano-$TiO_2$ during the stage of manufacturing.

Based on the quantitative data, the task of cleaning/maintenance seem to result in a higher exposure compared to the task of manufacturing and bagging. This is remarkable as the process of bagging is expected to have the highest exposure potential. A possible explanation is the difference in occupational conditions and risk management measures. The bagging data are from a continuous, semi-automatic bagging process provided with LEV, mechanical and natural ventilation. The literature source identified for the process of cleaning suggests that no specific occupational conditions and risk management measures are in place during the process of cleaning. As exposure to nanomaterials is the result of a lot of different factors, this is just one of the possible explanations. However, the data learn us that risk management measures should not be applied for the process of bagging only. Performing the activity of cleaning/maintenance can be responsible for a high exposure value as well.

The qualitative assessment with Stoffenmanager Nano results in a high priority for implementation of risk management measures for the task of waste treatment. This priority changes in medium after correction for the actual time of exposure.

### *6.3.2.3 Risk assessment during production of paint/coating using nano-$TiO_2$*

A quantitative risk assessment is performed for the process steps of storage, loading and waste treatment. The process steps mixing, filling cans, sampling and cleaning are qualitatively assessed using Stoffenmanager Nano. Results are summarized in table 6.6.

Table 6.6 Risk assessment production of paint/coating using nano-$TiO_2$[1]

| Production of paint/coating using nano-$TiO_2$ | | | | | |
|---|---|---|---|---|---|
| Process step | Threshold value | Task exposure | Day exposure | Risk indication (Task) | Risk indication (Day) |
| Storage | 830,000 #/cm3 | 24,580 #/cm3<br>(3:12 min) | 164 #/$cm^3$<br>(480 min) | No | No |
| Loading | 830,000 #/cm3 | 875,333 #/cm3<br>(12:32 min) | 22.850 #/$cm^3$<br>(480 min) | Yes | No |
| Mixing | Band D | Class 1<br>(4-8 hours) | Class 1<br>(4-8 hours) | Medium | Medium |
| Filling cans | Band D | Class 1<br>(4-8 hours) | Class 1<br>(4-8 hours) | Medium | Medium |
| Sampling | Band D | Class 1<br>(1-30 min) | Class 1<br>(4-8 hours) | Medium | Medium |
| Cleaning | Band D | Class 1<br>(1-30 min) | Class 1<br>(4-8 hours) | Medium | Medium |

| | | | | | |
|---|---|---|---|---|---|
| Waste | 830,000 #/cm3 | 1,300,336 #/cm3<br>(4:43 min) | 12.787 #/cm3<br>(480 min) | Yes | No |

[1] Results of a quantitative risk assessment (storage, loading, waste treatment) are not comparable with the results of a qualitative risk assessment (mixing, filling cans, sampling, cleaning) as both methods are not comparable.

Looking at this set of quantitative exposure data, the task of waste treatment seems to results in the highest exposure potential. For the process of storage/transport, both task and day exposure values are below the threshold value. This indicates that no risk is expected from performing only the task of storage/transport for the whole working day or for the specified period that day. Due to differences in the task duration, the process step of loading provides the highest contribution to exposure over the working day. Both task exposure values of the activities loading and waste treatment are above the threshold value. This indicates that a health risk is expected in case of performing the task of loading or waste treatment for the whole working day. It should be noted that these exposure values are not corrected for the use of a respirator. Workers were equipped with respirators during both activities. A respirator providing 40% protection reduces the exposure levels of both activities below the threshold value. The day exposure values for loading and waste treatment are below the threshold value indicating that no health risk is expected in case of performing only the task of loading or waste treatment for the specified period that day.

Both the process steps loading/charging and waste treatment are short tasks with relatively high exposure values. As acute hazard effects are described for Nano-$TiO_2$, those exposure values need to be referred to a 15 min threshold value as well. As a rule of thumb, the 15 min threshold value is twice the 8 hour threshold value. Hence, the 15 min threshold value is 1,660,000 #/cm3 in this case. The task exposure values of both loading/charging and waste treatment are below this 15 min threshold value indicating that no acute hazard effects are expected due to the short term exposure from loading/charging and waste treatment.

In practice, the actual health risk is caused by the exposure from all different tasks performed with nanomaterials on each working day. Due to the absence of quantitative exposure data covering the process step of mixing, filling, sampling and cleaning, it is impossible to judge the actual health risk due to exposure to Nano-$TiO_2$ during the stage of paint production.

Based on the quantitative data, the task of waste treatment seem to result in a higher exposure compared to the task of storage/transport and loading/charging. This is remarkable as the process of loading is expected to have the highest exposure potential. A possible explanation is the difference in occupational conditions and risk management measures. During loading, LEV and wet suppression techniques were applied to reduce worker exposure. No technical risk management measures were in place during waste treatment. As exposure to nanomaterials is the result of a lot of different factors, this is just one of the possible explanations. However, the data learn us that risk management measures should not be applied for the process of loading/charging only. Performing the activity of waste treatment can be responsible for high exposure values as well.

The qualitative assessment with Stoffenmanager Nano results in a medium priority for implementation of risk management measures for the tasks of mixing, filling cans, sampling and cleaning. This priority does not change after correction for the actual time of exposure.

#### *6.3.2.4 Risk assessment during application of Nano-TiO$_2$*

Due to a lack of workplace exposure data of enough quality, a qualitative risk assessment is performed based on the Stoffenmanager Nano Exposure bands. Results are summarized in table 6.7.

Table 6.7 Risk assessment application of Nano-TiO$_2$

| Application | | | | | |
|---|---|---|---|---|---|
| Process step | Threshold value | Task exposure | Day exposure | Risk indication (Task) | Risk indication (Day) |
| Loading | Band D | Class 2<br>(1-30 min) | Class 1<br>(4-8 hours) | Medium | Medium |
| Spraying | Band D | Class 2<br>(2-4 hours) | Class 2<br>(4-8 hours) | Medium | Medium |
| Rolling | Band D | Class 1<br>(4-8 hours) | Class 1<br>(4-8 hours) | Medium | Medium |
| Cleaning | Band D | Class 1<br>(1-30 min) | Class 1<br>(4-8 hours) | Medium | Medium |

The qualitative assessment with Stoffenmanager Nano results in a medium priority for implementation of risk management measures for all the process steps identified in the stage of application of Nano-TiO$_2$. This priority does not change after correction for the actual time of exposure.

The result is remarkable as the process of spraying has the highest exposure potential. This expectation is underpinned with the quantitative exposure sources presented as illustration in table 6.4 and section 6.2.2.3.1. It should be noted that a spray cabin with an efficacy of 10 ACH is assumed as risk management measure for the process of spraying. The exposure class corresponding to the process of spraying exceeds the exposure class corresponding to the other activities but the final risk indication is equal. This illustrates the insufficiency in discrimination functionality of control banding methods as described in section 6.2.3.3.

### 6.3.3 *Risk assessment of Nano-Ag use in the paint industry*

#### *6.3.3.1 Characterization*

The characterization data of the nano-silver used to derive the DNEL is limited to a primary size 18–19 nm. Data from literature source no 9 and 10 are used for the risk assessment during the stage of manufacturing. Source no 9 reports a primary particle size of 20-50 nm. Source no 10 shows an electron micrograph with agglomerated/aggregated silver nano particles.
The available data provide little characterization data which makes it difficult to compare the substances used for the toxicology and exposure studies. This improves the uncertainty of the final risk assessment.

However, the available data underpin the choice of hazard band D corresponding to particles < 50 nm in case of a qualitative risk assessment with Stoffenmanager Nano.

### *6.3.3.2 Risk assessment during manufacturing of Nano-Ag*

A quantitative risk assessment is performed for the process steps of manufacturing, and cleaning. The process steps of bagging and waste treatment are qualitatively assessed using Stoffenmanager Nano. Results are summarized in table 6.8.

Table 6.8 Risk assessment manufacturing of Nano-Ag[1]

| Manufacturing | | | | | |
|---|---|---|---|---|---|
| Process step | Threshold value | Task exposure | Day exposure | Risk indication (Task) | Risk indication (Day) |
| Manufacturing | 4000 #/cm3 | 6122.4 #/cm3<br>(223 min) | 2844.4 #/cm3<br>(480 min) | Yes | No |
| Bagging | Band D | Class 3<br>(4-8 hours) | Class 3<br>(4-8 hours) | High | High |
| Cleaning | 4000 #/cm3 | 6100 #/cm3<br>(30 min[2]) | 381 #/cm3<br>(480 min) | Yes | No |
| Waste | Band D | Class 3<br>(1-30 min) | Class 2<br>(4-8 hours) | High | Medium |

[1] Results of a quantitative risk assessment (manufacturing, bagging, cleaning) are not comparable with the results of a qualitative risk assessment (waste treatment) as both methods are not comparable.

[2] Exposure time is assumed to be 30 min as this parameter is not provided in literature.

Looking at the set of quantitative exposure data, the exposure potential of the task of manufacturing seems to be equal to the task of cleaning. The task of manufacturing provides the highest contribution to exposure over the working day. The task exposure values of both manufacturing and cleaning are above the threshold value. This indicates that a risk is expected from performing only the task of manufacturing or cleaning for the whole working day. The day exposure values for manufacturing and cleaning are below the threshold value indicating that no health risk is expected in case of performing only the task of manufacturing or cleaning for the specified period that day.

In practice, the actual health risk is caused by the exposure from all different tasks performed with nanomaterials on each working day. Due to the absence of quantitative exposure data covering the process step of bagging and waste treatment, it impossible to judge the actual health risk due to exposure to Nano-Ag during the stage of manufacturing.

The qualitative assessment with Stoffenmanager Nano results in a high priority for implementation of risk management measures for the tasks of bagging and waste treatment. For bagging, there is no difference between the task exposure and day exposure as a task duration of 4-8 hours is considered reasonable practice. In case of waste treatment, this priority changes in medium after correction for the actual time of exposure.

#### 6.3.3.3 *Risk assessment during production of paint/coating using Nano-Ag*

Due to a lack of workplace exposure data, a qualitative risk assessment is performed based on the Stoffenmanager Nano Exposure bands. Results are summarized in table 6.9.

Table 6.9 Risk assessment production of paint/coating using Nano-Ag

| Production of paint/coating using Nano-Ag | | | | | |
|---|---|---|---|---|---|
| Process step | Threshold value | Task exposure | Day exposure | Risk indication (Task) | Risk indication (Day) |
| Storage | Band D | Class 3<br>(1-30 min) | Class 2<br>(4-8 hours) | High | Medium |
| Loading | Band D | Class 3<br>(1-30 min) | Class 2<br>(4-8 hours) | High | Medium |
| Mixing | Band D | Class 1<br>(4-8 hours) | Class 1<br>(4-8 hours) | Medium | Medium |
| Filling cans | Band D | Class 1<br>(4-8 hours) | Class 1<br>(4-8 hours) | Medium | Medium |
| Sampling | Band D | Class 1<br>(1-30 min) | Class 1<br>(4-8 hours) | Medium | Medium |
| Cleaning | Band D | Class 1<br>(1-30 min) | Class 1<br>(4-8 hours) | Medium | Medium |
| Waste | Band D | Class 3<br>(1-30 min) | Class 2<br>(4-8 hours) | High | Medium |

The qualitative assessment with Stoffenmanager Nano results in a high priority for implementation of risk management measures for the tasks of storage/transport, loading and waste treatment. This priority changes in medium after correction for the actual time of exposure. A medium priority for implementation of risk management measures is derived for the task of mixing, filling cans, sampling and cleaning. This priority does not change after correction for the actual time of exposure.

The process steps in the stage of paint production are subdivided in wet and dry processes. During the task of storage/transport, loading/charging and waste treatment, the worker is exposed to pure, powdered nano-silver. During the process of mixing, filling cans, sampling and cleaning, the worker is exposed to liquid paint formulated with a limited percentage of nano-silver. The exposure potential of activities performed with pure powdered nano product exceeds the exposure potential of activities performed with liquid paint production. This explains the lower risk priority corresponding to the wet process tasks compared to the dry process tasks. This difference is not visible in the time weighed priority bands representing the risk indication for the day. This illustrates the insufficiency in discrimination functionality of control banding methods as described in section 6.2.3.3.

#### 6.3.3.4 *Risk assessment during application of Nano-Ag*

Due to a lack of workplace exposure data of enough quality, a qualitative risk assessment is performed based on the Stoffenmanager Nano Exposure bands. Results are summarized in table 6.10.

Table 6.10 Risk Assessment application of Nano-Ag

| Application | | | | | |
|---|---|---|---|---|---|
| Process step | Threshold value | Task exposure | Day exposure | Risk indication (Task) | Risk indication (Day) |
| Loading | Band D | Class 2<br>(1-30 min) | Class 1<br>(4-8 hours) | Medium | Medium |
| Spraying | Band D | Class 2<br>(2-4 hours) | Class 2<br>(4-8 hours) | Medium | Medium |
| Rolling | Band D | Class 1<br>(4-8 hours) | Class 1<br>(4-8 hours) | Medium | Medium |
| Cleaning | Band D | Class 1<br>(1-30 min) | Class 1<br>(4-8 hours) | Medium | Medium |

The qualitative assessment with Stoffenmanager Nano results in a medium priority for implementation of risk management measures for all the process steps identified in the stage of application of nano-silver. This priority does not change after correction for the actual time of exposure.

The result is remarkable as the process of spraying has the highest exposure potential. This expectation is underpinned with the quantitative exposure sources presented as illustration in table 6.4 and section 6.2.2.3.1. It should be noted that a spray cabin with an efficacy of 10 ACH is assumed as risk management measure for the process of spraying. The exposure class corresponding to the process of spraying exceeds the exposure class corresponding to the other activities but the final risk indication is equal. This illustrates the insufficiency in discrimination functionality of control banding methods as described in section 6.2.3.3.

### 6.3.4 *Uncertainties in risk assessment of MNOs*

#### *6.3.4.1 Quantitative risk assessment for MNOs*

The primary uncertainty concerns the similarity between the MNOs encountered at the workplace and the MNO used to obtain the toxicity data and reference value. Differences can occur for characteristics such as primary particle size (including size distribution), mass density, shape, crystallinity, agglomeration state and chemical modifications. Due to limitations in this characterization (related to both MNO identification and their state during experimental conditions) it is unclear to what extent the effect level is relevant for the actual human exposure.

The quantitative risk assessment methodology described above is based on the regulatory risk assessment under REACH which is accepted by authorities for conventional substances. The applicability of this method for risk assessment for MNOs is under debate as it is unclear if the set of underlying toxicity studies need to be equal for convential substances and MNOs. Besides this, the use of assessment factors is under debate.

Uncertainty also exists about experimental methods and differences in experimental exposure conditions. Importantly, the available toxicity studies have not investigated all relevant data: neurotoxicity parameters, detailed histopathological examination of the central nervous system and respiratory tract.

A critical issue in risk assessment of MNO is the choice of metric. In general, a reference value expressed as unit mass/volume (mg/m$^3$) derived from an experimental study is used for risk assessment. However it is uncertain whether this metric is the most appropriate one for risk assessment for the prediction of health effects in humans. Besides that, the outcome of a comparison between exposure and reference values might differ dependent on the metric (i.e. mass, number concentration, surface area) used. Exposure or dose metrics can be recalculated from one to another, if the MNOs are sufficiently characterized. For definite conclusions however, one should know the appropriate metric for comparison.

#### *6.3.4.2 Qualitative risk assessment for MNOs*

Qualitative methods are not underpinned with toxicological and exposure data. Therefore, they do not provide any reassurance for safe use. In addition, the distinctive character of those methods is small due to a lack in knowledge on both hazard and exposure.

### 6.3.5 *Conclusions on occupational risk assessment*

In the risk assessment, process steps are indicated with risk depending on the comparison between hazard and exposure values. Due to the high uncertainties in hazard, exposure and risk assessment, no conclusions on health risks or control of health risks can be drawn from this risk assessment. However, if the exposure value exceeds the threshold value, the process step can be prioritized for control measures.

When comparing quantitative task based exposure values to threshold values, the following process steps are prioritized: manufacturing and cleaning in the manufacturing stage of Nano-Ag and loading and waste treatment in the stage of production of paint using Nano-$TiO_2$. This indicates that a risk is expected from performing only these tasks for the whole working day. When compensating for task durations and assuming that the task is the only task performed with the nanomaterial during the day, none of these tasks exceeds the DNELs any longer. In reality however, a worker will perform several tasks with certain duration consecutively during the day. As a consequence of the different methods used (qualitatively vs quantitatively) it was not possible to calculate the realistic exposure resulting from the combination of tasks.

Using Stoffenmanager Nano, additional tasks are prioritized for control measures: bagging during the manufacturing of Nano-Ag and waste treatment in both the manufacturing stage of Nano-$TiO_2$ and Nano-Ag. The tasks of storage, loading and waste treatment are prioritized during the stage of production of paint using Nano-Ag. Although not prioritized, it is worthwhile mentioning that also other process steps leave room for improvement. It should be noted however that this risk banding tool is still under development and therefore can only be used as indicative.

Given the current knowledge, no additional risk of exposure to the nano particles caused by fracturing/abrasion of surfaces treated with nanocoatings is assumed. The current hypothesis is that the nano particles are embedded in the solid matrix and nano particles are not released as “free” primary particles. However, this hypothesis is uncertain and future research will further clarify this.

The most important uncertainty in the final risk assessment concerns the similarity between the MNOs encountered at the workplace and the MNO used to obtain the toxicity data and reference value. In this study it is known that hazard and exposure data concern Nano-$TiO_2$ and Nano-Ag respectively, however, the MNO are not thoroughly enough characterized with respect to size, morphology, surface functionalization to ascertain that the MNO used for hazard and exposure assessment are really the same substances.

# 7 Environmental exposure assessment

Central in the debate on the use of nanomaterials and nanoproducts is the environmental fate of these materials and their possible adverse effects on the environment. One of the reasons for assessing adverse effects on the environment in parallel to human toxicity is the observation that nanomaterials that are toxic to humans may be less toxic for environmental organisms and vice versa. Examples thereof are nano-ZnO and Nano-Ag that are only mildly toxic for humans but extremely toxic for aquatic organisms (Kahru and Dubourgier 2009), or carbon nanotubes that are considered to be toxic for humans but much less so for aquatic organisms.

In this chapter, the two cases (1) a Nano-$TiO_2$ containing paint and (2) a Nano-Ag containing paint are used to sketch what is currently known on the life cycle of these nano particles used in paints, their emissions from the “paint-chain” to the environment and their possible environmental fate. The following questions will be addressed:

1. Mass flow of nanomaterials (nano-$TiO_2$ and Nano-Ag) through the paint-chain
   - How much nanomaterial (raw material) is being produced?
   - How much nanomaterial is used for paint production?
   - How much nanomaterial “gets lost” during paint production?
   - How much nanomaterial “gets lost” during application?
   - What happens during the use and waste phase of the paint?
2. What is the relative contribution of the emission to the environment of nanomaterials used in paints compared to other sources?
3. Is a PEC/NEC approach possible to assess the possible risks to the environment?
4. In what form do nanomaterials reach the environment (as nanoparticle, aggregate, agglomerate or embedded in a matrix)?
5. What is known about the fate of Nano-$TiO_2$ and Nano-Ag in the environment?

These questions do result in the qualitative study described below on the known’s and unknowns regarding the environmental health and safety issues of Nano-$TiO_2$ and Nano-Ag in particular and aims to provide a more general understanding on the elements that play a role while assessing possible adverse effects on the environment as a consequence of the use of nanomaterials in paints.

## 7.1 Emissions to the environment

Nanomaterials can enter the environment at different stages during their life cycle. In the manufacturing phase of the raw material and paint production phase of the nanopaint emissions are due to accidental releases, airborne emissions, emissions to waste water, landfill leakages and waste incineration processes. During the use phase of the paint nanomaterials can enter the environment via to spills, airborne emissions, emissions to waste water, disposal of left-over product (upon application), and during service and maintenance of the applied paint system, wear and tear of the paint, and finally during the end of life phase due to the removal of the paint. In the following subsections the life cycle of nanopaints and the various stages where emission of nanomaterials (MNO) to the environment may occur are described.

### 7.1.1 *Emissions during manufacturing of MNO*

Emissions may take place during the manufacturing phase of the MNO. Typical moments in which emissions are to be expected are:

- during the actual manufacturing process (e.g. emissions via exhaust ventilation);
- during the collection of the MNO manufactured (e.g. spills, waste materials, transportation and packaging);
- during quality control activities (e.g. spills or emissions during sampling, removal of analyzed samples);
- during cleaning and maintenance activities of the manufacturing equipment and the production location (e.g. waste water, residuals, solid waste like cleaning cloths, filters etc.).

Needless to say is that the emissions during manufacturing do strongly depend on the work practice, the hygienic protocol, the air filtration measures and the waste management implemented in the manufacturing facility.

For Nano-$TiO_2$ the manufacturing is better documented than Nano-Ag and for that reason the manufacturing of Nano-$TiO_2$ and the emissions during this manufacturing are further described in the subsections below.

#### *7.1.1.1 Manufacturing specifics for Nano-$TiO_2$*

Nano-$TiO_2$ is being manufactured by a large diversity of manufacturing processes (Robichaud *et al.* 2009) as described in section 4.

From Robichaud *et al.* (2009) is derived that in 2009, there were at least seven established Nano-$TiO_2$ producing companies, of which DuPont was the only one producing also bulk $TiO_2$.

Table 7.1 Different established companies producing Nano-$TiO_2$

| Company | Country | Nano-$TiO_2$ manufacturing process | Ref. |
|---|---|---|---|
| Dupont | US | Undisclosed plasma process | Robichaud *et al.* (2009) |
| NanoPhase | US | Physical vapor synthesis | Robichaud *et al.* (2009) |
| NanoGram | US | Laser Pyrolysis | Robichaud *et al.* (2009) |
| Advanced NanoTech | US | Mechanical Milling | Robichaud *et al.* (2009) |
| NanoGate | Germany | Sol-gel process | Robichaud *et al.* (2009) |
| Degussa (BASF) | Germany | Unknown | Robichaud *et al.* (2009) |
| Altairnano | US | Hydrochloride process, incl. spray hydrolysis, calcining and milling | Robichaud *et al.* (2009) |
| Start-up in 2009 | Vietnam | Altairnano-process → capacity expected is 5.000-10.000 t/a | Robichaud *et al.* (2009) |
| Tronox | EU | According to TDMA the main manufacturing process is the Chloride process | TDMA |
| Kronos | EU | | TDMA |

$TiO_2$ as a nanomaterial (ultrafine $TiO_2$) is engineered to have primary particles smaller than 100 nm in order to optimize properties for non-pigmentary applications e.g. catalyst supports ($DeNO_X$ stationary and automotive), UV-absorbers

(Cosmetics) and photo-catalysts. Due to their smaller size nano particles are transparent. Pigment grade $TiO_2$ on the other hand is manufactured to optimize the scattering of visible light and the consequently white opacity. This requires a primary particle size of approximately half the wavelength of the light to be scattered, which is half of 400 - 700nm for visible light.

In order to obtain better insight in the dominant routes and practices for the manufacturing of nano-$TiO_2$ in Europe, the TDMA (Titanium Dioxide Manufacturers Association) was consulted for more information on:

1. the dominant manufacturing processes applied;
2. approximate manufacturing volumes of nano-$TiO_2$;
3. potential emissions to the environment in the manufacturing phase of the material;
4. possible releases of nano-$TiO_2$ from applied coatings.

The chloride process accounts for a majority of pigment grade $TiO_2$ produced globally and within the U.S. The chloride process is preferred over the sulfate process due to economic and environmental concerns. A third process, the sol-gel process, is used to produce specifically nano-$TiO_2$. Large volume manufacturing of nano-$TiO_2$ takes place via the chloride (Pyrogenic) or the sulphate process (Klaessig, 2010). The sol-gel process is described for the manufacturing of especially amorphous Nano-$TiO_2$. All these processes are reviewed in more detail by US EPA. In the chloride process the following process steps are defined:

- Ti-ore converted to volatile $TiCl_4$;
- $TiCl_4$ vaporized in an oxygen rich environment;
- $TiO_2$ particles captured from gas stream;
- Post treatment by fluid-bed or slurry system.

In their response, the TDMA states that "*common precursors for the manufacturing of ultrafine* $TiO_2$ *are intermediates of the pigmentary production process e.g. titanium tetrachloride – mainly converted to titanium oxychloride (chloride technology) - and titanium oxysulfate and titanium oxyhydrate (sulfate technology). These intermediates are further processed by precipitation, thermal hydrolysis or flame hydrolysis. Secondary steps are milling, coating and then milling again. It is unknown to what extent organometallic precursors like Titanium alcoholates are used in an industrial scale. Nearly all of these processes are proprietary knowledge and patent protected and not commercially available.*"

#### *7.1.1.2 Estimated manufacturing volumes of Nano-$TiO_2$ and Nano-Ag*

Different studies have modeled the possible emissions of MNO to the environment and, in order to do so, assumed yearly manufacturing volumes based on the information available. Table 7.2 summarizes estimated total manufacturing volumes of Nano-$TiO_2$ and Nano-Ag obtained these sources. In table 7.4, the different derived predicted environmental concentrations (PECs) are summarized that were based on these manufacturing volumes. It is important, to emphasize the existing uncertainty in the overall market volumes. Hendren *et al*. (2011) did point this out in a study where they compared the data quality related to the manufacturing and use of MNO, among which Nano-$TiO_2$ and Nano-Ag, concluding that there exists a serious lack in verifiable data. For Nano-$TiO_2$ only two of the eight US-companies involved in that study agreed to communicate manufacturing data in the form of patent information, one of which actually stopped manufacturing Nano-$TiO_2$ in 2003 (which was in fact one of the companies used by the Müller and Nowack study to estimate their world-wide manufacturing volumes). Consequently, Hendren *et al.* (2011) concluded the quality of the manufacturing data for $TiO_2$ to be weak. For Nano-Ag the data quality was concluded slightly better as three US companies (out of ten) were willing to share information.

Table 7.2 Estimates of the total manufacturing volumes of the US-only, European (EU) and world-wide (w-w) manufacturing of Nano-$TiO_2$ and Nano-Ag.

| **Year** | **Nano-$TiO_2$ (US-only t/a)** | **Nano-$TiO_2$ (US-only t/a)** | **Nano-$TiO_2$ (w-w t/a)** | **Nano-$TiO_2$ (EU t/a)** | **Nano-Ag (US-only t/a)** | **Nano-Ag (w-w t/a)** |
|---|---|---|---|---|---|---|
| | **Robichaud *et al.* (2009)** | **Hendren *et al.* (2011)** | **Müller and Nowack (2008)** | **TDMA (2011)[12]** | **Hendren *et al.* (2011)** | **Müller and Nowack (2008)** |
| 2002 | 3.000 | | | | | |
| 2006 | 40.000 | | | | | |
| 2008 | 43.000 | | 5.000 – 64.000 | | | 500 – 1.230 |
| 2009 | 44.400 | | | | | |
| 2011 | | 7.800 –38.000 | | 10.000 | 2,8 - 20 | |
| 2015 | 260.000 | | | | | |

In order to model possible releases on MNO to the different environmental compartments, Mueller and Nowack (2008) modeled the user phase and waste phase of the different products to include waste treatment scenario's that will prevent the MNO from entering the environment. In reaction to the modeling approach by Mueller and Nowack (2008), Robichaud *et al*. (2009) estimated environmental exposure to Nano-$TiO_2$ based on the worst case assumption that all Nano-$TiO_2$ produced should eventually end up in the environment. A worst case scenario: '*what goes in must come out'* has been adopted by Robichaud *et al.* (2009) in terms of total manufacturing volumes.

### *7.1.1.3 Emissions to the environment specific for Nano-$TiO_2$*

In their response to the question regarding possible emissions to the environment during $TiO_2$ manufacturing, the TDMA refers to "*The BAT reference document "Large volume inorganic chemicals – solids and others" (EC, 2007) formally adopted by the European Commission under the IPPC directive describes in Chapter 3 the Best Available Technology (BAT) for the manufacturing of $TiO_2$ (sulfate and chloride technology) giving details to raw materials consumption, energy and water consumption as well as emissions into water and air. In this document no differentiation is made between pigmentary $TiO_2$ and ultrafine $TiO_2$. In most cases ultrafine $TiO_2$ manufacturing is integrated in the production sites of pigmentary $TiO_2$.*" This suggests that emissions to the environment are closely intertwined with the emissions resulting from the pigmentary production of $TiO_2$. This also suggests that the total emissions (so Nano-$TiO_2$ plus pigmentary $TiO_2$) do meet the BAT description. In this BAT document, emissions to the environment are specified in high detail and allocated to the various process steps. Overall in 2002, the Choride process emitted an average of 0.6 kg Ti/ton $TiO_2$ to water, 0.1 kg particulates (non specified)/ton $TiO_2$ to air and 962 kg non-hazardous solid waste

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[12] Sharing nano-knowledge in the value-chain of coatings, TDMA response to IVAM questions, summer 2011. Approximated manufacturing volume is 1% of the total pigment grade $TiO_2$, which accounts for 1.000.000 t/a.

/ton $TiO_2$ to landfill. For the sulphate process, this was 6 kg Ti/ton $TiO_2$ to water, 0.7 kg particulates (non specified)/ton $TiO_2$ to air and 4.7 kg SOx-$TiO_2$/ton $TiO_2$ to air, and a total of about 1200 kg of different solid wastes /to $TiO_2$ to landfill or a chemical waste incinerator. It is difficult to say what fraction of these emissions should be alocated to the manufacturing of Nano-$TiO_2$. On might suggest 1% as the manufacturing volume of Nano-$TiO_2$ is about 1% of the total pigmentary $TiO_2$ produced. However, since his number is nowhere validated, here is not the place to speculate about the emissions during Nano-$TiO_2$ manufacturing. Alternatively, US EPA did model possible emissions to the environment during this manufacturing (US EPA, STREAMS).

Environmental emission sources due to process releases are described and estimated in table 7.3. Table 7.3 is based on EPA Office of Pollution Prevention and Toxics (OPPT) conservative models that are used when site-specific data are not available (U.S. EPA, 2010). These release estimates assume the Nano-$TiO_2$ manufacturer collects the Nano-$TiO_2$ as a solid powder from the production line and then repackages the Nano-$TiO_2$ for sale. It is conservatively assumed that the Nano-$TiO_2$ is sold as a solid powder without further formulation into liquid (exposure to powder forms results in formation of fugitive dusts and corresponding dermal and inhalation exposures).
Table 7.3 summarizes the potential release sources and associated quantities. The exact environmental media to which Nano-$TiO_2$ is released depends on the waste handling and cleanup practices employed by the manufacturer. The quantity of dust emissions to air from handling and packaging solid powders depends on the air pollution control devices employed. The facility’s practices for cleaning equipment, cleaning or disposal of spent containers, and handling spills are determinants of the environmental emissions to other media. For example, cleaning conducted with water and released to the facility’s wastewater stream may introduce Nano-$TiO_2$ into the wastewater. However, if a facility handles waste streams that potentially contain Nano-$TiO_2$ as non-hazardous solid waste or as hazardous waste, then introductions to water would be less likely. Actual industrial practices employed by individual manufacturers are uncertain. Therefore, the release estimates and environmental media presented in.

Table 7.3 also summarizes the potential risk management measures used for each activity. These engineering controls are described by DuPont in their submission to the EPA Nanoscale Materials Stewardship Program (NMSP) for their Light Stabilizer manufacturing process. However, it is uncertain if these engineering controls are applicable to other U.S. Nano-$TiO_2$ manufacturers or for the production of Nano-$TiO_2$ for applications other than UV stabilizers for plastics.

Table 7.3 Summary of Process Releases of Nano-$TiO_2$ to Environmental Media during Manufacturing (US EPA)

| **Potential Environmental Media**[1] | **Daily Release Rate (wt% of daily through-put)** | **Release Freq. (d/y)** | **Activity** | **Risk Management Measures**[2] | **Release Basis**[1] |
|---|---|---|---|---|---|
| Air (non-captured emissions);<br>Water or Incineration or Landfill (captured emissions) | 0.5% | 250 | Transferring solid Nano-$TiO_2$ from product collector to packaging mechanism. | Automatic packing machines.<br>Dust collectors<br>Baghouse with 99.98% efficiency<br>0.02% to air.<br>99.98% to water or landfill. | EPA/OPPT Dust Emissions from Solids Transfers Model estimates 0.5% of the solids transferred are released as dust emissions to uncertain media. |
| Water (non-captured aqueous releases);<br>Incineration or Landfill (captured aqueous releases or solid or hazardous waste) | 1% | 250 | Cleaning solid Nano-$TiO_2$ residuals (powders) in process vessels. | On-site wastewater treatment with flocculation.<br>99.3% removal efficiency.<br>99.3% to landfill / recycle.<br>0.7% pass through to surface water. | EPA/OPPT Solid Residuals in Process Vessels Model estimates 1% residual in process vessels. |
| Incineration or Landfill | 1% | 250 | Cleaning or discarding lining from product collector container. | Landfill | EPA/OPPT Solid Residuals in Transport Containers Model estimates 1% residual remains in emptied containers. |

[1] Values estimated using EPA/OPPT models.

[2] Data obtained from DuPont's NMSP submission[3].

To date, no environmental emission modelling has been done for Nano-Ag. However, similar to the manufacturing of nano-$TiO_2$, Nano-Ag is being produced under contained process conditions, meaning that exposure to the environment is most likely to occur during sampling (for quality control), unloading and transferring for packaging, cleaning and maintenance activities at the MNO production site, and transportation and storage.

#### 7.1.1.4 *Resulting emissions of Nano-$TiO_2$ and Nano-Ag to the environment during their manufacturing*

In section 7.1.1.2 and Table 7.2, variations in the assumed manufacturing volumes of Nano-$TiO_2$ and Nano-Ag have been summarized. Together with the modeled emissions during the manufacturing of Nano-$TiO_2$ in section 7.1.1.3 and assuming these are similar for the manufacturing process of Nano-Ag (which is in fact a rough assumption) this would result in the emissions during manufacturing summarized in Table 7.4.

Table 7.4 Emission flows of $TiO_2$ to the environment as a consequence of production and formulation of paint for the different estimated annual production volumes.

| Emissions of MNO during MNO Manufacturing | | | |
|---|---|---|---|
| Environmental compartments | Yearly release $TiO_2$ (%) # | Nano-$TiO_2$ (t/a) | Nano-Ag (t/a) |

| Total produced (t/a) | | 5.000* (W-W) | 10.000** (EU) | 64.000*** (W-W) | 500 (W-W) | 1.230 (W-W) |
|---|---|---|---|---|---|---|
| Emissions to Air | 0.5 | 25 | 50 | 350 | 2,5 | 6,15 |
| Emissions to Water | 1 | 50 | 100 | 640 | 5,0 | 12,3 |
| Emissions to Landfill | 1 | 50 | 100 | 640 | 5,0 | 12,3 |

# Yearly release of nano-$TiO_2$ under the assumption that no special measures were taken to prevent for this release (see Table 7.3).

* Min world-wide production.

** Estimated European production

*** Max. World-wide production.

Clearly and unsurprisingly from this table, the emissions in the manufacturing phase of the MNO depend strongly on the assumed manufacturing volumes. Uncertainties in the manufacturing volumes will similarly affect all emissions along the full life cycle of the nanocoating and it is therefore essential to the quality of future risk assessments that the yearly manufacturing volumes of MNO become known.

### 7.1.2 *Emissions during production of paint/coatings containing MNO*

The exposure sources resulting from the processing of nano-$TiO_2$ will vary with each application depending on the specific unit operations that are involved. Activities generating environmental releases may be expected to be similar to those observed during manufacturing. If processors receive nano-$TiO_2$ from manufacturers as solid powders, then the processors may expect dust emissions from handling the solid powder as well as solid residuals in the shipping containers. The processors may further expect solid residuals in any equipment used to process the solid powders.

Many of the applications require Nano-$TiO_2$ to be formulated into a liquid suspension or polymer resin. In these applications, processors may expect potential environmental releases of Nano-$TiO_2$ contained in liquid or solid resin releases.

Table 7.5 summarizes the potential sources and quantities of process releases and their respective environmental media. Similarly as with manufacturing, the exact environmental media to which nano-$TiO_2$ is released depends on the waste handling and clean-up practices employed by the processor. Facilities may employ air pollution control devices to control dust emissions to air. Facilities' practices for cleaning equipment, cleaning or disposing of spent containers, and handling spills may also vary. For example, cleaning conducted with water and released to the facility's wastewater stream may introduce Nano-$TiO_2$ into the wastewater. If a facility handles waste streams that potentially contain Nano-$TiO_2$ as non-hazardous solid waste or as hazardous waste, then introductions to water would be less likely. Similarly as with manufacturing, the actual industrial practices employed by processors are uncertain; therefore, the release estimates and environmental media presented in Table 7. are based on EPA Office of Pollution Prevention and Toxics (OPPT) conservative models that are used when site-specific data are not available. Information on potential engineering controls used by processing facilities has not been identified.

