| Project Partners:	SAbyNA
1. LEITAT 2. IOM 3. CEA 4. TECNALIA 5. UKCEH 6. CNRS 7. RIVM 8. GAIKER 9. FIOH 10. ISTEC 11. THINKWORKS 12. ALLIOS 13. LATI 14. NOURYON 15. SYMLOG 16. DUKE UNIVERSITY	H2020-NMBP-15-2020 Simple, robust and cost-effective approaches to guide industry in the development of safer nanomaterials and nano-enabled products Start date of the project: 01/03/2020 Duration 48 months # D7.1 Identification of sector-specific practices and relevant nanosafety alerts

WP	7	Implementation and verification of SAbyNA Guidance Platform in sector-specific case studies	
Dissemination level[1]	PU	Due delivery date	28/2/21
Nature[2]	R	Actual delivery date	1/3/21

| Lead beneficiary	IOM
Contributing beneficiaries	WP7 partners

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[1] Dissemination level: **PU** = Public, **PP** = Restricted to other programme participants (including the JU), **RE** = Restricted to a group specified by the consortium (including the JU), **CO** = Confidential, only for members of the consortium (including the JU)

[2] Nature of the deliverable: **R** = Report, **P** = Prototype, **D** = Demonstrator, **O** = Other
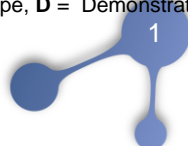
Version	Date	Author	Partner	Email	Comments[3]
1	4/1/21	Emma Innes	IOM	Emma.Innes@iom-world.org	Created section on paints
1	4/1/21	James Hanlon	IOM	James.Hanlon@iom-world.org	Created section on additive manufacturing
1	4/1/21	James Hanlon	IOM	James.Hanlon@iom-world.org	Added stakeholder information
1	8/2/21	William Brown	IOM	William.Brown@iom-world.org	Comments and edits
1	8/2/21	Matthew Boyles	IOM	Matthew.Boyles@iom-world.org	Comments and edits
2	10/2/21	James Hanlon	IOM	James.Hanlon@iom-world.org	Created new version
3	15/2/21	James Hanlon	IOM	James.Hanlon@iom-world.org	Edits from comments received from WP7 partners
4	24/2/21	James Hanlon	IOM	James.Hanlon@iom-world.org	Edits from internal review
4	1/3/21	James Hanlon	IOM	James.Hanlon@iom-world.org	Edits from internal review

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[3] Creation, modification, final version for evaluation, revised version following evaluation, final
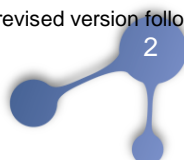
Deliverable abstract

The aim of task 7.1 (T7.1) has been to collect sector-specific typical activities that can be associated to relevant releases of nanoforms (NFs) to the environment or to direct human exposure for the paint and 3D printing sectors. The current deliverable D7.1 compiles the results of T7.1

Interviews were held with the industrial Work Package 7 (WP7) partners, ALLIOS and Nouryon for paints and LATI and LEITAT-3D Hub for 3D printing in order to identify sector-specific activities, relevant releases to the environment or direct human exposure and to identify commonly used nanomaterials and matrix materials in these sectors. This has been complimented with a joint questionnaire with WP6 partners for companies and a joint SAbyNA-SbD4Nano questionnaire (preliminary results are presented for the SAbyNA-SbD4Nano questionnaire).

A literature review has been performed for the paints and 3D printing sectors to identify sector-specific activities and releases of associated nanoforms. For the paints sector, 52 relevant papers were identified and 28 papers for the 3D printing sector including non-academic literature, i.e. The National Institute for Occupational Safety and Health (NIOSH) publications. The identified papers were reviewed for information on activities, measurements and other parameters. The literature review is presented in section 7 (for paints) and section 8 (for 3D printing).
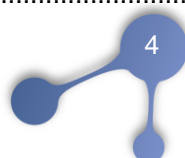
Lists of activities have been generated for the paints and 3D printing sectors along with information on their release potential, key release determinant factors and measurements. Lists of commonly used nanomaterials, matrices and standards have also been compiled. These tables and a summary are provided in sections 5 (paints) and 6 (3D printing) of this deliverable.

These can be used by the other work packages in the course of their activities. The literature database from this deliverable for the two sectors also produced by this deliverable will be updated during the project for use by WP2-6.

Table of Content

1. Abbreviations

ABS	Acrylonitrile Butadiene Styrene
ACGIH	The American Conference of Governmental Industrial Hygienists
AM	Additive Manufacturing
APS	Aerodynamic Particle Sizer
ASA	Acrylic Styrene Acrylonitrile
ASTM	American Society for Testing and Materials
BG	Background
BS	British Standard
CMD	Count Median Diameter
CNT	Carbon nanotube
DIN	Deutsches Institut für Normung e.V.
DLP	Digital Light Processing
DMLS	Direct Metal Laser Sintering
DoW	Description of Work
DPP	Diketopyrrolopyrrole
EC	Elemental Carbon
ELPI	Electrical Low Pressure Impactor
EN	European Standards
NF	Engineered Nanomaterial
ETAG	European Technical Approval Guidelines
FDM	Fused Deposition Modelling
FE	Field Emission
FFF	Fused Filament Fabrication
FMPS	Fast Mobility Particle Sizer
GMD	Geometric Mean Diameter
GWIT	Glow Wire Ignition Temperature
HEPA	High Efficiency Particulate Air
HIPS	High Impact Polystyrene
HSE	Health and Safety Executive
IARC	International Agency for Research on Cancer
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
IEC	International Electrotechnical Commission
IN	Inconel
IOM	Institute of Occupational Medicine
ISO	International Standardization Organization
LCA	Life Cycle Assessment

LEV	Local Exhaust Ventilation
LOD	Limit of Detection
MCA	Micronized Copper Azole-treated lumber
MDF	Medium Density Fibreboard
ME	Material Extrusion
MFR	Melt Mass Flow Rate
MJF	Multi Jet Fusion
MPD	Molten Polymer Deposition
MVR	Melt Volume Flow Rate
MWCNT	Multi Walled Carbon Nanotubes
NEP	Nano-Enabled Product
NF	Nanoform
NIOSH	The National Institute for Occupational Safety and Health
NM	Nanomaterials
NOAA	Nano-Objects and their aggregates and agglomerates
NP	Nanoparticle
PBZ	Personal Breathing Zone
PC	Polycarbonate
PCTPE	Plasticised Copolyamide TPE
PEEK	Polyetheretherketone
PES	Plastic Exposure Scenario
PETG	Polyethylene Terephthalate Glycol
PLA	Polylactic Acid
PPBV	Parts per Billion by Volume
PRISMA	Preferred Reporting Items for Systematic Reviews and Meta-Analysis
PROC	Process Category
PSD	Particle Size Distribution
PVC	Pigment Volume Concentration
PVDF	Poly(vinylidene) Fluorine
PVOH	Poly(vinyl) Alcohol
QC	Quality Control
REL	Recommended Exposure Limit
RMM	Risk Mitigation Measure
RT	Room Temperature
SbD	Safer by Design
SBD4Nano	Safe by Design for Nano
SEM	Scanning Electron Microscopy
SHS	Selective Heat Sintering

SLA	Stereolithography
SLM	Selective Laser Melting
SLS	Selective Laser Sintering
SME	Small and Medium Enterprise
TPU	Thermoplastic Polyurethane
TVOC	Total Volatile Organic Compounds
TWA	Time Weighted Average
UFP	Ultra Fine Particles
UL	Underwriters Laboratories
UV	Ultra Violet
VOC	Volatile Organic Compound
WoS	Web of Science
WP	Work Package

2. Introduction

The objective of SAbyNA is to simplify and distil safe-by-design (SbD) approaches into methods that industry can adopt. The main objective of WP7 is to provide sector-specific information for two sectors (paints and 3D printing) to allow other SAbyNA work packages (WP2-WP6) to simplify SbD approaches, models and tools for these two sectors and to implement SbD guidance into a number of sector-specific case studies.

The information collected in WP7 will be used by WP2-WP6 partners to simplify models and tools, to improve existing databases with sector-specific parameters, to identify relevant test methods to be used for knowledge gaps, and to optimise the SbD approach in the paints and 3D-printing sectors specifically.

This deliverable discusses the results of task 7.1 (T7.1).

3. Description of the tasks

The aim of T7.1 is to collect information on sector-specific activities for the paint and 3D printing sectors which could be associated with nanoform (NFs) releases to the environment and/or direct human exposure. To collect this information, the following steps have been performed:

- Literature review for the paint and 3D sectors.
- Interviews with WP7 industrial partners (ALLIOS and Nouryon for the paints sector; LATI and LEITAT-3D Hub for the 3D printing sector).
- Questionnaires with selected industry companies alongside WP6. This information has also been used for WP6 and for deliverable 7.2.
- Joint questionnaire for companies and industrial associations with the SbD4Nano (Safe by Design for Nano) project. This questionnaire closed on the 28th of February 2021.

3.1 Literature Review

The literature review was conducted in accordance with the PRISMA guidance (Preferred Reporting Items for Systematic Reviews and Meta-Analysis)[1]. This ensures the transparency and reproducibility of the review and consists of establishing search terms, setting the eligibility criteria for inclusion/exclusion through a two-stage screening process; defining the parameters of data extraction followed by data analysis and interpretation of the results.

3.1.1 Sources of information and the review process

The literature searching was undertaken using a Boolean search strategy. The search terms presented in Annex 1) were carefully chosen to ensure that release information on a broad range of scenarios was gathered, including occupational, consumer and environmental releases. Two biographical databases Web of Science (WoS) and PubMed were used as sources, as well as Google Scholar. The list was further supplemented with:

1. Additional literature (including relevant published reports) that was known to be relevant to the area under investigation, but had not been obtained through the Boolean search strategy.
2. Other papers of interest, brought to the attention of the authors through reading of the available literature contained in the reference list.

3.1.2 Study selection and data extraction

All the references retrieved from the Boolean searches were first gathered to an Endnote library where duplicates were removed, either automatically or manually. The list of references was then imported into DistillerSR® (Evidence Partners, Ottawa, Canada), a web-based systematic review software, which was used

to conduct a two-stage review process. Firstly, a title and abstract screening was conducted to remove studies that were not relevant for the review objective (e.g. not focused on the paints/3D printing industry). Following this, the remaining references underwent a full text screening to identify a final list of studies for inclusion in the review.