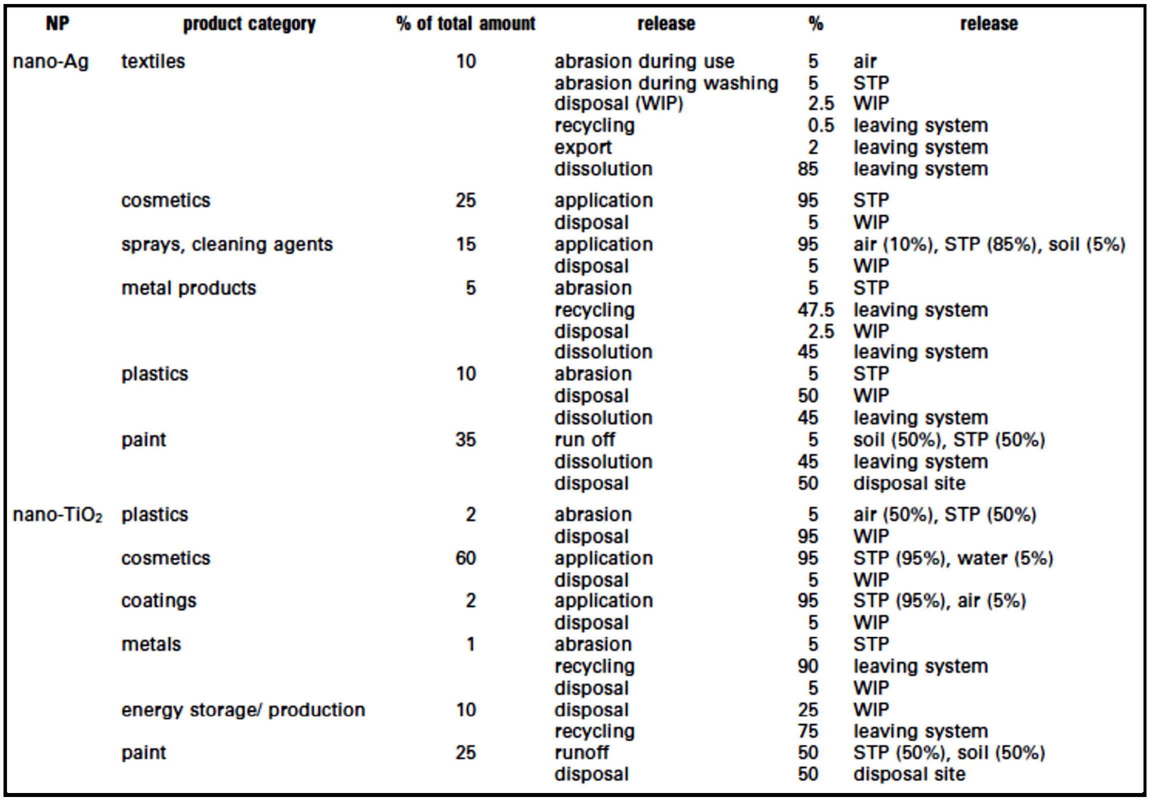
Table 7.5 Summary of Process Releases of Nano-TiO2 to Environmental Media during Processing (US EPA)

| **Potential Environmental Media** | **Daily Release Rate (wt% of daily through-put)** | **Release Frequency (days/year)** | **Activity** | **Release Basis** |
|---|---|---|---|---|
| Air (non-captured emissions);<br>Water or Incineration or Landfill (captured emissions) | 0.5% | 250 | Unloading Nano-$TiO_2$ from packaging and charging hopper or other process vessel. | EPA/OPPT Dust Emissions from Solids Transfers Model estimates 0.5% of the solids transferred are released as dust emissions to uncertain media. |
| Water (non-captured aqueous releases);<br>Incineration or Landfill (captured aqueous releases or solid or hazardous waste) | 1% | 250 | Cleaning solid Nano-$TiO_2$ residuals in process vessels. | EPA/OPPT Solid Residuals in Process Vessels Model estimates 1% residual in process vessels. |
| Incineration or Landfill | 1% | 250 | Cleaning or discarding product packaging. | EPA/OPPT Solid Residuals in Transport Containers Model estimates 1% residual remains in emptied containers. |
| Water (non-captured aqueous releases);<br>Incineration or Landfill (captured aqueous releases or solid or hazardous waste) | 2% | 250 | Cleaning liquid residuals containing Nano-$TiO_2$ from process vessels. | EPA/OPPT Multiple Process Vessel Residual Model estimates 2% residual from multi-vessel and other equipment processes. |

To date, no environmental emission modelling has been done for Nano-Ag. However, similar to the production of Nano-$TiO_2$ paints, Nano-Ag paint is being formulated under controlled process conditions, meaning that exposure to the environment is most likely to occur during transportation and storage of the raw MNO, charging the paint resin (=adding the MNO to the base paint), sampling (for quality control), cleaning and maintenance activities and packaging of the nanopaint. Assuming both MNO are delivered in a powdery form, similar emissions to the environmental may be assumed as a first reasonable estimate (of cause depending on the dusty ness of the powder). When the MNO is delivered to the downstream user as a liquid dispersion or paste, any emission of dust during packaging and unloading is unlikely. Emissions as a consequence of cleaning operations may nevertheless remain similar.

#### 7.1.2.1 *Resulting emissions of Nano-$TiO_2$ and Nano--Ag to the environment during paint production*

In order to estimate possible emissions of Nano--$TiO_2$ and Nano-Ag in the production phase of nanopaints one should have an idea on the total volume of these MNO that are actually used for paint applications. Müller and Nowack (2008) modeled the emission of Nano--$TiO_2$ and Nano-Ag to the environment based on the total world-wide turnaround of these nanomaterials in different product categories and the estimated releases from the different end-user products. In their allocation of the MNO over the different product categories, shown in Figure 7.1, they estimate that 25% of all nano-$TiO_2$ is used in paints. In the case of Nano-Ag, 35% of the world-wide production volume is used in paints.



| NP | product category | % of total amount | release | % | release |
|---|---|---|---|---|---|
| nano-Ag | textiles | 10 | abrasion during use | 5 | air |
| | | | abrasion during washing | 5 | STP |
| | | | disposal (WIP) | 2.5 | WIP |
| | | | recycling | 0.5 | leaving system |
| | | | export | 2 | leaving system |
| | | | dissolution | 85 | leaving system |
| | cosmetics | 25 | application | 95 | STP |
| | | | disposal | 5 | WIP |
| | sprays, cleaning agents | 15 | application | 95 | air (10%), STP (85%), soil (5%) |
| | | | disposal | 5 | WIP |
| | metal products | 5 | abrasion | 5 | STP |
| | | | recycling | 47.5 | leaving system |
| | | | disposal | 2.5 | WIP |
| | | | dissolution | 45 | leaving system |
| | plastics | 10 | abrasion | 5 | STP |
| | | | disposal | 50 | WIP |
| | | | dissolution | 45 | leaving system |
| | paint | 35 | run off | 5 | soil (50%), STP (50%) |
| | | | dissolution | 45 | leaving system |
| | | | disposal | 50 | disposal site |
| nano-$TiO_2$ | plastics | 2 | abrasion | 5 | air (50%), STP (50%) |
| | | | disposal | 95 | WIP |
| | cosmetics | 60 | application | 95 | STP (95%), water (5%) |
| | | | disposal | 5 | WIP |
| | coatings | 2 | application | 95 | STP (95%), air (5%) |
| | | | disposal | 5 | WIP |
| | metals | 1 | abrasion | 5 | STP |
| | | | recycling | 90 | leaving system |
| | | | disposal | 5 | WIP |
| | energy storage/ production | 10 | disposal | 25 | WIP |
| | | | recycling | 75 | leaving system |
| | paint | 25 | runoff | 50 | STP (50%), soil (50%) |
| | | | disposal | 50 | disposal site |

Figure 7.1 Allocation of world-wide substance flows of nano$TiO_2$ and Nano-Ag as a percentage of the estimated world-wide production volume and the eventual release in to the environment specific for the situation in Switzerland. STP = Sewage Treatment Plant, WIP = Waste Incineration Plant

Specific for Europe, the Titanium Dioxide Manufacturers Association (TDMA) approximated in 2011 in a written communiqué to IVAM UvA BV that the amount of Nano-$TiO_2$ used for coating applications in Europe is on the order of 100 - 200 t/a, about 1 – 2% of all Nano-$TiO_2$ produced in Europe. Any statistics on the European market share for the manufacturing of Nano-$TiO_2$ is lacking to date and therefore one cannot directly compare this 1 – 2% to the 25% estimate by Müller and Nowack (2008). In 2007, the European production of pigmentary $TiO_2$ accounted for 37% of the world-wide (pigmentary) $TiO_2$ market. It is uncertain whether or not this number may be indicative for the nano market as well. The different assumptions regarding the application volumes of Nano-$TiO_2$ and Nano-Ag in different products are summarized in Table 7.6.

Table 7.6 Differences in assumptions on the uses of $TiO_2$ and Ag in different product categories used in different models

| **Product category** | **Market share bulk-$TiO_2$ (V%)** | **Market share Nano-$TiO_2$ (V%)** | **Market share Nano-$TiO_2$ (V%)** | **Market share Nano-Ag (V%)** |
|---|---|---|---|---|
| | **Robichaud *et al.* (2009)** | **Müller and Nowack (2008)** | **TDMA (2011)** | **Müller and Nowack (2008)** |
| Paints, Pigments and Lacquers | 57% | 27% | 1-2% | 35% |
| Plastics | 26% | 2% | ~ 98% | 10% |
| Paper | 13% | - | | |
| Cosmetics | <4% | 60% | | 25% |
| Energy storage/production | - | 10% | | |
| Sprays and cleaning agents | | | | 15% |
| Textiles | | | | 10% |

From these percentages and the yearly manufacturing summarized in Table , one can estimate the amount of Nano-$TiO_2$ and Nano-Ag that is actually used on a yearly basis in paints. Using then the modeled emission percentages during paint production summarized in Table 7.5, actual emission flows of Nano-$TiO_2$ and Nano-Ag can be estimated (provided that a similar emission pattern is assumed to be valid for the production of Nano-Ag paints). The result of this exercise is shown in Table 7.7.

Table 7.7 Emission flows of $TiO_2$ to the environment as a consequence of production of paint for the different estimated annual production volumes.

| Emissions of MNO during paint production | | | | | | |
|---|---|---|---|---|---|---|
| Environmental compartments | Yearly release TiO2 (%) # | Nano-TiO2 (t/a) | | | Emission Nano-Ag (t/a) | |
| Total applied (t/a) | | 1.250* | 100** | 16.000*** | 175 | 430 |
| Emissions to Air | 0.5 | 6,25 | 0,5 | 80 | 0,88 | 2,15 |
| Emissions to Water | 2 | 25 | 2 | 320 | 1,75 | 4,3 |
| Emissions to Landfill | 1 | 12,50 | 1 | 160 | 1,75 | 4,3 |

# Yearly release of Nano-$TiO_2$ under the assumption that no special measures were taken to prevent for this release (see Table 7.5).
* Min world-wide production.
** Estimated European production
*** Max. World-wide production.

From the above, there is a clearly shown discrepancy between the allocation of Nano-$TiO_2$ end-uses as approximated by the TDMA (for Europe, being 1-2% for the use in paints) and Müller and Nowack (for the world-wide use of $TiO_2$, being 25% for the use in paints). The reason for this difference remains uncertain. Part may be due to “product grouping” as Mueller and Nowack did also include ink and varnishes in the group of paints. Other reasons may e.g. be that Europe only produces a small fraction of all Nano-$TiO_2$ paints produced world-wide, or that the TDMA only provides 1-2% of its European produced Nano-$TiO_2$ to European paint manufacturers. However, certain is that current uses or applications of MNO (including Nano-$TiO_2$ and Nano-Ag) are very difficult to recognize (if recognizable at all) from the products perspective and are no where registered by their manufacturer, with the exception of a limited (but growing) number of voluntary initiatives.

### 7.1.3 *Emissions during application of paints*

In the application phase of a coating, this coating is being prepared for use, applied to an object, the remaining coating material is disposed of and the instrumentation is cleaned. In practice, it may be difficult to distinguish between any corresponding emissions to the environment. Moreover, true emissions will strongly depend on the situation, depending on the specific work environment (indoor or outdoor use), on the paint characteristics (e.g. water or solvent borne coatings), on the MNO characteristics (e.g. volatility), on the behaviour of the workers involved and on parameters like weather conditions.

A typical percentage of 15% of paint loss has been described by *Determination method Environmental Performance Buildings and Infrastructure and Water Works* of SBK (SBK, 2011) for the total of all activities involved in the application of industrial paints. This may be accurate for architectural coatings applied outdoors, but in the case of automotive coatings applied inside a spraying cabin, this percentage of actual emission to the environment may be much smaller. According to ‘expert judgement’ this percentage lays more typically around 1%[13]. However, it should be noted that this percentage isn’t accurately known. From a previous project conducted in the context of exposure characteristics to volatile organics (the AWARE-pilot), it was being concluded that during spraying only 40 – 70% of the coating actually reaches the surfaces that should be coated, depending on factors like the specific working conditions, the coating characteristics and the spraying-nozzle. The rest (30 – 60%) is lost and will be (at least partly) captured on the wall, floor and ceiling, as well as by the ventilation exhaust system and the filters inside.

The main part of all losses will leave the workplace as solid waste as it can be assumed that the paint is attached in dry form to e.g. used rollers, empty cans, protective clothing or wiping tissues. This fraction of solid waste is typically incinerated as chemical waste. A smaller fraction of liquid waste might get flushed down the drain.

The Technical guidance document on Risk Assessment (TGD part II) of the European Chemical Agency describes a typical range of emission to air of 0% (Nano-$TiO_2$ and Nano-Ag are not volatile), between 1 – 5% emission to water and around 0,5% emission to soil. The subsections below present a more qualitative description of emissions occurring during the application phase of a paint.

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[13] A rough estimate obtained from Valspar and FOCWA.

#### *7.1.3.1 Preparation of nano based coatings*

Industrial and automotive coatings may consist of a one or a two component system. When the ready-for-use coating consists of two components, these are to be mixed on site. During mixing there is a potential exposure as a consequence of:

- Vaporisation;
- Spillage;
- Cleaning of the instrumentation (emission to e.g. solid waste, on-site landfill, municipal waste or waste water treatment plant).

Losses as a consequence of preparation are expected to be small compared to losses that will occur during application of the pain with a brush or roller or during spraying operations.

#### *7.1.3.2 Brush or roller application*

This type of application will be involved in only a small fraction of the total volume of coatings applied. Significant emissions can be expected through spillage, generation of wastes (e.g. disposable rollers, wiping tissues, personal protective clothing) and cleaning during and after coating activities. Minor emissions of MNO might be expected from evaporation of the nano based coating.

#### *7.1.3.3 Spray application*

Significant emissions can be expected through spillage and cleaning activities during and after coating activities. As a rough estimate one can assume that the spraying efficiency is a direct estimate of the fraction of the coating that might be released to the environment. This environmental exposure route is likely to dominate the emission during application in exterior workplaces. Minor emissions might be expected from evaporation of the nano based coating.

For indoor activities main exposure routes can be expected from the disposal of solid and liquid waste to landfill (construction area) or to the municipal waste water treatment plant.

For outdoor application the emission to the environment occurs as a consequence of the average efficiency of the spraying equipment used. This emission is originally airborne, but will quickly deposit as solid waste onto the ground. Given the typical “urban area”, this fraction will therefore be treated as emission to surface water or soil.

### 7.1.4 *Emissions during service life*

Emission of MNOs occurring during the service life of a paint system is largely depending on the stability of the paint system and the way the MNO is integrated in the paint matrix. Emissions do also depend on the frequency of service and maintenance, i.e. how often is a paint system repaired or partly removed. For the emission potential of MNOs to the environment, especially the freedom of migration of the MNO in the paint matrix is of importance, because this strongly affects the bioavailability. In the case of Nano-$TiO_2$ and Nano-Ag, two MNOs that are typically not chemically bound to the paint matrix but are physically contained, some mobility might be expected. Moreover, as Nano-Ag is soluble in water, for this MNO even a certain degree of leaching of $Ag^+$ ions is to be expected. However, other MNOs like $SiO_2$ that chemically do react with specific binder materials forming an exceptionally strong and dense maze, mobility within the matrix is less likely.

To date, there are two studies describing the weathering and emission patterns of Nano-$TiO_2$ and Nano-Ag containing wall coatings to the environment: Kaegi *et al.* (2008) and (2010) respectively. No studies are found that describe the weathering of automotive coatings, but as these type of coatings are typically more durable and erode much more slowly than wall coatings the data described here can well be considered an absolute worst case.

### *7.1.4.1 Emissions of Nano-$TiO_2$ to the environment during service life*

For $TiO_2$, erosion of the surface layer has been described as a consequence of oxidation due to natural weather conditions. This “chalking” of the surface leaves $TiO_2$ exposed at the surface. Kaegi *et al.* (2008) studied the appearance of nano-sized $TiO_2$ in the runoff of exterior facades covered with $TiO_2$-paints and in the urban runoff at the point in place just before the water mingles with the surface water. They find $TiO_2$ in the size range between 20 and 300 nm in the runoff from both new and aged (2 year old) facades. Most often, these $TiO_2$ nano particles are detected to be embedded in the organic binder material of the original paint, suggesting the $TiO_2$ and the binder erode from the surface together and a first emission of $TiO_2$ to the environment from exterior wall coatings will be a bound form. Kaegi *et al.* (2008) do also find elevated concentrations of Nano-$TiO_2$ in urban runoff water samples. The particle compositions suggest they stem from the same source as the façade runoffs measured. However, in the case of the urban runoffs, part of the $TiO_2$ nano particles observed are no longer embedded in the organic binder matrix of the paint, suggesting the binder dissolves during the transport from the façade to the surface water system leaving the “unbound” $TiO_2$ nano particles. This information is key in the assessment of the actual bio-availability of Nano-$TiO_2$ emitted from façade coatings. One might reason that if part of the binder dissolves, eventually all will dissolve and consequently all $TiO_2$ eroded from the surface will end up in an unbound state in the environment.

The actual particle concentration of $TiO_2$ that will reach the surface waters via this route will strongly depend on parameters like the actual weather conditions and the density of product application. Based on this one study, one therefore cannot derive a typical emission flow. Keagi *et al.* (2008) however does detect particle concentration <100nm of about $10^7$ $TiO_2$ particles $l^{-1}$ runoff water and about $10^8$ $TiO_2$ particles $l^{-1}$ runoff water for particles <300 nm. These number concentrations might provide a first insight in the order of magnitude that can be expected in the assessment of the emission of Nano-$TiO_2$ from exterior surfaces.

### *7.1.4.2 Emissions of Nano-Ag to the environment during service life*

In a follow-up study, Kaegi *et al.* (2010) determined the runoff of Nano-Ag from paints used in outdoor applications. Similar to $TiO_2$ they find that Nano-Ag typically comes off as a composite colloid and is embedded in the paint’s binder. However, in contrast to $TiO_2$ they find that the mass fraction of Ag that is lost from the surface over a period of one year is much higher (approximately 30% of all Ag initially applied) than that of $TiO_2$ (which was less than 1%). Interestingly also, about 80% of all Nano-Ag that was lost over one year, was emitted within the first 8 rain events. After half a year, the runoff concentration of Nano-Ag stabilized to approximately 1 $\mu g\ l^{-1}\ m^{-2}$. This pattern was very similar or $TiO_2$ although the initial runoff concentrations were much higher (almost 10x) and the runoff concentrations after 6 months were much lower (less than 0.1 µg $l^{-1}$ $m^{-2}$). After one year, concentrations of both ENPs were below the detection limit of 0.08 µg $l^{-1}$. Moreover, it is interesting to note that the runoff concentration appeared not to be correlated to the runoff volume, suggesting the availability of ENP for runoff depends on the erosion rate of the surface layer.

For the Ag nano particles emitted from the paint surface, Kaegi *et al.* (2010) found evidence for a possible complexation of Ag to sulfur, forming $AgS_2$, i.e. by reacting with $H_2S$ from the atmosphere. Such a complex formation would strongly influence the eventual toxicity profile of the Ag nano particles as $AgS_2$ is much less toxic to environmental organisms than $Ag^+$ or Ag. It is not unrealistic to suggest that Ag nano particles may react with sulfur containing species prior to reaching the ecosystem of natural surface waters. Another fate of the particles can be oxidation forming $Ag_2O$, which is also less toxic than Ag or $Ag^+$.

These two works by Keagi *et al.* do show that Nano-$TiO_2$ and Nano-Ag are both emitted from exterior surfaces. The ENPs appear to be primarily contained by the binder material. Emission seems mainly due to erosion of the surface matrix. Emission can be as high as 30% of all ENP present in the paint but depends strongly on i.e. the type of paint and the ENP present. Keagi *et al.* also show that once the emitted particles are taken up in water, the binder material can degrade leaving free ENP behind. However, the fate of these free ENP is uncertain as they may interact with other substances present in the environment such as pollutants or natural organic matter that may influence their chemical nature, toxicity and mobility.

#### *7.1.4.3 Concluding remarks for emissions during service life*

Concluding the above, first scientific data do suggest that approximately 1% of all Nano-$TiO_2$ applied on an exterior surface may be lost from an exterior surface within one year due to the erosion of the paint matrix. When the MNO is soluble and has the possibility to leach from the matrix, this fraction may increase to at least 30% as was found for Nano-Ag. It should be noted though that the presence of Nano-Ag in paints for outdoor applications is questionable and that for interior use a 30% emission is not to be expected (unless the surface, which can be a wall, floor, table top or kitchen table, is actually cleaned with water).

In the context of the results described above, it is furthermore important to note that the emission observed is influenced also by the homogeneity of the paint system. Nanocoatings in which MNOs do add specific surface characteristics are typically designed such that the active MNO ingredients do concentrate at the surface to make optimum use of their performance. In that situation, erosion may result in a higher emission than in a situation in which a similar amount of MNO is equally distributed within the paint layer. It would therefore be premature to conclude a specific fraction to the emission of MNO during the service life of coatings. However, one can conclude that depending on the type of paint, the paint morphology, the speed of erosion and the type of MNO, the service life may be an important phase in the total life cycle emission of MNO to the environment and should therefore be carefully assessed during paint-product design.

### 7.1.5 *Emissions during the waste phase*

Only very little is published concerning the possible emissions of MNO during the waste phase of MNO containing products. Müller and Nowack (2008) modeled the emission of Nano-$TiO_2$ and Nano-Ag to the environment based on the total world-wide turnaround of these nanomaterials in different product categories and estimated releases from the different end-user products. In their allocation of the MNO over the different product categories, which was shown in Figure 7.1, they estimate that of all Nano-$TiO_2$ used in paints 50% ends up in the environment during the product's functional life-phase via runoff from the painted surfaces. The other 50% is "actively" disposed during the end-of-life phase and ends up at a disposal site. In the case of Nano-Ag, 45% of all Nano-Ag used in paints dissolves as $Ag^+$ during the product's functional life-phase, 2,5% was assumed to end up in soil and 2,5% ends up in a sewage treatment plant.

In 2011, The Dutch Health Council published a *Signalement Nanomaterialen in Afval* (Nanomaterials in waste), where they did look specifically at the information available on recycling, incineration and waste water purification of waste streams containing nanomaterials from consumer products. The signalement does conclude that for incineration and waste water treatment there is evidence suggesting that MNO may not be fully removed from the waste and will consequently end up in the residual waste streams. MNO may become airborne during incineration or may remain part of the effluent of waste water treatment plants and enter the environment via those routes. MNO with bactericidal activity may furthermore adversely affect bacterial purification systems of waste water treatment plants.

Up to 2010, only one study by Kiser *et al.* (2009) does report on actual environmental abundances of Nano-$TiO_2$ in waste water effluents. In this work, the efficiency of waste water treatment plants (WWTP) towards the removal of nano-$TiO_2$ was studied, showing first evidence that waste water treatment plants, though quite efficient in removing larger $TiO_2$-moieties (on the order of 80%), are less well equipped for removing the smaller nano-sized entities (on the order of 42%). With the current growing use of nano-sized $TiO_2$ in all sorts of products, this finding suggests that an undesirable increase in the concentration of Nano-$TiO_2$ in surface waters is to be expected in the near future. For silver, Tiede *et al.* (2010) did show that approximately 90% of all Nano-Ag was removed during waste water treatment, suggesting that waste water treatment may in fact be efficient for Nano-Ag.

Nothing is published about possible remaining MNO in the ash residuals of incineration. For recycling practices, no specific conclusions were drawn as it is not yet known what effect current recycling practices have on nanomaterials and nanoproducts. Still, the Dutch waste management sector does put great emphasis on the separate collection and recycling of nanomaterials and nanoproducts.

An important issue influencing the current unknowns is the lack of methods available to routinely identify and quantify the possible abundance of MNO in the residual waste streams like water and air.
The current lack of transparent communication on the presence of MNO in products, also for coatings, does hamper a further precautionary waste management strategy for nanomaterials and nanoproducts.

The signalement therefore recommends that in accordance with the precautionary principle MNO waste should be minimized as much as possible and that the government should encourage manufacturers and importers of nanomaterials and nanoproducts to adopt smart design of products and technologies, involving also experts from the waste sector in this process. For the design, production and application of paints, this is an important issue. The major part of the total paint layer applied to an object will be removed (e.g. during service and maintenance activities) and will be transported to a waste incineration plant, or alternatively, gets removed as part of the destruction phase of e.g. a building, bridge or sound barrier. In both cases it is uncertain if the waste treatment facilities in place are sufficient for removing the MNO, preventing an emission to the environment.

## 7.2 Environmental fate

When assessing environmental exposure and the corresponding adverse effects, it is important to realize that in the case of Nano-$TiO_2$ and Nano-Ag containing materials, one should distinguish the two situations:

1. the exposure to the individual MNO or aggregates or agglomerates containing this MNO
2. the exposure to MNO contained or embedded in a matrix (i.e. a paint system)

Especially in the production phase of the MNOs of $TiO_2$ and Ag and of the materials containing these MNOs a direct emission of these MNOs to the environment, can be expected. During the use stage (i.e. during the preparation of a coating or the painting of an exterior façade or a car) and during service life (e.g. the functional life at the façade or on the car) however, the environment will rather be exposed to parts or particles of the whole paint system which includes besides the MNOs also binder material, stabilizers and pigments. Whether or not in that situation the environment will be exposed to the MNOs depends on the fate of these MNOs as an integral part of the paint system.

Typical parameters that determine the environmental fate are (a non-exclusive list):
- Dissolution
- Settling/Sedimentation
- Adsorption potential to soil
- Zeta-potential (describing the colloidal behavior)
- Aggregation / Agglomeration
- Adsorption to other substances (for example organic/inorganic suspended particulate matter)
- Speciation: Adsorption of hazardous pollutants (for example cadmium)
- Degradation / (bio) persistence

In the subsections below the current knowledge on the environmental fate of Nano-$TiO_2$ and Nano-Ag is summarized. It is important though, to realize that the information provided has been derived from studies that looked at different forms of Nano-$TiO_2$ and Nano-Ag that may vary with respect to (i.e.) their crystal structure, size range, agglomeration or aggregation state and surface functionalization. To date, there is not one coherent data set describing the different environmental properties for one single defined form of Nano-$TiO_2$ and Nano-Ag. The environmental behavior and fate of MNO do depend strongly on their specific chemical and physical characteristics. Consequently, the information below should be interpreted as possible scenarios for action and not as given facts.

### 7.2.1 *Environmental fate and behavior in air*

The fate and behavior of MNO in air, although not yet studied in detail for MNO, has been studied intensively in aerosol science for gases and ultra fine particulates. From that work, basic knowledge is available on possible behavior, transport mechanisms and fate of airborne nanomaterials. Still, caveats in knowledge do exist with respect to the effect of particle morphology and agglomeration on the behavior and ageing of the MNO in air. Aitken *et al.* (2004) does discuss the behavior of MNO in air. The ENRHES study that overview the information on behavior and fate of MNO up to 2009 identified a potential of four general factors that do play a key role:

| | |
|---|---|
| Particle diffusion | The smaller the particle, the higher its mobility in air and the more rapid mixing with the aerosol system will occur. A rapid dispersion and a potential to travel over large distances is to be expected. |
| Agglomeration | The agglomeration rate is governed by the particle mobility and particle number density. Both are inversely proportional to the particle size suspecting that agglomeration is a fast process for MNO. This would also imply that the MNO emitted are only shortly recognizable (and as such detectable) as MNO but will quickly become indistinguishable from the background aerosols. |
| Deposition | Deposition of particles depends on their gravitational settling coefficient (approximated by 800/rho) which is proportional to the aerodynamic diameter of the particle. Typically, settling will therefore be slower for MNO than for larger particles and does facilitate longer transport distances. |
| Potential re-suspension of agglomerates | In theory, agglomerates may re-suspend in reaction to external factors. However, when MNO are held together by Van der Waals forces, it may not be easy to re-suspend them as a lot of energy is required for this process to happen. |

However, to date no MNO specific information on behavior and fate in air is available. From the above a rough and preliminary picture can be drawn of rapidly mixing MNO that quickly agglomerate (with themselves or with other aerosols) and may be transported over large distances. This in contrast to their more course particle forms that may settle more quickly and mix less rapidly with the aerosol system. If this would lead to an increased or a decreased environmental health risk of MNO compared to larger particles is difficult to deduce and cannot be expressed in a general trend.

### 7.2.2 *Environmental fate and behavior in water*

Similar to the current understanding of the environmental fate and behavior of MNO in air, at this moment, the mechanisms influencing the fate and distribution of nanomaterials in the water environment are only beginning to be understood. In the absence of more Nano-specific knowledge, environmental modeling is yet based on classical colloid chemistry, traditional chemical fate modeling or a combination thereof. These models are based on typical chemical properties like boiling point, vapor pressure, solubility and partition coefficients, reactivity and biological degradation. However, these same properties potentially change at the nm-size scale. Solubility for example is a function of the particle surface area and the electronic properties of substances can be strongly dependent on size and shape. In the following subsections, current knowledge on nanospecific behavior and fate in water is summarized for most important parameters in the determination of environmental fate and behavior of MNO in water, i.e. aggregation, agglomeration, degradation, dispersion stability, solubility, bioaccumulation and carrier capacity.

#### *7.2.2.1 Degradation*

According to Aschberger *et al.* (2011) only few studies have been published on the degradation of nano particles in the environment. Nano-$TiO_2$ is expected to be non-biodegradable in analogy to its bulk-form. However, Nano-$TiO_2$ can be coated, for example to prevent aggregation or to prevent the formation of reactive oxygen species in the case of application in sun creams. Auffan *et al.* (2010) showed that a typical siloxane, used to coat $TiO_2$ to optimize its dispersion behavior in cosmetics, oxidizes in a water environment. Consequently can be expected that also in those cases that the nanoparticle itself is not biodegradable its surface functionalization might well be. For Nano-Ag this will be no different, depending on the exact nature of the coating. This implies that the behavior of the nanoparticle (chemically and physically) can change significantly due to degradation processes in the environment, influencing its reactivity, toxicity and fate.

#### *7.2.2.2 Dispersion stability*

The dispersion stability of Nano-$TiO_2$ and Nano-Ag is of high importance influencing the mobility of the particles. Factors that play a key role are i.e. the concentration of natural organic matter and the ionic strength and acidity (pH) of the environment and the surface charge of the nanoparticle. Observed trends are the following (Aschberger *et al.* 2011 and references therein):

- <u>In surface waters at natural acidity (pH ~ 7)</u>, low ionic strength (fresh water instead of a marine environment) and high NOM generally cause the stabilization of nanoparticle dispersions and hence long range transportation of these particles.
- <u>In porous media (soil and sediment)</u>, small pores and the presence of clay and NOM seems to lead to an increased immobilization of nano particles.

For Nano-$TiO_2$ in natural surface waters, transport distances of 5 – 10km have been reported. In an alkaline environment at pH 10 a dispersion of Nano-$TiO_2$ can be stable for of at least 10h.
Gao *et al.* (2009) does show that the aggregation of Nano-Ag in water increases with the ionic strength of the medium (following classical Derjaguin-Landau-Verwey-Overbeek theory on colloidal stability). Hence, as for the concern of ionic strength, aggregates of Nano-Ag may be more stable in seawater than in fresh water environments. However, NOM was observed to aggregate strongly to Nano-Ag, preventing the formation of larger silver agglomerates, but also as the NOM is suspended in water, in principle facilitating an elongation of transportation distances

of the MNO. Similar behavioral trends were observed for various metal oxide MNOs like aluminum oxide and iron oxide (ENRHES 2009 en references therein) hinting at a more general mechanism. However, it was also observed that the presence of certain acids may induce disaggregation instead of aggregation of MNO, pointing at the complexity of the interplay between substances influencing the eventual fate and behavior of the MNO in the environment.

In addition to pH, ionic strength and NOM concentration, the Zeta-potential of MNO may be an important factor determining its dispersion stability. For copper MNO, Li *et al.* (2007) showed that that the higher the absolute value of the Zeta-potential of the MNO, the better it dispersed in water and the greater its dispersion stability was. This directly impacts on e.g. sedimentation and transportation characteristics. However, no similar studies did look at the characteristics for Nano-Ag and Nano-$TiO_2$.

### *7.2.2.3 Solubility*

Solubility, or the dissolution of MNO, is an important issue in the assessment of environmental risks. By enlarging the surface to volume ratio, the dissolution rate of MNO may be enhanced significantly (Liu *et al.* 2010). This effect is well known and commonly explored in the design and optimization of e.g. drug delivery systems. Nano-$TiO_2$ is typically found to be non-soluble in water (also in the smaller size ranges). Nano-Ag on the other hand becomes more and more soluble with increasing surface to mass ratio, leading to the release of $Ag^+$ ions (Liu *et al*. 2010).

Additionally to surface to mass ration, the exact environmental conditions do affect dissolution. Studies have been published that do suggest that solubility of Nano-Ag might also be influenced by environmental factors such as the interaction with bacteria and natural organic matter, NOM, (Aschberger *et al.* 2011 and references therein). NOM present in the environment was described to lower the solubility of Nano-Ag by coating the particle. Results by Bradford *et al.* (2009), might point in this same direction showing a negligible effect of Nano-Ag on the bacterial diversity in estuarine sediments. Interaction of Nano-Ag with bacteria on the other hand was described by Aschberger *et al.* (2011) and references therein to induce a local release of $Ag^+$ ions, increasing the solubility of silver.

For metallic MNO, solubility and the release of metal-ions is an important factor in the possible toxic behavior of the particle. The available literature to date suggests that it are typically the metal ions that (when present) dominate the adverse effects observed. Nano-ZnO for example, has been shown more toxic to algae than Nano-Ag of similar size and shape, which were both more toxic than Nano-$TiO_2$. Their individual impacts did correlate with the extend of metal ion formation during the experiments (ZnO was fully ionized, Ag was partly ionized and $TiO_2$ was not ionized).

### *7.2.2.4 Bioaccumulation*

The possibility of bioaccumulation of nano particles does determine the possibility for these particles to cause long term adverse effects and be transported up the food chain. A number of scientific studies did look at the possibility for bioaccumulation in organisms (fish, bacteria, and algae), plants and terrestrial invertebrates (Aschberger *et al.* 2011 and references therein; Cifuentes *et al.* 2010;

Ferry *et al.* 2010; Morgalev *et al.* 2010). Uptake or adhesion to the outside of the organism is typically observed, also for Nano-Ag and Nano-$TiO_2$. The information available is still too scarce to draw the bioaccumulation-tree of Nano-$TiO_2$ and Nano-Ag up the food chain. A recent study by Judy *et al.* (2011) on gold nano particles however does show the first evidence of trophic transfer of MNO from a terrestrial organisms to a first consumer as well as the first evidence of biomagnifications of MNO within a terrestrial food web. Judy *et al.* (2011) thereby highlight that "*past experience with chemicals such as methylmercury, DDT, and PCBs have revealed dietary uptake at lower trophic levels and accumulation up the food chain to be an important route of contaminant exposure, resulting in chronic or even acute toxicity to a variety of ecoreceptors as well as humans*".

#### *7.2.2.5 Carrier capacity*

Scientific evidence is building up that nano-sized $TiO_2$ can function as carrier particle for pollutants, increasing the bio-availability of these substances to water organisms. Zhang *et al.* (2007) does describe the enhanced uptake of cadmium in fish in the presence of Nano-$TiO_2$, Hartman *et al.* (2010) describe the enhancement of the bioavailability of cadmium to Algae by the presence of Nano-$TiO_2$. For Nano-Ag no such effects have been studied. However, the carrier potential of MNO may differ strongly from one MNO to the other. Carbon black nano particles for example are described to reduce toxicity of specific pesticides (Knauer *et al.* 2007).

#### *7.2.2.6 Concluding fate and behavior in water*

There are many different properties of MNO that determine their behavior and fate in water. Typically, these properties are the same properties that determine the behavior and fate of all chemical substances, however, the size and surface to volume ratio of MNO specifically affect their behavior with respect to solubility, dispersion stability, bioaccumulation and degradation, which, in turn causes MNO to behave differently than they would have behaved in a larger particle dimension. If their nano-properties gives rise to e.g. longer transportation distances or a higher bioaccumulation or not, depends on the actual environmental conditions. Based on the current knowledge one cannot draw simple trends other than the observation that MNO typically seem to be more soluble in their nano-form than in larger micrometer forms.

### 7.2.3 *Environmental fate and behavior in soil*

As with the transport and fate of MNO in water, there is a general lack of knowledge on the nanospecific behavior and fate of MNO in soil and sediment. ENRHES (2009) did summarize the state of knowledge up to 2009 describing that MNO are likely to eventually adhere to soil or sediment and that transportation through soil or sediment depends on the attachment-detachment balance of the MNO to the soil or sediment medium, which on its own depends on factors like MNO surface charge and the pH and ionic strength of the medium. For example, positively charged (metal) particles were found to adhere more strongly to soil or sediment than negatively charged ones.

In 2011, the Swedish University of Agricultural Sciences did publish an evaluation on the fate of nano-silver and silver nitrate in soil media (Oromieh 2011). In his master's thesis, Oromieh does suggest that sorption of Nano-Ag to clay is slightly higher than to sand, possibly because of the higher cation exchange concentration of the clay compared to sand and the finer texture of the clay. He also looked at the solubility of Nano-Ag and silver ions as a function of pH, finding that a high pH (more basic medium) induces higher sorption to soil. Despite these, more specific data on the behavior and fate of Nano-Ag and nano$TiO_2$ in soil is still lacking.

### 7.3 Environmental toxicity profile

The environmental hazard of any substance is formed by the close interplay between the inherent toxicity of this substance and its fate in the different environmental compartments (water, soil and air). This is also true for MNO. In addition to the uncertainties with respect to the environmental behavior and fate of MNO, there are also still many uncertainties with respect to the inherent toxicity of MNO. One of the issues assessing the environmental toxicity of MNO is the absence of standardized tests to quantify the toxicity of MNO in a systematic manner. More and more evidence is emerging; pointing out that the toxicity of MNOs should be assessed by a particle toxicity approach rather than following the traditional toxicological methods.
In the subsections below the current knowledge on the environmental toxicity of Nano-$TiO_2$ and Nano-Ag is summarized. It is important though, to realize that the information provided has been derived from studies that looked at different forms of Nano-$TiO_2$ and Nano-Ag that may vary with respect to (i.e.) their crystal structure, size range, agglomeration or aggregation state and surface functionalization. To date, there is not one coherent data set describing the different environmental properties for one single defined form of Nano-$TiO_2$ and Nano-Ag. The toxicity of MNO in the environment does depend strongly on their specific chemical and physical characteristics. Consequently, the information below should be interpreted as possible scenarios for action and not as given facts.

Factors influencing the environmental toxicity of MNO are, for one, its shape, size and aspect ratio, affecting directly the migration of the particles. A general trend observed is: the smaller the particle, the easier it migrates through biological cell structures. Closely related to these are the factors surface area, surface charge and reactivity that do affect for example transport mechanisms across membranes, adsorption to the exterior of environmental organisms and the potential to adversely react with exterior or internal cell structures like enzymes or DNA. A most recent and comprehensive review is presented by Som *et al.* (2011).

In 2010, Karhu and Dubourguier published an overview of the current status of viewpoints regarding nano-ecotoxicology in relation to the ideas developed in the context of ecotoxicology (Karhu 2010). Part of this review included a collection of the present data on the environmental toxicity of Nano-$TiO_2$ and Nano-Ag, shown in

Table 7.8. Comparison of the toxicity data shown in this table do suggest that variations between the nano and bulk form do vary with the test organism. In a quick glance, Nano-$TiO_2$ seems more toxic than its bulk form for most organisms. However, as will be described in the next subsection, this pattern is influenced by the agglomeration and aggregation state of the MNO, by the surface modification of Nano-$TiO_2$ and by the photo activity of the MNO. Especially the agglomeration or aggregation state of the MNO is described to be difficult to control in the current toxicity tests. For Nano-Ag a comparison on toxicity of the non-nano form is difficult to make additionally because the nanoparticle does dissolve forming $Ag^+$. Quantification of this process was shown difficult in the available literature.

Table 7.8 Overview of the available quantitative data on the environmental toxicity of nano sized $TiO_2$, and Nano-Ag in the scientific literature as published by Karhu (2010) and references therein unless otherwise indicated. Classification according to EU-directive 93/67/EEC classification scheme.

| Group of organisms | Nano-$TiO_2$ | $TiO_2$ bulk | Nano-Ag | $Ag^+$ | Ag as $AgNO_3$ |
|---|---|---|---|---|---|
| | L(E)C50 (mg $l^{-1}$) | L(E)C50 (mg $l^{-1}$) | L(E)C50 (mg $l^{-1}$) | NOEC (mg $l^{-1}$) | L(E)C50 (mg $l^{-1}$) |
| Crustaceans | 76.7 | 20000 | 0.040 | | |
| Bacteria | 6003 | 20000 | 7.60 | | |
| Algae | 65.5 | 60 | 0.23 | 0.002-0.010[a] | 0.125[a] |
| Fish | 300 | 500 | 7.1 | | |
| Ciliates | - | - | 39.0 | | |
| Nematodes | 80.1 | 137 | - | | |
| Yeasts | 20000 | 20000 | - | | |
| Classification | Harmful | Harmful | Extremely toxic | | |

[a] Ratte (1999) and references therein

In a recent review by Aschberger *et al.* (2011) oxidative stress was described as a generic adverse effect found for metals and metal oxides in fish, aquatic invertebrates, algae and sediment organisms. Typically Nano-$TiO_2$ is less toxic than Nano-Ag. Among the different organisms, algae appeared to be the most sensitive organisms for metals and metal oxides. In addition to oxidative stress, also cytotoxicity and growth reduction were observed. In the larger organisms (fish and aquatic invertebrates) mortality, morphological changes and effects on reproduction were identified. In plants on the other hand, adverse effect observed were more variable, showing for example only a low toxicity for Nano-ZnO and Nano-Ag and specific for spinach a positive effect on root growth and photosynthetic activity in reaction to exposure to Nano-$TiO_2$.

In all studies summarized the adverse effects observed are induced by a combination of factors that acts on:

1. The bio-availability of the MNO;
2. The physic interaction of the MNO with the organism;
3. The chemical interaction of the MNO with the organism.

For MNO used in a paint system, it should be kept in mind that the question of bio-availability is the first for assessing a potential toxicity. In the two sections below, the known's and unknowns for Nano-$TiO_2$ and Nano-Ag are highlighted in some more detail.

### 7.3.1 *Knowns and unknowns for Nano-$TiO_2$*

The toxicity of Nano-$TiO_2$ has been described to depend on the actual particle size distribution and on the crystal structure of the substance, being crystalline rutile, crystalline anatase or amorphous. Hund-Rinke *et al*. (2006) studied the toxicity of 25 nm (mainly anatase) and 100 nm (100% anatase) diameter $TiO_2$ particles in algae *Desmodesmus subspicatus*, finding the smaller particles to be more toxic. Aruoja (2008) studied the toxicity of $TiO_2$ particles in the diameter range of 25-70 nm in algae *Psuedokircheriella. subcapitata* but did not specify the crystal structure of the $TiO_2$ (being anatase or rutile), which does impact on the toxicity of the substance. Both find a similar NOEC (No Observed Effect Concentration) for Nano-$TiO_2$. Ji *et al.* (2011) determined the toxicity of 5 – 10 nm anatase $TiO_2$ and 50 nm rutile $TiO_2$ in the green algae *Chlorella* sp. and found that rutile $TiO_2$ showed no significant toxicity whereas the anatase form greatly inhibited the algae growth with a EC50 of 30 mg $l^{-1}$ within 6 days.

A recent review on environmental adverse effects of Nano-$TiO_2$ is presented by U.S. EPA (2010). They cite various references suggesting that Nano-$TiO_2$ is only of low acute toxicity to fish (rainbow trout). However, subtle biochemical disturbances were observed in the brain and evidence of accumulation of Nano-$TiO_2$ in different organs was observed upon dietary ingestion. Also, various studies conducted on *Daphnia magna* and various bacterial strains do show only low toxicity (U.S. EPA, 2010 and references therein). Only one study for toxicity on terrestrial organisms (wood lice) was reviewed showing also only low toxicity.

However, the toxicity described above may change once the Nano-$TiO_2$ is photo active and is present in an environment where it is (or can be) irradiated by solar radiation. Only limited work has been done studying the effect of photo activity on possible adverse effects to environmental organisms. Hund-Rinke *et al.* (2006) study the effect of UV illumination of Nano-$TiO_2$ on algae and *Daphnia magna*. They find first indications that the observed inhibition of growth of algae and the immobilization of *Daphnia* does occur as a consequence of the photo activity of Nano-$TiO_2$. Furthermore, they show evidence of a “lasting-effect” of Nano-$TiO_2$ remaining photo active for some time after illumination.

#### *7.3.1.1 Derived PNECs for Nano-$TiO_2$*

For Nano-$TiO_2$, two scientific studies have reported a NOEC in a water environment. Aruoja (2009) derived a $NOEC_{nTiO2}$ of 1 mg Ti $l^{-1}$ (corresponding to 1.67 mg $TiO_2$ $l^{-1}$) in *Daphnia magna* and Hund-Rinke *et al.* (2006) derived a slightly lower $NOEC_{nTiO2}$ of 0.98 mg Ti $l^{-1}$ (corresponding to 1.63 mg $TiO_2$ $l^{-1}$) in *Pseudokirchneriella subcapitata*. In a review article by Karhu (2010) an overview of available $L(E)C_{50}$ data on Nano-$TiO_2$ is given.
The lowest $L(E)C_{50}$ value reported there is 65.5 mg $TiO_2$ $l^{-1}$ derived by Aruoja (2009) and Hund-Rinke *et al.* (2006). These data used by Gottschalk *et al.* (2010) to derive a $PNEC_{nTiO2}$ (water) of 1 µg Ti $l^{-1}$ (= 1.67 mg $TiO_2$ $l^{-1}$), acknowledging the high uncertainty of the underlying data by using an assessment factor of 1/1000 for the conversion of the NOEC to a PNEC. In this same work by Gottschalk *et al.* (2010) tentative PNECs were derived for the air and soil compartments based on the limited data available. These PNECs are summarized in Table 7.9.

Table 7.9 PNECs as derived for Nano-$TiO_2$ and Nano-Ag by Gottschalk *et al.* (2010) based on the limited data available.

| | **Nano-$TiO_2$** | **Nano-Ag** |
|---|---|---|
| **$PNEC_{water}$** | 1.67 mg $TiO_2$ $l^{-1}$ | 0.696 ng Ag $l^{-1}$ |
| **$PNEC_{air}$** | 10 µg $TiO_2$ $m^{-3}$ | 0.1 µg Ag $m^{-3}$ |
| **$PNEC_{soil}$** | >1 mg $TiO_2$ kg | - |

Given the traditional toxicological approach of expressing toxicity in units of mass per volume, one should acknowledge that the present PNEC might, and can be expected to, include a significant uncertainty with respect to the real-life nano-PNEC that will be effected by (among other nano-specific effects) the actual size distribution of Nano-$TiO_2$ particles in the environment and factors like pH, ionic strength and NOM (Natural Organic Matter). Aschberger *et al.* (2011) therefore advocates speaking about an Indicative No Effect Concentration (INEC) instead of a PNEC. Even though the procedure arriving at a INEC is similar to the procedure for deriving a PNEC, the “I” indicates the preliminary value of the exercise, acknowledging the current lack of systematic toxicity studies investigating the toxicity of MNOs.
This INEC should then be expressed as “an order of magnitude” only.

### 7.3.2 *Knowns and unknowns for Nano-Ag*

Silver is known to be an effective biocide and has been applied for that reason in various products. A review of the status on the knowns and unknowns on Nano-Ag in 2009 is presented by Wijnhoven *et al.* (2009). Wijnhoven *et al*. (2009) and references therein do find that Nano-Ag may provide for a reservoir of toxic silver ions, which may be of concern to environmental organisms. They hypothesize that “Because of the different physico-chemical properties and biological activities of nano-silver when compared with the regular metal, it cannot be excluded that the increased reactivity of nano-silver (because of the large surface area) leads to increased toxicity due to the activity of free silver ions released by the nano particles”. Since 2009, much work has been done to better understand the toxicity of Nano-Ag. It is now indeed shown by Liu (2010) that Nano-Ag, because of its high surface to volume ratio, is typically shown to be more soluble than more course silver, resulting in higher release of silver cations. In fact, it has been shown by Kvitek *et al*. (2011) that Nano-Ag can be similarly toxic to bacteria as ionic silver (suggesting it fully ionizes). Nano-Ag is observed to affect reproduction, cause DNA damage and cause cell damage in bacteria, fish and mammals (Wijnhoven *et al*. 2009 and references therein). Furthermore, research with zebra fish showed that Nano-Ag may affect early development of fish embryos (Lee *et al.* 2007).

Uncertainty though, does remain regarding the bioavailability of Nano-Ag and the actual release of $Ag^+$ ions in the various environmental compartments. For example, recent research does show a rapid conversion of $Ag^+$ to silver sulphide in real-life (non-laboratory) environments (Som *et al*., 2011 and references therein). Since silver sulphide is significantly less toxic to environmental organisms that silver ions, this potential fate of Nano-Ag may have a large impact on its environmental risk assessment. Furthermore, there still exists uncertainty on the relative contribution of Nano-Ag to the overall environmental silver toxicity, including also the course metal particles.

#### *Bacterial resistance to $Ag^+$*

However, despite the current lack of a complete toxicity profile for Nano-Ag, the following information is available and points to an alarming situation developing at this moment. One of the most essential applications of Nano-Ag used to be, and still is, for medical treatment of highly sensitive wounds, bacterial infections or as a disinfectant for bacterial strains that are very persistent and/or have become resistant towards other antibiotics. However, despite this valuable application, misuse may contribute to the development of bacterial resistance to silver. Various studies do point out that different types of bacteria may build-up resistance against $Ag^+$ (Silver 2003; Percival *et al.* 2005; Silver *et al*. 2006) and indicate that this resistance is in principle transferable to other bacterial strains. Since resistance involves the silver ion this resistance implies both to course silver and to Nano-Ag treatment.

To date, studies linking an development of bacterial resistance to $Ag^+$ in the environment to actual emissions of (nano)-Ag are inconclusive. However, Chopra (2007) does find silver ion resistance in bacteria from environmental sources and Cunningham *et al.* (2010) show by in vivo testing in Mixed-Culture Bioreactors (simulating biological waste water treatment systems) that silver ion resistance can be promoted by an already existing bacterial resistance to antibiotics. The antibiotic-biocide (i.e., AMX (amoxilin)-Ag+) cross-resistance found in this study is of environmental significance for its potential adverse effects on human health also. In this light, the current development of “silver-products”, e.g. food packaging, consumer products, sports gear, clothing, washing machines, silver coated kitchen surfaces, silver coated walls), are of high concern and should be minimized as much as possible.

#### *7.3.2.1 Derived PNECs for Nano-Ag*

To date, in the scientific literature no NOEC values have been published on Nano-Ag. In the absence of any NOEC, the PNEC for Nano-Ag is to be derived from the $EC_{50}$ or $LC_{50}$ data, when these are available. Karhu (2010) did present an overview on available $EC_{50}$ and $LC_{50}$ data for Nano-Ag, of which the lowest reported $L(E)C_{50}$ was 0,040 mg Ag $l^{-1}$ (measured in crustaceans). In addition to their values Griffitt *et al.* (2008) determined a $LC_{50}$ value in *Ceriodaphnia dubia* as low as 0,696 µg Ag $l^{-1}$, which value has been cited by Müller and Nowack (2008), Gottschalk *et al.* (2010) and Musee (2010) to obtain the $PNEC_{nAg}$ (water). All used the same assessment factor of 1/1000 to convert this $LC_{50}$ to the PNEC (water), acknowledging the high uncertainty of the underlying data and arriving at a $PNEC_{nAg}$ (water) of 0,696 ng Ag $l^{-1}$. Gottschalk *et al.* (2010) furthermore derives a $PNEC_{air}$. The different PNEcs derived for Nano-Ag are summarized in Table 7.9.

The observed toxicity is primarily caused by the $Ag^+$-ion. In its nano-form, the solubility of Ag is much larger than it is in the “bulk” form of silver because of the much larger surface to mass ratio (Liu *et al.* 2010). However, depending on the specific environmental conditions (e.g. pH, ionic strength, NOM, temperature) the solubility of silver can be still sufficiently slow to obtain a combined particle - ion effect in the environment. In the one extreme situation, this may result in a toxicity profile of Nano-Ag that is similar to that of $Ag^+$. In the other extreme situation, this may result in a toxicity profile of Nano-Ag that is dominated by the particle behavior of silver for the uptake of the silver by organisms and a highly localized ion-toxicity by $Ag^+$ prior to uptake (Aschberger *et al*. 2011). Given the present uncertainty with respect to environmental fate and toxicity of Nano-Ag and similar to Nano-$TiO_2$, Aschberger *et al*. (2011) advocates using an INEC instead of a PNEC, expressed as “an order of magnitude” only, like was described previously for Nano-$TiO_2$. To date, there is insufficient information to establish a PNEC for Nano-Ag for the environmental compartment soil.

## 7.4 Environmental risk assessment

In the field of environmental risk assessment, using the PEC/PNEC ratio is a well established method to determine the potential (environmental) risk of substances in the environment. The PEC (Predicted Environmental Concentration) is normally based on predicted environmental concentration values of the chemical (ECB, 2003). Depending on the ratio PEC/PNEC the abundance of a substance in the environment can be categorized in 3 different risk categories:

| | | |
|---|---|---|
| PEC/PNEC | <1 | Substance is not of immediate concern and is not expected to cause harm to the environment in the present concentration, unless new evidence will prove otherwise |
| PEC/PNEC | 1-10 | Substance is of concern |
| PEC/PNEC | >10 | Substance is of high concern |

### 7.4.1 *Predicted environmental concentrations of Nano-$TiO_2$ and Nano-Ag*

Assuming the range of manufacturing volumes approximated by the different sources described in section 7.1, predicted environmental concentrations (PECs) are derived by Boxall *et al.* (2007), Gottschalk (2009), Müller & Nowack (2008) and Blaser *et al*. (2008). Their results are summarized in Table 7.10 and Table 7.11 for Nano-$TiO_2$ and Nano-Ag respectively. One other study by Musee (2011) did model predicted environmental concentrations of a number of MNOs, among which Nano-$TiO_2$ and Nano-Ag, specifically for the urban area and direct surroundings of the City of Johannesburg South-Africa, and is for that reason not included here.

Unsurprisingly given the high uncertainties in the underlying data and the amount of approximations and/or assumptions going into the different models (for example regarding the manufacturing volumes of MNO;. see references for a detailed outline of each model), large variations in predicted environmental concentrations in Table 7.10 and Table 7.11 are evident. Predicted environmental abundances for Nano-$TiO_2$ for example are observed to vary between 0.002 and 24.4 μg $l^{-1}$ $TiO_2$ in the water compartment (a factor of $10^4$). Nano-Ag abundances in the water environment are predicted between 0.1 and 320 ng $l^{-1}$ Ag (a factor $10^3$). Also for the compartments air and soil, similar variations in predicted concentrations are observed. However, the different studies summarized in Table 7.10 and Table 7.11 do show a similar abundance pattern predicting that Nano-$TiO_2$ and Nano-Ag are both expected to concentrate in soil and sediment and are expected to be relatively much less abundant (eventually) in surface water or air. What is lacking from Table 7.10 and Table 7.11 is any information related to the relative contribution per phase of the paint life cycle.

Each of these studies mentioned above did assess the full life cycle of the MNO, including manufacturing, transportation, application, use and the end-of life, but presented the resulting environmental concentration as one value only. Consequently, for the purpose of this study looking at possible emissions of Nano-$TiO_2$ and Nano-Ag from paint application there is no information on the PEC resulting from each individual phase of the life cycle of MNO in paints. In principle, based on all environmental data presented here, it is possible to conduct an environmental risk assessment along the lines described within REACH to obtain this information. Such an exercise would be interesting and of great value to further investigate the contribution of the emissions of MNO per life phase in terms of predicted environmental concentrations resulting from emissions during manufacturing, paint production, paint application, service life and the end of life phase of the paint system individually. Even though, given the present uncertainties with respect to the behavior and fate of MNO in the environment and the resulting toxicity profile, the outcomes of this assessment could only serve as preliminary values.

Table 7.10 Calculated PECs for Nano-TiO$_2$; ME = Minimum exposure scenario / RE = Realistic exposure scenario / HE = High exposure scenario

| **Nano-TiO$_2$** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **NM** | **Environmental compartment** | | | | **STP effluent** | **Sludge treated soil** | **Region** | **Reference** |
| **year** | **Water (µg l$^{-1}$)** | **Soil (µg kg$^{-1}$)** | **Air (µg m$^{-3}$)** | **Sediment (µg kg$^{-1}$ y$^{-1}$)** | **(µg l$^{-1}$)** | **(µg kg$^{-1}$ y$^{-1}$)** | | |
| 2006 | 24.5 | 1030 | 7 | - | - | - | UK | Boxall *et al.* (2007) |
| 2008 | 0.015[a] | 1.28[b] | <0.0005 | 358 | 3.47 | 89.2 | EU | Gottschalk (2009) |
| 2008 | 0.002 | 0.53 | <0.0005 | 44 | 1.75 | 42.0 | US | Gottschalk (2009) |
| 2008 | 0.010 | 2.13 | <0.003 | 499 | 4.28 | - | Swiss | Gottschalk (2009) |
| 2008 | 0.7 | 0.4 | 0.0015 | - | - | - | Swiss; RE | Müller & Nowack (2008) |
| 2008 | 16 | 4.8 | 0.042 | - | - | - | Swiss; HE | Müller & Nowack (2008) |

[a] surface water concentration

[b] present as predicted yearly increase in units of µg kg$^{-1}$ y$^{-1}$

Table 7.11 Calculated PECs for Nano-Ag; ME = Minimum exposure scenario / RE = Realistic exposure scenario / HE = High exposure scenario

| **Nano-Ag** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **NM** | **Environmental compartment** | | | | **STP effluent** | **Sludge treated soil** | **Region** | **Reference** |
| **year** | **Water (ng l$^{-1}$)** | **Soil (ng kg$^{-1}$)** | **Air (ng m$^{-3}$)** | **Sediment (µg kg$^{-1}$ y$^{-1}$)** | **STP effluent (ng l$^{-1}$)** | **Sludge treated soil (µg kg$^{-1}$ y$^{-1}$)** | | |
| 2006 | 10 | 430 | - | - | - | - | UK | Boxall *et al.* (2007) |
| 2008 | 0.8 | 22.7 | 0.008 | 0.952 | 43 | 1.58 | EU | Gottschalk (2009) |
| 2008 | 0.1 | 8.3 | 0.002 | 0.195 | 21 | 0.66 | US | Gottschalk (2009) |
| 2008 | 0.4 | 11.2 | 0.02 | 1.203 | 39 | - | Swiss | Gottschalk (2009) |
| 2008 | 30 | 20 | 1.7 | - | - | - | Swiss; RE | Müller & Nowack (2008) |
| 2008 | 80 | 100 | 4.4 | - | - | - | Swiss; HE | Müller & Nowack (2008) |
| 2008 | 4 - 40 | - | - | 40 – 2000[a] | 2000[b] | - | NL/DE; Rhine; ME | Blaser *et al.* (2008) |
| 2008 | 30 - 320 | - | - | 300 – 14000[a] | 18000[b] | - | NL/DE; Rhine; HE | Blaser *et al.* (2008) |

[a] in micrograms per kg sediment

[b] inflow concentration (before STP treatment)

### *7.4.1.1 Actual measured environmental concentrations of Nano-TiO$_2$ and Nano-Ag*

In order to judge whether or not the PECs shown in Table 7.10 and Table 7.11 make sense, these should preferably be compared to environmental concentration measurements. Up to 2010, only one study by Kiser *et al.* (2009) does report on actual environmental abundances of Nano-$TiO_2$: measurements of Nano-$TiO_2$ in waste water effluents. In this work, the efficiency of waste water treatment plants (WWTP) towards the removal of Nano-$TiO_2$ was studied, showing that in 2008 the $TiO_2$ in the effluent of 8 different WWTPs in the US was dominated by particles and aggregates smaller than 700nm with a concentration range of 5 – 15 µg $l^{-1}$. The results by Kiser *et al.* (2009) are in line with the modeled PECs by Müller and Nowack (2008) and Boxal *et al.* (2007) and do provide a first indication that the emission of Nano-$TiO_2$ through the effluent of WWTP could be of actual environmental concern, assuming a $PNEC_{water}$ for Nano-$TiO_2$ of 1µg $l^{-1}$.

For silver, the World Health Organization, WHO (1996), did summarize that average silver concentrations (mainly in the form of silver ions, silver complexed to organic matter, silver chloride, silver nitrate or silver sulfide) in natural waters are 0.2–0.3 µg/liter. However, in the case of drinking water, concentrations may be higher when this water is treated with silver as disinfectant. Water treated with silver may have levels of 50 µg/litre or higher, for which most of the silver will be present as nondissociated silver chloride. Silver levels in drinking water in the USA that had not been treated with silver for disinfection purposes varied between "non-detectable" and 5 µg/litre. In a survey of Canadian tap water, only 0.1% of the samples contained more than 1–5 ng of silver per litre. Lenntech.com further adds that seawater typically contains approximately 2-100 ppt of silver. River water generally contains approximately 0.3-1 ppb of silver. The phytoplankton concentration is 0.1-1 ppm (dry mass), leading to a $10^4$-$10^5$ bio concentration factor in seawater. In oyster tissue concentrations of approximately 890 ppm (dry mass) were found. Dissolved in water silver mainly occurs as $Ag^+$, and in seawater as $AgCl_2^-$. No abundances are known for Nano-Ag in particular. It is even questionable whether or not environmental abundances will be easily detectable because of its solubility under the right environmental conditions.

### 7.4.2 *PEC/PNEC of Nano-$TiO_2$ and Nano-Ag*

Assuming the PNECs for Nano-$TiO_2$ and Nano-Ag approximated in section 7.3.1.1 and 7.3.2.1 and the PECs modeled by the different research groups PEC/PNEC, or rather PEC/INEC ratio's can be established to assess the actual possible environmental health risk caused by nano$TiO_2$ or Nano-Ag. As the PECs and PNECs are of the same order of magnitude (of the order of µg $l^{-1}$ for Nano-$TiO_2$ and of the order of ng $l^{-1}$ for Nano-Ag for the water compartment), combining Table 7.9 with Table 7.10 and Table 7.11 results in the following picture for the protential risk of these MNOs.

For Nano-$TiO_2$, the predicted concentrations in air and soil do suggest that this substance is not yet of concern to the environment (PEC/PNEC < 1). For air, this is not very surprising as Nano-$TiO_2$ is non-volatile and will not easily migrate to air by other mechanisms than by powder dispersion during the manufacturing of the MNO or the production of the paint. For the water compartment, only two modeled scenario's led to predicted environmental concentrations that may be of concern for the initiation of possible adverse effects to the environment: i.e. the scenario described by Boxall *et al.* (2007) for the UK and the high exposure scenario worked out for Switzerland by Müller & Nowack (2008).

For Nano-Ag, the predicted concentrations in air do suggest that this substance is not yet of concern to the environment (PEC/PNEC < 1), similar to the observation for Nano-$TiO_2$. For the water compartment, predicted environmental concentrations are more worrying. Boxall *et al.* (2007) for the UK and both the high exposure and low exposure scenario's worked out for Switzerland by Müller & Nowack (2008) do suggest predicted environmental concentrations that may be of high concern to the environment. This has been acknowledged also by the Advisory Committee on Hazardous Substances Report on Nanosilver, Defra (2009), who suggest environmental abundances of dissolved silver may even be higher than predicted by Müller & Nowack (2008) and may be different EU wide than the specific results for Switzerland do suggest (for example as a consequence of the use of sewage sludge to amend agricultural soils, which is not common practice in Switzerland but does occur in other EU member states).

The results show that there might indeed be reason of concern about the possible environmental concentrations of both Nano-$TiO_2$ and Nano-Ag that would deserve further attention. However, it should also be emphasized that the different studies followed a worst case approach in modeling possible environmental concentrations. Taking into account the high uncertainties in the model, for example regarding the environmental fate of MNO or total production volumes, these PEC/INEC ratios do show the urgency to take precautionary measures, but provide no hard proof for a direct environmental concern. The study by Kiser *et al.* (2009) though, does measure an abundances of Nano-$TiO_2$ between 5 – 15 µg $l^{-1}$ in waste water effluents of 8 different US waste water treatment plants, very similar to the modeled PECs of Nano-$TiO_2$ by Boxal er al (2007) and Müller and Nowack (2008). It is thereby the first work that shows Nano-$TiO_2$ can be a substance of environmental concern. For silver, environmental total silver abundances are shown to lay between 0.2–1 µg Ag $l^{-1}$ in natural waters (Canadian tap water typically 1–5 ng Ag $l^{-1}$) and between 2 – 100 ng Ag $l^{-1}$, without specifying any Nano-Ag contribution to these numbers. The various models do suggest an additional concentration of silver as a consequence of Nano-Ag applications on the order of 0.1 – 80 ng Ag $l^{-1}$ in the environmental compartment water. Depending on the geographical region this would imply adding 1 – 10% of silver to the existing silver concentration in fresh water. Depending on the fate and behavior of the Nano-Ag, this 1 – 10% may turn out to be a worrisome addition to the environmental silver.

### 7.4.3 *Present gaps preventing a robust environmental risk assessment*

The ENRHES project (Engineered Nano particles: Review of Health and Environmental Safety 2008-2009) does indicate the gaps that existed in 2009 that prevented then for a robust and reliable risk assessment specific for Nano-$TiO_2$ and Nano-Ag. For one, is the fact that current standards to define toxicity of chemicals do focus on solubility and do evaluate the toxicity on a mass base, whereas for MNO particle toxicity is thought to be a better measure. As a consequence, effects on toxicity due to for example agglomeration, aggregation and (low) solubility characteristics are difficult to quantify. Given this situation and valuing the data that is available, they concluded that the following elements where missing:

1. There is a lack of information on manufacturing volumes of Nano-$TiO_2$ and Nano-Ag, and especially also on their different forms;

2. There is a lack of information on the type of nanoproducts at the market that contain Nano-$TiO_2$ or Nano-Ag, on their market penetration, the total product volume and their MNO content;
3. There is a lack of information on the behavior during waste water treatment;
4. There is a lack of monitoring field data measuring concentrations in different environmental compartments;
5. There is a lack of ecotoxicity data (aquatic and terrestrial), and especially also regarding long-term effects;
6. There is a lack of information about the interaction of Nano-$TiO_2$ and Nano-Ag with organisms such as adsorption, uptake and bioaccumulation.

Of these gaps indicated in 2009, most are still valid anno 2011, although more and more information is becoming available that allows for the better understanding of the possible behavior of MNO in the environment.
For the waste water treatment, first evidence does suggest that Nano-$TiO_2$ is not as well filtered out as the more course $TiO_2$, resulting in elevated concentrations of Nano-$TiO_2$ in the effluent of various waste water treatment plants that were studied in the US. To date there is no such study performed in Europe. For silver Tiede *et al.* (2010) did show that approximately 90% of all Nano-Ag was removed during waste water treatment, suggesting that waste water treatment may in fact be efficient for Nano-Ag.

### 7.5 Concluding remarks

Given the predicted environmental concentration described in the previous section the question remains on “what is the actual contribution of paints to the modeled abundance of Nano-$TiO_2$ and Nano-Ag in the environment?”. From the allocation table of Müller and Nowack (2008) presented in Figure 7.1, one can approximate the relative contribution of the various product groups to the overall emission of MNO to the various environmental compartments. The result is shown in the table below (Table 7.13). For this approximation has been assumed that no emissions occur during waste incineration in a waste incineration plant (WIP) and no emission to the environment takes place as a consequence of landfill (both theoretical best practices). For all MNO that goes to a sewage treatment plant (STP) at the end of life the purification efficiency was assumed (i.e. 90% for Nano-Ag and 42% for Nano-$TiO_2$). For the remaining MNO in the effluent of the STP and for the fraction of the MNO specified in Figure 7.1 to end up in dissolution, was furthermore assumed that all MNO was emitted to surface water. Emissions to air, soil, “leaving the system” and recycling were not taken into account (i.e = zero emission).

Table 7.13 Contributions by the different product categories to the total emission of Nano-$TiO_2$ or Nano-Ag to water

| Product category | Allocation (% Total production volume) | End of life treatment STP (%) | Emission to water from STP effluent (% Total production volume)* | End of life Dissolution (%) | Emissions to water due to dissolution (% Total production volume) |
|---|---|---|---|---|---|
| **Nano-TiO2** | | | | | |
| plastics | 2 | 2.5 | 0.13% | | |

| Product category | Allocation (% Total production volume) | End of life treatment STP (%) | Emission to water from STP effluent (% Total production volume)* | End of life Dissolution (%) | Emissions to water due to dissolution (% Total production volume) |
|---|---|---|---|---|---|
| cosmetics | 60 | 90 | 31.32% | | |
| coatings (non-paint) | 2 | 90 | 1.04% | | |
| metals | 1 | 5 | 0.03% | | |
| energy storage | 10 | | 0.00% | | |
| paint | 25 | 25 | 3.63% | | |
| **Nano-Ag** | | | | | |
| textiles | 10 | 5 | 0.05% | 85 | 8.50% |
| cosmetics | 25 | 95 | 2.38% | | 0.00% |
| sprays/ cleaning agents | 15 | 80.7 | 1.21% | | 0.00% |
| metal products | 5 | 5 | 0.03% | 45 | 2.25% |
| plastics | 10 | 5 | 0.05% | 45 | 4.50% |
| paints | 35 | 2.5 | 0.09% | 45 | 15.75% |

* Emission to water taking into account the current knowledge on STP efficiencies of 42% for Nano-$TiO_2$ and 90% for Nano-Ag.

The results in Table 7.13 suggest that cosmetic products are suspected to be the most dominant source of Nano-$TiO_2$ for the water environment. About 30% of all Nano-$TiO_2$ applied in products may end up in the water environment as a consequence of its use in cosmetic products. Under the current assumptions, the application of 25% of all Nano-$TiO_2$ in paints does result in the emission of 3 – 4% of all Nano-$TiO_2$ applied in products to the water environment. This is approximately 9% of the total emission to the water environment.

For Nano-Ag, Table 7.13 suggests that the dominant route to the water environment is via dissolution. This, because of the high efficiency of sewage treatment plants (STP) to remove Nano-Ag from the waste water. Here, the application of Nano-Ag in paints shows to be dominant. Almost 16% of all Nano-Ag produced is suggested to enter the water environment through its use in paints (about 50% of all Nano-Ag emitted to water). Textiles, the second most important source, are responsible for almost 9%. However, there is a significant risk of over-interpretation of the available data. For example, in reality, it is most likely to expect that Nano-Ag containing paints will be developed primarily for indoor application. Consequently, dissolution of Nano-Ag from the applied paint system will most likely occur during cleaning activities (instead of rainfall) and the resulting $Ag^+$ ions will end up in waste water (to be treated in a STP). This would suggest that not ~16% but rather ten percent thereof, i.e. 1.6% of all Nano-Ag manufactured per year, would be emitted to the water environment due to its use in paints. The contribution by paints to the total emission of Nano-Ag to the water environment then becomes similar to the emission as a consequence of the use of Nano-Ag in cosmetics or textile products. However, then still paint products remain an important source, though no longer the dominant source, of $Ag^+$ to the water environment.

### 7.5.1 *Future perspectives*

According to Robichaud *et al.* (2009), with few exceptions, most of the current bulk $TiO_2$ market could benefit from and will eventually shift to using Nano-$TiO_2$. They base this statement on company interviews, and (scientific) study the interaction and function of $TiO_2$ in products. The eventual substitution will depend on the balance between improved product performance due to applying Nano-$TiO_2$ and additional costs. Som *et al.* (2011) refer that in 2015, 15% – 30% of all façade coatings will be enhanced by using nanotechnology. However, from own experience in the Netherlands pilot scale or small scale productions of some nanocoatings did seize (instead of grow) as a consequence of the prolonged uncertainty on health and safety issues of MNO and nanoproducts in general, involving also the present uncertainty with respect to near future regulatory actions at national and international level. In addition to this, the observation is that more and more often the more course alternatives are applied if the Nano-scale is not ubiquitous for the final (ready-for-use) product. Consequently, the future market will depend strongly on near future decisions to make as well as on technical advantages or possible adverse (environmental) health and safety effects.

# 8 Barriers in selection and cooperation with users of Nano-$TiO_2$ and Nano-Ag in the paint industry

## 8.1 Introduction

One of the goals of the pilot was to carry out exposure measurements of airborne nano particles at paint manufacturers workplaces and at workplaces of downstream users of nano-coatings in the car body repair sector and in the painters sector, with a total of seven workplaces. For this purpose, paint manufacturers as well as downstream nanomaterials-using companies had to be identified. However, serious barriers were faced to find suitable downstream companies working with nanomaterials. Several efforts were made but with little success, which led to the decision of the pilot to refrain from further search for companies and instead to identify clear reasons why most of the attempts failed. The leading question was:
*“What is the reason that nanomaterial using companies cannot be identified?”*

Important for answering this question is to have a closer look at the strategy of the partners in the pilot used to find and involve companies. Secondly, it is important to evaluate if there is a general tendency for the experienced problems: *“What are the main reasons for the limited traceability of users of nanomaterials”.*

At the beginning of the pilot, while composing the project team, three paint manufacturers were identified by the VVVF to become actively involved in the pilot. Each manufacturer was active in the field of formulating paints with nanomaterials. The amount of three formulators was thought to be sufficient to get an impression on how communication on “nano” finds its way through the production chain, so initially no further activities were employed to involve more manufacturers. During the pilot, the emphasis therefore was brought to the involvement of downstream users, two car body repair shops and two painting contractors. This task was allocated to the branch organizations active in the pilot: the paint manufacturers association (VVVF), the Vehicle Builders & Repairers Association (FOCWA) and the Painters Association (FOSAG). TNO and IVAM would become informed about the selected companies, and were supposed to make further contacts.

An important factor influencing the identification of companies to some extent might be the focus of the pilot on the types of nanomaterial for more elaborate research. To optimize the structure of the pilot it was decided that the focus would be only on two nanomaterials: $TiO_2$ and a second nano-substance to be determined at the start of the pilot. This second nano-substance was deliberately chosen. Different “frequently used” nanomaterials were considered, e.g. Ag, Al, Fe, Zn, Silica fume, Carbon Black, and some others. A first selection was made for carbon black with the highest priority, and silica fume as a material of second choice. Carbon black was selected as “most frequently used”, but was decided to be less interesting for the pilot because CB is not really an “engineered” nanomaterial. Silica was thought to have the highest innovation potential. However, both CB and silica would raise technical problems in measuring these substances because of the potential background sources of carbon and silica. Reconsideration and deliberation of the project team led to the selection of Nano-Ag as “model” for the use and possible exposure in the production chain in addition to Nano-TiO2. This, despite the fact that the FOCWA made clear that to their knowledge Nano-Ag was not used in automotive coatings.

Another important factor that appeared to prevent for identifying downstream users was one of the pilot boundary conditions that limited the scope to the Dutch market: Dutch manufacturers communicating with Dutch downstream users.

## 8.2 Barriers experienced by branch organizations

To find an answer to the questions on the limited success for finding companies, both FOCWA and FOSAG were interviewed. Summaries are presented in section 8.1.1-8.1.2; full interview minutes can be found in Annex 6 and 7. Independently the VVVF summarized their own ideas concerning existing barriers (8.1.3).

### 8.2.1 *FOCWA*

Two relative straight forward reasons found to be limiting the search for downstream users of nano$TiO_2$ and Nano-Ag automotive coatings are (1) the fact that the market is an international one instead of Dutch and (2) the fact that Nano-Ag is not known to be used. A third and most import reason is the current lack of traceability of nano in the production chain. This is the key issue. Identifying nano-using companies amongst car body repair shops generally fails due to the lack of information whether the product is nano-based. This can be due to the fact that nano-details are not reported on the SDS, the downstream user is not “focused” on this information and doesn’t record it as being important, or a product is marketed as nano but isn’t really formulated using nanomaterials. Neither the management, nor the workers in car body repair shops know whether they are confronted with cars that are coated with a nano-lacquer or whether they use nanoproducts for refinishing. As a consequence they don’t know whether there is a risk for exposure to nano particles.

The information is not supplied to them by the paint manufacturers, nor by the suppliers of the cars. The involved management in the branch does not have the chemical knowledge to demand upstream information from suppliers or manufacturers about the coating composition (and especially on the nano content). It seems that many paint and coating manufacturers keep their use of nanomaterials in products confidential

### 8.2.2 *FOSAG*

The frequency and extent of use of nanoproducts is small among Dutch painting contractors at the moment. FOSAG comes forward with the innovative character of nanoproducts as possible reason. In general, Dutch painting contractors are conservative and skeptical of working with new products because of the possible business risks and losses. Only after a brand new product has proven itself in practice, companies are willing to use this product on a larger scale. This does not apply to nanomaterials according to FOSAG.

FOSAG did not experience any ignorance among the companies contacted. The companies were convinced that they know whether their products contain nano particles.

Besides this, FOSAG did not experience anxiety for the possible health effects of nano particles among painting contractors. Painting contractors are confident with implementation of risk management measures. Hence, this issue is considered surmountable.

One formulator hesitated in cooperation due to the image of nanoproducts. Painting contractors did not come forward with this argument.

In conclusion, the frequency and extent of use seemed to be the main barrier in identifying and recruitment of companies for cooperation within the project Communication in the product chain paint and lacquers. A longer period of recruitment of companies was necessary to find suitable companies.

### 8.2.3 *VVVF*

The following barriers that may hamper the identification of nanoproduct-using downstream users are:

- Nanocoatings are only used incidentally
- Companies appear to have no clear definition for a nanocoating, which may be confusing. It is not clear to many companies under what conditions a coating is denominated as a "nanocoating".
- Downstream users are generally not informed whether they are working with a nanoproduct
- There is some restraint amongst downstream users to become identifiable as user (or applicant) of nanoproducts. This because of a possible "bad" image.
- There are commercial considerations not to become involved in nanoprojects

A positive remark was that the cooperation between VVVF, FOCWA and FOSAG is considered to be good.

## 8.3 Producers of Nano-Ag containing paints

The project team did decide to select Nano-Ag as the second nanomaterial in the pilot for more detailed studies. However this choice turned out to be a limiting factor for the involvement of paint manufacturers themselves. One of the committed paint manufacturers produces custom-made Nano-Ag paint. The only customer of this paint did not want to get involved or even be known in the context of the pilot. Moreover, this customer did demand the paint manufacturer not to communicate any details on the production of this Nano-Ag paint. Their argument, as brought forward by the manufacturer, was that the paint has a strictly confidential recipe and any risk to unveil this recipe should be avoided. This made it impossible to carry out measurements during the commercial production. As an alternative the good-willing manufacturer offered to produce a small Nano-Ag batch, with a different formulation, a different Nano-Ag supplier, without a predetermined client. However calculating the costs for this batch, and the time needed for starting up this batch made the pilot decide to skip this option.

Efforts of VVVF to find another paint manufacturer making Nano-Ag paint in the Netherlands failed. Apparently the amount of Nano-Ag paint manufacturers in the Netherlands is very limited.