The data extraction process collected information relating to the engineered nano material (NF) (name, size), matrix (identify, physical state), measurement strategies (online/offline analysis), study conditions, release information and authors' conclusions. A data extraction template was designed specifically for this purpose based upon that used by Basinas et al.[2]

Studies were categorised according to their release domain: (i) release to the environment, or (ii) exposure to humans), and further ordered according to life cycle stage (synthesis, formulation, use, and end-of-life).

3.1.3 Differentiation of release and exposure

As the literature review has focussed on both release and exposure, it is important to distinguish between them. VdL (German Paint and Printing Ink Association) differentiate between release and exposure [3]. Release refers to when pieces of matter such as particles, droplets or agglomerates are separated by external forces from a nanostructured materials, such as powder or suspension and are then transferred to the environment. Exposure refers to if the released particles are transported to an exposure region, such as the breathing zone.

A recent publication by Gohler *et al.* used propagation modelling to derive an exposure estimation based on experimental particle release data[4]. This focused on 3 release scenarios from nano-enabled materials including (i) dry wiping of a coated panel, (ii) sanding of a coated panel, and (iii) spray application of a liquid coating. While relying on a number of assumptions, the authors concluded that the level of exposure was largely influenced by the release scenario, the type of ventilation present and the positioning of the worker/consumer. This highlights the importance of contextual and process information during exposure assessment.

3.2 Interviews with industrial partners

In-depth interviews were held with ALLIOS and Nouryon for paints and with LATI and LEITAT for 3D printing. Information was collected on materials/products to be used in the project; tons of material/product used annually, exposure/chemical safety assessments and potential release domain for T7.1.

3.3 Questionnaires with industrial companies and associations

Selected questions related to tons of material/product used annually, exposure/chemical safety assessments and potential release domain were included in a joint questionnaire with SAbyNA WP6 and WP8 to selected companies (included in this deliverable).

Industry associations and companies were also asked about potential release scenarios in a joint questionnaire with the SbD4Nano project.

Note: Questionnaire responses received up to the 1st of February 2021 are included.

4. Description of the work and main achievements

4.1 Summary of the Literature Review

4.1.1 Paints Results

A total of 456 references were identified for the paints sector, and this was reduced to 423 after removing duplicates. Out of the 423 references, 123 remained for full-text screening and 52 were selected for inclusion in

the review. Papers were excluded for a number of reasons including; not focussing on use in the paints industry; the paints described were not nano-enabled; and papers that were themselves literature reviews. Of these 29 were relevant for human exposure and 23 for release into the environment.

The following paragraphs summarise the literature findings where release was identified across the following life-cycle stages defined as:

i. **Synthesis of nanomaterial and formulation:**
   Synthesis of nanomaterial to be used in paints application as a nano-additive. Paint formulation where nano-additive is incorporated into composition to produce the product for market. Includes powder handling, weighing and mixing.

ii. **Service life:**
   Professional and consumer use of the paint including; application of the paint (brushing, rolling and spray painting), contact with applied paints, weathering/aging of applied paints, and removal of applied paints.

iii. **End-of-life:**
   Processes that occur when the paints have reached the end of its useful life. This includes disposal and waste management processes such as incineration and recycling.

4.1.2 3D printing

A total of 299 references were identified, and this reduced to 296 after removing duplicates. Out of the 296 references, 97 remained for full-text screening and 28 were selected for inclusion in the review. Papers were excluded for a number of reasons including; papers not focussing on 3D printing; no information on exposure/release; and papers that were themselves literature reviews.

Of these 24 were relevant for human exposure, 1 was relevant for both human and environmental exposure, and 3 were either not applicable (N/A) or unclear. No papers were identified focussed on release into the environment exclusively.

The following paragraphs summarise the literature findings where release was identified across the following life-cycle stages defined as:

i. **Filament production:**
   Synthesis of the filament containing nanomaterials to be used for 3D printing.

ii. **Pre-processing:**
   Pre-processing activities where release could occur, for example loading and sieving.

iii. **Printing:**
   Professional and consumer application of 3D printing using different techniques. This includes binder jetting, directed energy deposition, material extrusion, material jetting, powder bed fusion, sheet lamination, and Vat photopolymerisation (defined in ISO (International Standardization Organization)/ASTM 5200:2015).

iv. **Post-processing:**
   Activities post-printing where release could occur. This includes activities on the printed articles (such as abrasion and the use of solvents or other chemicals on the object), cleaning activities, and maintenance activities.

v. **End of life:**
   Processes that occur when the 3D printer filaments/products have reached the end of its useful life. This includes disposal and waste management processes such as incineration and recycling. No relevant studies were identified for end of life.

5. Sector specific practice- paints sector

Paints are a liquid suspension of pigment particles composed of the following ingredient classes, each performing a specific function:

- Binder (resin) – usually organic polymers used to form a film upon drying. These provide surface adhesion, hardness and bind the pigment and additive particles into the film.
- Pigment – used to provide colour.
- Solvent(s) – a single or mixture of liquids used to form a non-reactive solution with the other constituents. Solvents can be volatile or water-based.
- Additives - provide unique functions such as plasticizers, stabilizers, surfactants or rheological agents. These are generally added in small quantities (approx. 0.5-5%).

This section provides a summary for the literature review, interviews with industrial partners and the questionnaire for associations/companies for the paints sector. This includes information on nanomaterials, matrix materials, standards used and release scenarios.

5.1 Interviews with industrial partners WPs

Interviews were held with Nouryon and ALLIOS to collect sector-specific information.

ALLIOS

The objective of ALLIOS within SAbyNA is to optimise the paint formulation and to improve air quality both internally and externally by the decrease of the pollution made by volatile organic compounds (VOC). The production of paints with nano-sized titanium dioxide (TiO_2) is presently performed at R&D scale, with the slurry produced in a glovebox. In terms of activities involved in the manufacturing of nano-engineered paints, there are seven identified steps involved in the process which are described in Figure 1. This figure is useful for input into WP2 for exposure and WP5 for process design.
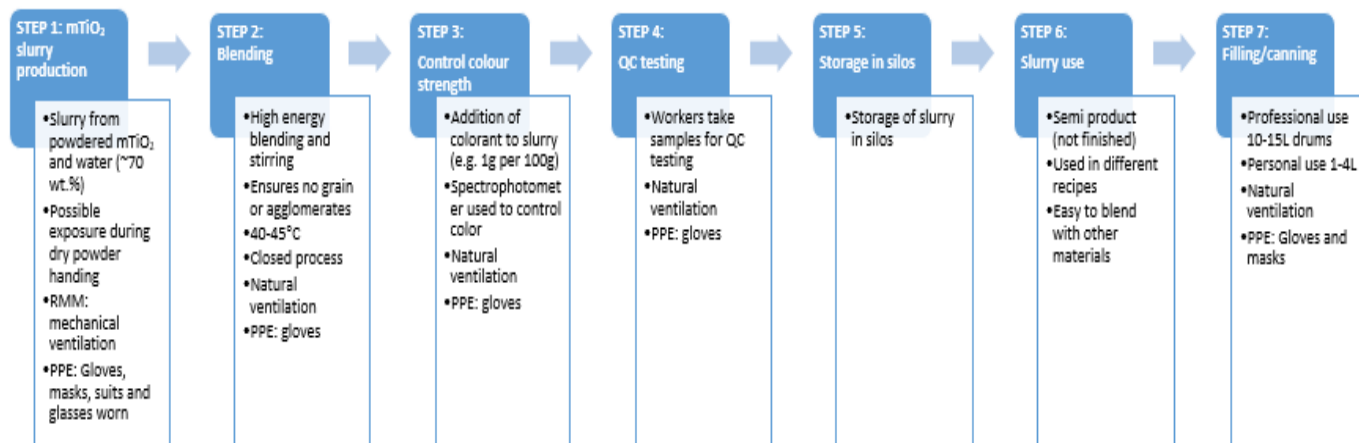
Figure 1. Manufacture of Paints (ALLIOS)

Nouryon

Nouryon manufacture colloidal amorphous nano-SiO_2. This silica can be added as an additive to paints for anti-fouling properties. The objective in SAbyNA is to optimise this surface modification to minimise the hazard. Exposure is thought to be low due to the process being automated and enclosed. There are six identified steps involved in producing colloidal amorphous silica (Figure 2). This figure is useful for input into WP2 for exposure and WP5 for process design.
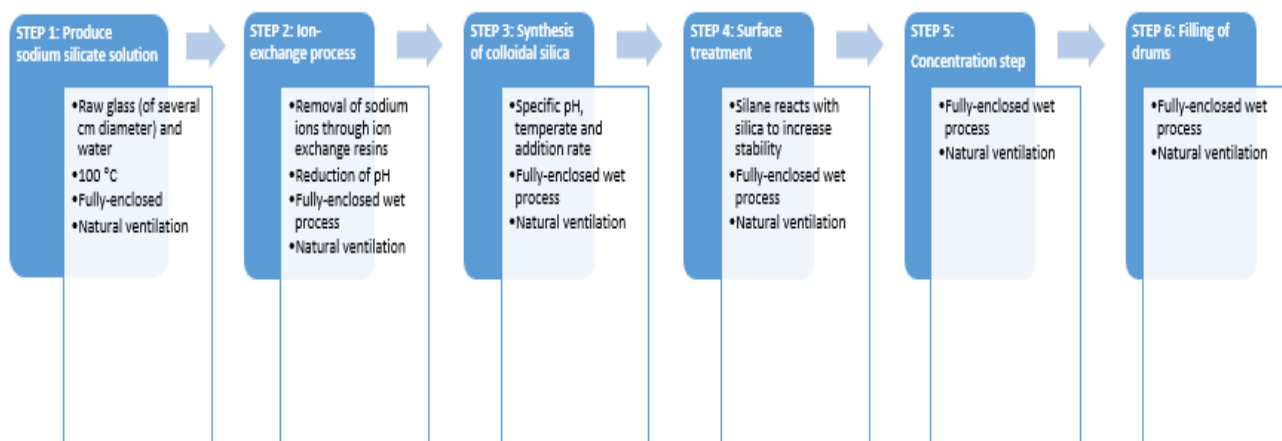
Figure 2. Manufacture of nano-SiO$_2$ (Nouryon)

5.2 Questionnaires with industrial associations/companies

5.2.1 SAbyNA questionnaire

A number of companies in the paint sector (also involved in other sectors) responded to the questionnaire. Nanoforms are used in the following activities (with RMMs in place such as engineering controls, RPE and PPE) in under 10 tons per year:

- Weighing
- Mixing
- Extrusion
- Powder handling
- Spray drying and spray application
- Grinding/milling
- Mechanical abrasion/polishing
- Drying
- Chemical vapour techniques
- Other (spin coating- occasionally)

5.2.2 Joint questionnaire with SbD4Nano

As of 1st February 2021, two companies involved in the paints sector (alongside other sectors) had responded to the joint questionnaire. For nanoforms used, only graphene was indicated as being used. For processes identified, graphene is used in the spray application of liquids. Other processes used are transfer, compression, fracturing powders, granules, or pelletized material, fracturing and abrasion of solid objects and the application of liquids in high speed processes.

Graphene nanoplatelets has been identified as being used for paints by one company who responded to the questionnaire.

5.3 Commonly used nanoforms in the paints sector

Table 1 lists the nanoforms that have been studied in the literature for the paint sector. Titanium dioxide is by far the most studied nanoforms, followed by silicon dioxide (these two are used by the WP paint industrial partners). This finding also correlates with that of the industrial WP partners, in which these two materials have

been/are being used. Zinc oxide and silver have also been used in a number of studies, whilst a number of nanoforms are only subject to either one or a few studies.

Table 1. Summary of total number of release studies by type of engineered nanoform

NF	Exposure to humans	Release to the environment	Total
Literature Review			
TiO_2	10 (32%)	15 (37%)	25 (35%)
SiO_2	5 (16%)	6 (15%)	11 (15%)
ZnO	4 (13%)	4 (10%)	8 (11%)
Ag	-	7 (17%)	7 (10%)
(MW)CNT	1 (3%)	4 (10%)	5 (7%)
CeO_2	1 (3%)	1 (2%)	2 (3%)
Fe_2O_3	3 (10%)	1 (2%)	4 (6%)
Carbon black	4 (13%)	-	4 (6%)
Cu_2O	-	1(2%)	1 (1%)
CuO	1 (3%)	-	1 (1%)
DPP	-	1 (2%)	1 (1%)
Cu-phthalocyanine	-	1 (2%)	1 (1%)
Fe_3O_4	1 (3%)	-	1 (1%)
FeO(OH)	1 (3%)	-	1 (1%)
Materials Identified from interviews/questionnaires			
TiO_2			
SiO_2			
Graphene nanoplatelets			

5.3.1 Commonly used matrix materials

Table 2 lists the matrix materials used in the literature. The most common matrix materials used in paints are acrylic-based matrices in the literature. In some cases, only limited information is provided for the matrix materials in the literature, such as only the solvent used (i.e. water based or organic based) or this information is not supplied in the study. These findings correspond to the matrix materials used by the industrial partners (mineral-based and organic-binder based). For mineral-based systems, two papers have very recently been accepted for publication by WP partners.

Table 2. Summary of materials used for matrix from the literature review

Paint system	Total
Literature Review	
Water-based	7 (18%)
Acrylic	7 (18%)
Styrene-acrylic	3 (8%)
Acrylate	3 (8%)
Water-based acrylic	2 (5%)
Polyvinyl acetate	2 (5%)
Water-based, styrene–acrylic copolymer	1 (3%)
Water, propylene, glycol, Uradil AZ XP 601Z44, and others	1 (3%)
Water, propylene glycol, Uradil AZ XP 601Z44	1 (3%)
Styrene acrylate polymer	1 (3%)
Polyvinyl chloride	1 (3%)
Polyvinyl acetate and acryl binder	1 (3%)
Polyurethane	1 (3%)

Polyacrylate	1 (3%)
Poly(methyl methacrylate)	1 (3%)
Organic solvent based	1 (3%)
Latex, aqueous	1 (3%)
Aqueous dispersion with polyacrylate	1 (3%)
alkyd and melamine	1 (3%)
acrylic and polyester polymers	1 (3%)
Materials identified from interviews	
Mineral based (i.e. silicate)	
Organic binder (i.e. acrylate)	
Additional materials identified from internal review	
Silicone-based	

5.4 Relevant standards

Standards which are used in the paint sector for durability/quality assurance testing (such as wear factor, leaching and weathering) have been collected from the literature and the WP7 industrial partners. These standards are described in Table 3. For manufacturing, ISO 9001 (quality management) and 14001 (environmental management) standards are also used. Only one method, ISO 21683:2019 references nano in its title/abstract.

Table 3. Standards used in the paint sector from the literature review

Testing	Reference	Name
Abrasion	EN (European Standard) ISO 7784-1	Paints and varnishes — Determination of resistance to abrasion — Part 1: Method with abrasive-paper covered wheels and rotating test specimen
	EN ISO 7784-2	Paints and varnishes — Determination of resistance to abrasion — Part 2: Method with abrasive rubber wheels and rotating test specimen
	ISO 11998:2006	Paints and varnishes – Determination of wet-scrub resistance and cleanability of coatings
	ASTM D 4060	Standard Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser
	ASTM D 6307	Standard Test Methods for Dry Abrasion Mar Resistance of High Gloss Coatings
	ASTM D 1044	Standard Test Method for Resistance of Transparent Plastics to Surface Abrasion by the Taber Abraser
Leaching	ISO 2812-2:2018	Paints and varnishes — Determination of resistance to liquids — Part 2: Water immersion method
	BS (British Standard) EN 12457-3:2002	Characterisation of waste - Leaching - Compliance test for leaching of granular waste materials and sludges
	ISO 11507:2007	Paints and varnishes — Exposure of coatings to artificial weathering — Exposure to fluorescent UV lamps and water
	ISO 7784-2:2016	Paints and varnishes – Determination of resistance to abrasion – Method with abrasive rubber wheels and rotating test specimen
Mechanical treatment	ISO 21683:2019	Pigments and extenders — Determination of experimentally simulated nano-object release from paints, varnishes and pigmented plastics
Weathering	ISO 4892-1:2016	Plastics — Methods of exposure to laboratory light sources — Part 1: General guidance
	ISO 4892-2:2013	Plastics — Methods of exposure to laboratory light sources — Part 2: Xenon-arc lamps
	ISO 4892-3:2013	Plastics — Methods of exposure to laboratory light sources — Part 3: Fluorescent UV lamps (2013)
	ISO 11507:2007	Paints and varnishes — Exposure of coatings to artificial weathering — Exposure to fluorescent UV lamps and water (withdrawn and replaced with ISO 16474)

	ISO 16474-1:2013	Paints and varnishes — Methods of exposure to laboratory light sources — Part 1: General guidance
	ISO 16474-2:2013	Paints and varnishes — Methods of exposure to laboratory light sources — Part 2: Xenon-arc lamps
	ISO 16474-3:2014	Paints and varnishes — Methods of exposure to laboratory light sources — Part 3: Fluorescent UV lamps
	EN 927-6: 2018	Paints and varnishes — Coating materials and coating systems for exterior wood — Part 6: exposure of wood coatings to artificial weathering using fluorescent UV lamps and water
	ETAG (European Technical Approval Guidelines) 004	External Thermal Insulation Composite Systems with Rendering (27-06-2013) (EOTA, 2000).
Environment	EU Ecolabel	COMMISSION DECISION of 28 May 2014 establishing the ecological criteria for the award of the EU Ecolabel for indoor and outdoor paints and varnishes and following amendments

5.5 Release Scenarios

Identified release scenarios for the paint sector from the review are described in Table 4. Release rates for common nanoforms, where these are available from the literature review and supplied by industrial partners have been added although for more information, it is recommended to review the tables in section 7. These tables give more information on the nanoforms, matrices used and the testing used. In Annex 2, there is a summary table for the release scenarios with exposure route.

Table 4. Paint activities

Process	Activities	Release potential, Key release determinant factors	Reported release rates	Reported environmental release rates
Formulation	Synthesis (i.e. synthesis of colloidal silica)	Low release potential- performed in solution and closed systems	Collodial silica: low Iron oxide: median mass concentration: 0.083 mg/m^3 median particle number: 66,800 #/cm^3; 80% under 100 nm[5]	N/A
	Powder handling	Considered in the literature to be low. Key release factors include amount of material, RMM and process steps	TiO$_2$[6]: Reported BG = 10899 #/cm^3; PBZ = 23536 #/cm^3 and BG = 25497 #/cm^3, PBZ = 23671 #/cm^3 Multi Walled Carbon Nanotubes (MWCNT)[7]: 8-h Time Weighted Average (TWA) EC of 0.1-0.9 µg/m^3	N/A
	Weighing	Low release potential. Key release factors include manual/automated process, volume handled	MWCNT[7]: 8-h TWA EC of 0.1-0.9 µg/m^3	N/A
	Mixing	Low release potential. Key release factors include manual/automated process, volume handled	MWCNT[7]: 8-h TWA EC of 0.1-0.9 µg/m^3	N/A
	Blending (high energy blending and stirring)	Low release potential- performed on a slurry; closed process	N/A	N/A
	Colour control step (addition of colorant to a slurry)	Low release potential- performed in solution	N/A	N/A
	QC (Quality Control) testing		N/A	N/A