## 8.4 Discussions

Communication in the production chain about the use of nanomaterials, the use of nanoproducts or the release of nano particles from products during intended use of the products containing nanomaterials is limited. Communication about the use of nanoproducts with third parties seems even to be even less. At the same time however a difference can be observed between the level of information of car body repair shops and the construction painters. The information about materials used in articles in the automotive sector and (as a consequence) information about the possible release of nanomaterials from these articles during handling is limited. There is no, or almost no downstream communication in the automotive chain about the details of the assembling components. Information on new products though, e.g. coatings used for repair and refinishing of vehicles, is expected to be more extensive, at least according to remarks made by the paint manufacturing industry. But according to the FOCWA coatings used for refinishing are not necessarily identical to the original coatings applied on the vehicle, i.e. even if an original nanocoating would have been applied the refinishing coating may as well be a non-nanocoating.

For painting contractors, mainly active in the construction industry, the level of information seems to be less of a problem. According to the observation of the FOSAG contractors are generally informed about the fact that “nanopaints” are demanded for the project. It is the special request of the architect or customer that makes painting contractor choose for a nanopaint. However, the use of nanopaints seems to be only incidentally, because of the typically higher product costs, but possibly also due to the rather conservative behavior of paint contractors and their risk avoiding attitude towards innovative paints. The limited use is confirmed by some paint manufacturers, who indicate that the production of nanopaint takes place only incidentally over the year, and only on a special demand.

Based on these observations the idea might raise that painting contractors are better informed about the possible nano-character of their products than the car body repair shops. This conclusion however may be premature. It is questionable whether painting contractors would become properly informed as well about the nano-character of the materials they are handling for example in maintenance or restoration activities. (Experience with former communication issues, for example about former lead-containing paints shows that knowledge about the character of former paint layers is rapidly lost). Since nanopaints are relatively new though, it is unlikely that painting contractor when asked for maintenance and restoration of surfaces will be confronted with a surface that was already been treated with nanomaterials.

It can be concluded that employers and employees in car body repair shops do often not exactly know whether they are working with nanomaterials or that nano particles might be released during work. This holds for the company management, their employees, but as well for the institutions responsible for the health & safety management. An upstream oriented activity of car body repair shops, trying to generate more nano-information, is according to the FOCWA, bound to fail. They base their idea on the fact that it concerns too many products for which information would be required and consequentially it would take too much time for the shops to collect the info. Additionally the shop generally lacks the knowledge to ask for the right details on the nanomaterials.

### 8.4.1 *Traceability*

The issue of traceability is a well-recognized problem. To find out whether used products contain nanomaterials is not a simple job. Several initiatives were employed to generate more information, but it seems that confidentiality about product information is still a dominating factor.

### 8.4.2 *Voluntary reporting scheme*

One of the first initiatives to identify MNO in products was the Voluntary Reporting Scheme (VRS), developed by the British Department for Environment, Food and Rural Affairs (DEFRA). It was aimed at collecting data concerning free engineered nanomaterials from manufacturers, commercial users, research and the waste industry. For the purposes of the collection, the VRS used a very narrow definition with the following criteria: the material is engineered deliberately (*i.e.* not material which is created naturally or unintentionally as a by-product of other processes); the material shows in two or more dimensions an extension of up to 200 nm, or is in two or more dimensions roughly within the nanoscale; the material “is free within any environmental media at any stage of a products life cycle”. During the period of data collection (September 2006 – September 2008) only twelve completed responses were submitted. Therefore this voluntary scheme must be deemed as little successful.

There are a few other voluntary reporting initiatives, but all with limited success.

### 8.4.3 *France mandatory reporting scheme*

A recent, more powerful initiative to make the reporting of the use of nanomaterials in products mandatory was initiated in France within the context of the French environmental legislation *Lois Grenelle* [14]. This law demands the manufacturers, importers and distributors to report (and make public availability) the identity of nanomaterials and uses, and the quantities on the market. There is a possibility to ask for information to stay confidential. The identity of downstream users must be reported as well, but is considered to be confidential information. Important to mention here is the fact that the scope of the reporting scheme is on *substances at the nanoscale on its own, or contained in a mixture without being linked to it* and that it is focused on *articles with intended release of nanomaterials*. The implementation of the decree will take place in 2013 for nanomaterials put on the market in 2012.

### 8.4.4 *Retailers’ initiative*

Another initiative in this context comes from Swiss retailers organizations, which in 2008 developed a Code of Conduct[15] as a voluntary instrument for retailers. The Code obliges retailers to take a responsible approach to nanotechnology products. The retail trade undertakes to provide consumers with full information on nanotechnology and to label as such only those products that really do have nanotechnology-based components or modes of action. The collection of information is organized with an upstream questionnaire. According to the IGDHS the reporting scheme functions little slow, but reasonably. Additional effort should be developed to make it  stronger instrument.

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[14] Luc Maurer 2011.French mandatory reporting scheme on nanomaterials, presentation at seminar “working with nanomaterials”, Brussels 29 November 2011.

[15] IG DHS code of conduct for nanotechnologies. 18.4.2008

### 8.4.5 *SDS*

Recently an adaption was published by the European Chemical Agency[16] for the format of the Safety Data Sheet for chemical substances. Adaptations in section 3 and 9 are proposed. Section 3 of the safety data sheet describes the chemical identity of the ingredient(s) of the substance or mixture, including impurities and stabilizing additives. In this section appropriate and available safety information on surface chemistry shall be indicated. It should be noted that the term “surface chemistry” as used is intended to refer to properties that may arise as a result of the particular surface properties of a (solid) substance or mixture (e.g. due to having certain dimensions in the nano range). The second adaptation concerning “nano” refers to section 9 concerning (a) appearance: the physical state (solid (including appropriate and available safety information on granulometry and specific surface area if not already specified elsewhere in the safety data sheet), liquid, gas) and the colour of the substance or mixture as supplied shall be indicated. Here properties of nanomaterials should be taken into account such as size and size distribution, shape, porosity, pour density, aggregation/agglomeration state, morphology, surface area ($m^2$/mass), surface charge/zeta potential and crystalline phase. To date, October 2011, it is not clear whether info on the SDS on new nanoproducts will be reported according to this guidance. Actual remaining barrier is the fact that a definition for a “nanoproducts” is lacking.

## 8.5 Conclusion

Although differing amongst sectors and companies, in may cases it appears to be unknown whether the used articles and products contain nanomaterials or not. More information seems to be available for downstream users purchasing special nanopaints or –coatings. For downstream users, purchasing these *new* products it is at least clear *that* they are using a nanoproduct. The identity of used nanomaterials in these products is not necessarily clear.

Several initiatives are underway that may shed some more light on the (nano)character of new products being brought on the market. The revised MSDS may give a small contribution. More can be expected from the French initiative provided that this gets a European recognition and follow-up.

For products being used in a complex production chain like the automotive sector and the car body repair shops therein, being active in maintenance and restoration, identification of the “nano-character” of the articles and products requires an additional approach. An extra emphasis on improving the chain communication for these situations is required. This holds especially for dispersive nanomaterials that may be released during intended activities (not necessarily intended release during use). Some scientific publications note that activities like abrasion, drilling do not generate the original nanomaterials, but that these are emitted in clusters, contained in the hardened coating-matrix. However, so far there is no indication that this information is transferred in the production chain towards downstream users.

The difficulties in identification of downstream companies working with nanomaterials are strongly related to the issue of limited information supply to these

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[16] ECHA 2011. Guidance on the compilation of safety data sheets Version 1.0 – September 2011. http://guidance.echa.europa.eu/docs/guidance_document/sds_en.pdf

companies. However, there are some more reasons contributing to obscure the users of nanomaterials. These can be summarized as follows:

- Relatively limited knowledge about nanomaterials amongst employers, employees as well as health & safety management
- Many companies prefer to remain out of screen when using nanoproducts or nanomaterials to avoid questions or adverse reactions. Some fear for a bad image when associated with nanomaterials-use
- The use of, or experimenting with nanomaterials has a high competitive character, leading to confidential behavior.
- Apparently, the use of “nano” is not discussed between members of branch organizations.
- Some companies used the lacking definition of nanomaterials as a reason why they cannot answer whether they work with nanomaterials. Now this definition is published this should not be an argument any more.
- Lacking information about the risk of nanomaterials may be a reason for some companies to stay out of screen. (even when they assume that conventional protective measures are sufficient).

Finally, many downstream companies welcome specific expert attention for nano-issues brought to them in mutual contact. It may help the companies to overcome resistance towards the use of nanomaterials, and also it may help to identify already existing use of nanomaterials in their own companies.

# 9 Conclusions

## 9.1 Conclusions regarding health risks for workers

This pilot project investigated the availability and subsequent gaps in current knowledge on hazard of, and exposure to Nano-$TiO_2$ and Nano-Ag used in all life cycle stages and corresponding process steps of the paint supply chain. Based on available data, the risks of Nano-$TiO_2$ and Nano-Ag for humans and the environment are assessed, using a tiered approach in which data are gathered and used conform a specific hierarchy.

### 9.1.1 *Hazard assessment*

Compared to other MNOs, relatively much hazard data are available for Nano-$TiO_2$ and Nano-Ag. For both Nano-$TiO_2$ and Nano-Ag, human health hazard data were found on all levels in the above described hierarchy.

Gaps in knowledge on nano hazard data consist of a lack of scientific consensus on how to obtain good quality hazard data and how to interpret the obtained data correctly. As a consequence the data are accompanied by high levels of uncertainty. Issues like the influence of medium used to perform toxicity tests and sameness of the particles used for different tests remain unclear.

### 9.1.2 *Exposure assessment*

Worker exposure datasets are very scarce for scenarios from the paint supply chain. Nevertheless, a relatively large number of exposure datasets is found for the stage of manufacturing of differing quality. Only very few datasets are found for the stage of paint production, end use and service life. In general, more data are found for Nano-$TiO_2$ compared to Nano-Ag.

Gaps in knowledge on exposure data consist of the methods of gathering and interpretation of those data. Hence, in all cases occupational exposure data on MNOs are, accompanied by many uncertainties. An important factor in this uncertainty is the lack of contextual information provided with the data. Besides that, information is often lacking about the type of data presented (e.g. AM, GM, 90-percentile, maximum). A harmonized measurement strategy, taking into account the difficulties related to activity and background exposure is currently not available, hampering straight forward interpretation of exposure data.

### 9.1.3 *Risk assessment*

A prerequisite for risk assessment is the similarity between the MNOs encountered at the workplace and the MNO used to obtain the toxicity data and threshold value. In this study the MNOs are not thoroughly enough characterized to ascertain that the MNO used for hazard and exposure assessment are identical substances. This is an important factor of uncertainty in the final risk assessment.

In the quantitative risk assessment, process steps are indicated with risk depending on the comparison between hazard and exposure values. If the exposure value exceeds the threshold value, the process step can be prioritized for control measures. Doing so, the following process steps are prioritized: manufacturing and cleaning in the manufacturing stage of Nano-Ag and loading and waste treatment in the stage of paint production using Nano-$TiO_2$.

Using a qualitative approach (Stoffenmanager Nano), additional tasks are prioritized for control measures: bagging during the manufacturing of Nano-Ag and waste treatment in both the manufacturing stage of Nano-$TiO_2$ and Nano-Ag. The tasks of storage, loading and waste treatment are prioritized during the stage of paint production using Nano-Ag.

Due to the high uncertainties in hazard, exposure and risk assessment, no conclusions on health risks or control of health risks can be drawn from this risk assessment.

Given the current knowledge, no additional risk of exposure to the nano particles caused by fracturing/abrasion of surfaces treated with nanocoatings is assumed. The current hypothesis is that the nano particles are embedded in the solid matrix and nano particles are not released as “free” primary particles. However, this hypothesis is uncertain and future research will further clarify this.

It is advised to persist on the precautionary principle (minimization of exposure) until more data are available. Besides that, it is recommended to gather more data in practice in order to fill in the gaps in current knowledge on hazard of, and exposure to MNOs used in the paint supply chain. Acquiring knowledge on hazard of and exposure to MNOs in the paint supply chain enables a reliable and representative occupational risk assessment in the future.

## 9.2 Conclusion regarding environment

Analysis of the available environmental data on Nano-$TiO_2$ and Nano-Ag, does show that both these MNO may cause adverse effects to environmental organisms. However, the sincerity of these effects has been observed to strongly depend on the actual environmental conditions. Based on the PNECs derived and model predictions of environmental concentrations, indicative risk quotients (PEC/PNEC ratios) were calculated, suggesting that there might indeed be reason of concern regarding the possible environmental concentrations of both Nano-$TiO_2$ and Nano-Ag that should deserve further attention. First studies investigating the environmental abundance of these MNOs are in line with the derived PNECs, supporting the reason of concern.

To date, there are no studies describing MNO emissions per phase in the life cycle of a paint system. Combination of the data available for the different life phases however do suggest that for Nano-$TiO_2$ emissions may be of the same order of magnitude during manufacturing, paint production, application, service life and the end-of-life phase, but will depend strongly on the actual handling of the material by the individual worker. For Nano-Ag, the service-life appears the important phase for emissions to the environment as a consequence of its solubility.

The relative contribution of paints to the total emission of these MNO to the environment is difficult to deduce. Because of the high uncertainty on the actual uses and market volumes of products containing Nano-$TiO_2$ or Nano-Ag one can only speculate about the relative contribution of paints to the total emission of these MNO to the environment. The preliminary data available do suggest that for Nano-$TiO_2$, about 4% of all Nano-$TiO_2$ produced may enter the water environment as a consequence of its use in paints, which is about 9% of all Nano-$TiO_2$ emissions to water. The major fraction of Nano-$TiO_2$ emitted to water is suggested to originate from its use in cosmetics. For Nano-Ag, the contribution by paints may be much higher. About 1.6 – 16% of all Nano-Ag produced is suggested to enter the water environment as a consequence of its use in paints via dissolution during the paint's functional life. This is a significant fraction of all assumed emissions of Nano-Ag to water. However, this derivation for actual emissions of Nano-$TiO_2$ and Nano-Ag to water is based on one model only. It should be emphasized, that the different studies modeling environmental concentrations aimed at following a worst case approach. None however did focus on modeling the Dutch (or the EU) situation. Acknowledging the high uncertainties and many unknowns on the environmental abundance, behavior, fate and toxicity of Nano-$TiO_2$ and Nano-Ag, the available data do show the urgency to take precautionary measures preventing emission of these MNO, but provide no hard proof for a direct environmental concern.

However, despite the current lack of a complete toxicity profile, for Nano-Ag there is another reason to motivate not to use Nano-Ag in paints but safe it for very specific applications. One of the most essential applications of Nano-Ag used to be, and still is, for medical treatment of highly sensitive wounds, bacterial infections or as a disinfectant for bacterial strains that are very persistent and/or have become resistant towards other antibiotics. However, despite this valuable application, misuse may contribute to the development of bacterial resistance to silver. Various studies do point this out and moreover indicate that once developed, this resistance is in principle transferable to other bacterial strains as well. In this light, the current development of "silver-products", e.g. food packaging, consumer products, sports gear, clothing, washing machines, silver coated kitchen surfaces, silver coated walls), are of high concern and should be minimized as much as possible.

## 9.3 Conclusion regarding barriers encountered in pilot company selection

Barriers encountered in the search for companies where exposure measurements could be performed are identified on two levels:
- Barriers in identifying possible pilot companies
- Barriers in obtaining companies' cooperation

The main barriers may be summarized as follows: the transparency concerning the presence of nano particles in products is relatively low. As a consequence companies do not always know whether or not they work with nanoproducts. Moreover, in many cases it is unclear to people what is meant with nanoproducts. A complicating factor lies in the negative image of 'nano' labeled products, reducing the willingness to make publically known that a company works with nanoproducts. And, once identified as 'nanocompany' all kinds of initiatives come your way, which is not always appreciated by companies.

A relatively small group of companies appear to use nanoproducts to date on an irregular basis and in low quantities. Within this group a relatively low number of different nano particles are used. The companies operate in an international market.

Points of consideration for coming projects :
- Choose pilot nanomaterials that are amongst the most abundantly used to enlarge the pool of potential pilot companies
- Do not limit to the Dutch market
- Due to the incidental character: identifying companies is the most urgent task and should preferably be done before the start of a project.
- Possibly a longer project period would be more convenient to ascertain that activities with nanoproducts take place within the project period.

Transparency is a challenge. It would be good to find ways to communicate about nanomaterials in a way that all persons involved know what they are working with and what the points of attention are, without causing unnecessary anxiety.

# 10 Signatures

23/3/2012

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| Dr. A.A.M.G. Spooren | M. le Feber |
| Head of Department TARA | Project leader |

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# Annex 1; More detailed description of paint production processes

### Production of Nano-$TiO_2$ paints

Nano-$TiO_2$ for paint production is typically supplied as powder, delivered in bags or drums, or in liquid dispersions. For the actual process of paint production, industrial paints and automotive coatings are being distinguished.

- *Industrial and architectural paints*

In the Netherlands, Nano-$TiO_2$ paints are produced on the conventional production lines for batch production. Consequently, the production process occurs roughly similar to the non-nano one. Nano-additives are either added manually or via an automatic dosing system. The nano-additive is normally supplied to the paint formulator as powder (transported in a bag or drum) or in liquid form.

When manually adding nano-additives in powder form, the nano batch process may differ from other batches. One company that implemented a number of precautionary measures to limit exposure to MNOs listed the following (precautionary) adaptations to the "normal" process:

- Storage of the nano-additive: Keeping (storing) the nano-additive at the workfloor prior to use is not allowed. It is only collected from its place of storage when it will actually be added to the coating;
- Personal protective measures: When the nano-additive is added to the mixing vessel, the worker has to take additional personal protective measures, namely wear a Tyvek overall (non-woven plastic), use a respirator mask with P3 filter and Tyvek overshoes (non-woven plastic);
- Waste treatment: Empty bags of the nano-additive are being disposed off separately as chemical waste. This also holds for the personal protective equipment used. Leftovers of the nano-additive are not saved for later use but removed as chemical waste;
- Service and maintenance: The Cycloon filter of the ventilation system is serviced after the addition of the nano-additive. The filter is beaded empty and the captured (nano) dust is being removed as chemical waste. No wastes are internally recycled;

There is no specific information available on the method of sampling and quality control, suggesting these are carried out according to usual protocol. The (precautionary) adaptation described above though, may not be representative for the average Nano-$TiO_2$ using paint manufacturer.

Chapter 6 presents a summary of available data on the actual particle number concentrations in air during various steps in the production of Nano-$TiO_2$ paints. The particle number concentrations do not necessarily distinguish Nano-$TiO_2$ particles in the measures air from other nano particles emitted to air as a consequence of the specific production step (e.g. as a consequence of running electric equipment). As a consequence one cannot simply assign the concentrations measured to the abundance of Nano-$TiO_2$ in the breathing zone of the worker involved in the activity. However, it does provide some first insight in possible exposure ranges. Industrial and automotive paint are not distinguished.

- *Automotive coatings*

Automotive coatings containing Nano-$TiO_2$ are formulated using a batch process, as often as about 40 times a year (almost once a week). As a first step, the Nano-$TiO_2$ powder is deposited in a vessel for mixing. During deposition of the powder and mixing of the paint ingredients, the vessel is covered by a lid. Local exhaust ventilation is placed close to the lid opening required for the mixer to go through and at the position where the Nano-$TiO_2$ is added. Adding the Nano-$TiO_2$ by manually dumping the $TiO_2$ from the bag is a task that may take about 10 min. Mixing of the formulation may take about 1.5 hours, depending on the size of the batch, but during the mixing operation the vessel is fully closed (except for the opening for the mixer).

When the coating is ready, it is tapped automatically into the product cans. This is an open process where local exhaust ventilation is available. Closing the cans by putting the lids in place is done either manually or automatically depending on the production line. Quality control takes place by spraying a test object with a sample from the batch in a spraying cabin in the quality control department. Tests are performed only on the colour performance.
There is no specific information available on the method of sampling and quality control, suggesting these activities take place according to usual protocol, which is in a spraying cabin.

### Production of Nano-Ag paints

Nano-Ag containing paints are still considered a niche market. In the Netherlands, only two paint manufacturers could be identified that are actually producing Nano-Ag paints. Paints containing Nano-Ag are typically prepared in relatively small batches compared to the company’s total paint turnover, and only a few times per year (typically on the order of 1 to 10 times per year per producing company). Nano-Ag is found to be delivered as course granulate or as a paste.

Blending of the Nano-Ag granulates is performed by using a vacuum dissolver[17] to prevent for airborne nano particles diffusion. Blending normally takes 1 to 5 minutes. The workplace is equipped with a mechanical ventilation system. Packaging of the formulated paint is a fully automatic and closed process. Sampling for quality control is done manually and takes place ones per batch. The sample preparation and removal of the analyzed sample by the analyst in the laboratory is also performed manually and takes place ones per batch. For these activities there is no information on the personal protection measures taken by the analyst. In case of Nano-Ag dispersed in a paste, blending takes place via “injection” into the base paint formulation.

There is no literature data on the possible exposure to Nano-Ag during paint production. When the granulate form is used, one can typically expect a higher risk of exposure to airborne MNOs than in the case of using a paste. The same holds for possible exposure risks during storage and transportation. Once the Nano-Ag is added to the paint, similar exposure risks are to be expected when packaging the final paint formulation, sampling the paint, performing quality control or cleaning and maintaining the used equipment.

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[17] It is uncertain what a “vacuum dissolver” looks like and what type of process actually takes place.

# Annex 2; Table 1 Summary on exposure data available for Nano-$TiO_2$

| Life cycle stage | Process Description of sources | Specific data | Analogous data | Stoffenmanager Nano Exposure banding |
|---|---|---|---|---|
| **Manufacturing**<br>Manufacturing of Nano-$TiO_2$ by specific industrial processes | ***Source no 1***<br>Indicative workplace measurement<br>Manufacturing of Nano-$TiO_2$<br>Type of manufacturing process unknown.<br>Monitoring of a closed reactor process<br>Production amount 250 kg Nano-TiO2<br>Natural ventilation.<br><br>***Source no 10***<br>Data from two different manufacturing locations.<br>Location 1; Research institute<br>Manufacturing of Nano-$TiO_2$ by chemical synthesis.<br>Production amount 5g/h<br>Reactor operation and Nano-$TiO_2$ collection using a brush<br>Fume hood | ***Source no 10***<br>*Task measurements*<br>*Location 1*<br>*Mass concentration data*<br>*Personal and area sampling*<br>*Min-Max values, N4.*<br>Manufacturing 0.12-0.50 mg/$m^3$<br>$TiO_2$ collection 0.55-4.99 mg/$m^3$<br><br>*SMPS data*<br>*Min value*<br>Background 14000 #/$cm^3$<br>*Max value*<br>Manufacturing and $TiO_2$ collection 45889 #/$cm^3$ | ***Source no 1***<br>*Task measurement*<br>*No background measured*<br><br>*CPC data*<br>Total number concentration; Manufacturing 12766 #/cm3<br>*SMPS data (AM)*<br>Particle concentration < 100 nm: Manufacturing 11265 #/cm3<br>Particle concentration > 100 nm: Manufacturing 2095 #/cm3 | ***Source no 18***<br>Task based<br>2<br>Time weighed<br>2 |

| Life cycle stage | Process Description of sources | Specific data | Analogous data | Stoffenmanager Nano Exposure banding |
|---|---|---|---|---|
| **Manufacturing**<br>Manufacturing of Nano-$TiO_2$ by specific industrial processes | *Location 2*; Research institute<br>Manufacturing of Nano-$TiO_2$ by chemical synthesis.<br>Production amount 5 kg/h<br>Reactor operation and removal of the Nano-$TiO_2$ collection vessel<br>Large scale reactor surrounded by a vinyl curtain. Collection vessel in glove box.<br><br>***Source no 9***<br>Batch manufacturing of Nano-$TiO_2$<br>Specific process unknown<br>Production amount 5-10 kg<br>Creation of slurries by manual loading/unloading inside a booth and dumping into a mixing tank<br>Focused LEV. | *Location 2*<br>*Mass concentration data*<br>*Personal and area sampling*<br>*Min-Max values*<br>Manufacturing (*N7*) 0.095-0.89 mg/$m^3$<br>Collection *(N1)* 0.48 mg/$m^3$<br><br>*SMPS data*<br>Background 12000 #/$cm^3$<br>*Max value*<br>Manufacturing and removal of collection vessel 66695 #/$cm^3$<br><br>***Source no 9***<br>*Task measurements*<br>*Data presentation*<br>*(AM, GM, Max not clear)*<br>*CPC data*<br>*(background corrected);*<br>Dumping 3500 #/$cm^3$<br>Manual loading/unloading 15500 #/$cm^3$ | | |

| Life cycle stage | Process Description of sources | Specific data | Analogous data | Stoffenmanager Nano Exposure banding |
|---|---|---|---|---|
| **Manufacturing**<br>Bagging manufactured Nano-$TiO_2$ | ***Source no 1***<br>Bag/bin filling<br>Amount of product is 250 kg Nano-$TiO_2$<br>Continuous semi-automatic process provided with LEV.<br>Both mechanical and natural ventilation | ***Source no 1***<br>*Task measurement*<br>*Non activity represents background*<br>*CPC data*<br>Total number concentration; Bagging 22725 #/$cm^3$<br><br>*SMPS data (AM)*<br>Particle concentration < 100 nm:<br>Bagging 12897 #/$cm^3$<br>Non activity 4252 #/$cm^3$<br>Particle concentration > 100 nm:<br>Bagging 1182 #/$cm^3$<br>Non activity 395 #/$cm^3$ | | ***Source no 18***<br>Task based 3<br>Time weighed 3 |
| | ***Source no 2***<br>Bag/bin filling<br>LEV | ***Source no 2***<br>*Task measurements*<br>*Mass concentration data*<br>Bin filling (*N1*) 0.18 mg/$m^3$<br>Bag filling *(N1)* 0.23 mg/$m^3$ | | |

| Life cycle stage | Process Description of sources | Specific data | Analogous data | Stoffenmanager Nano Exposure banding |
|---|---|---|---|---|
| | | *SMPS data*<br>*Data presentation*<br>*(AM, GM, Max not clear)*<br>Bin filling 19931#/$cm^3$<br>Bag filling 33413 #/$cm^3$ | | |
| **Manufacturing**<br>Cleaning and Maintenance equipment of manufacturing process | ***Source no 9***<br>Spray dryer drum changeout | ***Source no 9***<br>*Task measurement*<br>*Data presentation*<br>*(AM, GM, Max not clear)*<br>*CPC data*<br>*(background corrected);*<br>144800 #/$cm^3$ | | ***Source no 18***<br>Task based 3<br>Time weighed 2 |
| **Manufacturing**<br>Treatment of waste contaminated with powdered nano material | | | | ***Source no 18***<br>Task based 3<br>Time weighed 2 |
| **Paint production**<br>Receipt, storage and transport | ***Source no 19***<br>*Company 2*<br>Picking up and transport of 10 bags of nano-$TiO_2$ | ***Source no 19***<br>*Task measurement*<br>*Philips Aerasense data (AM)*<br>*(Background corrected)*<br>24580 #/$cm^3$ | | ***Source no 18***<br>Task based 3<br>Time weighed 2 |

| Life cycle stage | Process Description of sources | Specific data | Analogous data | Stoffenmanager Nano Exposure banding |
|---|---|---|---|---|
| **Paint production**<br>Loading/Charging of powdered Nano-$TiO_2$ | **Source no 19**<br>*Company 1*<br>Loading/charging manually<br>Amount of product 170 kg<br>Half enclosed mixing vessel provided with LEV.<br>Wet suppression techniques applied | **Source no 19**<br>*Company 1*<br>*Task measurement*<br>*Philips Aerasense data (AM)*<br>*(Background corrected)*<br>875333 #/$cm^3$ | | ***Source no 18***<br>Task based 3<br>Time weighed 2 |
| **Paint production**<br>Loading/Charging of powdered Nano-$TiO_2$ | *Company 2*<br>Loading/charging manually<br>Amount of product 100 kg<br>Half enclosed mixing vessel provided with LEV.<br>Careful work practices. | *Company 2*<br>*Task measurement*<br>*Philips Aerasense data (AM)*<br>*(Background corrected)*<br>2485 #/$cm^3$ | | |
| | ***Source no 3***<br>Production of Paint<br>Dumping Nano-TiO2 into a vessel, containing water.<br>Amount of product is 200 kg<br>Natural ventilation, mechanical ventilation and LEV | ***Source no 3***<br>*Task measurement*<br>*Non activity represents background*<br>*CPC data (AM)*<br>Total number concentration;<br>Loading 35627 #/cm3,<br>Non-activity 23928 #/cm3<br>*SMPS data (AM)* | | |

| Life cycle stage | Process Description of sources | Specific data | Analogous data | Stoffenmanager Nano Exposure banding |
|---|---|---|---|---|
|  | ***Source no 4***<br>Production of printing ink<br>Emptying bags in filling station<br>Amount of product 40 kg<br>Only the front of the filling station is open.<br>LEV present<br>***Source no 11***<br>Mixing area of a Nano-$SiO_2$ epoxy molding compound plant<br>Feeding fumed silica into a ball grinder<br>Amount of product 40 kg<br>Enclosed space with limited general ventilation.<br>Capturing hood with low effectiveness | Particle concentration < 100 nm;<br>Loading 51877 #/cm3<br>Non-activity 32515 #/cm3<br>Particle concentration > 100 nm;<br>Loading 3305 #/cm3<br>Non activity 2572 #/cm3 | ***Source no 4***<br>*Task measurement*<br>*Non activity represents background*<br>*CPC data (AM)*<br>Total number concentration;<br>Loading 10242#/cm3<br>Non activity 9756#/cm3<br>***Source no 11***<br>*Shift measurements*<br>*Area sampling (N3)*<br>*Respirable mass concentration*<br>1963 ug/m3<br>*SMPS/APS data*<br>Background 3700 #/cm3<br>Peak 19000 #/cm3 |  |

| **Life cycle stage** | **Process Description of sources** | **Specific data** | **Analogous data** | **Stoffenmanager Nano Exposure banding** |
|---|---|---|---|---|
| **Paint production**<br>Mixing/Blending/Dissolving | | | | ***Source no 18***<br>Task based 1<br>Time weighed 1 |
| **Paint production**<br>Filling cans with liquid coating | | | | ***Source no 18***<br>Task based 1<br>Time weighed 1 |
| **Paint production**<br>Sampling of liquid coating | | | | ***Source no 18***<br>Task based 1<br>Time weighed 1 |
| **Paint production**<br>Cleaning and Maintenance of equipment of paint production process | | | | ***Source no 18***<br>Task based 1<br>Time weighed 1 |
| **Paint production**<br>Treatment of waste contaminated with powdered nano material | ***Source no 19***<br>*Company 1*<br>Discharging remainings, draining of buckets, sweeping up spillage.<br>Mechanical ventilation present.<br><br>*Company 2*<br>Discharging of empty bags to the waste container. | **Source no 19**<br>*Company 1*<br>*Task measurement*<br>*Philips Aerasense data (AM)*<br>*(Background corrected)*<br>1300336 #/cm$^3$<br><br>*Company 2*<br>*Task measurement*<br>*Philips Aerasense data (AM)*<br>*(Background corrected)*<br>Activity concentration not increased. | | ***Source no 18***<br>Task based 3<br>Time weighed 2 |

| **Life cycle stage** | **Process Description of sources** | **Specific data** | **Analogous data** | **Stoffenmanager Nano Exposure banding** |
|---|---|---|---|---|
| **Application**<br>Loading of application equipment with coating | | | | ***Source no 18***<br>Task based 2<br>Time weighed 1 |
| **Application**<br>Application of coating by spraying | ***Source no 8***<br>Indicative workplace measurement<br>Spray painting in the car repair industry.<br>Application of both coatings with nano particles and regular coatings Spray activities were performed using high pressure in a spray cabin.<br><br>***Source no 15***<br>Indicative simulation experiment in a laboratory setting.<br>Gas propellant spray can consumer product based on Nano-$TiO_2$ particles<br>The laboratory room simulated a home environment with a high ceiling and low air exchange rate of 0.34 air changes per hour.<br>Several intermittent short spray periods of 5 seconds lasting for 2.5 min. | | ***Source no 8***<br>*Task measurement*<br>*No background measurement*<br><br>*Philips Aerasense data*<br>Mean 39.000 #/cm3<br>Peak 1.100.000 #/cm3<br>Data not explained by presence of nano particles<br><br>***Source no 15***<br>*Simulation data*<br>*SMPS data*<br>130.000 #/cm3<br>*mass concentration data – number concentration*<br>Total ;<br>3.4 mg/m3/160.000#/cm3<br>< 100 nm;<br>170 ug/$m^3$ /120.000 #/cm3 | ***Source no 18***<br>Task based 2<br>Time weighed 2 |

| Life cycle stage | Process Description of sources | Specific data | Analogous data | Stoffenmanager Nano Exposure banding |
|---|---|---|---|---|
| | ***Source no 16***<br>Indicative simulation experiment in a laboratory setting.<br>Hand pump spray can consumer product containing nano $TiO_2$ particles and ethanol.<br>Surface spraying was performed using about 8 g of product over a max period of 25 s. | | ***Source no 16***<br>30000000 #/cm3 per g product | |
| **Application**<br>Application of coating including by rolling/brushing | | | | ***Source no 18***<br>Task based 1<br>Time weighed 1 |
| **Application**<br>Cleaning and Maintenance of equipment used in the stage of application | | | | ***Source no 18***<br>Task based 1<br>Time weighed 1 |
| **Service life**<br>Fracturing/Abrasion of coated surfaces | ***Source no 8***<br>Indicative workplace measurement<br>Sanding of surfaces coated with both coatings formulated with nano particles as regular coatings using a handheld sanding machine | | ***Source no 8***<br>*Task measurement*<br>*Philips Aerasense data*<br>Background 14000 #/cm3<br>Activity 18000 #/cm3<br>Difference not explained by presence of nano particles | ***Source no 18***<br>Not covered |

| Life cycle stage | Process Description of sources | Specific data | Analogous data | Stoffenmanager Nano Exposure banding |
|---|---|---|---|---|
| | ***Source no 12***<br>Indicative simulation experiment in a laboratory setting.<br>Abrasion of a surface treated with a Nano-ZnO coating.<br>Low energy process<br><br>***Source no 13***<br>Indicative simulation experiment in a laboratory setting.<br>Sanding using a handheld, orbital sander<br>Sanding of surfaces treated with coatings with and without nano particles including $SiO_2$.<br>Human exposure chamber<br>Mechanical ventilation air exchange rate of 9.2 ± 0.8 per hour. | | ***Source no 12***<br>*Simulation data*<br>*SMPS and CPC data*<br>No significant particle release < 100 nm.<br>*TEM/SEM/EDX data*<br>ZnO particles < 100 nm embedded in coarse wear particles.<br><br>***Source no 13***<br>*Simulation data*<br>*FMPS and APS data*<br>Fine particles dominate the particle number concentrations<br>No clear effect of nano particles in coatings on dust emissions from sanding | |

| Life cycle stage | Process Description of sources | Specific data | Analogous data | Stoffenmanager Nano Exposure banding |
|---|---|---|---|---|
| | ***Source no 14***<br>Indicative simulation experiment in a laboratory setting.<br>Sanding using a miniature sander<br>One abrasion wheel 1.83 m/s,<br>Pressure of 10 kPa.<br>Sanding of surfaces treated with coatings with and without nano particles including ZnO.<br>Sanded surface 13 $cm^2$. | | ***Source no 14***<br>*Simulation data*<br>*FMPS, LAP and CPC data*<br>Sanding results in generation of nano particles No significant difference in released particles < 100 nm of coatings with and without nano particles including ZnO.<br>*SEM/ TEM data*<br>ZnO particles embedded in the wear particles. | |

# Annex 2; Table 2 Summary on exposure data available on nano-silver

| **Life Cycle stage** | **Process description of sources** | **Specific data** | **Analogous data** | **Stoffenmanager Nano exposure banding** |
|---|---|---|---|---|
| **Manufacturing stage**<br><br>Manufacturing of Nano-Ag by specific industrial processes | ***Source no 5***<br>Manufacturing of metal-based nano particles using a gas-phase production process<br>Pilot-scale production facility.<br><br>***Source no 6***<br>Batch manufacturing of nano-silver based on a wet-chemical reaction<br>Commercial production facility<br>Opening the reaction hatch for sampling<br>A vent hood is installed<br><br>***Source no 9***<br>Manufacturing of nano-silver using a gas phase condensation process.<br>Emission measurements on the passivator tumbler exhaust port<br>Opening of the reactor<br>No control measures present. | ***Source no 6***<br>*Task measurement*<br>*SMPS data*<br>*(background corrected);*<br>Total number concentration<br>11.020.000 #/cm3<br>Particle concentration 100 nm;<br>Manufacturing 6.1000 #/cm3<br>Sampling 120.000 #/cm3<br><br>***Source no 9***<br>*Task measurement*<br>*Data presentation*<br>*(AM, GM, Max not clear)*<br>*CPC data*<br>*(background corrected);*<br>Manufacturing 5970 #/cm$^3$<br>Opening reactor 85900 #/cm$^3$ | ***Source no 5***<br>*Shift measurement*<br>*CPC/SMPS data*<br>Average background<br>(*17 days, 7 positions*)<br>8.512 #/cm$^3$<br>*Max value*<br>Manufacturing 59.100 #/cm$^3$ | ***Source no 18***<br>Task based<br>2<br>Time weighed<br>2 |

| Life Cycle stage | Process description of sources | Specific data | Analogous data | Stoffenmanager Nano exposure banding |
|---|---|---|---|---|
| **Manufacturing stage**<br>Manufacturing of Nano-Ag by specific industrial processes | ***Source no 10***<br>Location 1; Industrial setting<br>Manufacturing by induced coupled plasma process<br>Large-scale pilot reactor<br>Production amount of 5 kg/day.<br>Manufacturing including silver powder injection and tube connection to the collector.<br>Natural ventilation | ***Source no 10***<br>*Task measurement*<br>*Location 1;*<br>*Mass concentration data*<br>*Personal sampling*<br>*Min-Max values, N2.*<br>Manufacturing<br>0.00012-0.00102 mg/m$^3$<br>*SMPS data*<br>*Min-Max values*<br>Manufacturing<br>534.6-6657 #/cm$^3$ | | |
| | ***Source no 10***<br>Location 2; Industrial setting<br>Manufacturing by mixing sodium citrate with silver nitrate<br>Production amount of 1 kg/day.<br>Manufacturing including weighing raw materials, adding, stirring, pumping, cleaning. to make it soluble.<br>Room ventilation and fume hood | ***Source no 10***<br>*Location 2;*<br>*Mass concentration data*<br>*Personal and area sampling*<br>*Min-Max values, N10*<br>Manufacturing<br>0.00003-0.00118 mg/m$^3$<br>*SMPS data*<br>*Min-Max values*<br>Manufacturing<br>393.9-3525.8 #/cm$^3$ | | |

| Life Cycle stage | Process description of sources | Specific data | Analogous data | Stoffenmanager Nano exposure banding |
|---|---|---|---|---|
| **Manufacturing stage**<br>Bagging manufactured Nano-Ag | | | | ***Source no 18***<br>Task based 3<br>Time weighed 3 |
| **Manufacturing stage**<br>Cleaning and maintenance of equipment contaminated with Nano-Ag | ***Source no 9***<br>Cleanout of the reactor without and with the presence of LEV. | ***Source no 9***<br>*Task measurement*<br>*CPC data*<br>*(background corrected);*<br>Without LEV 6100 #/cm$^3$<br>With LEV 0 | | ***Source no 18***<br>Task based 3<br>Time weighed 2 |
| **Manufacturing**<br>Treatment of waste contaminated with powdered nano material | | | | ***Source no 18***<br>Task based 3<br>Time weighed 2 |
| **Paint production**<br>Receipt, storage and transport | | | | ***Source no 18***<br>Task based 3<br>Time weighed 2 |
| **Paint production**<br>Loading/Charging of powdered Nano-Ag | | | | ***Source no 18***<br>Task based 3<br>Time weighed 2 |
| **Paint production**<br>Mixing/Blending/Dissolving | | | | ***Source no 18***<br>Task based 1<br>Time weighed 1 |

| Life Cycle stage | Process description of sources | Specific data | Analogous data | Stoffenmanager Nano exposure banding |
|---|---|---|---|---|
| **Paint production**<br>Filling cans with liquid coating | | | | ***Source no 18***<br>Task based 1<br>Time weighed 1 |
| **Paint production**<br>Sampling of liquid coating | | | | ***Source no 18***<br>Task based 1<br>Time weighed 1 |
| **Paint production**<br>Cleaning and Maintenance of equipment of paint production process | | | | ***Source no 18***<br>Task based 1<br>Time weighed 1 |
| **Paint production**<br>Treatment of waste contaminated with powdered nano material | | | | ***Source no 18***<br>Task based 3<br>Time weighed 2 |
| **Application**<br>Loading of application equipment with coating | | | | ***Source no 18***<br>Task based 2<br>Time weighed 1 |
| **Application**<br>Application of coating by spraying | ***Source no 8***<br>Indicative workplace measurement<br>Spray painting in the car repair industry.<br>Application of both coatings with nano particles and regular coatings<br>Spray activities were performed using high pressure in a spray cabin. | | ***Source no 8***<br>*Task measurement*<br>*No background measurement*<br>*Philips Aerasense data*<br>Mean 39.000 #/cm3<br>Peak 1.100.000 #/cm3 | ***Source no 18***<br>Task based 2<br>Time weighed 2 |

| Life Cycle stage | Process description of sources | Specific data | Analogous data | Stoffenmanager Nano exposure banding |
|---|---|---|---|---|
| | ***Source no 17***<br>Indicative simulation experiment in a laboratory setting.<br>Gas propellant spray can consumer product based on Nano-Ag particles<br>Spray events of 1s and repeated 3 times. | | ***Source no 17***<br>*Simulation data*<br>*SMPS data (N3)*<br>Particle concentration < 100 nm;<br>14000 #/cm3 | |
| **Application**<br>Application of coating by rolling/brushing | ***Source no 7***<br>Indicative workplace measurement<br>Manual rolling /brushing of coating based on Nano-Ag<br>Open air. | | ***Source no 7***<br>*Task measurement*<br>*Philips Aerasense data*<br>Activity concentration not increased.<br>Background 19.000 #/cm3 | ***Source no 18***<br>Task based 1<br>Time weighed 1 |
| **Application**<br>Cleaning/Maintenance of equipment used in the stage of application | | | | ***Source no 18***<br>Task based 1<br>Time weighed 1 |
| **Service life**<br>Fracturing/Abrasion of coated surfaces | ***Source no 8***<br>Indicative workplace measurement<br>Sanding of surfaces coated with both coatings formulated with nano particles as regular coatings using a handheld sanding machine | | ***Source no 8***<br>***Task measurement***<br>*Philips Aerasense data*<br>Background 14000 #/cm3<br>Activity 18000 #/cm3<br>Difference not explained by presence of nano particles | ***Source no 18***<br>Not covered |

# Annex 3; Description of occupational exposure data sources

## 1. Nanex data set 1.

Nanex reports the results of a Nanosh exposure survey performed during the manufacturing of Nano-$TiO_2$. Activity measurements were performed on monitoring the reactor, and handling the manufactured product. SMPS and CPC equipment was used for measurements on particle concentration and size distributions. No information is available on background concentrations and/or product identification. The amount of product manufactured is considered to be 250 kg. Specific information on the type of process used for manufacturing is not available. Monitoring of a closed reactor process is measured during 97 minutes. Natural ventilation is available during the manufacturing process. Due to the absence of a background measurement, these data are considered to be specific, but only indicative for the process step of manufacturing of Nano-$TiO_2$ by specific industrial processes.