Process	Activities	Release potential, Key release determinant factors	Reported release rates	Reported environmental release rates
	Ion exchange (use of ion exchange resins for removing ions)	Low release potential-performed in solution and closed systems	N/A	N/A
	Concentration step	Low release potential-performed in solution and closed systems	N/A	N/A
	Surface treatment (i.e. treatment to increase stability)	Low release potential-performed in solution and closed systems	N/A	N/A
	Storage in silos		N/A	N/A
	Filling/canning (drum size depending on personal use/professional use)	Low release potential- in solution	N/A	N/A
Service life	Paint brushing	Low release potential	SiO_2[7]: BG 1136 #/cm^3 – 85076 #/cm^3; PBZ: 7147 #/cm^3 – 53793 #/cm^3	N/A
	Paint rolling		SiO_2[7]: BG 1136 #/cm^3 – 85076 #/cm^3; PBZ: 7147 #/cm^3 – 53793 #/cm^3 Hand painting MWCNTs[8]: Respirable below 1 µg/m^3; inhalation fraction: 1.52-2.29 µg/m^3	N/A
	Drying	Low potential release. Key release factors include if the paint is water-borne or solvent-borne	Solvent-borne carbon black: (3.2×10^5-1.4×10^6 #/cm^3) sized 9.31 nm[9]	N/A
	Spray painting/spray applications	High potential release. Key release factors include matrix composition, agglomeration, overspraying and type of spraying performed	ZnO, Fe_2O_3, SiO_2: Release in magnitude of 5×10^8-3×10^{10} particles per gram ejection mass[10] SiO_2[6]: Particle concentrations of 14,000-800,000 #/cm^3 ZnO: Total aerosol concentrations of 96 mg/m^3 for area samples and 84 mg/m^3 for personal samples[11] Aqueous TiO_2: GM particle number emission rate 1.9×10^{10} s^{-1}; mean mass emission rate of 381 µgs^{-1}. Particle deposition rate up to 15 h^{-1} for < 1 µm-size[12] MWCNT[8]: Inhalable EC concentrations within spray booth (0.99 µg/m^3). The background corrected inhalable fraction was 12.31–14.94 µg/m^3 TiO_2: Mean concentration of 0.7 mg/m^3 for respirable TiO_2; NOAA of 100-500 nm[13]	N/A

Process	Activities	Release potential, Key release determinant factors	Reported release rates	Reported environmental release rates
	Sanding (mechanical process)	High potential release. Key release factors include the abrasive material used, contact force/pressure applied, matrix embedded, grit size of the sandpaper and area of contact.	Dermal contact for CuO: 0.9 and 2.5 ng/ cm^2 for non-sanded and sanded paint[14] TiO$_2$ (2.06×10^5 - 2.57×10^5 #/cm^3)[15] Generally high amounts released (see Table 16)	N/A
	Sawing	Low potential release.	SiO$_2$:[7] Background concentration of 13081 #/cm^3; PBZ of 15827 #/cm^3	
	Weathering	Potential for release. Key release factors include dissolution and photo degradation of the matrix		TiO$_2$ release rates: 0.001% (Azimzada et al., 2020[16]), 0.007% (Al-Kattan et al., 2013[17]) and <1% (Kaegi et al., 2008[18]) Ag: Release of 0.5 mg/m^2; <1% of the initial coating[19,20] CeO$_2$[21]: Ce release between 2.8 ± 0.3 - 6.0 ± 2.4 mg/m^2
	Abrasion	Potential for release. Type of coating and formulations are release factors		ZnO and polyurethane: No significant release observed in particle concentration <100 nm[22] TiO$_2$ water-based: Low release with no free NP present. Released fragments larger than 100 nm[23]
End of life	Sandblasting	Low release potential	CNT: No free CNT above Limit of Detection (LOD) (1.3×10^{-4} wt. %)[24]	SiO$_2$ with acrylic: (1.7% of the SiO$_2$)
	Incineration		N/A	N/A
	Leaching	Low release potential. Key release factors include pH, ionic composition, polymer matrix composition	N/A	NPs in the paint) for paint formulated with higher PVC value (63%)[25] Cu$_2$O: 0.21% from aluminium and 1.76% from Wood[26] TiO$_2$, Ag and SiO$_2$ (weathered): Ag (detection limit) and Ti (0.00015 wt.%) and Si loss was about 1.8 wt.%[25]

Process	Activities	Release potential, Key release determinant factors	Reported release rates	Reported environmental release rates
	Landfill	Low release potential	N/A	SiO_2- and TiO_2-containing leachates effectively contained[27]

6. Sector specific practices – 3D printing

6.1 Categorisation systems

There are a number of standards that exist for 3D printing categorisation which are discussed in this section.

ISO-ASTM 52900:2015 standard (Additive Manufacturing – General principles – Terminology) classifies 3D printing into seven different techniques. These are:

- Binder jetting. This additive manufacturing process is where the liquid binding agent is deposited separately for the purpose to join powder materials.
- Directed energy deposition. This involves thermal energy (energy source) being used for fusing materials by melting during deposition.
- Material extrusion. This involves the material being selectively dispensed through an orifice or nozzle.
- Material jetting. This involves droplets of build material being selectively dispensed.
- Powder bed fusion. This is when thermal energy is used to selectively fuse the regions of a powder bed.
- Sheet lamination. This process involves sheets of materials being bonded to form a part
- Vat polymerisation. This process involves a liquid photopolymer which is contained in a vat which is then selectively cured by light-activated polymerisation.

ISO 17296-2: 2015 (Additive Manufacturing. General principles. Overview of process categories and feedstock) classify 3D printing technologies into seven families. These families are:

- Fused Deposition Modelling (FDM or FFF)
- Direct metal laser sintering (DMLS) or Selective Laser Sintering (SLS)
- Stereolithography or Vat photopolymersation
- Material jetting
- Electron Beam Melting
- Binder jetting
- Sheet lamination

ISO-ASTM 52900:2015 has been used as a starting point for categorisation and based on the literature reviews and interviews/questionnaires has been further subcategorised based on differing factors leading to releases which are described in the following sections.

6.2 Interviews with industrial partners WPs

Interviews were held with LATI and LEITAT-3D Hub to collect sector-specific information. The aim of LATI in SAbyNA is to improve the filament materials, have a better risk understanding in the supply chain and also having a tool which has broad acceptance with Small and Medium Enterprises (SMEs). LEITAT-3D Hub are interested in anti-static and biocide applications, printing with new polymers, evaluating particle release of new materials with nanoparticles processed by 3D techniques and evaluating safe-by-design methodology.

Within the SAbyNA consortium, LATI is making available 3D printing filaments produced by innovative composite thermoplastic materials. Namely the filaments are SWCNT modified polycarbonate/glass fibre

filament and a nanosilver based filament. There are five steps (steps 1 and 2 are combined for clarity in the figure) involved in the filament manufacturing which are weighing and mixing; extrusion; pelletisation and drying; and filament production. Previous measurements have been performed at LATI for exposure during extrusion which are provided in Table 5.

Table 5. Extrusion measurements (GM (GSD) presented)

Material	FMPS	APS	EC (personal, µg/m^3)	Respirable dust (personal, µg/m^3)
Polyamide (blank)	44,839 (1.68)	151 (1.05)	< LOD	44.5 (N/A)
Polyamide and CNT (master batch):	30,116 (1.34)	109 (1.2)		46.7 (22.1)
Polyamide and CNT (powder)	23,045 (1.09)	135 (1.4)	11.2 (1.4)	56.1 (9.2)

The filaments will then be used by LEITAT-3D Hub, with three steps involved in 3D printing (pre-processing, Additive Manufacturing and post-processing). The steps involved in 3D printing are described in Figure 3. This figure is useful for input into WP2 for exposure and WP5 for process design.
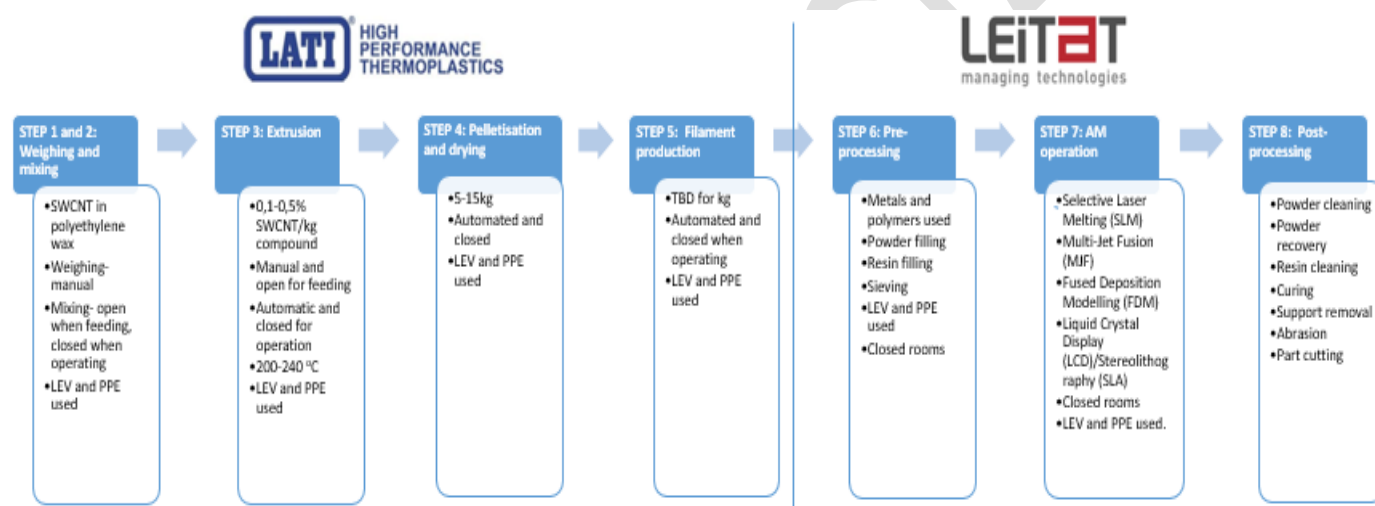
Figure 3. 3D printing process

6.3 Questionnaires with industrial associations/companies

6.3.1 SAbyNA Questionnaire

A number of companies in the 3D printing sector responded to the questionnaire. Nanoforms are used under 10 tons per year in the following activities (with the use of engineering controls, RPE and PPE):

- Weighing
- Mixing
- Extrusion
- Powder handling
- Spraying applications
- Mechanical abrasion/polishing
- Grinding/milling
- Drying
- Other (printing applications)

6.3.2 Joint Questionnaire with SBD4Nano

As of 1st Feb 2021, two companies involved in additive manufacturing had responded. The nanoforms used are CNTs and MWCNTs. The processes in which nanoforms are used are in transfer operations, compressing operations, fracturing of powders, granules or pelletised material (i.e. size reduction), movement and agitation, handling of contaminated objects, liquid operations (i.e. transfer, spraying, and application in high speed processes) and fracturing and abrasion of solid objects.

It is unclear if all these processes are relevant for 3D printing as these companies also indicated that they were also involved in other sectors (i.e. liquid operations).

6.4 Commonly used nanoforms in the 3D Printing sector

6.4.1 NFs used in filaments

The primary focus on the studies in the literature were on release during printing activities with specific filament materials. For those studies where nanoforms were discussed (three studies) this was for carbon nanotubes.

An additional literature search in Web of Science has been performed for listing nanoforms that have been used in filaments. Table 6 lists the nanoforms used in filaments. Carbon nanotubes are the main engineered nanomaterial used in filaments (20 studies) along with graphene nanoplatelets (11 studies). Single Wall Carbon Nanotubes (SWCNTs) are also being used in filaments as part of the experimental work being performed in SAbyNA and have also been identified as being used in the joint SAbyNA-SbD4Nano questionnaire.

Table 6. Nanoforms used in filaments (from literature review)

NF	Total
Literature Review	
Carbon nanotubes (SWCNT)	12 (21%)
Graphene nanoplatelets	11 (19%)
Multi walled carbon nanotubes (MWCNT)	8 (14%)
Nanoclay	4 (7%)
TiO_2	3 (5%)
Graphene oxide	2 (4%)
Zinc oxide	2 (4%)
Cloisite	2 (4%)
Cellulose nanocrystal	2 (4%)
organically modified montmorillonite (OMMT)	2 (4%)
Mixture of MWCNTs and GNPs	1 (2%)
Inorganic Fullerene Tungsten Sulphide (IF-WS2)	1 (2%)
Ag nanocomposite	1 (2%)
mesoporous nano carbon (NC)	1 (2%)
high-structured carbon black (Ketjenblack) (KB)	1 (2%)
Silica	1 (2%)
Gold	1 (2%)
WS inorganic nanotubes (WS-NT)	1 (2%)
Antimony (Sb) doped Tin Oxide (SnO) nanoparticle	1 (2%)
Materials Identified from interviews/questionnaires	
Single Walled Carbon Nanotubes (SWCNT)	
Silver	

6.4.2 Matrix materials

The most commonly used matrices identified in the literature for filaments are polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS) as listed in Table 7. This corresponds with those used by the WP industrial partners (ABS, PLA plus others which are listed in the table).

Table 7. **Summary of matrix materials used in filaments**

Matrix material	Total
Polylactic acid (PLA)	13 (30%)
Acrylonitrile butadiene styrene (ABS)	12 (28%)
thermoplastic polyurethane (TPU)	3 (7%)
polyether ether ketone (PEEK)	3 (7%)
poly(vinyl alcohol) (PVOH)	2 (5%)
Polyetherimide	2 (5%)
High Density Polyethylene	1 (2%)
Thermoplastic polyurethane (TPU)	1 (2%)
Polypropylene	1 (2%)
Nylon 6 (PA 6)	1 (2%)
Polybutylene terephthalate	1 (2%)
Surlyn (Dow trade name for various acrylic copolymers Ionomers)	1 (2%)
PMM	1 (2%)
poly(vinylidene fluoride) (PVDF)	1 (2%)
Polyamide	Used by Industrial Partner
Polyetheretherketone (PEEK)	Used by Industrial Partner

6.4.3 Metal powders

A variety of metal powders have been identified as being used for metal AM from the literature review and information from WP partners (Table 8). The metal powders used in printing are not nanosized (typically on the microscale), however printing using metal powders can result in the release of nanosized particles (see section 7).

Table 8. **Identified metal powders for metal 3D printing**

Metal Powder
Stainless steel 316L
Maraging steel MA300
Aluminium magnesium caesium
Titanium
Inconel
Nickel-based Inconel 939 (IN939)
Copper alloy (high copper content with aluminium coating)
Cobalt
Chromium, nickel and cobalt alloy

6.5 Relevant standards

Standards which are used in the 3D printing sector for filament manufacturing (Table 9) and printing (discussed in section 5.1) have been collected from the literature and the WP industrial partners. These standards are described in Table 9. The methods listed for plastics are general methods for plastics which are applicable also to 3D printing and the manufacturing of filaments. For manufacturing, ISO 9000 (quality management) and 14001 (environmental management) standards are also used.

Table 9. Standards employed in filament and additive manufacturing (general plastic methods listed)

Method Reference	Name
ISO 527-1:2012	Plastics — Determination of tensile properties — Part 1: General principles
ISO 1133-1:2011	Plastics — Determination of the melt mass-flow rate (MFR) and melt volume-flow rate (MVR) of thermoplastics — Part 1: Standard method
ISO 1133-2:2011	Determination of the melt mass-flow rate (MFR) and melt volume-flow rate (MVR) of thermoplastics — Part 2: Method for materials sensitive to time-temperature history and/or moisture
ISO 3451	Plastics - Determination of ash
ASTM D 11.11	Surface Resistance Measurement of Static Dissipative Planar Materials
ASTM D 618-08	Standard Practice for conditioning plastics for testing
ASTM D 2863-08	Measuring the minimum concentration to support candle-like combustion of plastics (oxygen index).
International Electrotechnical Commission (IEC) 60112:2009	Method for the determination of the proof and the comparative tracking indices of solid insulating materials under moist conditions
UL 746A	Polymeric Materials-Short Term Property Evaluation
IEC 60695-2-10:2013	Fire hazard testing - Part 2-10: Glowing/hot-wire based test methods - Glow-wire apparatus and common test procedures
IEC 60695-2-11	Fire hazard testing – Part 2-11: Glowing/hot-wire based test methods – Glow-wire flammability test method for end-products
(IEC) DIN (Deutsches Institut für Normung e.V.) EN 60695-2-13	Glowing/hot-wire based test methods – Glow-wire ignition temperature (GWIT) test method for materials
IEC 60695-11-10	Flammability classification
ISO 62:2008	Plastics — Determination of water absorption
ISO 1791-1:2010	Plastics — Determination of Charpy impact properties — Part 1: Non-instrumented impact test
ISO 178:2010	Plastics — Determination of flexural properties
UL94 5VA & 5VB	Flammability standard
ISO 291:2008	Plastics — Standard atmospheres for conditioning and testing
ISO 307:2019	Plastics — Polyamides — Determination of viscosity number
ISO 3105:1994	Glass Capillary Kinematic Viscometers - Specifications And Operating Instructions
ISO 604:2002	Plastics — Determination of compressive properties
ISO 4589-1:2017	Plastics — Determination of burning behaviour by oxygen index — Part 1: General requirements
ISO 4589-2:2017	Plastics — Determination of burning behaviour by oxygen index — Part 2: Ambient-temperature test
ASTM D2240	Durometer Hardness- Shore A & D
ASTM D256	Izod Impact
ISO 4589-3:2017	Plastics — Determination of burning behaviour by oxygen index — Part 3: Elevated-temperature test
ISO 8256:2004	Plastics — Determination of tensile-impact strength
IEC 60695-2-2	Fire hazard testing - Part 2: Test methods - Section 2. Needle-flame test
ASTM D648	Deflection Temperature of Plastics Under Flexural Load
ASTM D1525	Vicat Softening Temperature of Plastics
UL Standard 746B	Polymeric Materials, Long-Term Property Evaluation
Additive Manufacturing Methods	
ISO 17296-3:2014	Additive manufacturing — General principles — Part 3: Main characteristics and corresponding test methods
ISO/ASTM 52900:2015	Additive manufacturing — General principles — Terminology
ISO/ASTM CD 52932	Additive manufacturing — Environmental health and safety — Standard test method for determination of particle emission rates from desktop 3D printers using material extrusion

ISO/ASTM WD 52933	Additive manufacturing — Environment, health and safety — Consideration for the reduction of hazardous substances emitted during the operation of the non-industrial ME type 3D printer in workplaces, and corresponding test method

6.6 Release scenarios

Identified release scenarios for the 3D printing sector from the review are described in Table 10. Release rates where these are available from the literature review and industrial partners have been added although for more information, it is recommended to review the tables in section 8. These tables give more information on the nanoforms, matrices used and the testing used. A table is also presented in Annex 2 for the release scenarios and potential exposure routes.

Table 10. 3D printing release scenarios

Process	Activity	Release potential, Key release determinant factors	Release rates
Filament production	Weighing	Potential for release. Key release factors include if manual or automated process, dustiness of powder, particle size	CNTs: No free CNTs above LOD $(2.5 \times 10^{-2}$ wt. %$)$[24]
	Mixing	Potential for release. Key release factors include if manual or automated process, dustiness of powder, particle size	
	Extrusion	Possible potential for release. Key release factor is agglomeration	Polyamide (blank): 44.5 µg/m³ for personal respirable dust; Fast Mobiliity Particle Sizer (FMPS): GM(GSD): 44,839 (1.68) Polyamide and CNT (masterbatch): 46.7 µg/m³ for personal respirable dust; FMPS: GM(GSD): 30,116 (1.34) Polyamide and CNT (powder): 56.1 µg/m³ for personal respirable dust; FMPS: GM(GSD): 23,045 (1.09)
Pre-processing	Powder filling/powder handling	High potential for release. Key release factors include use of metal powders (risk related to exposure/pyrophoricity), cleaning printer heads/nozzles and heating nozzles	CNT in ABS, PLA and PLC: No free CNT on filament surface[28]
	Resin filling		
	Sieving		
AM	Binder jetting	Potential for release of nanoparticles and VOCs during additive manufacture. Key release factors include filament composition, technology used and temperatures	N/A
	Directed energy deposition		N/A
	Material extrusion – includes Fused Filament Fabrication (FFF) and Fused Deposition Modelling (FDM)*		Varies (see Table 24) i.e. CNT/ABS: up to 1010 ultrafine particles per gram printed (diameter <100 nm); 106-108 respirable particles per gram printed (diameter of ~0.5-2 µm)[28] ABS printers had total Ultra Fine Particles (UFP) emission rates of nearly a magnitude higher then lower temperature PLA printers $(1.8-2.0 \times 10(11)$ # min^{-1} versus