At the same production facility, bag/bin filling is measured using a continuous semi-automatic process provided with LEV. This measurement includes a non-activity measurement which is referred to as background measurement. SMPS and CPC equipment was used for measurements on particle concentration and size distributions. The amount of product handled is considered to be 250 kg. Both mechanical and natural ventilation are available during the process of bag/bin filling. These data are considered to be specific for the process step of bagging manufactured Nano-$TiO_2$. Bag/Bin filling was measured twice. Worst case values are provided in the summary table. Results are reported in Annex 2.

## 2. Nanex data set 2.

Nanex reports the results of a workplace exposure characterization during $TiO_2$ nanoparticle production. Results are presented at the 3rd International Symposium on Nanotechnology. Activity measurements were performed on both bag and bin filling of powdered Nano-$TiO_2$ with a particle size of 15 nm. Bin and bag filling was measured during 3.5 and 1.75 hours respectively. A local exhaust system is present. SMPS equipment was used for measurements on particle concentrations and size distributions. Mass concentrations are presented as well. No information is available on background concentrations and/or product identification. These data are considered to be specific for the process step of bagging manufactured Nano-$TiO_2$. Exposure due to the performance of activities was monitored over two years. Exposure values decrease due to improvements on the LEV system. Highest exposure values are reported in Annex 2.

## 3. Nanex data set 3.

Nanex reports the results of a Nanosh exposure survey performed during the production of paint. Powdered TiO2 application in photocatalytic paints and plasters was studied. SMPS and CPC equipment was used for measurements on particle concentration and size distributions. No information is available on background concentrations and/or product identification. Powders were handled in bags and the material was dumped into a large vessel, containing water. Different applied powder materials were mixed in the large vessel. The workplace was provided with both natural and mechanical ventilation and LEV was present. These data are considered to be specific for the process step of loading/charging Nano-$TiO_2$ in the stage of paint production. Annex 2 reports the exposure values measured during loading/charging 200 kg of TiO2.

### 4. Nanex data set 4.

Nanex reports the results of a Nanosh exposure survey during the production of printing ink based on Nano-$TiO_2$. Activity measurements were performed on emptying bags of pure powdered Nano-$TiO_2$ (40 kg) in a filling station. CPC equipment was used for measurements on particle concentrations. No information is available on background concentrations and/or product identification. Only the front of the filling station is open. LEV present at the filling station. Time duration is 5-10 min/task. This activity is considered comparable with the activity of charging Nano-$TiO_2$ in the paint industry. The difference in sector and relative low amount of product makes this dataset an analogous data set for the process step of loading/charging Nano-$TiO_2$ in the stage of paint production. The activity was measured twice. The dataset with the largest difference between activity and non-activity periods are reported in Annex 2.

### 5. Nanex data set 5.

Nanex reports a study of Demou A et al, 2008. This study investigated workers' real time exposure to metal-based nano particles in a gas-phase production process of pilot-scale production facility. Measurements are performed during 17 measuring days at 7 positions. SMPS and CPC equipment was used for measurements on particle concentration and size distributions. Information is available on background concentrations. A characterization of particles was not reported in the Nanex database. No information on specific activities, operational conditions and risk management measures are available in the Nanex database. Researchers state that data could be used as a rough indication of exposure levels of nano-silver manufacturing. Hence, these data are considered to be analogous for the process step of manufacturing of nano-silver by specific industrial processes. Annex 2 presents the maximum particle concentrations achieved during the steady state production phase.

### 6. Nanex data set 6.

Nanex reports a study of Junsu Park et al, 2009. The release of silver nano particles during a liquid-phase manufacturing process in a commercial production facility is studied. Bulky silver is synthesized by the liquid-phase reaction of Silver Nitrate (AgNO3) with Nitric Acid. A colloidal suspension of silver is produced by the reduction of AgNO3 in the presence of dispersing agent. Reaction mixing time is typically 24 h. After the reaction Process, the resulting Ag nano particles are filtered and dried in a dryer to remove volatile organic materials and water. After the drying process, silver nano particles (powder) are transferred to the grinding process. SMPS equipment was used for measurements on particle concentration and size distributions. Samples were taken in order to identify and characterize the particles from the process. Measured activities include opening the reaction hatch for sampling, opening the dryer door and opening the grinder hatch for packaging. Opening the reaction hatch for sampling silver nano particles results in the highest exposure values. The reactor hatch is opened for about 1 hour for sampling. A vent hood is installed. Collected samples showed that Ag nano particles were aerosolized into the work place; researcher explain that nano particles of 50-60 nm form agglomerates that will evolve to larger agglomerates depending upon particle mobility and concentration. This data are considered specific for the process step of manufacturing of nano-silver by specific industrial processes. Annex 2 presents the maximum exposure levels during opening the reaction hatch for sampling.

## 7. Data field study “Vervaardiging en gebruik van nano-eindproducten in Nederland”

The study “Vervaardiging en gebruik van nano-eindproducten in Nederland” by TNO and RIVM reports an indicative workplace measurement on manual rolling and brushing of liquid coating based on nano-silver in the open air. The measurement on the product based on nano-silver took 10 min. A surface area of max 3.2 m2 was treated. No protective equipment was used. Traffic and a diesel engine were reported as secondary sources. Philips Aerasense equipment was used to measure particle concentrations between 10-300 nm. Measured particles were not characterized/identified. Background concentrations were compared to particle concentrations measured during the activity. The application of liquid nanocoating is a wet process. The Philips Aerasense equipment does not distinguish between wet aerosols in the range of 10-300 nm and solid nano particles. It is not clear if this dataset is representative for the paint industry as the task duration is short and the applicated surface area small. This dataset is considered analogous for exposure to wet and solid particles in the range of 10-300 nm during manual rolling and brushing in the open air. Results are reported in Annex 2.

## 8. Data field study “Vervaardiging en gebruik van nano-eindproducten in Nederland”

The study “Vervaardiging en gebruik van nano-eindproducten in Nederland” by TNO and RIVM reports an indicative workplace measurement on spray painting in the car repair industry. Both coatings formulated with nano particles and regular coatings were applicated. Spray activities were performed using high pressure in a spray cabin. Philips Aerasense equipment was used to measure particle concentrations between 10-300 nm. The application of liquid nanocoating is a wet process. The Philips Aerasense equipment does not distinguish between wet aerosols and solid nano particles in the range of 10-300 nm. This dataset is considered indicative for exposure to wet and solid particles in the range of 10-300 nm during spray activities in a cabin. However, measured particles were not characterized/identified and no background concentration was determined. Hence, it is impossible to identify the type and amount of nano particles generated by the process from the type and amount of nano particles from secondary sources. The absence of a characterization makes it also impossible to judge the differences in particles released by spraying of coatings formulated with nano particles compared to the particles released by spraying of a regular coating.

Within the same company the activity of sanding of surfaces coated with both coatings formulated with nano particles as regular coatings was measured. A handheld sanding machine was used for sanding. Philips Aerasense equipment was used to measure particle concentrations between 10-300 nm. This measurement includes a background measurement, but measured particles were not identified/characterized. Due to the absence of characterization/identification, the actual source of the particles is unknown. The absence of a characterization makes it also impossible to judge the differences in particles released by sanding of nanocoatings compared to the particles released by sanding of a regular coating.

The researchers conclude that differences in particle release observed could not be explained by the presence of nano particles in a coating. This conclusion applies for both spraying and sanding activities measured at this workplace.
This dataset is considered an analogous but only indicative dataset for the application of coating by spray activities and for sanding activities. Because of the absence of information on the type of nanoparticle observed. The dataset is presented in Annex 2.

## 9. Methner, M. et al. 2010. Nanoparticle Emission Assessment Technique (NEAT) for the Identification and Measurement of Potential Inhalation Exposure to Engineered Nanomaterials – Part B: Results from 12 Field Studies. Journal of Occupational and Environmental Hygiene. 6th January 2010. 7:163-176.

Methner et al, 2010 present the results of 12 field studies in which emission measurements were performed to identify potential emission points or sources that could result in worker exposure. Facilities measured include a manufacturer of both nano titanium dioxide and nano-silver. CPC and OPC equipment was used for measurements on particle number concentrations and size distributions. CPC equipment measured in a size range of 10-1000 nm. OPC results are presented in two parts; one part in the range of 300-500 nm and one part in the range of 500-1000 nm. All results are corrected for background concentrations. TEM and EDX were used in some cases to characterize the particles from the process. Equipment was positioned as close as possible to the source of emission to identify worst-case scenarios. The researchers declare that the results represent a worst case situation and should not be interpreted as directly representative of full shift worker exposure.

Measurements were performed during batch manufacturing of 5-10 kg titanium dioxide with a particle size of 40 nm. Activity measurements include the creation of slurries by manual loading/unloading inside a booth and dumping into a mixing tank using focused LEV. These data are considered to be specific for the process step manufacturing of Nano-$TiO_2$ by specific industrial processes. CPC results are presented in Annex 2.

Besides that, the change out of a spray dryer drum was measured which can be considered as a maintenance activity. Information on OCs and RMMs is available, but not correlated to this activity. These data are considered specific for the process step of service/maintenance of equipment of the TiO2 manufacturing process. CPC results are presented in Annex 2.

In another facility, the manufacturing of silver using a gas phase condensation process was measured. Activity measurements during the stage of manufacturing include measurements on the passivator tumbler exhaust port and during the opening of the reactor (no LEV). These data are considered to be specific for the process step manufacturing of nano-silver by specific industrial processes. CPC results are presented in Annex 2.

Besides that, activity measurements were performed during cleanout of the reactor with and without the presence of LEV. These data are considered to be specific for the process step of service/maintenance of equipment of the Ag manufacturing process. CPC results are presented in Annex 2.

### 10. Lee, Ji Hyun. et al. 2011. Exposure assessment of workplaces manufacturing nanosized TiO2 and silver. Inhalation Toxicology. 23(4): 226-236.

Lee et al, 2011 monitored exposure to nano particles at 4 workplaces that manufacture Nano-$TiO_2$ and Nano-silver. The SMPS and dust monitor were used to monitor the particle size distribution. Particles sizes measured were 15-710.5 nm for the SMPS, and 0.3 – 20 um for the dust monitor. TiO2 and Ag nano particles were characterized using STEM/EDX analysis. Personal and area samples were taken for measurements on gravimetric concentrations.

Manufacturing of Nano-$TiO_2$ by chemical synthesis was measured at two different Research institutes. At the first location the entire manufacturing process lasted 4 hours and was conducted in a fume hood. The $TiO_2$ powder was collected after the reaction by workers using a brush. Powder collection required workers to put their head inside the fume hood. The amount of $TiO_2$ produced was 5 g/h. Results indicate that nano particles can be released from the manufacturing equipment into the workplace air. Number concentrations increased more due to increased temperature during the manufacturing process than due to harvesting of powdered nano-$TiO_2$. Particle sizes show that agglomeration and aggregation of particles takes place during the manufacturing process. This is confirmed by the TEM filters which show no individual $TiO_2$, but clumped structures. These data are considered to be specific for the process step manufacturing of Nano-$TiO_2$ by specific industrial processes. However, the production amount may not be representative for the manufacturers serving the paint industry with nano particles.

The second location was a $TiO_2$ powder manufacturing laboratory that uses a large-scale reactor surrounded by a vinyl curtain. The vessel used to collect the $TiO_2$ is located in a glove box. The amount of $TiO_2$ produced was 5 kg/h. Measured particle number concentrations were not the result of the manufacturing process only. Two secondary sources (Vacuum pump and welding operations were also involved in increasing the particle number concentrations). These data are considered to be specific for the process step manufacturing of Nano-$TiO_2$ by specific industrial processes. However, the influence of secondary sources increase the uncertainty of the data set. Results are presented in Annex 2.

Manufacturing of nano-silver was measured in two industrial settings. At the first location, a large-scale pilot reactor performed an induced coupled plasma process resulting in a daily production amount of 5 kg/day. Activities include Silver powder injection and tube connection to the collector. The workplace was ventilated by natural air. Results indicate that very few silver particles were released from the process into the workplace air. The researchers explain this by the fact of the presence of a complete closed system. TEM analysis showed agglomerated/aggregated silver nano particles. These data are considered to be specific for the process step manufacturing of Nano-Ag by specific industrial processes.

At the second location, silver nano particles were produced by mixing sodium citrate with silver nitrate resulting in a daily production amount of 1 kg/day. Activities include weighing of sodium citrate, adding and stirring to make it soluble. A solution of sodium citrate and silver nitrate were then pumped into the reactor to form silver nano particles. Cleaning activities are included as well. The workplace was equipped with a fume hood and well ventilated. Results show very low number concentrations including both particles generated by handling of the raw materials as nano-silver particles from the process. These data are considered to be specific for the process step manufacturing of Nano-Ag by specific industrial processes.

Results are presented in Annex 2.

## 11. Tsai, Chuen-Jinn. et al. 2011. Exposure assessment of nano-sized and respirable particles at different workplaces. J Nanopart Res.

Tsai et al, 2011 performed exposure measurements in the mixing area of a Nano-$SiO_2$ epoxy molding compound plant. In this area fumed silica with a primary diameter of 15 nm was mixed with other materials using a batch process. The main process was feeding raw materials including 40 kg of fumed silica into a ball grinder. The measurement location consists of an enclosed space with limited general ventilation. A large plastic tube is available near the inlet for Nano-$SiO_2$ with a connection to a small baghouse. The tube was intended as capturing hood. However, the researchers criticize the effectiveness of this measurement. Sampling was conducted tree times during a period of 6-8 hours. Equipment was positioned as close to the particle emission source as possible to represent the worse case scenario. TEM Analysis was used to judge the morphology of the silica fume used. Filters from Cyclones and MOUDIs were used for measurements on mass concentration. MOUDI equipment was used to identify the mass distribution of particles at the workplace. Filters from the Cyclones and MOUDIs were used for chemical analysis to quantify the content of manufactured nano particles in the collected samples. The SMPS was used for measurements on particle concentrations.

The mass concentration of nano particles (2.8 ug/m3) is low compared to the respirable particle mass (1963 ug/m3) and the total mass concentration (4653 ug/m3) . Besides that, the measured mass median aerodynamic diameter is 4611 nm. Chemical analysis shows SiO2 in the respirable particle mass, but not in the Nano particle fraction. TEM analysis shows loose agglomerates of silica. Researchers conclude that due to agglomeration airborne particles at these nanopowder workplaces are super-micron rather than nano-sized in terms of mass concentration.

Researchers observe that nano particle number and mass concentrations of manufactured materials were close to the background level. Number concentrations are elevated during loading or bagging processes. However, the researchers conclude that increase in particle number concentration is due to particles > 100nm. Increase in particles < 100 nm was not observed. The difference in type of particle and sector makes this dataset an analogous dataset for loading/charging of powdered Nano-$TiO_2$. Annex 2 reports Respirable particle mass concentrations and number concentrations.

### 12. Vorbau, Manuel. et al. 2009. Method for characterization of the abrasion induced nanoparticle release into air from surface coatings. Aerosol Science. 40. 209-217.

Vorbau et al, 2009 studied the particle release due to abrasion of a surface treated with a Nano-ZnO coating using a slow abrasion treatment test simulation experiment in a laboratory setting. A Taber Abraser consisting of two abrasion wheels moving by rotation of the sample with Nano-ZnO was used to simulate a low energy abrasion process. SMPS and CPC equipment was used for measurements on particle concentration and size distributions. CPC equipment analysed the total particle concentration in the range of 6 nm to > 10 m. SMPS equipment analysed the size distributions in a size range of 16-626 nm. TEM/SEM and EDX were used to characterize the particles from the abrasion process. In this study abrasion did not result in the release of a significant amount of particles < 100 nm. TEM/SEM analysis showed ZnO < 100 nm embedded in coarse dust particles from the abrasion process.

The difference in type of particle and the setting makes this dataset an analogous but only indicative dataset for low energy abrasion of surfaces treated with Nano-$TiO_2$ at the workplace.

### 13. Koponen, Ismo Kalevi. et al. 2010. Comparison of dust released from sanding conventional and nanoparticle-doped wall and wood coatings. Journal of Exposure Science and Environmental Epidemiology. 1-11.

Koponen et al, 2010 studied particle release due to sanding of surfaces using a handheld sanding machine during a simulation experiment in a laboratory setting. Surfaces were treated with paints, lacquers and fillers formulated with and without nano particles including SiO2. The experiment was conducted in a human exposure chamber provided with an air exchange rate of 9.2 ± 0.8 per hour. Sanding was performed using a handheld, orbital sander provided with grit size 240 sanding paper. All sanding experiments were performed by the same person using the same protocol. Sanding experiments were separated in three parts. The first part consisted of a background measurement, the second of a measurement on emission of the sanding machine. During the third part, repeated sanding periods of 1-2 min over 15-30 min were measured. APS and FMPS equipment was used for measurements on particle concentration and size distributions. APS equipment measured particles in the range of 0.542-19.81 um. FMPS measured particles in a smaller range of 5.6 - 542 nm. Particles were not characterized by TEM/SEM/EDX analysis.

Fine particles dominate the particle number concentrations. However, the motor from the sanding machine is the dominant source of particles < 100 nm. The shape of the size distributions is considered similar for coatings with and without engineered nano particles. The concentration of particles in each size distribution mode differ for coatings with and without nano particles. However, this differences cannot be explained by the presence of nano particles as they are not consistent. The researchers conclude that no clear effect is revealed on the presence of nano particles in coatings on dust emissions from sanding a surface treated with that coating. The difference in type of particle and the setting makes this dataset an analogous but only indicative dataset for high energy abrasion of surfaces treated with Nano-$TiO_2$ at the workplace.

## 14. Gohler, Daniel. et al. 2010. Characterization of Nanoparticle Release from Surface Coatings by the Simulation of a Sanding process. Ann. Occup. Hyg. Pp.1-10.

Gohler et al, 2010 studied particle release due to sanding of surfaces using a miniature sander in a simulation experiment performed in a laboratory setting. The sander consists of one abrasion wheel rotating with a speed of 1.83 m/s handled with a pressure of 10 kPa. Surfaces handled were treated with coatings formulated with and without nano particles including ZnO. The sanded surface was 13 cm2. 10 aerosol measurements for each coating were achieved. FMPS, LAP and CPC equipment was used for measurements on particle concentration and size distributions. FMPS measured particles in a range of 5.6 - 560 nm. For measurements of particles in the range of 0.3-30 um, LAP equipment was used. CPC equipment measured particles in the range of 6 nm till a few micrometers. Particles were characterized by TEM/SEM/ analysis. Results show a considerable generation of nano particles during the sanding process. No significant difference was detected between the number concentrations of released particles < 100 nm of the regular coatings compared to the coatings formulated with nano particles. The SEM and TEM images clearly prove that the additive particles are still embedded in the wear sample. No free ZnO particle could be collected of additionally counted. The difference in type of particle and the setting makes this dataset an analogous but only indicative dataset for high energy abrasion of surfaces treated with Nano-$TiO_2$ at the workplace. Results are described in Annex 2.

## 15. Chen, Bean T. et al. 2010. Nano particles-containing spray can aerosol: Characterization, exposure assessment and generator design. Inhalation Toxicology. 22(13): 1072-1082

Chen et al, 2010 studied nanoparticle release due to spraying of a spray can consumer product containing nano TiO2 particles in a simulation experiment performed in a laboratory setting. The product contains a gas propellant spray and is intended as bathroom cleaner/sanitizer. The laboratory room simulated a home environment with a high ceiling and low air exchange rate of 0.34 air changes per hour. Each experiment consisted of several intermittent short spray periods of 5 seconds lasting for 2.5 min. A combination of the Grimm analyzer, APS and SMPS equipment was used to measure particle size distributions. Particles were characterized using SEM/EDX analysis. The researchers conclude that the aerosol contains primary particles for more than 90%. Filters show TiO2 particles in a range of 40 nm-3.5 um. The comparison in setting, application time and spray method of this simulation experiment and the paint industry is small. Hence, this dataset is considered an analogous but only indicative dataset for the application of coating including Nano-$TiO_2$ by spray activities. Results are presented in Annex 2.

### 16. Norgaard, Asger W. et al. 2009. Release of VOCs and Particles During Use of Nanofilm Spray Products. Environ. Sci. Technol.

Norgaard et al, 2009. studied nanoparticle release due to spraying of a hand pump spray can consumer product containing Nano-$TiO_2$ particles and ethanol in a simulation experiment performed in a laboratory setting. Surface spraying was performed using about 8 g of product over a max period of 25 s. A combination of APS and FMPS equipment was used to measure particle size distributions. This dataset is considered an analogous but only indicative dataset for the application of coating including Nano-$TiO_2$ by spray activities. Results are presented in Annex 2.

### 17. Hagendorfer, Herald. et al. 2009. Size-fractionated characterization and quantification of nanoparticle release rates from a consumer spray product containing engineered nano particles. J Nanopart Res.

Hagendorfer et al, 2009 studied nanoparticle release due to spraying of a consumer product containing nano-silver particles using both pump and gas propellant spray techniques in a simulation experiment performed in a laboratory setting. SMPS equipment was used to measure particle size distributions in the range of 10-500 nm. Particles were characterized and quantified using TEM analysis. Each spray event was performed during 1 s and was repeated three times. The pump spray situation shows no measurable particle release, whereas in case of the gas spray, a significant release of nano-silver particles was observed. TEM images show Ag clusters. Most of the clusters were smaller than 100 nm. Total particle number concentrations peak right after the spray event. This peak value represents a worst case situation. This dataset is considered an analogous but only indicative dataset for the application of coating including nano-silver by spray activities. Worst case values are presented in Annex 2.

### 18. Stoffenmanager Nano

### 19. Occupational exposure measurements dutch paint producers

Within this pilot project, occupational exposure data were gathered during the production of paint/coating containing nano-$TiO_2$ at two different sites. Philips Aerasense equipment was used to measure particle concentrations between 10-300 nm. Background measurements were performed to correct for secondary sources. Particles were characterized using SEM/EDX analysis.

At company 1, measurements were performed during loading/charging of powdered nano-$TiO_2$ and the treatment of waste contaminated with powdered nano-$TiO_2$.
Loading/charging was performed manually using 170 kg of nano-$TiO_2$. A half enclosed mixing vessel was used provided with LEV. Wet suppression techniques were applied to prevent dust exposure.
Waste treatment consisted of discharging remainings, draining of buckets and sweeping up spillage in the presence of mechanical ventilation.
SEM/EDX analysis determine exposure to nano-$TiO_2$ during the activities.
These data are considered to be specific for the process step of loading/charging of Nano-$TiO_2$ and waste treatment in the stage of paint production. Background corrected exposure values are reported in Annex 2.

At company 2, measurements were performed during transport, loading/charging of powdered nano-$TiO_2$ and the treatment of waste contaminated with powdered nano-$TiO_2$.
The activity of transport consisted of picking up and transport of 10 bags of nano-$TiO_2$ from the storeroom to the paint production facility.
Loading/charging was performed manually using 100 kg of nano-$TiO_2$. A half enclosed mixing vessel was used provided with LEV. Loading/Charging was performed very careful.
Waste treatment consisted of discharging of empty bags to the waste container.
SEM/EDX analysis determine exposure to nano-$TiO_2$ during the activities.

These data are considered to be specific for the process step of transport, loading/charging of Nano-$TiO_2$ and waste treatment in the stage of paint production. Background corrected exposure values are reported in Annex 2. The individual company reports are documented in Annex 8 and 9.

# Annex 4; Measurement strategy for the VVVF pilot

## Introduction

A risk assessment framework for the use of manufactured nano-objects in the paint supply chain has been developed. In addition, this framework has been complemented with available information. Missing information for risk assessment will be complemented on:

- Human toxicity
- Occupational exposure
- Ecotoxicity
- Environmental emissions

This document provides a measurement strategy to complement missing information on occupational exposure only. The objective of the measurements is to complement the missing information for risk assessment of occupational exposure to Nano-$TiO_2$ and Nano-Ag in the Dutch paint chain.

In this project, the paint chain is defined as:

- (manufacturing of nanomaterials),
- Production of paint, and
- application of paint (incl. working with paint processed material/removing layers of old paint).

Since the manufacturing of nanomaterials is not located in The Netherlands, this phase will not be included in the measurements. In addition, the paint chain is limited to the fields of application in which the members of the FOSAG and FOCWA operate. Within these application fields the focus is restricted to the production and application of paint/coatings containing Nano-$TiO_2$ and Nano-Ag. In the past, TNO and IVAM have already conducted some measurements regarding the use of MNOs in the paint chain. Existing data on operational conditions, risk management and product information will be used to complement the information.

## Context of the measurements

### *Selection of measurement locations/companies*

Occupational exposure will be measured in different workplaces. The VVVF, VNCI, FOCWA and FOSAG provide a total of 6-8 companies.

### *Measurement/exposure scenarios*

In general, the scenarios will include activities involving the release of (dry) dusty nano particles or scenarios in which liquid aerosols are produced (i.e. spraying). Activities involving pastes or fluids with nano particles in non-aerosol forming processes are less likely to form airborne nano-objects and therefore seem less important in terms of a potential occupational exposure to nano-objects. After a telephone survey with the participating companies, it has become clear that in practice the following activities with Nano-$TiO_2$ and Nano-Ag take place:

Formulators:
- Warehouse: (un)loading, weighing, transport etc.
- R&D new paints and pilot scale production
- Mixing
- Filling
- Quality control (small scale quality control in a laboratory is less likely to form airborne nano-objects. Quality control will therefore only be measured in case of colour control by spraying)
- Cleaning vessels after production

Application rs:
- Preparation of paint
- Spraying (primer and paintwork)
- Cleaning paint pistol, brushes, etc.
- Sanding of surfaces containing Nano-$TiO_2$ or Nano-Ag (it might be difficult to determine of a surface contains the nanoparticle of interest)

In addition, other activities with the nano particles of interest, like bagging, dumping, sweeping, pouring, shaking, dipping, painting (brush/roller), etc., could take place in the four yet to be determined companies (application rs).

### *Identification of possible background sources of emission*

It might be useful to identify all possible sources of emission in and outside the workplace, other than the activity of interest, by taking into account all the activities, factors, pathways etc. which can cause emission of MNOs or other particles in the nano size range. The intention of this step is to compose a list of secondary sources which might disturb the measurement results. During the measurement day, background samples will be collected to adjust the measurement result for these sources of background emissions.

### *Gathering contextual information*

Contextual information will be gathered in order to completely understand the situation in which measurements are going to be conducted and therefore help to interpret the results.
A questionnaire will be used in order to gather the most important contextual information (questionnaire can be adapted to the activity).
In addition, photo and video material will be made (with consent of the company) to facilitate the interpretation and reporting of the measurement results.

### *Safety measurements*

Safety conditions will be evaluated for each individual measurement scenario. If necessary, safety measurements will be discussed with the companies.

## Measurements

### *On-line measurement instruments*

Number concentration and average particle diameter in the nano size range (10 to 300 nm) will be monitored with two NanoTracers (Philips Aerasense). Given the current state of art, the NanoTracer meets the criteria for this project the best (i.e. portable, easy to operate, suitable for personal measurements, accurate data, fast response time). NanoTracer works by diffusion charging, i.e. particles undergo diffusion charging enabled by a corona discharge.

In the advanced mode, the NanoTracer measures both particle concentration and average particle mobility diameter. In the fast mode, the NanoTracer measures only particle number concentration. Used in the advanced mode, the data can be used to calculate the lung deposited surface area. However, these values have to be interpreted with caution since there are no studies comparing these calculated values with measured values. At the moment we are still investigating whether the NanoTracer can be used for wet processes (e.g. spraying). This will be further discussed with Philips.

### *Measurement type and instrument location*

Measurements can be subdivided into source, work area, and personal measurements. Factors like surface deposition, evaporation, agglomeration, aggregation, and resuspension of deposited nano-objects can influence concentration and occurrence of MNOs in the workers breathing zone. Therefore, source or work area sampling cannot be interpreted as a representative of worker’s exposure. Personal measurements should be conducted in the worker’s breathing zone which represents a hemisphere (generally accepted to be 0.3 meters in radius) extending in front of the human face, centred on the midpoint of a line joining the ears (CEN.EN1540 1998). One NanoTracer will therefore be placed in the front pocket of a blouse or placed in the breathing zone using a belt. If the work area is large enough, a second Nanotracer will be placed at least 3 meters from the source in order to determine if other workers present in the work area are exposed to the MNOs.

### *Instrument operation*

The Nanotracer is a very easy to use instrument. When it is switched on, it measures continuously without further handling. Therefore, the Nanotracer does not require further operation. However, it is very important to keep up a task-time registration which can be used in order to analyse the relationship between activity and concentrations and investigate the influence of disturbing factors on the exposure level. The Nanotracer has the ability to mark a certain event. The mark will be displayed in the instrument output as a letter of the alphabet, which can be helpful with the task-time registration. The second Nanotracer (far field) can be used to mark the events since the other two Nanotracer (personal) are hard to reach without disturbing the worker.

In the advanced mode, the NanoTracer measures both particle concentration and average particle mobility diameter. In the fast mode, the NanoTracer measures only particle number concentration with an estimates size of 50 nm. Therefore, using the advanced mode will provide more accurate data and the fast mode can provide additional information in fast transient processes.

### *Measurement duration and frequency*

The aim is to measure during an activity and some time before and after the activity in order to determine the change in concentration once the activity has stopped. Observations combined with task-time registration can be used in order to analyse the relationship between activity and concentrations. Each company will be visit for one whole day (or less, depending on the duration of the activities with NMO); the aim is to maximize the amount of various activities measured during this visit. Therefore, the duration and frequency of the measurements will depend on the amount different activities taking place within a company.

### *Temperature and relative humidity*

Changes in temperature and relative humidity in the workroom can have significant impact on the particle dispersion and deposition (Asbach et al. 2009) and therefore on the personal exposure to MNOs. Several processes and factors (e.g. time of the day, heat production of machines/measurement devices) can change the temperature and humidity in the room. Therefore, temperature and relative humidity will be continuously monitored with a VelociCalc (TSI 8386)/Kimo KH200 data logger. If it is not possible to use this equipment, environmental data will gathered from the local weather station.

### *Background concentration*

A problem for assessing the exposure to MNOs is the background concentration of nano-objects in the air. Background nano-objects can be released as side products, such as fossil fuel combustion, equipment (compressors), secondary generation in the atmosphere and other work processes (Ono-ogasawara et al. 2009). On-line measurement devices nowadays available measure all particles within a certain size range and cannot make a distinction between background and MNOs, as a result that background nano-objects influence the quantitative exposure assessments. Therefore, it is useful to determine background concentration. There are various methods to determine background concentration near field and far field approach. Near-field measurements are conducted by monitoring before and/or after the activity at the workplace. Activity/time is therefore the variable of this background. Far-field measurements are performed by simultaneously measuring particle concentration at the workplace and at a selected reference site. Therefore, this type of background has distance as variable. The reference site, which represented the particle concentration at the workplaces during no work activity, has to be representative of the workplace environment. In practice, it is very hard to find a suitable reference site. Therefore, a near-field approach seems to be appropriate as a first approach to compare background concentrations with activity concentrations in case of task-based sampling. In case of a high background concentration, an effort should be made to identify and remove the source. Background concentrations should be measured for at least 10 minutes. The location and instruments used for the background measurement will be kept equal to the location and instruments used for the activity measurements.

### *Off-line analysis*

In order to investigate whether the worker is exposed to MNO or background nano particles, off-line analyses are performed. For these off-line measurements, particles are collected on a filter or a grid using a personal air sampling pump. Subsequently, the filter or grid is qualitatively analysed using scanning electron microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) for elemental analysis. This way, it can be determined if and in which configuration the particle that is under investigation is present in the air. In order to conduct off-line measurements, considerations will be given to the most suitable way to collect the samples and to analyze them.

### *Sampling method SEM*

In order to conduct SEM, particles need to be collected on a membrane filter. The filters can be coated in order to improve the conductivity. The most suitable pore size has to be determined. A pore size of 0.4 µm is the smallest size a personal pump with a flow rate of 1 l/m can handle. Samples will be collected on nickel-coated Nuclepore filters with a pore size of 0.4 µm. The off-line samples will be collected in the breathing zone of the worker by clipping the sampling head to the clothing of the worker.

An adequate particle loading onto the filters is important. Overloading the filter will cause the particles to pile, making the filter to become clogged. On the contrary, if the loading is too sparse, it might be impossible to conduct an accurate assessment of the particle characteristics. Therefore, the choice of flow rate will be determined based on the work situation and expected concentration of airborne particles. Using filters with 0.4 µm pore size, personal pumps can sample with a maximum flow rate of 1 l/min. If a higher flow rate is desired, it might be necessary to sample with high flow pumps. The downside to using high flow pumps is their size and weight. These pumps are not portable and can only be used for personal measurements if the activity is stationary.

Air samples will be gathered together with quantitative data during the activity (filter 1), after the activity (filter 2) and during the background measurements (filter 3). However, because analysing the filters is rather time-consuming and therefore expensive, it will be determined after the measurements which filters will be analysed.

### *Analysis of on-line measurement data*

Raw measurement data from the NanoTracer will be downloaded and visualised using NanoReporter software. Data will be visualised by presenting plots visualising background measurements and activity measurements. Activity measurements will be corrected for background measurements.

The most suitable method to interpret the results will be provided later on.

### *Time schedule*

Measurements are spread throughout the year in consultation with the various companies, taking into account the production line of the companies. Some activities, e.g. production of a batch containing Nano-$TiO_2$ and Nano-Ag, take place only a few times a year (2-3 times). Scheduling of measurements has to be adjusted to these sporadic occurring activities.

# Annex 5; Results assessments using Stoffenmanager Nano

| Life Cycle stage | Assumptions Stoffenmanager Nano | Result Stoffenmanager Nano |
|---|---|---|
| **Manufacturing stage**<br>Manufacturing of Nano-TiO$_2$/ Ag by specific industrial processes | 100% product<br>4-8 hours/day<br>Distance source-worker > 1 m<br>Workplace > 1000 $m^3$<br>Mechanical/Natural ventilation<br>Containment of the source with LEV | Task based exposure class; 2<br>Time weighed exposure class; 2<br>Time weighed exposure class corrected for FFP3; 2 |
| **Manufacturing stage**<br>Bagging manufactured Nano-TiO$_2$/ Ag | 100% product<br>Powder, High Dustiness (> 500 mg/kg), Low moisture content (<5%)<br>Handling of products with a relatively high speed/force which leads to dispersion of dust.<br>4-8 hours/day<br>Distance source-worker < 1 m<br>Workplace > 1000 $m^3$<br>Mechanical/Natural ventilation<br>LEV | Task based exposure class; 3<br>Time weighed exposure class; 3<br>Time weighed exposure class corrected for FFP3; 3 |
| **Manufacturing stage**<br>Cleaning and maintenance of equipment contaminated with Nano-TiO$_2$/ Ag | 100% product<br>Powder, High Dustiness (> 500 mg/kg), Low moisture content (<5%)<br>Handling of products with low speed or little force which leads to some dispersion or dust<br>1-30 min/day<br>Distance source-worker < 1 m | Task based exposure class; 3<br>Time weighed exposure class; 2 |

| Life Cycle stage | Assumptions Stoffenmanager Nano | Result Stoffenmanager Nano |
|---|---|---|
| | Workplace >1000 m3<br>Mechanical/Natural ventilation<br>LEV | Time weighed exposure class corrected for FFP3;<br>2 |
| **Manufacturing stage**<br>Treatment of waste contaminated with powdered nano material | 100% product<br>Powder, High Dustiness (> 500 mg/kg), Low moisture content (<5%)<br>Handling of products with low speed or little force which leads to some dispersion or dust<br>1-30 min/day<br>Distance source-worker < 1 m<br>Workplace >1000 m3<br>Mechanical/Natural ventilation | Task based exposure class;<br>3<br>Time weighed exposure class;<br>2<br>Time weighed exposure class corrected for FFP3;<br>2 |
| **Paint production**<br>Receipt, storage and transport of Nano-$TiO_2$/ Ag | 100% product<br>Powder, High Dustiness (> 500 mg/kg), Low moisture content (<5%)<br>Handling of products in situations where only low quantities of products are likely to be released.<br>1-30 min/day<br>Distance source-worker < 1 m<br>Workplace 100-1000 m3<br>Mechanical/Natural ventilation | Task based exposure class;<br>3<br>Time weighed exposure class;<br>2<br>Time weighed exposure class corrected for FFP3;<br>2 |
| **Paint production**<br>Loading/Charging of powdered Nano-$TiO_2$/ Ag | 100% product<br>Powder, High Dustiness (> 500 mg/kg), Low moisture content (<5%)<br>Handling of products with medium speed or force, which leads to some dispersion or dust<br>1-30 min//day<br>Distance source-worker < 1 m<br>Workplace >1000 m3 | Task based exposure class;<br>3<br>Time weighed exposure class;<br>2 |

| **Life Cycle stage** | **Assumptions Stoffenmanager Nano** | **Result Stoffenmanager Nano** |
|---|---|---|
| | Mechanical/Natural ventilation<br>LEV | Time weighed exposure class corrected for FFP3;<br>2 |
| **Paint production**<br>Mixing/Blending/Dissolving of coating formulated with Nano-$TiO_2$/ Ag | 1-10% nano in product<br>Liquid, medium viscosity<br>Handling of liquids using low pressure, but high speed<br>4-8 hours/day<br>Distance source-worker > 1 m<br>Workplace >1000 m3<br>Mechanical/Natural ventilation<br>LEV | Task based exposure class;<br>1 |
| | | Time weighed exposure class;<br>1 |
| | | Time weighed exposure class corrected for FFP3;<br>1 |
| **Paint production**<br>Filling cans with liquid coating | 1-10% nano in product<br>Liquid, medium viscosity<br>Handling of liquids using low pressure and low speed<br>4-8 hours/day<br>Distance source-worker < 1 m<br>Workplace >1000 m3<br>Mechanical/Natural ventilation<br>LEV | Task based exposure class;<br>1 |
| | | Time weighed exposure class;<br>1 |
| | | Time weighed exposure class corrected for FFP3;<br>1 |
| **Paint production**<br>Sampling of liquid coating formulated with Nano-$TiO_2$/ Ag | 1-10% nano in product<br>Liquid, medium viscosity<br>Handling of liquids in very small quantities<br>1-30 minutes/day<br>Distance source-worker < 1 m | Task based exposure class;<br>1 |
| | | Time weighed exposure class;<br>1 |

| Life Cycle stage | Assumptions Stoffenmanager Nano | Result Stoffenmanager Nano |
|---|---|---|
| | Workplace >1000 m3<br>Mechanical/Natural ventilation | Time weighed exposure class corrected for FFP3;<br>1 |
| **Paint production**<br>Cleaning and Maintenance of equipment of paint production process | 1-10% nano in product<br>Liquid, medium viscosity<br>Handling of liquids using low pressure, low speed with large of medium quantities<br>1-30 minutes/day<br>Distance source-worker < 1 m<br>Workplace >1000 m3<br>Mechanical/Natural ventilation | Task based exposure class;<br>1 |
| | | Time weighed exposure class;<br>1 |
| | | Time weighed exposure class corrected for FFP3;<br>1 |
| **Paint production**<br>Treatment of waste contaminated with powdered nano material | 100% product<br>Powder, High Dustiness (> 500 mg/kg), Low moisture content (<5%)<br>Handling of products with low speed or little force which leads to some dispersion or dust<br>1-30 min/day<br>Distance source-worker < 1 m<br>Workplace >1000 m3<br>Mechanical/Natural ventilation | Task based exposure class;<br>3 |
| | | Time weighed exposure class;<br>2 |
| | | Time weighed exposure class corrected for FFP3;<br>2 |
| **Application**<br>Loading of application equipment with coating formulated with Nano-$TiO_2$/ Ag | 1-10% nano in product<br>Liquid, medium viscosity<br>Handling of liquids using low pressure, low speed with large of medium quantities<br>1-30 min/day<br>Distance source-worker < 1 m<br>Workplace 100-1000 m3 | Task based exposure class;<br>2 |
| | | Time weighed exposure class;<br>1 |
| | | Time weighed exposure class corrected for FFP3;<br>1 |

| Life Cycle stage | Assumptions Stoffenmanager Nano | Result Stoffenmanager Nano |
|---|---|---|
| **Application**<br>Application of coating by spraying | 1-10% nano in product<br>Liquid, medium viscosity<br>Handling of liquids at high pressure resulting in substantial generation of visible mist or spray/haze<br>2-4 hours/day<br>Distance source-worker < 1 m<br>Workplace 100-1000 m3<br>Spray cabin | Task based exposure class;<br>2<br>Time weighed exposure class;<br>2<br>Time weighed exposure class corrected for FFP3;<br>2 |
| **Application**<br>Application of coating including by rolling/brushing | 1-10% nano in product<br>Liquid, medium viscosity<br>Handling of liquids using low pressure, low speed with large of medium quantities<br>4-8 hours/day<br>Distance source-worker < 1 m<br>Workplace 100-1000 m3 or Outdoor<br>Mechanical/Natural ventilation or Outdoor | Task based exposure class;<br>1<br>Time weighed exposure class;<br>1<br>Time weighed exposure class corrected for FFP3;<br>1 |
| **Application**<br>Cleaning and Maintenance of equipment used in the stage of application | 1-10% nano in product<br>Liquid, medium viscosity<br>Handling of liquids using low pressure, low speed with large of medium quantities<br>1-30 min/day<br>Distance source-worker < 1 m<br>Workplace >1000 m3<br>Mechanical/Natural ventilation | Task based exposure class;<br>1<br>Time weighed exposure class;<br>1<br>Time weighed exposure class corrected for FFP3;<br>1 |

| Life Cycle stage | Assumptions Stoffenmanager Nano | Result Stoffenmanager Nano |
|---|---|---|
| **Service life**<br>Fracturing/Abrasion of coated surfaces | | Not covered by Stoffenmanager Nano |

# Annex 6; Interview with FOCWA on barriers experienced to find pilot companies

Interview with: J. Horak, FOCWA (The Dutch Car Body Repairers Association), 8 October 2011
Main question: what barriers are experienced in practice in identifying companies in the car body repair sector that work with nanoproducts and where possibly exposure to airborne nano particles might occur.

As strategy for the selection of companies for practical exposure measures to nano particles the project used a tiered approach. The participating branch organizations made a first selection of potential companies and verified their willingness to cooperate. Consequently the names were given to the consultants to make further appointments and to carry out the exposure measurements.
The projects' choice was to monitor two nanomaterials: Nano-$TiO_2$ and Nano-Ag for detailed studies and to try to find companies that use one of these materials. The idea of JH is that car body repair shops do not use Nano-Ag based coatings or lacquers, since these type of coatings typically are used for "hygienic" purposes for the bactericidal properties.

A first effort of FOCWA was to send around an invitation to a few member-companies that were well-known from past participation projects, and were expected to be willing to participate. Two companies replied positively to be willing, but a further, more detailed inventory of used products showed that in the end, they were not using any nanoproducts. So this strategy failed.

A second effort to find companies was the initiative of JH to ask the account managers of FOCWA to suggest companies that use nanoproducts. The task of the account manager (AM) is to visit members companies in their region to discuss all sorts of questions related to professional activities. The AMs have a large action radius and they know quite a lot of companies at a very detailed level. They visit about 4 to 5 companies every day. Every member-company is visited about 1 time per year. It was asked to the AMs to combine their visits with the inquiry about the use of nanoproducts. Doing this, the AMs faced the problem that they were equipped with too little information. The question whether the car body repair shop uses products that contain Nano-$TiO_2$ or Nano-Ag appears not to be answerable. Car body repair shops are not informed, in any way about the nanocontent of their products. The available SDS of the used products do most often not mention "nano". Consequently the management does not know whether nanoproducts are being used. It might be, but it might as well not be. A more detailed search of products used in companies, followed up with a search at the producers of these products to find out which products *might* contain "nano" is too much work for the companies. They have many dozens of products with an SDS on stock and this producer-oriented (upstream) activity would cost them too much time. Additionally, these companies may even not be skilled enough "in nano" to ask the right questions or to insist to get information on product composition that is normally kept confidential by the paint manufacturer. Further search on the "nano-identity" of the used paint is neither a task for AMs. So this strategy failed as well.
A third effort to identify willing companies was along the line of the paint manufacturer: to try to get information from the paint manufacturer about the car body repair shops that use their "nanopaint".
The project cooperated with two paint manufacturers. One of the paint manufacturers appeared no useful source for identification of nanopaint-using repair shops as their production of automotive and car refinishing paints and lacquers is not located in the Netherlands. The nanocoating produced by the other paint-manufacturer in the project, was not used in the Netherlands. So this strategy failed as well.

It should be noted that FOCWA, with the help of those two paint manufacturers, was able to identify either downstream users abroad, or downstream users using nanoproducts produced abroad. None did match the Dutch Business to Business chain, though. The scope of the pilot and the number of manufacturers involved appeared to be too small to meet the pilot goals for measurements. One of the paint manufacturers was a relatively small vehicle refinishing paint manufacturer. Cooperation with this manufacturer turned out to be not a good choice for identification of a Dutch car body repair shop. The other paint manufacturer was a large company. However, production of automotive and car refinishing paints was located abroad. Because of the larger market and possibly more car body repair shops, the chance of finding a car body repair shop might have been larger if more large paint manufacturers cooperated in the pilot project.

At the same time one of the rumors in the sector is that one car trademark uses special transparent lacquers based on nano at least on their new luxury cars. It is not known whether this lacquer is used as well on cheaper new models, but it seems that older types did not use nano. The company strongly advises to use specific brands as repair lacquers. The sectors calls this “homologizing”. The choice for homologues seems to be largely a commercial driven demand to control the market, it is not a matter of the right colour. Normally the colour of the car (which may decolourize in time) is carefully checked at the car body repair shop with a photo spectrometer to assure the right colour and mixed upon the exact degree. It is not clear whether these homologues contain nano. The SDS of these products do not mention “nano”. The dealers themselves seem neither a source of information, because they are supposed not to be informed about the composition of the used paint on the new car, or if they would be asked, are expected to reply that this concerns confidential information. A possible choice just to involve a company specific repair shop in the project was not a choice, because brand specific car body repair shops do not exist and to do an at random measurement was not thought to be an option. As stated before, it was no option for car body repair shops to go back in the production chain to try to get the nano-information about the used coatings.
A by-pass was shortly considered, namely to organize a simulation experiment at one of the centers for vocational training. This idea however was not brought into operation because of the idea that simulation of a practice situation, with a working day-long exposure to (emissions of) nanocoatings or –lacquers would be difficult to organize in the setting of the students education. Anyway, the emphasis of the project was on real-life situations and the related risk communication, making a test situation less attractive.

Other possible dispersive nanoproducts used in car body repair shops, like polishing products, waxes, protection layers, as used for example by car polishing and reconditioning companies are not considered to be products within the scope of the actual project.

## Conclusion

Two relative straight forward reasons found to be limiting the search for downstream users of nano$TiO_2$ and Nano-Ag automotive coatings are (1) the fact that the market is an international one instead of Dutch and (2) the fact that Nano-Ag is not known to be used. A third and most import reason is the current lack of traceability of nano in the production chain. This is the key issue. Identifying nano-using companies amongst car body repair shops generally fails due to the lack of information whether the product is nano based. This can be due to the fact that nanodetails are not reported on the SDS, the downstream user is not “focused” on this information and doesn’t record it as being important, or a product is marketed as nano but isn’t really formulated using nanomaterials. Neither the management, nor the workers in car body repair shops know whether they are confronted with cars that are coated with a nano-lacquer or whether they use nanoproducts for refinishing. As a consequence they don’t know whether there is a risk for exposure to nano particles.
The information is not supplied to them by the paint manufacturers, nor by the suppliers of the cars. The involved management in the branch does not have the chemical knowledge to demand upstream information from suppliers or manufacturers about the coating composition (and especially on the nano content). It seems that many paint and coating manufacturers keep their use of nanomaterials in products confidential.

# Annex 7; Interview with FOSAG on barriers experienced to find pilot companies

Interview with: Edwin Meewsen FOSAG (The Dutch Painters Association),
18 October 2011

Main Questions:
- Which strategy was followed in identifying painting contractors processing nanoproducts?
- What barriers were experienced in identifying and cooperating with painting contractors processing nanoproducts?

## Strategy

A first effort of FOSAG to identify painting contractors handling nanoproducts was contacting the customers of the formulators of nanoproducts involved in the project. FOSAG asked the formulators for an alert in case of supplying nanoproducts to a customer. This effort resulted in 7 identified users.
Secondly, FOSAG contacted three other formulators of nanoproducts.
Besides this, FOSAG contacted 5 painting contractors from their own member list.

## Results and barriers

In general, painting contractors work on projects. The projects of the 7 formulator-mediated users were all finished at the moment these users were identified. No alerts were received from the formulators during the period established for recruitment of companies for cooperation within the project.
One of the three other formulators did not want to assist in identifying painting contractors processing nanoproducts, as they did not want to be associated with the use of nanoproducts. Both other formulators were willing to assist. However, one of them did formulate nanoproducts in such small extent that it was not possible to identify customers during the period of the project. There is an on-going contact with the last formulator. However, this contact did not result in identifying and cooperation with a painting contractor processing nanoproducts within the timeframe of the project.
One of the 5 painting contractors from the FOSAG member list was planning a pilot project using nanoproducts in the near future. Unfortunately, this pilot project was planned after the period established for recruitment of companies for cooperation within the project. The 4 other painting contractors were willing to cooperate, but did not have a project with nanoproducts during the recruitment period.

## Discussion

According to FOSAG, the frequency and extent of use of nanoproducts is small among Dutch painting contractors at the moment. FOSAG comes forward with the innovative character of nanoproducts as possible reason. In general, Dutch painting contractors are conservative and skeptical of working with new products because of the possible business risks and losses. Only after a brand new product has proven itself in practice, companies are willing to use this product on a larger scale. This does not apply to nanomaterials according to FOSAG.
FOSAG did not experience any ignorance among the companies contacted. The companies were convinced that they know whether their products contain nano particles.
Besides this, FOSAG did not experience anxiety for the possible health effects of nano particles among painting contractors. Painting contractors are confident with implementation of risk management measures. Hence, this issue is considered surmountable.
One formulator hesitated in cooperation due to the image of nanoproducts.
Painting contractors did not come forward with this argument.

In conclusion, the frequency and extent of use seemed to be the main barrier in identifying and recruitment of companies for cooperation within the project *Communication in the product chain paint and lacquers.* A longer period of recruitment of companies was necessary to find suitable companies.

# Annex 8; VVVF-project – Rapportage meetresultaten bedrijf B1

## Oriënterende metingen naar blootstelling aan nanodeeltjes tijdens aanmaken coating bij bedrijf B1

## *Pilot: “Kennisdelen Nano in de verfketen*

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Amsterdam, januari 2012

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## Colofon

ISO Doc. nr.
Project nr.

| | |
|---|---|
| Titel | **Oriënterende metingen naar blootstelling aan nanodeeltjes bij het aanmaken van een coating bij bedrijf B1** |
| Auteur(s) | F.A. van Broekhuizen, IVAM UvA<br>R.T.M. Cornelissen, IVAM UvA |
| Uitvoer metingen | R.T.M. Cornelissen, IVAM UvA<br>Babs van Manen - Vernooij, TNO Triskelion |
| Datum | Januari 2012 |

Deze rapportage is tot stand gekomen in het kader van het project Pilot Kennis delen in de verfketen. Het onderzoek uitgevoerd in opdracht van, met subsidie van het ministerie van.
Contactpersoon opdrachtgever:

Voor meer informatie over deze rapportage kunt u contact opnemen met:
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# 1. Pilot Kennisdelen in de verfketen

## 1.1 Toelichting Project

De inzet van de VVVF is om samen met de partijen uit de hele verfketen – de producent van de grondstof, de verffabrikant en de gebruiker – inzichten te verwerven betreffende het veilig werken met nanodeeltjes. Deze proactieve aanpak levert informatie en inzichten op die ingezet kunnen worden bij Europese (bijv. REACH) maar ook nationale beleidsontwikkelingen op het gebied van arbo- en milieuzorg. Daarnaast zijn de opbrengsten van direct belang voor bedrijven in de betrokken sectoren omdat het inzicht biedt in de mogelijke risico's van het werken met nanodeeltjes.

De Vereniging van Verf- en Drukinktfabrikanten (VVVF) wenst de kennisopbouw over nanotechnologie in de verf- en drukinktindustrie te stimuleren en wil daarom, samen met de grondstoffenleveranciers verenigt in de VNCI, participeren in een project om kennis te verzamelen en te delen over nanodeeltjes.
Dit project richt zich op de stoffen nano-$TiO_2$ en nano-Ag. Deze rapportage beschrijft de resultaten van blootstellingmetingen tijdens het gebruik van nano-$TiO_2$ binnen bedrijf B1.

Nanodeeltjes
Nanodeeltjes (deeltjes met een afmeting van 1 – 100 nm in één of meerdere dimensies) worden vanwege hun bijzondere chemisch/fysische eigenschappen in toenemende mate ontwikkeld en toegepast in producten om hieraan een bijzondere eigenschap te geven. Het betreft veelal onoplosbare en niet- (of slecht-) afbreekbare deeltjes, waarbij het kan gaan om anorganische materialen (bijv. metalen of metaaloxiden) of om op koolstof gebaseerde - of organische materialen (bijv. fullerenen of koolstofnanobuisjes).

In de praktijk onderscheidt men engineered nanodeeltjes (gefabriceerde nanomaterialen die bewust zijn gemaakt en worden toegepast in producten)(ENP), en ultrafijne deeltjes (UFP)(deeltjes die door natuurlijke of antropogene activiteiten worden gevormd en in de lucht aanwezig zijn als *achtergrondconcentratie* aan nanodeeltjes). Bij UFP kan men aan bronnen denken als verbranding, verhitting, roken e.d. ENP en UFP zijn deeltjes met vergelijkbare afmetingen, beiden in het nanogebied. Het "nanobeleid" richt zich vooral op de ENP, het inzicht verkrijgen in de risico's van deze deeltjes en het terugdringen van de emissie.

Grenswaarden
Voor het maken van een risicobeoordeling voor werken met nanomaterialen maak je idealiter gebruik van gezondheidskundige grenswaarden (OEL of DNEL). Christensen et al (2010) heeft de beschikbare gevaardata van $TiO_2$ geevalueerd en een DNEL voor inhalatie voorgesteld van 17 $\mu g/m^3$ (of wel $8.3 \times 10^5$ nanodeeltjes/$cm^3$). Christensen et al (2010) stelt dat deze DNEL momenteel niet voor regulatoire doeleinden kan worden gebruikt omdat er nog veel onzekerheid bestaat over de verzameling en interpretatie van nano gevaardata. Bij gebrek aan andere specifieke gevaardata wordt zal de gemeten blootstelling in de huidige rapportage vergeleken met deze DNEL. Voor de meeste nanodeeltjes zijn er momenteel nog geen gezondheidskundige grenswaarden beschikbaar. In de praktijk heeft een bedrijf meestal ook geen specifieke gevaar data voorhanden. Daarom zal de gemeten blootstelling tevens worden vergeleken met de NRV die wordt voorgesteld als tijdelijke referentiewaarde voor blootstellingbeoordeling in het geval van het ontbreken van een OEL of DNEL. De NRV zijn geen gezondheidskundige grenswaarden (zie onder voor toelichting). Dat betekent dat werkzaamheden niet per definitie als veilig kunnen worden beschouwd wanneer de blootstelling lager is dan de NRV. De NRV zijn gebaseerd op voorzorg en kunnen beschouwd worden als waarschuwingsniveau dat moet aanzetten tot de uitvoering van een zorgvuldige blootstellingsbeheersing van nanodeeltjes op de werkplek.

Nanoreferentiewaarden

Onder normale omstandigheden geven de grenswaarden voor beroepsmatige blootstelling het maximale blootstellingsniveau aan waarbij werkzaamheden veilig kunnen worden geacht (grenswaarde of DNEL)[18]. Deze grenswaarden zijn echter nog maar beperkt beschikbaar voor nanodeeltjes.

Nanoreferentiewaarden kunnen, zolang er nog geen grenswaarden voor beroepsmatige blootstelling zijn vastgesteld, hierin een oplossing bieden. Het is een generieke benadering voor een grenswaarde voor de verschillende ENP. Omdat onvoldoende toxiciteits- en blootstellingsgegevens beschikbaar zijn, zijn ze bepaald op basis van voorzorg en hebben ze een tijdelijk karakter. De onbekendheid van de specifieke giftigheid van nanodeeltjes, en tegelijkertijd de verwachting dat deze niet verwaarloosd kan worden brengt grote onzekerheid in de risicobeoordeling. Dit leidt tot het toepassen van een benadering gebaseerd op voorzorg. Als meer gegevens beschikbaar komen kunnen ze vervangen worden door een normale grenswaarde of DNEL-waarde.

In Nederland zijn de nanoreferentiewaarden vastgesteld door het RIVM ([I]). Hierbij moet benadrukt worden dat het gaat om *tijdelijke* nanoreferentiewaarden. Het RIVM heeft zich hierbij gebaseerd op vergelijkbare initiatieven in Groot Brittannië en Duitsland, de “benchmark exposure levels” (vergelijkende blootstellingswaarden), voorgesteld door het British Standards Institue ([II]), en de methode zoals voorgesteld door het IFA ([III]). Het RIVM stelt voor om het IFA-model in Nederland te gebruiken.

*Tijdelijke* nanoreferentiewaarden worden als volgt gedefinieerd:

**Een tijdelijke nanoreferentiewaarde (NRV)** is een waarschuwingsniveau dat moet aanzetten tot de uitvoering van een zorgvuldige blootstellingsbeheersing van nanodeeltjes op de werkplek. De NRV is vastgesteld als een 8-uur tijd gewogen gemiddelde concentratie gecorrigeerd voor de achtergrondconcentratie aan ultrafijne deeltjes. Als dit niveau wordt overschreden dan moet de blootstelling worden geminimaliseerd: de bron(nen) van de nanodeeltjes moet(en) nauwkeurig worden vastgesteld, (indien mogelijk) moeten de deeltjes worden gekarakteriseerd, het risico worden beoordeeld en moet worden vastgesteld op welke wijze de emissie van nanodeeltjes kan worden gereduceerd en de blootstelling kan worden beheerst.

In tabel 1 is de NRV weergegeven en voor gangbare nanodeeltjes aangegeven in welke categorie ze vallen.

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[18] DNEL = Derived No-Effect Level

**Tabel 1 Nanoreferentiewaarden voor nanodeeltjes op de werkplek**

| | Omschrijving categorie | Dichtheid | Nanoreferentiewaarden ($NRV_{8u\text{-}TGG}$)* | Type |
|---|---|---|---|---|
| 1 | Koolstof nanobuisjes (CNT) (lengte diameterverhouding > 3:1 en lengte > 5µm) waarvoor geen testen omtrent asbestachtige effecten zijn uitgevoerd | | 0,01 vezels /$cm^3$<br>10.000 vezels/$m^3$ | SWCNT of MWCNT waarbij asbestachtige klachten niet zijn uitgesloten |
| 2 | biopersistente granulaire nanomaterialen met een primaire deeltjesgrootte in de 1 tot 100 nm range | > 6.000 kg/$m^3$ | 20.000 deeltjes/$cm^3$ | Ag, Au, $CeO_2$, CoO, Fe, $Fe_xO_y$, La, Pb, $Sb_2O_5$, $SnO_2$, |
| 3 | biopersistente granulaire nanomaterialen met een primaire deeltjesgrootte in de 1 tot 100 nm range | < 6.000 kg/m³ | 40.000 deeltjes/$cm^3$ | $Al_2O_3$, $SiO_2$, TiN, $TiO_2$, ZnO, nanoclay<br>Carbon Black, $C_{60}$, dendrimers, polystyrene<br>CNT zonder asbest achtige effecten |
| 4 | Ultrafijne vloeistof en oplosbare deeltjes | | Betreffende grenswaarde voor moedermateriaal | O.a. vetten,, koolwaterstoffen, siloxanes, NaCl |

Kortdurende blootstelling

In de methodiek van de DNEL en de tijdelijke nanoreferentiewaarden, is geen rekening gehouden met de beoordeling van werkplek concentraties aan een grenswaarde voor tijd gewogen gemiddelde van 15 minuten (TGG-15). In de praktijk blijkt de blootstelling aan nanodeeltjes veelal van kort durende aard te zijn. Het artikel van Christensen et al (2010) beschrijft acute gevaareffecten voor nano-$TiO_2$. Wanneer er acute gevaareffecten zijn beschreven voor de nanostof zou de blootstelling ook vergeleken moeten worden met de TGG-15. Hiervoor kan de vuistregel van de Nederlandse arbeidsinspectie worden gehanteerd, die een handreiking geeft voor een korte blootstellingstijd van 15 minuten:

NRV15min-TGG = 2 x 8uur-TGG. Voor de DNEL van nano-$TiO_2$ resulteert dit in een TGG-15 van 1.660.000 deeltjes/$cm^3$, voor de NRV van nano-$TiO_2$ in 80.000 deeltjes/$cm^3$

## 1.3 Meetapparatuur

NanoTracer

Voor het in kaart brengen van de persoonlijke real-time blootstelling aan nanodeeltjes is in dit onderzoek gebruik gemaakt van een aerosol meter van Philips Aerasense, de NanoTracer. De NanoTracer is een draagbare monitor voor het meten van de concentratie nanodeeltjes in de omgevingslucht. Hiermee worden continu, real-time ultrafijne- en nanodeeltjes (Φ = 10 - 300nm) gemeten, zowel de deeltjesconcentratie als de gemiddelde deeltjesgrootte.

De persoonlijke werker blootstelling aan nanodeeltjes is in dit onderzoek gemeten met de Philips NanoTracer bevestigd in de ademzone van de werknemer die activiteiten uitvoert met nanodeeltjes. De specificaties en de gehanteerde instellingen van de meter zijn opgenomen in tabel 7. Bij het meten van de blootstelling worden alle aanwezige deeltjes met een afmeting van 10-300nm gemeten. Het betreft hier zowel ENP als de nanodeeltjes die aanwezig zijn in de natuurlijke achtergrondconcentratie. Naast natuurlijke bronnen van nanodeeltjes (vrijkomen bij b.v. verbranding, verhitting) zullen er ook nanodeeltjes gevormd kunnen worden door de gebruikte elektrische apparatuur en het gebruik van verwarmingselementen. Dit zijn bronnen die de blootstellingsmeting van engineered nanodeeltjes kunnen verstoren. .Om een overschatting van de blootstelling aan synthetische nanodeeltjes tijdens het werkproces te voorkomen zijn achtergrondmetingen uitgevoerd. De blootstelling aan synthetische nanodeeltjes tijdens het werkproces is gecorrigeerd voor deze achtergrondwaarden.

tabel 2 Specificaties van de Philips Aerasense aerosol meter

| | |
|---|---|
| Gemeten parameters | - Aantal deeltjes [deeltjes /cm$^3$]<br>- Deeltjesgrootte (diameter) [ nm] |
| Range: Deeltjesgrootte | 10 – 300 nm |
| Smoothing algorithm | Geen |
| Aanzuigsnelheid ventilator | 0,4 l/min |
| Gebruikte instelling | Advanced mode |
| Meet interval | 16 seconden |
| Gevoeligheid | 1 fA [19] |
| Gebruikte ijkbron | $KNO_3$ aerosol |

De meetresultaten zijn geanalyseerd met behulp van de NanoReporter software (versie 1.0.4.0), Philips Aerasense) en met behulp van MS Excel (MS Office 2007) en SPSS.

Monstername pompen

Zowel tijdens de metingen aan de achtergrond als het werkproces zijn filtermonsters genomen. In de monstername is onderscheid gemaakt tussen het storten van de “normale poeders” en het nano materiaal Hombicat UV 100. Met behulp van Scanning Electron Microscopy (SEM) en Energy Dispersive Analysis of X-radiation (EDX) is de deeltjesgrootte, morfologie en chemische samenstelling van de nanodeeltjes bepaald.

Meer achtergrondinformatie over de meetopzet en de gebruikte meetmethoden en –technieken is opgenomen in Annex 4 van rapport V9445 Pilot “Kennisdelen Nano in de Verfketen.

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[19] femto Ampère (10 $^{-15}$)

# 2. Oriënterende metingen bij bedrijf B1

## 2.1 Nanomaterialen bedrijf B1

Bij bedrijf B1 is op 19 mei 2011 een bezoek gebracht aan een van de productielocaties voor het uitvoeren van oriënterende blootstellingsmetingen tijdens gebruik van ENP.

Bij dit bedrijf zijn metingen verricht tijdens het aanmaken van een watergedragen (latex) coating via een batch proces, waarbij gebruik gemaakt wordt van Hombicat UV 100; een additief in de nanovorm (nano-$TiO_2$). Ook zijn enkele achtergrondmetingen verricht in de productieruimte.

Nano-$TiO_2$ is verpakt in papieren zakken van 15 kg nano-$TiO_2$ per zak. Deze zakken worden door de leverancier op een pallet aangeleverd. Voor aanvang van de productie wordt de juiste hoeveelheid van het benodigde materiaal (in meervouden van 15 kg) door de medewerkers van het grondstoffenmagazijn klaargezet op een pallet en wordt het pallet met pakbon gereedgezet in de productieruimte. Op de betreffende meetdag is 170 kg grondstof (=12 zakken) gebruikt in de batch. Naast nano-$TiO_2$ zijn voor deze batch ook andere poedervormige grondstoffen gebruikt, waarbij één grondstof mogelijk een additief in de nanoschaal kan zijn geweest[20].

## 2.2 Productie nano-batch bedrijf B1

Productie van de batch vond plaats in een verfketel.

De verfketel was voorzien van een interne roerder die via een besturingspaneel bediend werd. De operators van de productie stonden op een bordes op circa 2m boven de grond, zodat de bovenkant van de ketel zich op heuphoogte bevond. Aan de ketel met water worden volgens recept en in volgorde van het recept grondstoffen toegevoegd.

Bij deze batch en op deze specifieke productielijn worden de grondstoffen handmatig toegevoegd uit zakken of uit emmers. Een deel van de grondstoffen wordt echter ook automatisch via het centrale feeder systeem toegevoegd. Dit betekent dat via een silo opslag de juiste hoeveelheid additief wordt afgewogen en via een leiding aan de ketel wordt toegevoegd.

Voor het handmatig toevoegen van de poedervormige additieven wordt het pallet met de gewenste grondstof met een vorkheftruck op bordeshoogte gebracht, waarvandaan de medewerkers de zakken pakken. Ze zetten de zak op een rooster bovenin de ketel, waarna ze de zak aan de onderzijde open snijden. Afhankelijk van het gewenste additief kan dit om 1 of om meerdere zakken gaan. Tijdens het toevoegen van de grondstoffen draait de roerder in de ketel.

Wanneer de meeste grondstoffen zijn toegevoegd wordt de latex ‘afgedraaid’ (kapotslaan en mengen van additieven). Vervolgens vindt een kwaliteitscontrole plaats en afhankelijk van de uitslag wordt het product afgemaakt, of worden er meer additieven toegevoegd. Afmaken betekend de laatste grondstoffen toevoegen.

Na de productie van de batch werden de lege zakken in een ton gestopt en afgevoerd en werd het filter dat gebruikt was voor afzuiging leeg geklopt. De afvaltonnen werden leeggezogen en gemorst product werd opgeveegd met stoffer en blik.

In principe wordt elke verf batch zo gemaakt en is deze nano-batch niet anders, op een klein aantal aangepaste werkzaamheden na.

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[20] In gesprek met de contactpersoon bij bedrijf B1 en na inspectie van het veiligeidsinfromatieblad en aanvullende informatie van internet bleek dit product te bestaan uit primaire deeltjes van ca. 25nm in diameter. de gemiddelde deeltjesgrootte van het product lag echter in het micrometer regime.

De preparatie van de nano-TiO2 batch verschilt ten op zichte van andere batches in:

- Het nano-additief mag niet op de werkplek aanwezig zijn en wordt pas gehaald op het moment dat de stof toegevoegd moet worden;
- Op het moment van toevoegen moeten medewerkers aanvullende pbm dragen (tyvek overall, volgelaatsmasker + P3 filterbussen + overschoenen van Tyvek;
- Lege zakken worden apart afgevoegd als chemisch afval, idem voor de PBM;
- De cycloonfilter van de afzuiginstallatie wordt na het toevoegen van het nano additief apart afgeklopt (leegkloppen). Het afgeklopte product wordt ook als chemisch afval afgevoerd en niet hergebruikt;
- Er worden geen zakken met restproduct bewaard. Er gaan alleen hele zakken in de batch;

## 2.3 Voorzorgsmaatregelen B1

Bij de toepassing van nano-$TiO_2$ als grondstof voor de coating worden diverse beheersmaatregelen genomen door bedrijf B1. Deze zijn onderstaand weergegeven volgens de verschillende niveaus van de arbeidshygiënische strategie:

1. Bronaanpak:

n.v.t

2. Technische maatregelen:

Het vat waarin de grondstof gedispergeerd wordt is voorzien van puntafzuiging en het is half afgesloten om de werking van de puntafzuiging te optimaliseren. Tijdens het toevoegen van nano-$TIO_2$ wordt door een tweede operator water verneveld boven het mengvat om stofvorming tijdens het storten van poeders tegen te gaan.

3. Organisatorische maatregelen

Er worden alleen maar hele zakken gebruikt in het proces om te voorkomen dat er geen aangebroken zakken opnieuw opgeslagen worden. Na gebruik van Hombikat (nano-$TiO_2$) worden de filters leeg geklopt en wordt het afval apart afgevoerd. (ook tijdens deze handelingen gelden de extra PBM)

4. Persoonlijke beschermingsmiddelen

De medewerker droeg werkkleding, handschoenen, veiligheidsbril en een FFP3 halfgelaatsmasker (combinatiefilter oplosmiddelen en stof).Tijdens de handelingen met het nano-additief werd over de overall een tyvek overall gedragen, inclusief overschoenen.

## 2.4 Resultaten Metingen B1

Kwalitatieve resultaten

Het filtermonster genomen tijdens het storten/mengen van Hombicat UV 100 is ruim beladen met $TiO_2$ clusters tussen de 0.5 en 10 um. Daarnaast zijn enkele losse ronde $TiO_2$ deeltjes rond de 100nm zichtbaar. De nano $TiO_2$ aanwezig in Hombicat UV100 lijken een sterke neiging tot agglomeratie te hebben. Naast $TiO_2$ is op het filter ook een laag percentage silicium met koolstof zichtbaar. Sommige van deze clusters zijn voorzien van een coating. Deze silicium/koolstof deeltjes lijken afkomstig van de poeders die eerder zijn gestort in de receptuur of uit de achtergrond concentratie (zie fig 3 en 4).

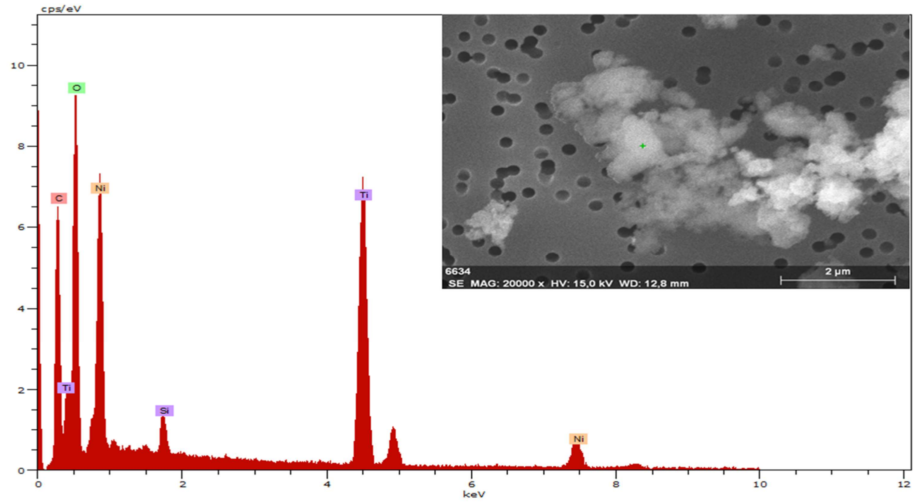

Fig 1. Filtermonster van storten/mengen Hombicat UV100. Cluster $TiO_2$ deeltjes met een coating van een organische siliciumverbinding

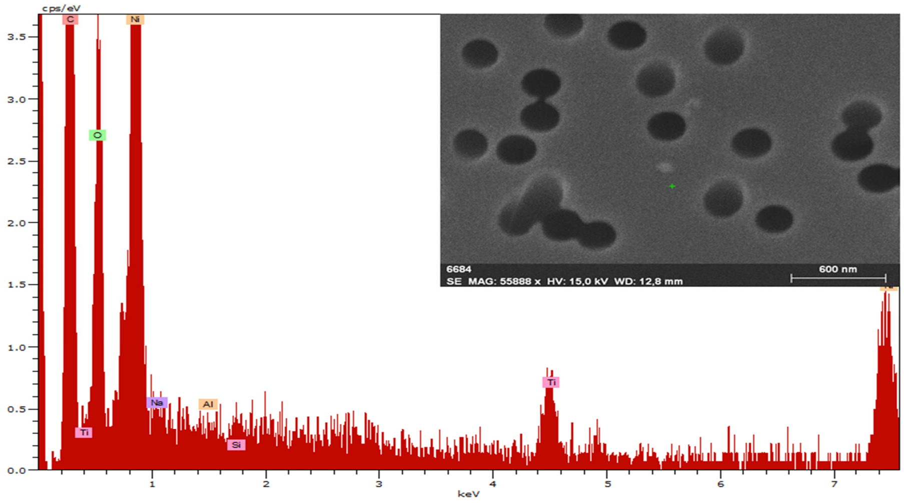

Fig. 2 Filtermonster van storten/mengen Hombicat UV100. Elementspectrum los $TiO_2$ deeltje (ca. 100nm)

Het filtermonster genomen tijdens het toevoegen van andere poeders in de formulering (o.a Sylowhite SM 405) is ruim beladen met clusters (wolken) van Si/Al/MgOx met NaCl van enkele um's groot. Daarnaast zijn meerdere losse silicabolletjes van 30-200nm zichtbaar. De clusters wolken bestaan meer uit hoekige deeltjes met een grote variatie in grootte, de silicabolletjes zijn echt rond met eenduidige afmetingen. SyloWhite™ SM 405 Silicate is een geprecipiteerd amorfe natrium aluminum silicaat met een deeltjes grootte kleiner dan 6.0 µm. Dit poeder vormt mogelijk de bron van de nano silica deeltjes.