Process	Activity	Release potential, Key release determinant factors	Release rates
			1.9-2.0 x 10(10) # min-[1] respectively[29] Release of VOCs in a number of studies
	Material jetting		VOCs (isopropanol, propylene and toluene)[30]
	Powder bed fusion: Includes - Direct Metal Laser Sintering (DMLS), Electron Beam Melting (EBM), Selective Heat Sintering (SHS), Selective Laser Melting (SLM) and Selective Laser Sintering (SLS		ABS[31]: Mean of 0.4 mg/m^3 from DustTrak, 5.2 mg/m^3 for stationary IOM sampler and 9.1 mg/m^3 for personal IOM sampler) Mean particle concentration of 16900 #/cm^3 Metal powders: release of nanoparticles (>300 nm) [32]
	Sheet lamination-includes Ultrasonic Additive Manufacturing (UAM) and Laminated Object Manufacturing (LOM)		N/A
	Vat polymerisation		Dust concentrations: 0.01 and 0.12 mg/m^3 (DustTrack), below LOD (IOM sampler)[31] Mean particle concentration of 8020 #/cm^3 [31] Release of fluorine, acetone and isopropanol[30]
Post-processing	Injection moulding	Potential for release. Key release factors can include feedstock (filament) composition and nanomaterial used	Particle number concentrations from 20,000-26,000 particles/cm^3; also detection of ethylbenzene, styrene, m,p-xylene and o-xylene[30]
	Part cutting		
	Support removal		
	Sandblasting/sanding		Particle concentration[31]: 11,000-15,000 particles/cm^3
	Shot peening		
	Curing		
	Abrasion/polishing		
	Handling of powders and objects		Peak particle concentration measurement of 16,000 p/cm^3 for metal powder printing using IN939[33]
Cleaning and maintenance	Cleaning (including the use of solvents)	High potential for exposure from solvent use. Release factors can also include AM technology used and cleaning process	Dust concentrations: (0.19-0.4 mg/m^3)[30] VOCs detected[31]
	Maintenance	Potential for higher exposure	
End of life	Disposal		

*As categorised at: https://www.lboro.ac.uk/research/amrg/about/

7. Paints Literature Review

7.1 Release scenarios: Human

A number of useful reviews have been published addressing human exposure to nanomaterials across their life cycle. Many of these reviews focused on workplace measurements and occupational exposure scenarios; often grouping release characteristics according to the type of occupational activity[2,34] or by nanomaterial identity[35]. Others have focused on evaluating the release of NFs from nano-enabled products[36,37].

These review articles provide an excellent source of information on human exposure to nanoforms in general, however none has been sector-specific, focusing solely on the paints and coating industry. For this reason, only studies specifically pertinent to paints have been included in this review. This allows a focused assessment at the pool of evidence related to this sector.

A Dutch industrial study in 2010-2011 highlighted workers in painting and coating applications as a high priority for exposure to manufactured nanomaterials[38]. While NFs are the focus of this review, it should be noted that other components of paints have been associated with negative health effects. Occupational exposure of painters was categorised as *carcinogenic to humans (group 1)* by the International Agency for Research on Cancer (IARC) due to the use of solvents, metals and dyes[39]

The reported studies contain both workplace measurements and laboratory simulations, with the latter being more prevalent, particularly during studies on the service life. The following release scenario groupings have been used: synthesis and formulation; service life (paint application, spray painting, dermal contact, and mechanical treatment); end-of-life (sand-blasting).

Synthesis of nano-additives

Paint manufacturers may synthesise their own nano-additives. The SAbyNA interviews as part of the WP6-WP7 joint consultation and questionnaire, indicated that a number of enterprises involved in the paints sector also produce nanoforms, although as nanoforms can have multiple applications, the synthesis process is not necessarily sector-specific. For example, SAbyNA partner NOURYON synthesise colloidal silica. While this is used as an additive in paints, it has multiple other industrial applications in a number of sectors (e.g. ceramic investment casting). It is also the case that paint manufacturers also purchase nanoadditives for use in their formulation processes. Similarly, SAbyNA partner, ALLIOS (paint manufacturer) purchase nano-additives to be added to their formulation.

One study was identified that conducted workplace exposure measurements during iron oxide nanomaterial pigment production for use in paints (Table 11)[5]. Static sampling was conducted in three locations where workers were most frequently positioned (calcination furnace, drying units and control room). As expected, particle concentrations varied with location and time. The median mass concentration in the facility was 0.083 mg/m^3 and a particle number of 66,800 #/cm^3. Over 80% of these particles were found to be under 100 nm in diameter. The study linked these exposure levels to the presence of oxidative stress markers in factory workers. However, they concluded that the current nano-iron oxide levels did not result in systemic effects.

Table 11. Summary of studies investigating release during nanomaterial synthesis

Ref	NF	NF size (nm)	Amount of NF handled	Nature of activity and measurements	Risk Mitigation Measure (RMM)	Release characteristics and findings
Pelclova et al[5]	α-Fe_2O_3 $FeO(OH)$ Fe_3O_4	N/A	N/A	Pigment production (static sampling points included by the calcination furnace, drying unit and control room) (P-TRAK, DustTrak, SMPS, APS)	N/A	Calcination furnace: 86100 #/cm^3, 0.069 mg/m^3 Drying unit: 15900 #/cm^3, 0.136 mg/m^3 Control room: 34100 #/cm^3, 0.243 mg/m^3

7.1.1 Formulation of paints

Measurements carried out in conventional paint factories have shown that exposure to NFs occurs[40]. However, few studies have focused specifically on nano-enabled paint production.

Two studies were identified for the use of TiO_2 in the formulation of paints. Van Broekhuizen *et al.* monitored exposure in a nano-paint manufacturing facility, among other occupational settings[6]. During addition of the solid components they observed no NF emissions linked to the handling of nano-TiO_2. In contrast, NPs were observed on the NanoTracer during addition of other conventional components such as bulk TiO_2. However, Bekker *et al.* during similar powder handling activities with nano-TiO_2 did indicate the release of nano-TiO_2 with exposure concluded as 'possible'[7]. The observed differences in these two studies is likely due to variances in the amount of handled material, risk management measures and process steps.

One study has been identified for the use of MWCNTs in paint formulation. Elemental carbon (EC) measurements during manual weighing and mixing demonstrated respirable and inhalable concentrations were below the NIOSH Recommended Exposure Level (REL) of 1 µg/m^3 (8-h TWA EC of 0.1-0.9 µg/m^3)[8]. Low emissions in terms of carbon was helped by the use of a chemical fume hood to contain any associated releases.

Table 12. Summary of studies investigating release during paint formulation

Ref	NF	NF size (nm)*	Functionality	Formulation	Nature of activity and measurements	RMM	Form of released NF	Release characteristics and findings
Van Broekhuizen et al.[6]	TiO_2	NA	NA	Water-based. Coarse TiO_2, $CaCO_3$, talc and (powdered) additives	Addition of solid powdered components (bulk TiO_2; nano-TiO_2; $CaCO_3$) into agitation vessel. Personal monitoring on workers using NanoTracer.	Exhaust ventilation	NA	No NP emissions linked to nano-TiO_2 handling (mean particle concentration was 1,495 #/cm^3, diameter of 46 nm). Other NP emissions associated with conventional components.
Bekker et al.[7]	TiO_2	100	NA	NA	Dumping powder manually during paint production Nanotracer (PBZ measurements). NanoID (near-field). SEM/EDXS	LEV	NA	Likelihood of exposure was 'presumable'. BG = 10899 #/cm^3 PBZ = 23536 #/cm^3

Ref	NF	NF size (nm)*	Functionality	Formulation	Nature of activity and measurements	RMM	Form of released NF	Release characteristics and findings
	TiO$_2$	50-100	NA	NA	Dumping powder manually during paint production Nanotracer (PBZ measurements). NanoID (near-field). SEM/EDXS	LEV	Pristine; agglomerated and aggregated	Likelihood of exposure was 'possible/not excluded'. BG = 25497 #/cm^3 PBZ = 23671 #/cm^3
Brame et al.[8]	MWCNTs	Width <100 nm; length of several hundred nanometers	Anticorrosive	Contained micron-sized Zn, primer and pigment	Manual weighing and mixing of dry MWCNTs (in fumehood); monitoring dispersion of batch using pneumatic mixer. Elemental carbon, TEM	Fume cupboard, ventilation, lab coat, safety glasses, nitrile gloves	Agglomerated; matrix-embedded	The workplace exposure study provided evidence for overall low exposures, with all respirable samples being below the NIOSH REL for CNTs.

*No information on the amount of NF handles has been provided in the studies

7.1.2 Service life

Paint application (manual application)

Bekker *et al.* carried out a broad-scale exposure study that included measurements during brushing and rolling of a SiO$_2$ coating[7]. While information of the process and measurement strategies were not given in detail, exposure to NOAA was deemed 'unlikely' during 3 separate brushing/rolling activities. Likewise, manual application of a nano-enabled interior wall paint did not release TiO$_2$ NPs[41].

A separate study focused on activities involving an anticorrosive coating containing MWCNTs. Elemental carbon measurements taken during hand painting found that the respirable concentrations of CNT were below the NIOSH REL of 1 µg/m^3; however this was exceeded for the inhalable fraction (1.52-2.29 µg/m^3)[8].

When the other activities performed over two 8-hour shifts were taken into account, exposure was concluded to be low. Jorgensen *et al.* investigated releases during paint drying from interior wall paints during the first week after application. Releases were low, however solvent-borne alkyd paint released higher NP values by a factor of 10^3 than the water-borne acrylic alternatives, but only for the initial 48 hours[9].

Table 13. Summary of studies investigating release during paint application (manual application)

Ref	NF	NF size (nm)	Functionality	Paint formulation	Nature of activity and measurements	RMM	Form of released NF	Release characteristics and findings
Bekker et al.[7]	SiO$_2$	N/A	N/A	N/A	Brushing and rolling Nanotracer (PBZ measurements). NanoID (near-field). SEM/EDXS	No LEV or respirator used	Agglomerated; Aggregated	Measurement 1: BG = 85076 #/cm^3 PBZ = 53793 #/cm^3 Measurement 2: BG =11536 #/cm^3 PBZ = 9075 #/cm^3 Measurement 3: BG = 11853 #/cm^3 PBZ = 7147 #/cm^3
Jørgensen et al.[9]	Carbon black	N/A	Pigment	Water-borne acrylic; Solvent-borne alkyd	Emissions during paint drying measured using FMPS in 6.78 m^3 test chamber for 1-week (23 degrees °C, 50% relative humidity, 0.5h^{-1} air exchange rate).	N/A		Release from water-borne acrylic paints was low. Solvent-borne paint showed the highest concentration (3.2x10^5-1.4x10^6 #/cm^3) sized 9.31 nm.