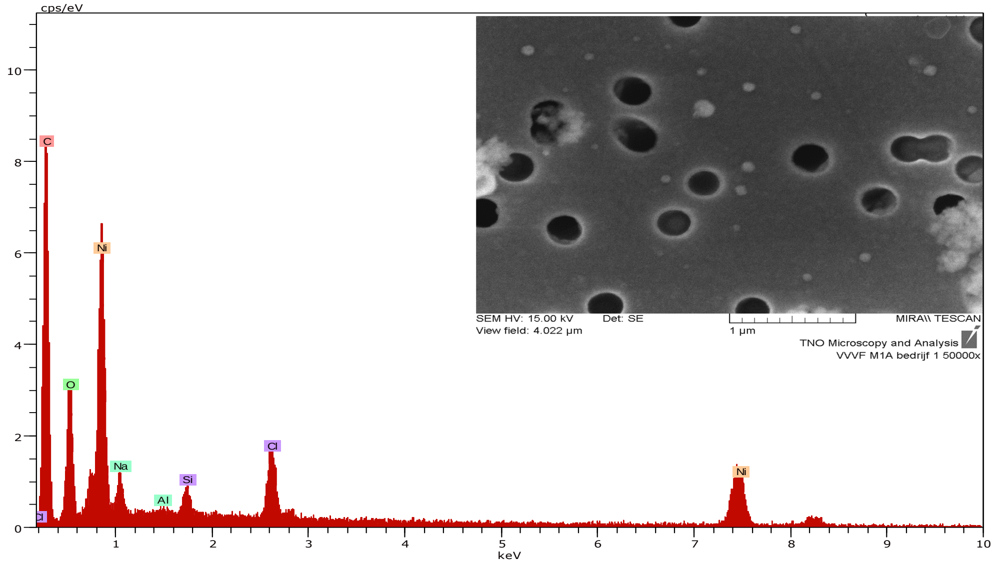

Fig 3. Filtermonster van storten/mengen van overige poeders in formulering (o.a Sylowhite SM 405). Clusters van Al/Mg-Silicaatdeeltjes met NaCl

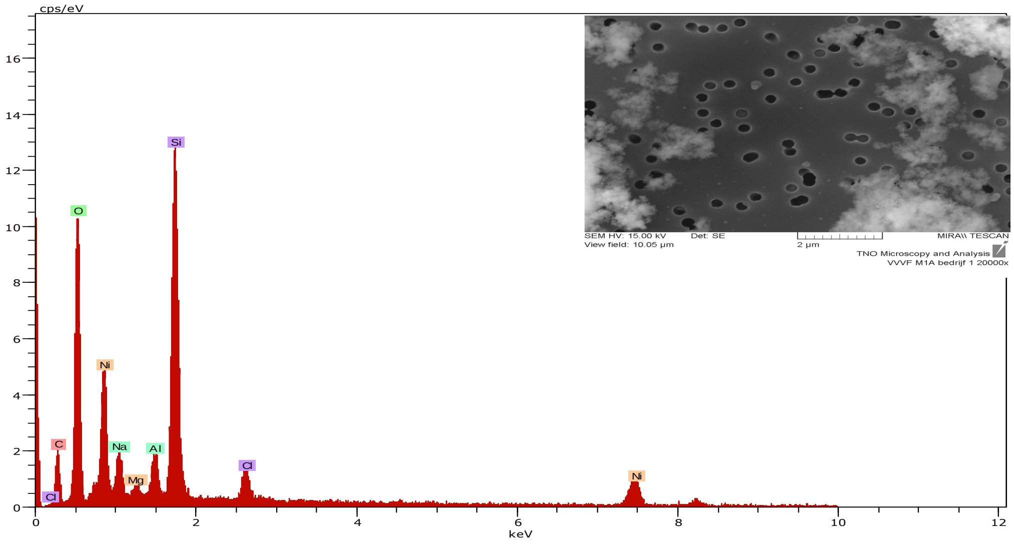

Fig. 4 Filtermonster van storten/mengen van overige poeders in formulering (o.a Sylowhite SM 405). Losse silicaatdeeltjes, diameter range 30 - 200nm

Op de filtermonsters genomen tijdens de achtergrondmeting is een lage belading zichtbaar van losse $TiO_2$ deeltjes van een afmeting 200-300nm. Daarnaast zijn enkele clusters van $TiO_2$ deeltjes (200-300nm) op grotere deeltjes Al/SiOx, CaO/CaCO3 en koolstof van enkele um's. Daarnaast zijn enkele CaCO3 en Al/SiOx deeltjes zichtbaar van enkele um's. Tevens zijn losse roetdeeltjes <100nm en roetconglomeraten tot enkele um's en grof organisch materiaal (vezels, schilfers, etc) van enkele um's tot tientalen um's waargenomen. De achtergrond monsters laten zien dat er tijdens de meting sprake was van een secundaire bron van nanodeeltjes in de vorm van roet. Daarnaast blijken er $TiO_2$ deeltjes in de achtergrond concentratie aanwezig waarvan de deeltjesgrootte aansluit op de deeltjesgrootte van de nano variant aanwezig in Hombicat UV100.

Bovenstaande resultaten laten zien dat er tijdens de formulering van een batch sigma impuls blootstelling aan nano $TiO_2$ en nano Silica plaatsvindt. Hombicat UV 100 en SyloWhite™ SM 405 zijn de potentiele bronnen van deze blootstelling.

Kwantitatieve resultaten
Op 19 mei zijn met behulp van 3 NanoTracers en PAS-pompen oriënterende metingen verricht bij bedrijf B1. Vertrouwelijke details over de betreffende activiteiten zijn niet opgenomen in het rapport. De metingen zijn zo uitgevoerd dat een zo goed mogelijk beeld verkregen werd van de potentiële blootstelling aan nanomaterialen van de uitvoerende medewerker. Mits anders is beschreven, is zoveel mogelijk in de ademzone gemeten. Vooraf aan elke meting is voor aanvang van de metingen enige tijd de achtergrondconcentratie in de betreffende ruimte bemonsterd alvorens de activiteiten te bemeten.

Specifieke ‘activiteiten’ zijn met markers in de meetdata aangegeven, zodat achteraf bepaald kan worden welke activiteiten op welk moment zijn uitgevoerd.

De belangrijkste activiteiten (events) die bemeten zijn tijdens de werkzaamheden zijn opgenomen in tabel 8 3. Een overzicht van de meetresultaten (persoonlijke metingen) is opgenomen in tabel 4. Voor de verschillende activiteiten zijn per gemeten parameter de volgende waarden bepaald:
Minimum : laagste gemeten waarde tijdens de bemeten activiteit
Mediaan : middelste van de naar grootte gerangschikte waarnemingen
AM : Rekenkundig gemiddelde
Maximum : hoogste gemeten waarde tijdens de bemeten activiteit

tabel 3 Belangrijkste te onderscheiden activiteiten tijdens het verwerken van nano-$TiO_2$

| **Event** [21] | **Tijdsduur (h:m:s)** | **Omschrijving meetlocatie/activiteit** |
|---|---|---|
| A | 0:25:47 | Achtergrondmetingen in de prodcutieruimte, voorafgaand aan de activiteiten |
| E | 0:04:58 | Toevoegen van additief waarvan verwacht wordt dat dit een nano-additief is obv nano Silica(sylowhite SM 405) |
| I | 0:12:32 | Toevoegen nano-TiO2 (Hombicat) |
| K | 0:04:43 | Afvoeren afval en leegkloppen filters na gebruik van Hombicat |

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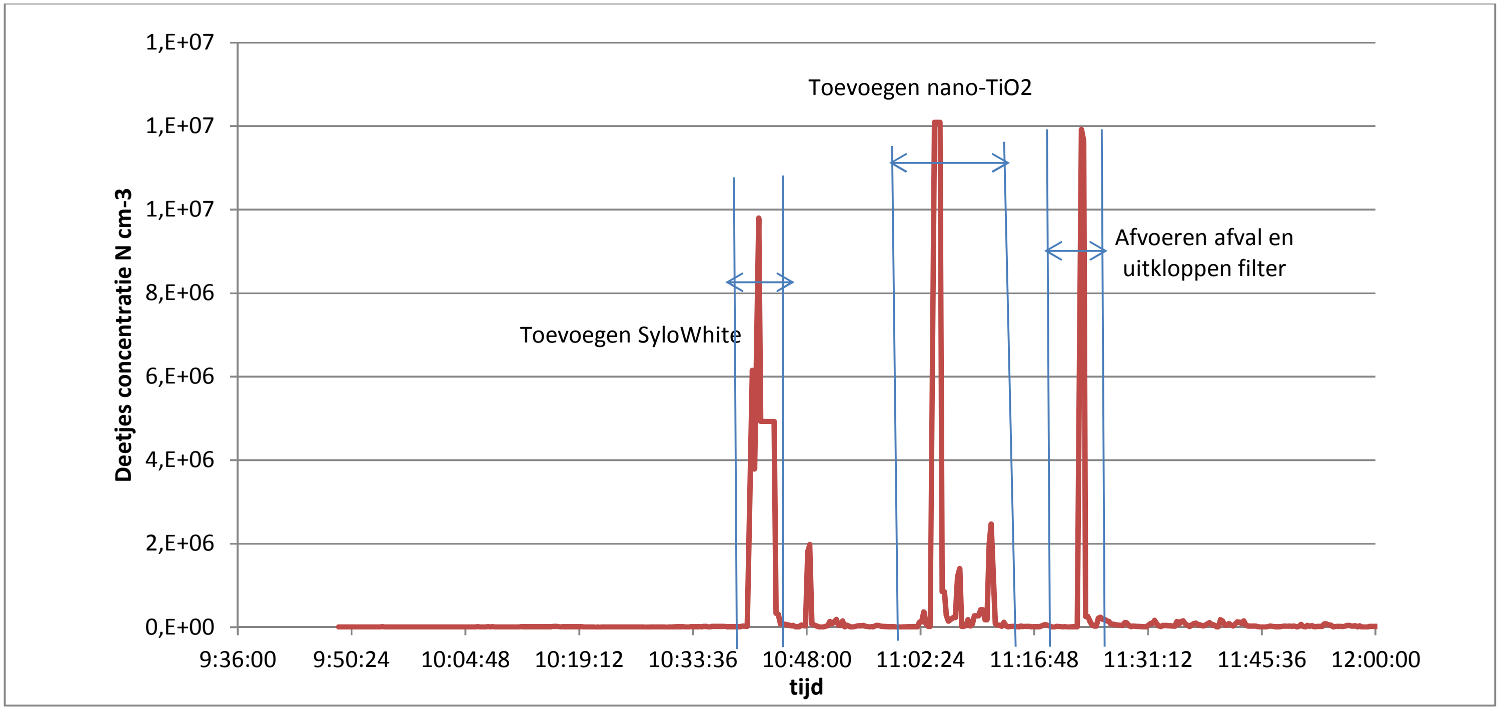
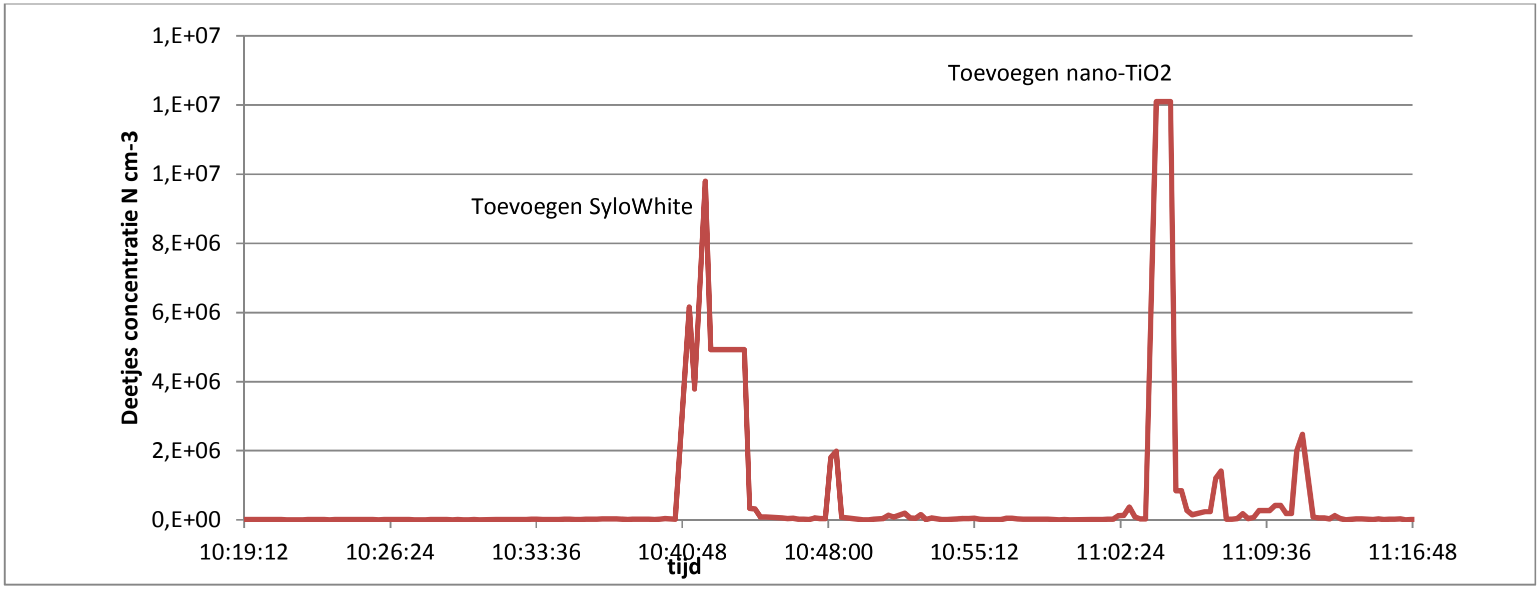
[21] De event nummers verwijzen naar de naamgeving van de events in de datafile met ruwe meetgegevens (logboek)

tabel 4 Kerngegevens gemeten concentratie nanodeeltjes per event – aanmaak coating (personal sampling)

| | aantal deeltjes per cm$^3$ [10 - 300nm] | | | | Gemeten Gemiddelde deeltjesgrootte (nm) | | | |
|---|---|---|---|---|---|---|---|---|
| Event | min | mediaan | AM | max | min | mediaan | AM | max |
| A (achtergrond) | 6.915 | 11.180 | 11.433 | 22.710 | 55 | 104 | 105 | 148 |
| E (Sylowhite) | 21.048 | 2.060.388 | 2.949.906 | 9.800.201 | 19 | 47 | 44 | 72 |
| I (nano-$TiO_2$) | 6.833 | 130.923 | 886.766 | 12.092.757 | 19 | 33 | 58 | 191 |
| K (afval verwijdering) | 6.973 | 29.526 | 1.311.769 | 11.925.880 | 19 | 55 | 69 | 210 |



Figuur 1 Grafische weergave van de persoonlijke blootstelling gedurende de toevoeging van SyloWhite (event E), nano-TiO2 (event I) en het afvoeren van afval en uitkloppen van de filter (event K). De blootstelling is gecorrigeerd voor de gemiddelde achtergrond concentratie in de productieruimte (event A, tabel 4).



Figuur 2 weergave Grafische weergave van de persoonlijke blootstelling gedurende de toevoeging van SyloWhite (event E) en nano-TiO2 (event I). De blootstelling is gecorrigeerd voor de gemiddelde achtergrond concentratie in de productieruimte (event A, tabel 4).

Voor vergelijking van de meetresultaten met de DNEL en tijdelijke nanoreferentiewaarden zullen de meetgegevens gecorrigeerd worden voor de aanwezige achtergrondconcentratie. In alle gevallen is “event A” als achtergrond concentratie gehanteerd. De uitkomsten van deze vergelijking zijn opgenomen in hoofdstuk **Error! Reference source not found.** van dit rapport.

# 3. Toetsing aan grenswaarden en discussie

De 8 uur TGG geldt voor de totale blootstelling van een werknemer aan nano-$TiO_2$ op een dag. De dagblootstelling wordt veroorzaakt door verschillende taken op een dag. Om inzicht te geven in de blootstellingbijdrage per activiteit en in de blootstelling door een combinatie van activiteiten zijn verschillende werkscenarios berekend.

Deze scenario’s zijn vergeleken met de DNEL, voorgesteld door Christensen et al (2010) en met de NRV. Omdat het werken met poeders ook kortdurende hoge blootstelling kan veroorzaken wordt de blootstelling aan ENP ook vergeleken met de $NRV_{TGG-15-min}$ (= 2*NRV) en de $DNEL_{15min}$ (=2*DNEL). De volgende scenario’s zijn berekend:

5. Scenario 1; Storten hombicat (event I); een werknemer stort de hombicat en komt vervolgens gedurende de dag niet meer in aanraking met dit product (enkel blootstelling door stort).
6. Scenario 2; Theoretische afleiding blootstelling voor 8 uur storten (blootstellingsniveau van event I gedurende een periode van 8 uur); Een werknemer stort 8 uur lang hombicat en doet verder niets anders gedurende de gehele werkdag.
7. Scenario 3; Afvalverwerking hombicat (event K); een werknemer doet afvalverwerking van hombicat en komt vervolgens gedurende de dag niet meer in aanraking met dit product (enkel blootstelling door afvalverwerking).
8. Scenario 4; Theoretische afleiding blootstelling voor 8 uur afvalverwerking (blootstellingsniveau van event K gedurende een periode van 8 uur); Een werknemer verwerkt 8 uur lang hombicat afval en doet verder niets anders gedurende de gehele werkdag.
9. Scenario 5; Storten hombicat (event I) + leegkloppen filters (event K); een werknemer stort hombicat en klopt de filters leeg, maar komt verder niet meer met het product in aanraking.

De vergelijking van de blootstelling aan nano-$TiO_2$ met de DNEL en Nanoreferentiewaarden is weergegeven in Tabel 5 en Tabel 6.

Tabel 5 Gemiddelde t-blootstelling, gecorrigeerd voor de achtergrond concentratie nanodeeltjes

| Activiteit | Taak -tijd (minuten) | Gemiddelde taakblootstelling ($N/cm^3$) | Gemiddelde blootstelling (8uur –TGG) ($N/cm^3$) | Gemiddelde blootstelling (15 min-TGG) ($N/cm^3$) |
|---|---|---|---|---|
| I (storten) | 0:12:32 | 875.333 | 22.795 | 729.444 |
| K(afval) | 0:04:43 | 1.300.336 | 12.868 | 411.773 |
| I&K (storten + afval) | 0:17:15 | 992.363 | 35.663 | 862.924 |

Tabel 6 Gemiddelde blootstelling, gecorrigeerd voor de achtergrond concentratie nanodeeltjes, vergeleken met de DNEL en NRV 8uur-TGG en 15min-TGG.

| Activiteit | Gemiddelde taakblootstelling (N/cm$^3$) | Gemiddelde blootstelling 8uur -TGG (N/cm$^3$) | Gemiddelde blootstelling 15-min TGG (N/cm$^3$) ) | DNEL (N/cm$^3$) | DNEL TGG-15min (N/cm$^3$) | NRV (N/cm$^3$) | NRV TGG-15min (N/cm$^3$) |
|---|---|---|---|---|---|---|---|
| I (storten) | 875.333 | 22.795 | 729.444 | 830.000 | 1.660.000 | 40.000 | 80.000 |
| K(afval) | 1.300.336 | 12.868 | 411.773 | 830.000 | 1.660.000 | 40.000 | 80.000 |
| I&K (storten + afval) | 992.363 | 35.663 | 862.924 | 830.000 | 1.660.000 | 40.000 | 80.000 |

Tabel 6 laat zien dat ruim 12 min. storten van nano-TiO$_2$ alleen (Scenario1) geen aanleiding geeft voor overschrijding van de DNEL of de NRV wanneer de blootstelling wordt gemiddeld over een hele werkdag. Zou je echter 8 uur lang als werknemer alleen maar storten (Scenario2), dan is dit wel het geval. Dit betekend dat er een indicatie is voor een gezondheidsrisico is wanneer een werknemer Hombicat UV100 stort gedurende de gehele werkdag, maar niet wanneer de tijdsduur beperkt is tot 12 min per dag.

Het storten van Hombicat UV100 is een korte taak met een relatief hoge blootstelling. Omdat er acute effecten zijn beschreven voor nano-TiO$_2$ zou de blootstelling ook vergeleken moeten worden met de TGG-15 min waarden. De 15 min TGG blootstelling overschrijdt de NRV TGG-15 min, maar niet de DNEL TGG-15 min. Dit betekent dat het waarschuwingsniveau dat uit voorzorg wordt gehanteerd wordt overschreden, maar dat er obv de huidige kennis geen acute gezondheidseffecten worden verwacht tgv het storten van Hombicat UV100.

Uit vergelijking van de blootstelling en de NRV kan je stellen dat je als werknemer niet langer dan ca. 22 min zou mogen storten om onder de NRV$_{8uur\text{-}TGG}$ te blijven. Daarbij zou je dan geen enkele andere activiteit met een nano-additief mogen uitvoeren. De DNEL is duidelijk soepeler dan de NRV en is ruim een factor 20 hoger voorgesteld. Houdt men deze DNEL aan dan betekend dit dat een werknemer ruim 455 min lang nano-TiO$_2$ zou mogen storten zonder deze DNEL te overschrijden. Dit betekent dat het waarschuwingsniveau dat uit voorzorg gehanteerd wordt na 22 min storten wordt overschreden, maar dat obv de huidige kennis er pas een gezondheidsrisico lijkt te zijn wanneer iemand langer dan 455 min stort.

Tabel 6 laat zien dat ruim 4 min. Afvalverwerking van nano-TiO$_2$ alleen (Scenario3) geen aanleiding geeft voor overschrijding van de DNEL of de NRV wanneer de blootstelling wordt gemiddeld over een hele werkdag. Zou je echter 8 uur lang als werknemer alleen maar afval verwerken (Scenario4), dan is dit wel het geval. Dit betekend dat er een indicatie is voor een gezondheidsrisico is wanneer een werknemer Hombicat UV100 afval verwerkt gedurende de gehele werkdag, maar niet wanneer de tijdsduur beperkt is tot ruim 4 min per dag.

Het verwerken van Hombicat UV100 afval is een korte taak met een relatief hoge blootstelling. Omdat er acute effecten zijn beschreven voor nano-TiO$_2$ zou de blootstelling ook vergeleken moeten worden met de TGG-15 min waarden. De 15 min TGG blootstelling overschrijdt de NRV TGG-15 min, maar niet de DNEL TGG-15 min. Dit betekent dat het waarschuwingsniveau dat uit voorzorg wordt gehanteerd wordt overschreden, maar dat er op basis van de huidige kennis geen acute gezondheidseffecten worden verwacht tgv het afvalverwerken van Hombicat UV100.

Wanneer je als werknemer 12 min. lang stort en vervolgens afval afvoert en de filters uitklopt gedurende ruim 4 min (Scenario 5), kom je voor een 8uur tijdgewogen gemiddelde onder de DNEL en NRV$_{8uur\text{-}TGG}$ uit.

Dit betekend dat er geen risico indicatie is wanneer de activiteit storten en afvalverwerking wordt gecombineerd in geval van een taakduur van respectievelijk 12 en 4 min en geen blootstelling aan nano-TiO$_2$ tgv andere activiteiten.

Interessant genoeg leidt niet alleen het werken met nano-$TiO_2$ tot een blootstelling aan nanodeeltjes. Ook bij het storten van andere poeders worden nanodeeltjes gemeten. Op de SEM/EDX zijn silicabolletjes van 30-200 nm met een coating zichtbaar. Dit suggereert dat er synthetische nanodeeltjes toegevoegd zijn aan een van de poeders die eerder gestort zijn in de receptuur. Te denken valt hierbij aan SyloWhite aangezien de verhoogde blootstelling aan nanodeeltjes optrad op het moment dat SyloWhite gestort werd (Zie tabel 4, event E). Gemiddeld gaat het hierbij zelfs om een veel hogere concentratie beduidend kleinere deeltjes dan voor het nano-$TiO_2$.Aangezien voor SyloWhite geen DNEL is voorgesteld is hier een vergelijking met de NRV op zijn plaats.

Tabel 7 Gemiddelde blootstelling, gecorrigeerd voor de achtergrond concentratie nanodeeltjes, vergeleken met de NRV 8uur-TGG en 15min-TGG.

| Activiteit | Taak tijd | Gemiddelde taak blootstelling (N/cm$^3$) | Gemiddelde blootstelling 8uur –TGG (N/cm$^3$) | Gemiddelde blootstelling 15 min-TGG (N/cm$^{3)}$ | NRV (N/cm$^3$) | NRV TGG-15min (N/cm$^3$) |
|---|---|---|---|---|---|---|
| E (storten) | 0:04:58 | 2.938.473 | 30.609 | 979.380 | 40.000 | 80.000 |

De 8uur-TGG ligt ruim onder de NRV (zie Tabel 7), maar de gemiddelde taakblootstelling overschrijdt de NRV. De TGG-15min komt uit op 979.380 N cm$^{-3}$, ruim 10x hoger dan waarop de NRV$_{15min-TGG}$ is gesteld. Dit betekent dat het waarschuwingsniveau dat uit voorzorg wordt gehanteerd voor systemische effecten wordt overschreden wanneer SyloWhite wordt gestort gedurende de gehele werkdag, maar niet wanneer de blootstelling beperkt blijft tot 5 min. Echter, het waarschuwingsniveau dat uit voorzorg wordt gehanteerd voor acute effecten wordt wel overschreden bij het storten met deze tijdsduur. Binnen dit project zijn de eventuele acute effecten van nano-silica niet onderzocht. Het is dan ook niet mogelijk om hier een indicatie voor een gezondheidsrisico te geven.
SyloWhite™ SM 405 Silicate is een geprecipiteerde amorfe natrium aluminum silicaat met een deeltjes grootte kleiner dan 6.0 µm. In totaal werd 170 kg Sylowhite SM 405 (Grace Down) uit 7 zakken van 25 kg toegevoegd. Uit de SEM/EDX analyse kan worden afgeleidt dat het bij SyloWhite inderdaad gaat om de emissie vanSi/Al/MgOx achtige complexen met mogelijk een NaCl coating georganiseerd in clusters/wolken en/of om silicabolletjes van 30-200nm met mogelijk een NaCl coating. De clusters/wolken bestaan meer uit hoekige deeltjes met een grote variatie in grootte, de silicabolletjes zijn echt rond met eenduidige afmetingen. Nadeel is dat het SEM/EDX sample voor het storten van SyloWhite ook emissies tijdens het storten van andere poeders aan de batch heeft opgevangen. Het is daarom lastig een directe link te leggen tussen de SEM metingen en de emissie door toevoeging van SyloWhite.

# 4. Conclusies en aanbevelingen

Uit de bovenstaande resultaten blijkt dat er geen risico indicatie is wanneer een werknemer alleen de activiteit storten hombicat, afvalverwerking of storten Sylowhite uitvoert gedurende de genoemde tijdsduur op een dag en de rest van de dag niet meer in aanraking komt met nanoproduct. (dagblootstelling waarden). Echter, wanneer deze activiteiten een gehele werkdag zouden duren zou er wel sprake zijn van een risico indicatie (taakblootstelling waarden). In de praktijk wordt werker blootstelling veroorzaakt door een combinatie van alle activiteiten met nanoprodukt. Omdat niet al deze activiteiten zijn bemeten is dit scenario niet uitgewerkt. Helaas kan er dan ook geen uitspraak worden gedaan over een “veilige” combinatie en maximale tijdsduur van activiteiten. Combineer je de verschillende taken “storten SyloWhite”, “storten Hombicat” en “afvoeren afval en uitkloppen filter” dan zie je dat, hoewel dit per situatie zal verschillen, het belangrijk is om je te realiseren dat een combinatie van kortdurende handelingen aanleiding kan geven tot een overschrijding van het waarschuwingsniveau.

Opvallend is verder dat het waarschuwingsniveau dat uit voorzorg wordt gehanteerd voor acute effecten wordt overschreden voor zowel de activiteit storten Hombicat, storten Sylowhite en afvalverwerking. In lijn met het voorzorgsprincipe is

Het handhaven en op punten aanscherpen van het huidige beheersregime en het dragen van beschermende kleding, handschoenen en adembescherming zoals in de huidige praktijk ook gebeurd is dan ook te adviseren.

De observatie dat ook niet-nano-gelabelde ingrediënten kunnen leiden tot een nano-blootstelling zet aan tot nadenken over het al dan niet herevalueren van eventuele blootstelling en bijbehorende beheersmaatregelen op de werkplek. In de hier bemeten werksituatie is het advies om het beheersregime voor het werken met SyloWhite overeenkomstig te maken met het beheersregime voor Hombicat UV100.

Het is overigens van belang om te benadrukken dat er typisch bij blootstellingsmetingen aan nanodeeltjes grote dag-tot-dag variaties worden waargenomen, bijvoorbeeld als gevolg van de luchtvochtigheid, de temperatuur van de ruimte en de overige activiteiten die zich in dezelfde ruimte afspelen. Zo is het bijvoorbeeld niet uit te sluiten dat een volgende keer wanneer een batch met nano-$TiO_2$ wordt gemaakt de DNEL wel wordt overschreden. Om dit te onderzoeken zou bijvoorkeur meerdere keren gemeten moeten worden om een beeld te krijgen van de spreiding in blootstelling. Daarnaast is de blootstelling sterk afhankelijk van het nanoproduct waarmee gewerkt wordt, zoals de stoffigheid en een eventuele behandeling van het product om klontering (agglomeratie) tegen te gaan. Tenslotte is blootstelling (bij vergelijkbare blootstellingsbeheersmaatregelen) sterk afhankelijk van de zorgvuldigheid waarmee de werknemer zijn of haar handelingen uitvoert. In dit specifieke geval werd de zak Sylowhite en nano-$TiO_2$ zodanig gestort dat de lucht in de directe nabijheid van de werknemer zichtbaar stoffig werd. Mocht het nu mogelijk zijn om de zak zo voorzichtig leeg te storten dat er minder opwerveling van nanodeeltjes plaatsvindt dan zal de blootstelling van de werknemer gedurende die activiteit naar verwachting afnemen. Het is aan te raden om werknemers te instrueren om zo zorgvuldig mogelijk te werken met poeders om zo veel mogelijk stofvorming te voorkomen, ook wanneer je niet werkt met een nanomateriaal.

**Mitsen en Maren**

Nanodeeltjes behoren momenteel tot de groep stoffen met onzekere en/of onbekende risicos. Daarnaast is de discussie omtrent de methoden die moeten worden toegepast om goede risicobeoordelingen uit te voeren nog in volle gang. Voor een toelichting op deze onzekerheden wordt verwezen naar rapport V9445 “kennisdelen Nano in de verfketen”. Ondanks de grote onzekerheden in data en methoden, geeft deze rapportage een risico indicatie op basis van de best beschikbare gegevens. Gezien de grote onzekerheid kunnen geen definitieve conclusies over veilig gebruik of beheersing van een gezondheidsrisico worden ontleend aan deze beoordeling. Er wordt geadviseerd het voorzorgsprincipe (minimalisatie van blootstelling) toe te passen tot er meer data beschikbaar komen. Daarnaast wordt geadviseerd specifieke data te genereren om de hiaten in kennis te kunnen vullen. Kennis vergaren op het gebied van zowel het gevaar van deeltjes als de blootstelling aan deeltjes kan het in de toekomst mogelijk maken betrouwbare en representatieve werker risicobeoordelingen uit te voeren.

# Annex 9; VVVF-project – Rapportage meetresultaten bedrijf B2

## Oriënterende metingen naar blootstelling aan nanodeeltjes tijdens aanmaken coating bij bedrijf B2

## *Pilot: “Kennisdelen Nano in de verfketen*

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Amsterdam, januari 2012

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## Colofon

|  |  |
|---|---|
| ISO Doc. nr. |  |
| Project nr. |  |
| Titel | **Oriënterende metingen naar blootstelling aan nanodeeltjes bij het aanmaken van een coating bij bedrijf B2** |
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| Datum | Januari 2012 |

Deze rapportage is tot stand gekomen in het kader van het project Pilot Kennis delen in de verfketen. Het onderzoek uitgevoerd in opdracht van, met subsidie van het ministerie van.
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Gegevens uit deze rapportage mogen worden overgenomen mits onder uitdrukkelijke bronvermelding.
IVAM UvA b.v. aanvaardt geen aansprakelijkheid voor eventuele schade voortvloeiend uit het gebruik van de resultaten van dit onderzoek of de toepassing van de adviezen.

# 1. Pilot Kennisdelen in de verfketen

## 1.1 Toelichting Project

De inzet van de VVVF is om samen met de partijen uit de hele verfketen – de producent van de grondstof, de verffabrikant en de gebruiker – inzichten te verwerven betreffende het veilig werken met nanodeeltjes. Deze proactieve aanpak levert informatie en inzichten op die ingezet kunnen worden bij Europese (bijv. REACH) maar ook nationale beleidsontwikkelingen op het gebied van arbo- en milieuzorg. Daarnaast zijn de opbrengsten van direct belang voor bedrijven in de betrokken sectoren omdat het inzicht biedt in de mogelijke risico's van het werken met nanodeeltjes.

De Vereniging van Verf- en Drukinktfabrikanten (VVVF) wenst de kennisopbouw over nanotechnologie in de verf- en drukinktindustrie te stimuleren en wil daarom, samen met de grondstoffenleveranciers verenigt in de VNCI, participeren in een project om kennis te verzamelen en te delen over nanodeeltjes.
Dit project richt zich op de stoffen nano-$TiO_2$ en nano-Ag. Deze rapportage beschrijft de resultaten van blootstellingmetingen tijdens het gebruik van nano-$TiO_2$ binnen bedrijf B2.

Nanodeeltjes
Nanodeeltjes (deeltjes met een afmeting van 1 – 100 nm in één of meerdere dimensies) worden vanwege hun bijzondere chemisch/fysische eigenschappen in toenemende mate ontwikkeld en toegepast in producten om hieraan een bijzondere eigenschap te geven. Het betreft veelal onoplosbare en niet- (of slecht-) afbreekbare deeltjes, waarbij het kan gaan om anorganische materialen (bijv. metalen of metaaloxiden) of om op koolstof gebaseerde - of organische materialen (bijv. fullerenen of koolstofnanobuisjes).

In de praktijk onderscheidt men engineered nanodeeltjes (gefabriceerde nanomaterialen die bewust zijn gemaakt en worden toegepast in producten)(ENP), en ultrafijne deeltjes (UFP)(deeltjes die door natuurlijke of antropogene activiteiten worden gevormd en in de lucht aanwezig zijn als *achtergrondconcentratie* aan nanodeeltjes). Bij UFP kan men aan bronnen denken als verbranding, verhitting, roken e.d. ENP en UFP zijn deeltjes met vergelijkbare afmetingen, beiden in het nanogebied. Het "nanobeleid" richt zich vooral op de ENP, het inzicht verkrijgen in de risico's van deze deeltjes en het terugdringen van de emissie.

Grenswaarden
Voor het maken van een risicobeoordeling voor werken met nanomaterialen maak je idealiter gebruik van gezondheidskundige grenswaarden (OEL of DNEL). Christensen et al (2010) heeft de beschikbare gevaardata van $TiO_2$ geevalueerd en een DNEL voor inhalatie voorgesteld van 17 $\mu g/m^3$ (of wel $8.3 \times 10^5$ nanodeeltjes/$cm^3$). Christensen et al (2010) stelt dat deze DNEL momenteel niet voor regulatoire doeleinden kan worden gebruikt omdat er nog veel onzekerheid bestaat over de verzameling en interpretatie van nano gevaardata. Bij gebrek aan andere specifieke gevaardata wordt zal de gemeten blootstelling in de huidige rapportage vergeleken met deze DNEL. Voor de meeste nanodeeltjes zijn er momenteel nog geen gezondheidskundige grenswaarden beschikbaar. In de praktijk heeft een bedrijf meestal ook geen specifieke gevaar data voorhanden. Daarom zal de gemeten blootstelling tevens worden vergeleken met de NRV die wordt voorgesteld als tijdelijke referentiewaarde voor blootstellingbeoordeling in het geval van het ontbreken van een OEL of DNEL. De NRV zijn geen gezondheidskundige grenswaarden (zie onder voor toelichting). Dat betekent dat werkzaamheden niet per definitie als veilig kunnen worden beschouwd wanneer de blootstelling lager is dan de NRV. De NRV zijn gebaseerd op voorzorg en kunnen beschouwd worden als waarschuwingsniveau dat moet aanzetten tot de uitvoering van een zorgvuldige blootstellingsbeheersing van nanodeeltjes op de werkplek.

Nanoreferentiewaarden

Onder normale omstandigheden geven de grenswaarden voor beroepsmatige blootstelling het maximale blootstellingsniveau aan waarbij werkzaamheden veilig kunnen worden geacht (grenswaarde of DNEL)[22]. Deze grenswaarden zijn echter nog maar beperkt beschikbaar voor nanodeeltjes.

Nanoreferentiewaarden kunnen, zolang er nog geen grenswaarden voor beroepsmatige blootstelling zijn vastgesteld, hierin een oplossing bieden. Het is een generieke benadering voor een grenswaarde voor de verschillende ENP. Omdat onvoldoende toxiciteits- en blootstellingsgegevens beschikbaar zijn, zijn ze bepaald op basis van voorzorg en hebben ze een tijdelijk karakter. De onbekendheid van de specifieke giftigheid van nanodeeltjes, en tegelijkertijd de verwachting dat deze niet verwaarloosd kan worden brengt grote onzekerheid in de risicobeoordeling. Dit leidt tot het toepassen van een benadering gebaseerd op voorzorg. Als meer gegevens beschikbaar komen kunnen ze vervangen worden door een normale grenswaarde of DNEL-waarde.

In Nederland zijn de nanoreferentiewaarden vastgesteld door het RIVM ([IV]). Hierbij moet benadrukt worden dat het gaat om *tijdelijke* nanoreferentiewaarden. Het RIVM heeft zich hierbij gebaseerd op vergelijkbare initiatieven in Groot Brittannië en Duitsland, de “benchmark exposure levels” (vergelijkende blootstellingswaarden), voorgesteld door het British Standards Institue ([V]), en de methode zoals voorgesteld door het IFA ([VI]). Het RIVM stelt voor om het IFA-model in Nederland te gebruiken.