Ref	NF	NF size (nm)	Functionality	Paint formulation	Nature of activity and measurements	RMM	Form of released NF	Release characteristics and findings
Brame et al.[8]	MWCNTs	width< 100 nm and lengths of several hundred nanometers	Anticorrosive	Contained micron-sized Zn, primer and pigment	Hand painting metal parts with CNT-based primer. Elemental carbon, Transmission Electron Microscopy (TEM)	Room exhaust ventilation, lab coat, safety glasses, nitrile gloves	Agglomerated; matrix-embedded	The workplace exposure study provided evidence for overall low exposures, with all respirable samples being below the NIOSH REL for CNTs.
Svedova et al.[41]	TiO_2	N/A	Photoactive	Water suspension	Coat of paint applied to ceiling area of 20m^2. Sampled using Electrical Low Pressure Impactor (ELPI$^+$)	None.		Before and during paint application, the highest number of particles in the grain-size class of 0.006–0.0175 μm was identified.

Spray painting

During spray application of coatings, exposure is a result of over-spraying which is defined as the fraction of the paint that does not adhere to the desired surface and is rebounded back to into the surrounding air. This can result in inhalation exposure, as well as possible dermal contact. Seven studies have investigated human exposure during spray painting of nano-enabled paints, 2 of which were conducted in real-life scenarios. Epidemiological evidence has shown that adverse health effects can result from occupational exposure in spray painting facilities[42]. While it was unclear in this study if the paints were nano-enabled, SiO_2 particles ranging from 2-20 nm in diameter we identified in the biopsies and pleural effusions of affected workers. However, it appears that the release rates are generally unaffected by the inclusion of NFs in the formulation compared to without the inclusion of NFs i.e. releases can be comparable to non-nanoenabled paints[10].

Golher *et al.* compared a number of domestic/handcraft spray application technologies for their airborne particle releases[10]. This included two types of commercial propellant spray cans and manual gravity spray guns. While particle releases were seen to be dependent on the formulation and spray unit, no systematic differences were observed between the nano-coatings and their non-nano reference coatings. The highest nanoparticulate fractions were seen for the standard spray cans (30-60%), while lowest fractions were observed for the spray gun (10-20%). ZnO and Fe_2O_3 were found to be matrix-embedded and SiO_2 seen in its agglomerated state. Similar results were reported by Cooper *et al.* during spray-application of wood treated with ZnO[11]. Nano-sized ZnO was contained within, or on the surface of larger matrix particles.

Field-studies in industrial settings highlighted spraying activities to represent a high exposure potential. Bekker *et al.* carried out measurements during a number of spray coating activities using nano-SiO_2 in a variety of sizes. Detailed information on the process parameters and measurement strategies were not given, however the study concluded the exposure was 'likely' during these activities. Particle concentration levels ranged between 14,000-800,000 #/cm^3 and filter analysis conducted in the personal breathing zone showed SiO_2 agglomerates/aggregates of 0.5-5 μm. Likewise, Brame *et al.* noted spraying to represent this highest exposure potential in the manufacture, application and testing of CNT coatings[8]. Results from West *et al.* supported these conclusions, reporting respirable TiO_2 concentrations above the NIOSH REL for ultrafine TiO_2 during airless spray painting[13]. Koivisto *et al.* also reported respirable concentrations above the NIOSH REL for TiO_2, with concentrations more than the double of the REL (0.7 mg/m^3 versus the REL of 0.3 mg/m^3) for airless spraying[12].

Whilst none of the literature monitored such activities, the cleaning of spray guns and applicators using nano-enabled paints will also provide a possible critical exposure scenario.

Table 14. Summary of studies investigating release during spray painting

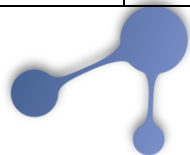| Ref	NF	NF size (nm)	Functionality	Paint formulation	Concentration of NF in polymers	Nature of activity and measurements	RMM	Form of released NF	Release characteristics and findings
Göhler et al.[10]	ZnO	75	N/A	Polyurethane or acrylate (with TiO_2 pigment)	1.3-2.0 wt.%	Three spray applicators - standard spray cans, SprayMax-cans and a manual gravity spray gun - tested within a spray channel (1635 mm long). Sampled with EEPS; FMPS; APS; CPC and SEM	N/A	Matrix-embedded	Release in magnitude of 5×10^8-3×10^{10} particles per gram ejection mass Releases were comparable to non-nano sized reference materials. Emitted particles consisted of matrix droplets where NMs were either as agglomerates and individual particles (ZnO and Fe_2O_3) or as agglomerates (SiO_2).
	Fe_2O_3	115		Polyurethane or acrylate (with TiO_2 pigment)	1.3-2.0 wt.%			Matrix-embedded	
	SiO_2	7		Water-based (with TiO_2 pigment) or organic solvent-based	1.2-1-.3 wt.%			Agglomerated	

Ref	NF	NF size (nm)	Functionality	Paint formulation	Concentration of NF in polymers	Nature of activity and measurements	RMM	Form of released NF	Release characteristics and findings
Bekker et al.[7]	SiO$_2$	Unknown	N/A	N/A	N/A	Spray coating (compressor sprayer)	No Local Exhaust Ventilation (LEV). Outdoor activity	Agglomerated /aggregated	BG = 14552 #/cm^3 PBZ = 16393 #/cm^3
	SiO$_2$	50-100	N/A	N/A	N/A	Spray coating (compressor sprayer)	No LEV. Outdoor activity		BG = 14210 #/cm^3 PBZ = 16468 #/cm^3
	SiO$_2$	20-50	N/A	N/A	N/A	Spray coating (high pressure system) Nanotracer (PBZ measurements). NanoID (near-field). SEM/EDXS	No LEV		BG = 31565 #/cm^3 PBZ = 827861 #/cm^3
Cooper et al.[11]	ZnO	NA	Wood sealant	NA	N/A	Spray conducted in environmentally controlled chamber. Spraying conducted with a Graco Magnum X5 airless paint/coating sprayer (0.1 gallon per minute, 3-4 minutes). 2 coats of paint. (SMPS, OPS SEM, TEM)	Respirator; Tyvek suit	Matrix-embedded	Bimodal particle size distribution with a peak of 6.5x10^4 particles at 187 nm and a second peak of 9,340 particles at 2.16 µm. Total aerosol concentrations of 96 mg/m^3 for area samples and 84 mg/m^3 for personal samples.

Ref	NF	NF size (nm)	Functionality	Paint formulation	Concentration of NF in polymers	Nature of activity and measurements	RMM	Form of released NF	Release characteristics and findings
Koivisto et al.[12]	TiO_2	5.5	Photocatalytic	Aqueous	0.2 wt%	Spraying was performed with an electrostatic spray system. In a 20.3 m^3 test chamber 23°C and 50% relative humidity, 0.5 H^{-1} air exchange rate. 15-150 seconds of spraying (coating rate 23m^2/min) (FMPS, ELPI, SMPS, CPC)	N/A	Agglomerated	The geometric mean particle number emission rate was 1.9×10^{10} s^{-1} and the mean mass emission rate was 381 μgs^{-1} The particle deposition rates were up to 15 h^{-1} for < 1 μm-size
Brame et al.[8]	MWCNTs	width< 100 nm and lengths of several hundred nanometers	Anticorrosive	Contained micron-sized Zn, primer and pigment	N/A	Spraying CNT paint formulation in spray booth Elemental carbon, TEM	Safety glasses, tyvek coveralls, 1/2 face respirator with organic vapour cartridges, nitrile gloves	N/A	Inhalable EC concentrations within spray booth (0.99 $\mu g/m^3$). The background corrected inhalable fraction was 12.31–14.94 $\mu g/m^3$
West et al.[13]	TiO_2	50-75	Photocatalytic	NA	NA	Spraying was performed with an airless sprayer (Graco Magnum X5) at a rate of 0.2 gallons per min. In an 82 m^3 test chamber with 2 air	Respirator, Tyvek suit and gloves	Matrix-embedded; agglomerated	The mean concentration of respirable TiO_2 (0.7 mg/m^3) was more than double the NIOSH REL (0.3 mg/m^3 as a 10-h TWA)

Ref	NF	NF size (nm)	Functionality	Paint formulation	Concentration of NF in polymers	Nature of activity and measurements	RMM	Form of released NF	Release characteristics and findings
						changes per hour. Spraying for 12-15 min. (SMPS, OPS)			Paint globules of 0.5 to >10um, with TiO_2 NOAA of 100-500nm.

Dermal contact

Three studies were identified that investigated the dermal transfer of nanoparticles from coated surfaces. This is an important exposure pathway through human skin contact, which can also lead to inadvertent ingestion. Of the identified studies, it was clear that NPs were released through dermal contact, particularly when the painted surface was aged either through weathering or mechanical processes.

Mackevica *et al.* employed a dermal wiping test to investigate CuO NP transfer from painted wooden blocks[14]. They demonstrated that CuO NPs were removed from wiping of the surface, and this was most significant after wear via sanding (0.885 and 2.5 ng/cm^2 without and with sanding, respectively). The released particles were sized at 79 nm (sanding) and 84 nm (no sanding), however agglomerates of up to 200 nm were observed by TEM.

Clar and colleagues noted that highest release was seen during the initial dermal contact events[43-44]. During continued wiping over a six-month period the amount of release gradually decreased to a steady state (after 2-6 contact events). Logically, the number of contact events governed material release. The application matrix was also seen to play an important role: water dispersion of ZnO or CeO$_2$ released greater quantities than the stain-based applications (CeO$_2$: 66 vs 36 mg/m^2 [44]); (ZnO[43]: 180 65 mg/m^2).

In all the reported studies, no free single NPs were observed, instead the studies found the NPs in agglomerates or aggregated with dislodged substrate material.

Table 15. Summary of studies investigate release during dermal contact simulation events

Ref	NF	NF size (nm)	Functionality	Formulation	Concentration of NF in polymers	Substrate	Amount applied	Nature of test	Form of released NF	Release characteristics and findings
Release from dermal contact										
Clar et al.[44]	CeO$_2$	10	UV inhibitor on outdoor surfaces	Milli-Q water or water-based wood stain	6 wt%	Micronized copper azole-treated lumber (MCA) Composite decking	110 mg	Outdoor weathering for 6-months during which time dermal contact was simulated using a modified version of the CPSC wipe method.	Aggregated; transformed	Application matrix affected release characteristics. Aqueous applications releasing greater quantities of CeO$_2$ than stain based applications, 66±12 mg/m^2 and 36±7 mg/m^2, respectively. Conversion of CeO$_2$ to a Ce(III) species in water applications.
Clar et al.[43]	ZnO	28 ± 23	UV protection	Milli-Q water or water-based wood stain	1.7%	Micronized copper azole-treated lumber (MCA) Composite decking	295 mg 187 mg	Simulated dermal contact using CPSC wipe method: on weathered (outdoor, indoor and pre-weathered) samples.	Aggregated; transformed	Application matrix affected release characteristics. 2.5–3.6% (water-based) and 0.2–1% for (stain-based) of initially applied Zn released through dermal contact events.