*Tijdelijke* nanoreferentiewaarden worden als volgt gedefinieerd:

**Een tijdelijke nanoreferentiewaarde (NRV)** is een waarschuwingsniveau dat moet aanzetten tot de uitvoering van een zorgvuldige blootstellingsbeheersing van nanodeeltjes op de werkplek. De NRV is vastgesteld als een 8-uur tijd gewogen gemiddelde concentratie gecorrigeerd voor de achtergrondconcentratie aan ultrafijne deeltjes. Als dit niveau wordt overschreden dan moet de blootstelling worden geminimaliseerd: de bron(nen) van de nanodeeltjes moet(en) nauwkeurig worden vastgesteld, (indien mogelijk) moeten de deeltjes worden gekarakteriseerd, het risico worden beoordeeld en moet worden vastgesteld op welke wijze de emissie van nanodeeltjes kan worden gereduceerd en de blootstelling kan worden beheerst.

In tabel 1 is de NRV weergegeven en voor gangbare nanodeeltjes aangegeven in welke categorie ze vallen.

---

[22] DNEL = Derived No-Effect Level

**Tabel 1 Nanoreferentiewaarden voor nanodeeltjes op de werkplek**

| | Omschrijving categorie | Dichtheid | Nanoreferentiewaarden ($NRV_{8u-TGG}$)* | Type |
|---|---|---|---|---|
| 1 | Koolstof nanobuisjes (CNT) (lengte diameterverhouding > 3:1 en lengte > 5µm) waarvoor geen testen omtrent asbestachtige effecten zijn uitgevoerd | | 0,01 vezels /$cm^3$<br>10.000 vezels/$m^3$ | SWCNT of MWCNT waarbij asbestachtige klachten niet zijn uitgesloten |
| 2 | biopersistente granulaire nanomaterialen met een primaire deeltjesgrootte in de 1 tot 100 nm range | > 6.000 kg/m³ | 20.000 deeltjes/$cm^3$ | Ag, Au, $CeO_2$, CoO, Fe, $Fe_xO_y$, La, Pb, $Sb_2O_5$, $SnO_2$, |
| 3 | biopersistente granulaire nanomaterialen met een primaire deeltjesgrootte in de 1 tot 100 nm range | < 6.000 kg/m³ | 40.000 deeltjes/$cm^3$ | $Al_2O_3$, $SiO_2$, TiN, $TiO_2$, ZnO, nanoclay<br>Carbon Black, $C_{60}$, dendrimers, polystyrene<br>CNT zonder asbest achtige effecten |
| 4 | Ultrafijne vloeistof en oplosbare deeltjes | | Betreffende grenswaarde voor moedermateriaal | O.a. vetten,, koolwaterstoffen, siloxanes, NaCl |

Kortdurende blootstelling

In de methodiek van de DNEL en de tijdelijke nanoreferentiewaarden, is geen rekening gehouden met de beoordeling van werkplek concentraties aan een grenswaarde voor tijd gewogen gemiddelde van 15 minuten (TGG-15). In de praktijk blijkt de blootstelling aan nanodeeltjes veelal van kort durende aard te zijn. Het artikel van Christensen et al (2010) beschrijft acute gevaareffecten voor nano-$TiO_2$. Wanneer er acute gevaareffecten zijn beschreven voor de nanostof zou de blootstelling ook vergeleken moeten worden met de TGG-15. Hiervoor kan de vuistregel van de Nederlandse arbeidsinspectie worden gehanteerd, die een handreiking geeft voor een korte blootstellingstijd van 15 minuten:

NRV15min-TGG = 2 x 8uur-TGG. Voor de DNEL van nano-$TiO_2$ resulteert dit in een TGG-15 van 1.660.000 deeltjes/$cm^3$, voor de NRV van nano-$TiO_2$ in 80.000 deeltjes/$cm^3$

## 1.3 Meetapparatuur

NanoTracer

Voor het in kaart brengen van de persoonlijke real-time blootstelling aan nanodeeltjes is in dit onderzoek gebruik gemaakt van een aerosol meter van Philips Aerasense, de NanoTracer. De NanoTracer is een draagbare monitor voor het meten van de concentratie nanodeeltjes in de omgevingslucht. Hiermee worden continu, real-time ultrafijne- en nanodeeltjes (Φ = 10 - 300nm) gemeten, zowel de deeltjesconcentratie als de gemiddelde deeltjesgrootte.

De persoonlijke werker blootstelling aan nanodeeltjes is in dit onderzoek gemeten met de Philips NanoTracer bevestigd in de ademzone van de werknemer die activiteiten uitvoert met nanodeeltjes. De specificaties en de gehanteerde instellingen van de meter zijn opgenomen in tabel 7. Bij het meten van de blootstelling worden alle aanwezige deeltjes met een afmeting van 10-300nm gemeten. Het betreft hier zowel ENP als de nanodeeltjes die aanwezig zijn in de natuurlijke achtergrondconcentratie. Naast natuurlijke bronnen van nanodeeltjes (vrijkomen bij b.v. verbranding, verhitting) zullen er ook nanodeeltjes gevormd kunnen worden door de gebruikte elektrische apparatuur en het gebruik van verwarmingselementen. Dit zijn bronnen die de blootstellingsmeting van engineered nanodeeltjes kunnen verstoren. .Om een overschatting van de blootstelling aan synthetische nanodeeltjes tijdens het werkproces te voorkomen zijn achtergrondmetingen uitgevoerd. De blootstelling aan synthetische nanodeeltjes tijdens het werkproces is gecorrigeerd voor deze achtergrondwaarden.

tabel 7 Specificaties van de Philips Aerasense aerosol meter

| | |
|---|---|
| Gemeten parameters | - Aantal deeltjes [deeltjes /cm$^3$]<br>- Deeltjesgrootte (diameter) [ nm] |
| Range: Deeltjesgrootte | 10 – 300 nm |
| Smoothing algorithm | Geen |
| Aanzuigsnelheid ventilator | 0,4 l/min |
| Gebruikte instelling | Advanced mode |
| Meet interval | 16 seconden |
| Gevoeligheid | 1 fA [23] |
| Gebruikte ijkbron | $KNO_3$ aerosol |

De meetresultaten zijn geanalyseerd met behulp van de NanoReporter software (versie 1.0.4.0), Philips Aerasense) en met behulp van MS Excel (MS Office 2007) en SPSS.

<u>Monstername pompen</u>

Zowel tijdens de metingen aan de achtergrond als het werkproces zijn filtermonsters genomen. In de monstername is onderscheid gemaakt tussen het storten van de “normale poeders” en het nano materiaal. Met behulp van Scanning Electron Microscopy (SEM) en Energy Dispersive Analysis of X-radiation (EDX) is de deeltjesgrootte, morfologie en chemische samenstelling van de nanodeeltjes bepaald.

Meer achtergrondinformatie over de meetopzet en de gebruikte meetmethoden en –technieken is opgenomen in het document: Annex 4 van rapport V9445 Pilot “Kennisdelen Nano in de Verfketen.

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[23] femto Ampère ($10^{-15}$)

# 2. Oriënterende metingen bij bedrijf B2

## 2.1 Nanomaterialen bedrijf B2

Bij bedrijf B2 is op 15 september 2011 een bezoek gebracht aan een van de productielocaties voor het uitvoeren van oriënterende blootstellingsmetingen tijdens gebruik van ENP.

Bij dit bedrijf zijn metingen verricht tijdens het aanmaken van een oplosmiddelhoudende coating, waarbij gebruik gemaakt wordt van een additief in nanovorm (nano-$TiO_2$). Hiernaast zijn ook enkele achtergrondmetingen verricht in de productieruimte en het magazijn. Tijdens het uitvoeren van de metingen is de grondstof gevolgd vanuit het grondstoffenmagazijn tot en met het gebruik in de productie (afdeling oplosmiddelhoudende coating).

Nano-$TiO_2$ is verpakt in enkelwandige papieren zakken van 10 kg en wordt aangeleverd op een pallet. Voor aanvang van de productie wordt de juiste hoeveelheid van het benodigde materiaal door de medewerkers van het grondstoffenmagazijn (zie figuur 1) klaar gezet op een pallet en wordt deze pallet met pakbon gereedgezet in de productiehal. Op de betreffende meetdag is 100 kg (10 zakken) grondstof gebruikt in de betreffende batch. Er werd naast nano-$TiO_2$ geen andere poedervormige grondstof gebruikt. In dit specifieke geval bleek de onderste zak op het pallet gescheurd.

Figuur 3 Overzicht magazijn met positie NanoTracer in het midden van het pad

## 2.2 Productie nano-batch bedrijf B1

Productie van de batch vond plaats in een mengketel (zie figuur 2). De grondstof nano-$TiO_2$ werd handmatig aan de coating toegevoegd. De zakken werden daarvoor op een stortrooster geplaatst dat op de mengketel geplaatst was (zie figuur 2). De mengketel was half afgesloten d.m.v. een deksel, waarop ook de puntafzuiging aangesloten was. De afzuiging zat aan het achterste deel van de ketel. De zakken $TiO_2$ worden toegevoegd aan de voorzijde van de ketel. De betreffende productiemedewerker deponeerde zeer netjes de zakken met grondstof in het mengvat, zodat er een minimale werveling van product optrad.

Figuur 4 links: Schuin boven aanzicht van de mengvat met stortrooster; Rechts: Leeg laten lopen van zak nano-TiO2

Er was eerder sprake van het ‘leeg laten lopen’ van de zakken dan van ‘leegschudden’ (zie figuur 2) Na gebruik werden de lege zakken opgevouwen en gedeponeerd in een kartonnen doos. De kartonnen doos werd na afloop van de werkzaamheden afgevoerd bij het restafval in de container buiten.

## 2.3 Voorzorgsmaatregelen B2

Bij de toepassing van nano-$TiO_2$ als grondstof voor de coating worden diverse beheersmaatregelen genomen door bedrijf B2. Deze zijn onderstaand weergegeven volgens de verschillende niveaus van de arbeidshygiënische strategie:

10. Bronaanpak:

n.v.t

11. Technische maatregelen:

De ketel waarin de grondstof gedispergeerd wordt is voorzien van puntafzuiging en de ketel is half afgesloten om de werking van de puntafzuiging te optimaliseren.

12. Organisatorische maatregelen

De werkhandelingen zoals uitgevoerd door de medewerker zijn er op gericht om stofvorming zoveel mogelijk te voorkomen. De medewerker laat de zak rustig leeglopen in plaats van dat er door middel van schudden extra stof opgewerveld wordt. Visueel was er geen stofvorming waarneembaar. Het legen van de zakken gebeurde door in de lengterichting de zak aan de onderzijde open te snijden. Na legen werd de zak voorzicht leeg geklopt om vervolgens te worden opgevouwen en te worden afgevoerd.

13. Persoonlijke beschermingsmiddelen

De medewerker droeg werkkleding, handschoenen, veiligheidsbril en een FFP3 halfgelaatsmasker (combinatiefilter oplosmiddelen en stof).

## 2.4 Resultaten Metingen B2

Kwalitatieve resultaten

Het filtermonster genomen tijdens het transport van grondstoffen is laag beladen met 2 typen $TiO_2$ deeltjes. Type 1 Titaniumdioxide komt het meeste voor in een deeltjesgrootte van ca. 100nm tot 2 µm.

De meeste deeltjes bestaan uit conglomeraten (clusters) van primaire $TiO_2$-deeltjes. De primaire deeltjesgrootte varieert van 100 tot 300nm en komen een enkele keer ook afzonderlijk als los deeltje voor (zie fig 1). Type 2 $TiO_2$ ziet er morfologisch anders uit en komt alleen voor als grotere conglomeraten (wolken) van ca. 500nm tot 2 µm opgebouwd uit primaire deeltjes van rond de 50nm. Deze deeltjes komen echter niet afzonderlijk voor als los deeltje. Zowel in type 1 als in type 2 $TiO_2$ conglomeraten zitten sporen aluminium en silicium die vermoedelijk afkomstig zijn van een coating op de deeltjes.

Naast $TiO_2$ komen ook silicaten veelvuldig voor. Deze deeltjes bestaan veelal uit aluminium/siliciumoxiden (Al-SiOx) met soms nog andere elementen zoals calcium, magnesium, kalium, ijzer. De deeltjesgrootte varieert van minimaal 500nm tot maximaal 5µm. Een aantal keer zijn sulfaten (SO4) aangetroffen met een deeltjesgrootte van ca. 200nm tot 2µm. De meeste sulfaten bestaan uit bariumsulfaat. Daarnaast is ook een spoor zinksulfaat en ijzersulfaat aangetroffen.

Meerdere keren is roet aangetroffen. Roetdeeltjes bestaan uit conglomeraten (clusters) van primaire roetdeeltjes en hebben een deeltjesgrootte van ca. 200nm tot 1µm. De primaire deeltjesgrootte is ca. 50nm, deze komen echter nooit afzonderlijk voor.

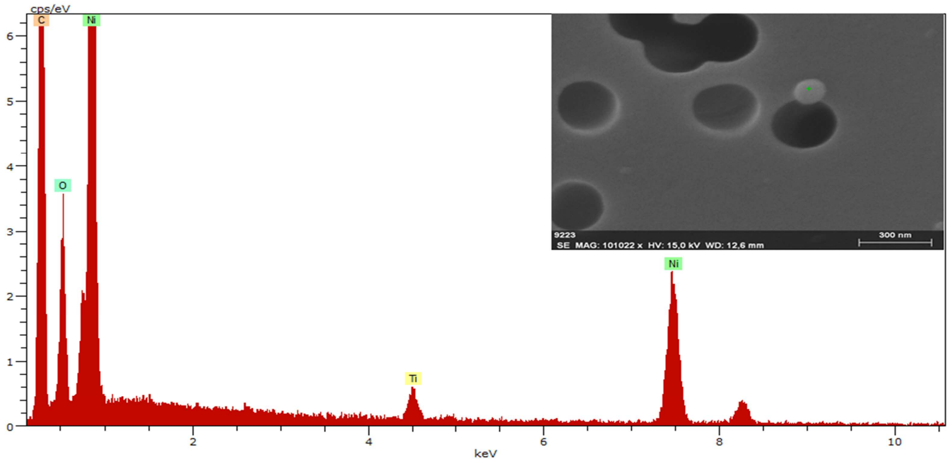
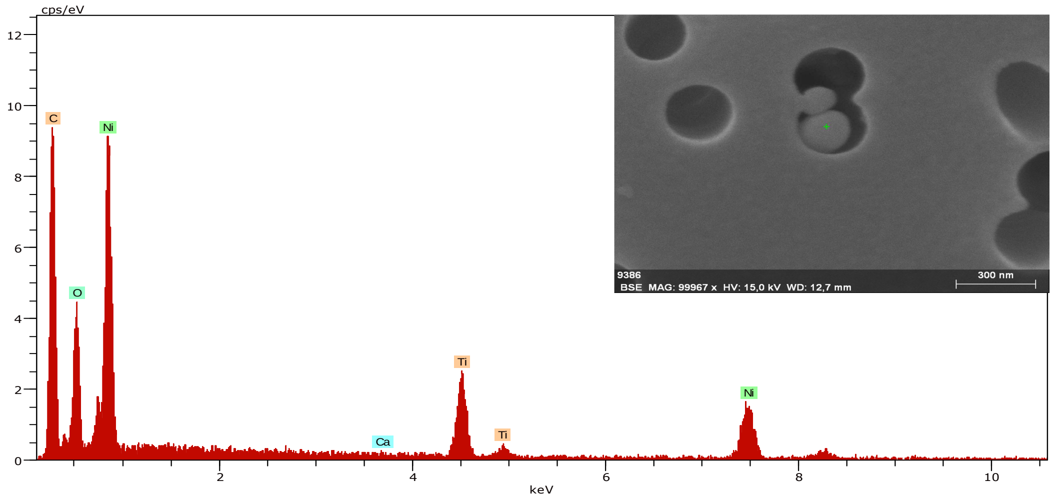


Fig 1 Los nano-$TiO_2$ deeltje op filtermonster van transport grondstoffen.

Het filtermonster genomen tijdens het storten is laag beladen met 2 typen $TiO_2$ deeltjes. De 2 vormen (typen) zijn ongeveer in vergelijkbare hoeveelheden aanwezig op het filter. Type 1 $TiO_2$ heeft een deeltjesgrootte van ca. 100nm tot 2 µm. De meeste deeltjes bestaan uit conglomeraten (clusters) van primaire $TiO_2$-deeltjes. De primaire deeltjesgrootte varieert van 100 tot 300nm en komen een enkele keer ook afzonderlijk als los deeltje voor. Type 2 $TiO_2$-deeltjes komt alleen voor als grotere conglomeraten (wolken) van ca. 500nm tot 5 µm opgebouwd uit primaire deeltjes van rond de 50nm (25-75nm). Deze deeltjes komen echter niet afzonderlijk voor als los deeltje. Zowel in type 1 als in type 2 $TiO_2$ conglomeraten zitten sporen aluminium en silicium die vermoedelijk afkomstig zijn van een coating op de deeltjes. Naast $TiO_2$ komen ook silicaten meerder keren voor. Deze deeltjes bestaan veelal uit aluminium/siliciumoxiden (Al-SiOx) met soms nog andere elementen zoals calcium, magnesium, kalium, ijzer. De deeltjesgrootte varieert van minimaal 500nm tot maximaal 5µm. In verhouding met de metingen tijdens laden en transport komen meer silicaten voor met ijzer (Fe-SiOx). Meerdere keren zijn NaCl kristallen aangetroffen. De NaCl kristallen op het filter zijn vermoedelijk afkomstig van water aerosolen; het opgeloste NaCl kristalliseert als de water aerosolen verdampen op het filter. De NaCl kristallen hebben een deeltjesgrootte van ca. 500nm tot 2µm Meerdere keren is roet aangetroffen. Roetdeeltjes bestaan uit conglomeraten (clusters) van primaire roetdeeltjes en hebben een deeltjesgrootte van ca. 200nm tot 1µm. De primaire deeltjesgrootte is ca. 50nm, deze komen echter nooit afzonderlijk voor.



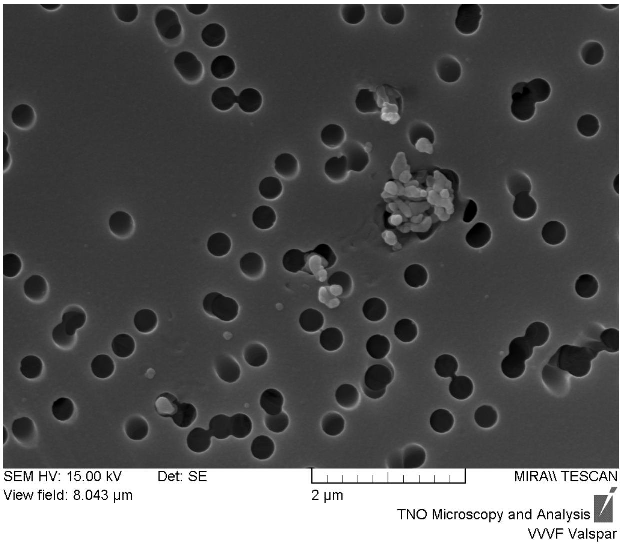


Fig 3 Clusters van $TiO_2$ deeltjes op filtermonster van storten grondstoffen

De resultaten laten zien dat er tijdens het transport van grondstoffen en tijdens het storten/mengen blootstelling plaatsvindt aan 2 typen $TiO_2$ deeltjes. Het Type 1 $TiO_2$ deeltje komt als los nano-$TiO_2$ deeltje voor maar voornamelijk als onderdeel van grotere agglomeraten. Daarnaast lijkt er een secundaire bron van nanodeeltjes aanwezig in de vorm van roetdeeltjes die zich als clusters gedragen.

Kwantitatieve resultaten

Op 21 oktober 2010 zijn met behulp van 3 NanoTracers en PAS-pompen oriënterende metingen verricht bij bedrijf B2. Vertrouwelijke details over betreffende activiteiten zijn niet opgenomen in het rapport. De metingen zijn zo uitgevoerd dat een zo goed mogelijk beeld verkregen werd van de potentiële blootstelling aan nanomaterialen van de uitvoerende medewerker. Indien anders beschreven is zoveel mogelijk in de ademzone gemeten. Vooraf aan elke meting is voor aanvang van de metingen enige tijd de achtergrondconcentratie in de betreffende ruimte bemonsterd alvorens de activiteiten te bemeten.
Specifieke ‘activiteiten’ zijn met markers in de meetdata aangegeven, zodat achteraf bepaald kan worden welke activiteiten op welk moment zijn uitgevoerd.

De belangrijkste activiteiten (events) die bemeten zijn tijdens de werkzaamheden zijn opgenomen in tabel 8. Een overzicht van de meetresultaten (persoonlijke metingen) is opgenomen in tabel 4. Voor de verschillende activiteiten is per gemeten parameter de navolgende waarden bepaald:
Minimum : laagste gemeten waarde tijdens de bemeten activiteit
Mediaan : middelste van de naar grootte gerangschikte waarnemingen
AM : rekenkundig gemiddelde
Maximum : hoogste gemeten waarde tijdens de bemeten activiteit

De uiteindelijke vergelijking van de gemiddelde blootstelling van een werknemer gedurende een activiteit met de NRV is gedaan op basis van het rekenkundig gemiddelde. Hiervoor zijn enkel de data afkomstig van de persoonlijke bemonstering meegenomen. Niet die van de far-field meters.

tabel 8 Belangrijkste te onderscheiden activiteiten tijdens het verwerken van nano-$TiO_2$

| **Event** [24] | **Tijdsduur (h:m:s)** | **Omschrijving meetlocatie/activiteit** |
|---|---|---|
| B | 00:05:30 | Meten van de achtergrondconcentratie in het grondstoffen magazijn |
| D | 00:02:24 | Rapen van zakken nano-$TiO_2$ in magazijn |
| K | 00:10:29 | Meten van de achtergrondconcentratie in de productieruimte |
| L | 00:18:40 | Verwerken van nano-TiO2 (storten en dispergeren in de coating) |
| N | 00:04:17 | Afvoeren van de lege zakken naar afvalcontainer |

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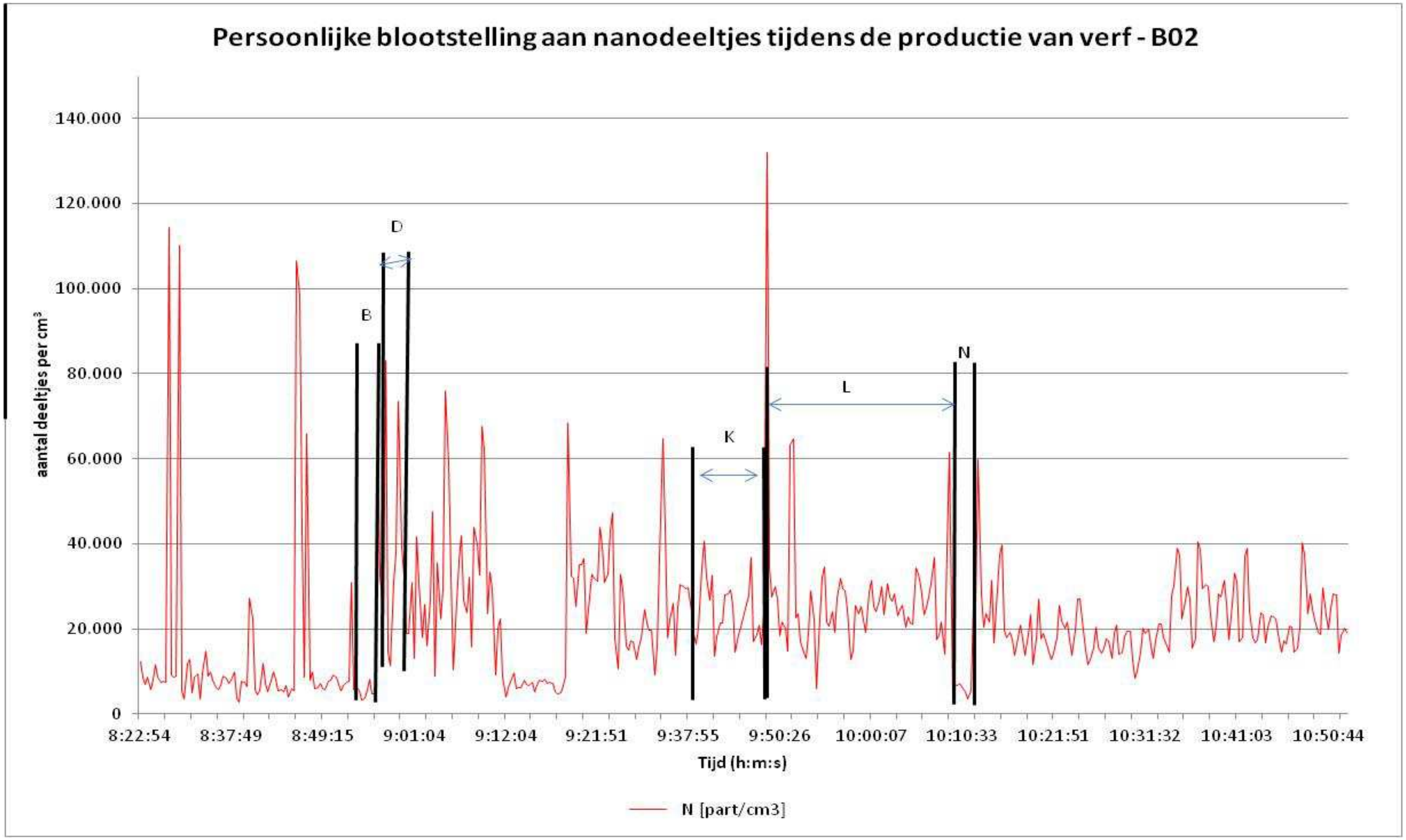
[24] De event nummers verwijzen naar de naamgeving van de events in de datafile met ruwe meetgegevens (logboek)

tabel 9 Kerngegevens gemeten concentratie nanodeeltjes per event – aanmaak coating (personal sampling)

| | aantal deeltjes per $cm^3$ | | | | Gemeten Gemiddelde deeltjesgrootte (nm) | | | |
|---|---|---|---|---|---|---|---|---|
| Event | min | mediaan | AM | max | min | mediaan | AM | max |
| B (achtergrond magazijn) | 3.311 | 6.903 | 7.978 | 30.958 | 29 | 69 | 92 | 266 |
| D (rapen zakken nano-$TiO_2$) | 11.244 | 32.444 | 32.558 | 83.117 | 25 | 37 | 46 | 66 |
| K (achtergrond productieruimte) | 10.226 | 24.161 | 24.629 | 40.728 | 44 | 97 | 98 | 314 |
| L (storten nano-$TiO_2$) | 5.803 | 24.629 | 27.114 | 132.011 | 25 | 51 | 54 | 198 |
| N (afvoeren van afval) | 3.381 | 6.809 | 19.114 | 61.484 | 25 | 64 | 58 | 128 |

In Figuur 5 is de persoonlijke blootstelling aan nanodeeltjes van de werknemer gedurende de hele meetochtend grafisch weergegeven in de tijd. In deze figuur zijn tevens de verschillende events gemarkeerd. Duidelijk is dat de achtergrondconcentratie nanodeeltjes in het magazijn lager is dan de achtergrondcondentratie in de productieruimte. Hoewel de gemiddelde blootstelling aan nanodeeltjes tijdens het werken met nano-$TiO_2$ laag is, kan je tijdens het storten wel mogelijk te maken krijgen met een kortdurende verhoogde blootstelling. In de figuur is aan het begin van het storten een verhoogde blootstelling waar te nemen.



Figuur 5 Blootstelling werknemer aan nanodeeltjes gedurende de gehele meetochtend tijdens het rapen (event D; event B is achtergrond magazijn), storten (event L; event K is achtergrond productieruimte) en afvoeren van lege zakken (event N) van nano-$TiO_2$. De data zijn niet gecorrigeerd voor de aanwezige achtergrond concentratie aan nanodeeltjes. Om 10:06, direct nadat nano-$TiO_2$ is toegevoegd (event L), werden de lege zakken afgevoerd naar de afval container.

Voor vergelijking van de meetresultaten met de tijdelijke nanoreferentiewaarden zullen de meetgegevens gecorrigeerd worden voor de aanwezige achtergrondconcentratie.

# 3. Toetsing aan grenswaarden en discussie

De 8 uur TGG geldt voor de totale blootstelling van een werknemer aan nano-$TiO_2$ op een dag. De dagblootstelling wordt veroorzaakt door verschillende taken op een dag. Om inzicht te geven in de blootstellingbijdrage per activiteit en in de blootstelling door een combinatie van activiteiten zijn verschillende werkscenarios berekend.

. Deze scenario's zijn vergeleken met de DNEL, voorgesteld door Christensen et al (2010) en met de NRV. Omdat het werken met poeders ook kortdurende hoge blootstelling kan veroorzaken wordt de blootstelling aan ENP ook vergeleken met de $NRV_{TGG-15-min}$ (= 2*NRV) en de $DNEL_{15min}$ (=2*DNEL). De volgende scenario's zijn berekend:

- Scenario 1; Het scenario waarin een werknemer enkel nano-$TiO_2$ uit het magazijn ophaalt en aflevert in de productieruimte (het zogenaamde "rapen") (event D) , maar verder niet meer met het product in aanraking komt.
- Scenario 2; Het theoretische scenario waarin een werknemer gedurende een 8 uur durende werkdag de hele dag enkel nano-$TiO_2$ zou rapen (event D voor 8 uur).
- Scenario 3; Het scenario waarin een werknemer nano-$TiO_2$ enkel stort in de mengketel (event L), maar verder niet meer met het product in aanraking komt.
- Scenario 4; Het theoretische scenario waarin een werknemer gedurende een 8 uur durende werkdag de hele dag enkel nano-$TiO_2$ zou stort in de mengketel (event L voor 8 uur).
- Scenario 5; Het scenario waarin een werknemer enkel lege zakken afvoert (event N)
- Scenario 6; Het scenario waarin een werknemer zowel de nano-$TiO_2$ raapt in het magazijn, stort in de mengketel en zakken afvoert (event D+L+N), maar verder niet meer met het product in aanraking komt.

Voor vergelijking met de NRV is voor de persoonlijke blootstelling van de werknemer het rekenkundig gemiddelde berekend. De resulterende blootstellingen voor de verschillende scenario's zijn gegeven in Tabel 10 en Tabel 11. Event B is gebruikt als achtergrond voor de blootstelling in het magazijn. Event K is de achtergrondconcentratie in de productieruimte (zie tabel 9).

Tabel 10 Gemiddelde blootstelling aan nanodeeltjes, achtergrond gecorrigeerd

| Activiteit | Taak-tijd (minuten) | Gemiddelde taakblootstelling ($N/cm^3$) | Gemiddelde blootstelling 8uur -TGG ($N/cm^3$) | Gemiddelde blootstelling (15 min-TGG) ($N/cm^3$) |
|---|---|---|---|---|
| D | 0:02:24 | 24580 | 128 | 4097 |
| L | 0:18:52 | 2485 | 98 | 1962 |
| N | 0:04:17 | Geen verhoging tov achtergrond | Geen verhoging tov achtergrond | Geen verhoging tov achtergrond |
| D+L+N | 0:25:33 | 4144 | 220 | nr |

Tabel 11 Gemiddelde taakblootstelling, achtergrond gecorrigeerd, vergeleken met de DNEL en de NRV voor nano-$TiO_2$ voor 8uur-TGG en 15min-TGG.

| Activiteit | Gemiddelde taakblootstelling ($N/cm^3$) | Gemiddelde blootstelling 8uur -TGG ($N/cm^3$) | Gemiddelde blootstelling (15 min-TGG) ($N/cm^3$) | $DNEL_{8uur\text{-}TGG}$ ($N/cm^3$) | $DNEL_{15min\text{-}TGG}$ ($N/cm^3$) | $NRV_{8uur\text{-}TGG}$ ($N/cm^3$) | $NRV_{15minr\text{-}TGG}$ ($N/cm^3$) |
|---|---|---|---|---|---|---|---|
| D | 24580 | 128 | 4097 | 830.000 | 1.660.000 | 40.000 | 80.000 |
| L | 2485 | 98 | 1962 | 830.000 | 1.660.000 | 40.000 | 80.000 |
| N | Geen verhoging tov achtergrond | Geen verhoging tov achtergrond | Geen verhoging tov achtergrond | 830.000 | 1.660.000 | 40.000 | 80.000 |
| D+L+N | 4144 | 220 | nr | | | | |

Tabel 11 laat zien dat de blootstelling van de werknemer aan nanodeeltjes tijdens het rapen van nano-$TiO_2$ uit het magazijn (event D) en tijdens het storten van deze nano-$TiO_2$ in de mengketel (event L) ruim onder de gestelde DNEL en NRV blijft wanneer deze blootstelling wordt gemiddeld over een 8 uur durende werkdag (Scenario 1 en 3). Zelfs als je deze handelingen zou beoordelen aan de hand van een 15min-TGG blijft de blootstelling ruimschoots onder de gestelde DNEL en $NRV_{15min\text{-}TGG}$. In het extreme geval dat je als werknemer 8 uur lang alleen maar nano-$TiO_2$ zou storten, of in het geval dat de werknemer 8 uur lang alleen maar nano$TiO_2$ uit het magazijn zou rapen (waar de hoogste blootstelling werd waargenomen) blijft de 8uur-TGG nog steeds onder de voorgestelde DNEL of NRV. (Scenario 2 en 4)
Het afvoeren van lege zakken (Event N) veroorzaakt geen verhoging tov van de achtergrond (Scenario 5). Er is zelfs een negatieve blootstelling gemeten. In dit geval was de achtergrondconcentratie in de productieruimte aan het begin van het toevoegen van nano-$TiO_2$ hoger dan na afloop van het storten van de zakken. De precieze reden hiervoor is lastig te duiden op basis van de uitgevoerde metingen. Tabel 6 laat verder zien dat de 8 uurs blootstelling bij een combinatie van de activiteiten rapen, storten en afval afvoeren bij genoemde taakduur beneden de DNEL en NRV blijft.

# 4. Conclusies en aanbevelingen

Uit de bovenstaande vergelijking tussen de gemiddelde taakblootstelling aan nano-$TiO_2$ en de voorgestelde DNEL voor nano-$TiO_2$ blijkt dat de getroffen beheersmaatregelen in de vorm van locale ventilatie en het zeer zorgvuldig werken tijdens het storten van het nanomateriaal voldoen voor het beheersen van de 8-uur TGG tot beneden de DNEL en de NRV, zelfs als je een hele dag nano-$TiO_2$ zakken zou rapen of de hele dag nano-$TiO_2$ zou storten. Dit betekent dat er, op basis van de huidige kennis, geen indicatie is voor een risico voor de beschreven scenarios. In de praktijk wordt werker blootstelling veroorzaakt door een combinatie van alle activiteiten met nanoprodukt. Omdat niet al deze activiteiten zijn bemeten is dit scenario niet uitgewerkt. Helaas kan er dan ook geen uitspraak worden gedaan over een “veilige” combinatie en maximale tijdsduur van activiteiten met nanoproduct.
Uit voorzorg is het handhaven van het huidige voorzorgsmaatregelen inclusief het dragen van beschermende kleding, handschoenen en adembescherming zoals in de huidige praktijk ook gebeurt desalniettemin te adviseren.

Ondanks dat tijdens de metingen in geen enkel geval een overschrijding van de DNEL of van de NRV is gevonden, is het van belang om te benadrukken dat er typisch bij blootstellingsmetingen aan nanodeeltjes grote dag-tot-dag variaties worden waargenomen, bijvoorbeeld als gevolg van de luchtvochtigheid, de temperatuur van de ruimte en de overige activiteiten die zich in dezelfde ruimte afspelen. Zo is het bijvoorbeeld niet uit te sluiten dat een volgende keer wanneer een batch met nano-$TiO_2$ wordt gemaakt de DNEL wel wordt overschreden. Om dit te onderzoeken zou bijvoorkeur meerdere keren gemeten moeten worden om een beeld te krijgen van de spreiding in blootstelling. Daarnaast is de blootstelling sterk afhankelijk van het nanoproduct waarmee gewerkt wordt, zoals de stoffigheid en een eventuele behandeling van het product om klontering (agglomeratie) tegen te gaan.

Tenslotte is blootstelling (bij vergelijkbare blootstellingsbeheersmaatregelen) sterk afhankelijk van de zorgvuldigheid waarmee de werknemer zijn of haar handelingen uitvoert. In dit specifieke geval werd de zak nano-$TiO_2$ zeer voorzichtig leeggestort waardoor niet tot nauwelijks werveling van nanodeeltjes werd waargenomen. Wordt er echter ruwer gestort dan is het de verwachting dat de blootstelling van de werknemer zal toenemen tijdens het storten.

## Mitsen en Maren

Nanodeeltjes behoren momenteel tot de groep stoffen met onzekere en/of onbekende risicos. Daarnaast is de discussie omtrent de methoden die moeten worden toegepast om goede risicobeoordelingen uit te voeren nog in volle gang. Voor een toelichting op deze onzekerheden wordt verwezen naar rapport V9445 “kennisdelen Nano in de verfketen”. Ondanks de grote onzekerheden in data en methoden, geeft deze rapportage een risico indicatie op basis van de best beschikbare gegevens. Gezien de grote onzekerheid kunnen geen definitieve conclusies over veilig gebruik of beheersing van een gezondheidsrisico worden ontleend aan deze beoordeling. Er wordt geadviseerd het voorzorgsprincipe (minimalisatie van blootstelling) toe te passen tot er meer data beschikbaar komen. Daarnaast wordt geadviseerd specifieke data te genereren om de hiaten in kennis te kunnen vullen. Kennis vergaren op het gebied van zowel het gevaar van deeltjes als de blootstelling aan deeltjes kan het in de toekomst mogelijk maken betrouwbare en representatieve werker risicobeoordelingen uit te voeren.

Daarbij is het de observatie op verschillende werkplekken waar gewerkt wordt met poeders dat ook niet-nano-gelabelde stoffen kunnen leiden tot een nano-blootstelling. Wanneer daarom de blootstelling aan nanodeeltjes op de werkplek wordt geëvalueerd voor het treffen van eventueel nader benodigde beheersmaatregelen, is het wellicht interessant om bij deze evaluatie niet alleen te kijken naar die grondstoffen waarvan bekend is dat het nanomaterialen zijn maar ook eens te kijken naar de overige (poedervormige) ingrediënten waarvoor dit niet is vermeld door de leverancier.

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[I] RIVM report 6010440001/2010, S.Dekkers, C. de Heer, Tijdelijke nano-referentiewaarden – Bruikbaarheid van het concept en van de gepubliceerde methoden.

[II] BSI - PD 6699-2:2007 Nanotechnologies –Part 2: Guide to safe handling and disposal of manufactured nanomaterials;

[III] IFA website: Technical Information → nanoparticles at the workplace : http://www.dguv.de/ifa/en/fac/nanopartikel/beurteilungsmassstaebe/index.jsp

IV Christensen et al. 2010. Nano-$TiO_2$-feasability and challenges for human health risk assessment based on open literature.

[IV] RIVM report 6010440001/2010, S.Dekkers, C. de Heer, Tijdelijke nano-referentiewaarden – Bruikbaarheid van het concept en van de gepubliceerde methoden.

[V] BSI - PD 6699-2:2007 Nanotechnologies –Part 2: Guide to safe handling and disposal of manufactured nanomaterials;

[VI] IFA website: Technical Information → nanoparticles at the workplace : http://www.dguv.de/ifa/en/fac/nanopartikel/beurteilungsmassstaebe/index.jsp

[IV] Christensen et al. 2010. Nano-$TiO_2$-feasability and challenges for human health risk assessment based on open literature.