Ref	NF	NF size (nm)	Functionality	Formulation	Concentration of NF in polymers	Substrate	Amount applied	Nature of test	Form of released NF	Release characteristics and findings
Release from dermal contact of sanded articles										
Mackevica et al[14]	CuO	30-50	Antifouling	Acrylic	1.5 %	Wood	5.7 ± 0.2 mg CuO per wooden block	Dermal wiping test following NIOSH guideline Elements on Wipes: Method 9102, with minor modifications. Characterisation with spICP Inductively Coupled Plasma)-MS. Manual sanding with 180 grit paper, three times (pressure of approximately 500 g/cm^3)	Agglomerated	The total mass of CuO released after three wiping events was 0.9 and 2.5 ng/ cm^2 for non-sanded and sanded paint, respectively, which is less than 0.01% of the CuO amount originally present in the painted surface per cm^2.

Mechanical treatment (sanding and sawing)

Sanding is a mechanical process where an abrasive material is used upon the surface of a material, matrix or product. The extent of release is generally related to the abrasive material used, contact force/pressure applied and area of contact. It is often conducted during finishing, polishing, renovation or removal of these products.

The reviewed literature shows that sanding gives rise to a considerable number of nanoparticles[45,46]. However it appears that the release rates are generally unaffected by the inclusion of NFs in the matrix i.e. sanding of coatings containing nano-additives gave similar total particles concentrations as shown for ZnO, Fe_2O_3 [11, 22,47]; and TiO_2, SiO_2, carbon black[13,15,45].

Koponen *et al.* also noted that the size distributions of the emitted dusts were not significantly affected by the addition of nano-additives in comparison to their reference products [48,49]. The study evaluated dust generated during sanding of 13 different coatings including paints, fillers and a lacquer with three different nano-additives (TiO_2, SiO_2 and carbon black). The average total number concentration in the aerosol collection chamber was 2.1×10^5 #/cm^3 and was dominated by particles in the 100-300 nm size range. This average total particle concentration was consistent with that reported by Gomez *et al*[15] for TiO_2 (2.06×10^5 - 2.57×10^5 #/cm^3). Despite this, Koponen *et al.* found no clear connection between the engineered NM and emission size distribution or total concentration. The same nano-enabled paints were further studied by Saber *et al.* who noted that sanding of the lacquer appeared to generate more particles in the nano-size range than the paints and fillers[50]. In almost all cases releases were matrix-embedded (Table 16). Gohler *et al.* and Gomez *et al.* specifically indicated that no free NPs were detected; instead NPs remained in the matrix-fragments. However, Nored *et al.* noted that while TiO_2 particles were agglomerated and encapsulated or on the surface on paint particles, these were still nano-sized (< 100 nm). Saber *et al.* noted pigment particles were generally liberated from the matrix as free particles, especially when sanding PVA-based paints. However they went on to demonstrate no inflammations, oxidative stress, or genotoxic effects of nanoparticles from the resulting paint dust.

The grit size of the sandpaper was found to be an influencing factor during sanding. Finer sandpaper grits resulted in increased particle number concentrations (147,000 ± 1,500, 235,000± 2,200 and 278,000 ± 2,300 #/cm^3 for grit sizes 40, 120 and 220, respectively)[46]. This make sense due to the finer sizes being able to dislocate small pieces of paint materials. It was also shown that there was no significant difference between surfaces coated with multiple paint layers (2-8 layers varied from 178,000 to 200,000 #/cm^3). It should be noted that in a number of studies the sanding machine contributed its own emission particles and therefore need to be considered when interpreting results[48].

Alongside the laboratory sanding tests, one field study was identified that studied mechanical sawing of nano-SiO_2 coated synthetic sheets[7]. Exposure was deemed 'unlikely', however process generated NPs were detected.

Table 16. Summary of studies investigating release from mechanical treatment

Ref	NF	NF size (nm)	Functionality	Paint formulation	Concentration of NF in polymers	Substrate	Amount applied	Nature of test	Form of released NF	Release characteristics and findings
Release from sanding										
Koponen et al.[48]	TiO$_2$ Carbon black	17 95	N/A	N/A N/A	N/A N/A	Medium Density Fibreboard (MDF) plates	N/A	Sanding using commercial handheld orbital sander (Metabo Model FSR 200 Intec). 240 grit size. Sanding for 1-2 minutes.	N/A	Dust emissions consisted of five size modes; three modes under 1 μm and two modes around 1 and 2 μm. Addition of NP caused only minor changes in the geometric mean diameters, but number concentrations varied in the different size modes. The sander was a main source of particles smaller than 50 nm.

Ref	NF	NF size (nm)	Functionality	Paint formulation	Concentration of NF in polymers	Substrate	Amount applied	Nature of test	Form of released NF	Release characteristics and findings
Göhler et al.[47]	ZnO Fe_2O_3	75% <100; 25% <100	Used in industrial and domestic applications.	Polyurethane; White-pigmented architectural coating	N/A N/A	Steel panel Fibre cement plate	Coating thickness: 41 µm 130-150 µm	Miniature sander (Model Dremel 400 Series Digital): one abrasion wheel that rotates with an adjustable peripheral speed in the range of 1.8-24 m/s. Contact force of 0.2-1 N, Contact pressure of 10,000-50,000 Pa	Matrix-embedded	Results show a considerable generation of NPs during the sanding process. Cumulative particle release from a 13 cm^2 sanding area varied between 2.4×10^6 to 2.5×10^8. No significant difference could be observed between coatings containing and not containing NP additives.
Koponen et al.[45]	TiO_2 SiO_2 Carbon black	17; <100; 200; 220 <50; 7 95		Polyvinyl acetate; Acryl binder Acryl binder; lacquer Acryl binder	2.5-33 wt%	Wooden-plates	N/A	Sanding using commercial handheld orbital sander (Metabo Model FSR 200 Intec). 22000 rpm, 240 grit size. Sanding for 1-2 minutes.	Matrix-embedded	Sanding of both reference and NM containing coatings released high amounts of airborne particles from < 100 nm to µm-size in diameter (5 size modes independent of product). Size-distributions were only affected to a minor degree by presence of NM and concentrations varied in unpredictable manner.

Ref	NF	NF size (nm)	Functionality	Paint formulation	Concentration of NF in polymers	Substrate	Amount applied	Nature of test	Form of released NF	Release characteristics and findings
Saber et al.[50]	TiO$_2$	17; <100; 200; 220		Polyvinyl acetate; Acryl binder	2.5-33 wt%	Wooden-plates	N/A	Sanding using commercial handheld orbital sander (Metabo Model FSR 200 Intec). 22000 rpm, 240 grit size. Sanding for 1-2 minutes.	Matrix-embedded; Mixed aggregates	No systematic difference was found in the particle number size distribution between dust generated by sanding NP-containing paint and conventional paint. The most abundant product-related sanding dust particles were in a 100–300 nm and 1–2 mm size modes.
	SiO$_2$	<50; 7		Acryl binder; lacquer					Pigment (TiO$_2$, kaolinite) was liberated from the matrix	
	Carbon black	95		Acryl binder						Sanding of the lacquer appeared to generate a much larger number of nm-size particles than the paints and fillers.
	Kaolin	30		PVA						

Ref	NF	NF size (nm)	Functionality	Paint formulation	Concentration of NF in polymers	Substrate	Amount applied	Nature of test	Form of released NF	Release characteristics and findings
Gomez et al.[15]	TiO$_2$ (Nano Amor; NaBond)	Reference 50 and 80 80	White pigment	Polyvinyl acetate Water, propylene, glycol, Uradil AZ XP 601Z44, and others. Water, propylene glycol, Uradil AZ XP 601Z44, and others.	0 36% (Nano Amor and NaBond) 36% (NaBond)	Wooden boards	N/A	Sanding using commercial handheld orbital sander (Metabo FSR200). 22 000 l min−1, paper with grit size of 120. Sanding for 30s.	Matrix-embedded aggregates	2.06x10^5 #/cm (ELPI) 2.50x10^5 #/cm (ELPI) 2.57x10^5 #/cm (ELPI) Similar Particle Size Distribution (PSD) for all paints. Sanding of the paints produced airborne particles mainly > 1µm in size. Free TiO$_2$ NPs were not observed.
Cooper et al.[11]	ZnO	N/A	Wood sealant	N/A	N/A	Plytanium® boards	N/A	Sanding using DeWalt 5-inch random orbital sander (100-grit) for 8-10 minutes	Matrix-embedded	No statistically significant difference in NP release from sanding treated and untreated wood

Ref	NF	NF size (nm)	Functionality	Paint formulation	Concentration of NF in polymers	Substrate	Amount applied	Nature of test	Form of released NF	Release characteristics and findings
Nored et al.[46]	TiO$_2$	N/A	N/A	Latex paint: water (49.6% w/w), non-volatile species (49.4% w/w), organic volatiles (0.9% w/w) and 2-amino-2-methyl-1-propanol (0.2% w/w). It also included crystalline silica (0.22% w/w) and cristobalite (0.11% w/w)	3.2 wt %	Wood panels	N/A	Sanding using manual using orbital sander (BDERO600 2.4 Amp 5 inches (12.7 cm)). The sandpaper grits were 40, 120 and 220. Sanding for 5 minutes	Matrix-embedded; agglomerated	Higher particle concentrations for paint dusts than wood dust (from sanding of bare wooden panel). The nano-size particle number concentrations increased for finer sandpaper grits and more paint coatings; albeit lower particle mass concentrations were estimated.

Ref	NF	NF size (nm)	Functionality	Paint formulation	Concentration of NF in polymers	Substrate	Amount applied	Nature of test	Form of released NF	Release characteristics and findings
Bekker et al.[7]	TiO$_2$	50-75	Photocatalytic	N/A	N/A	Plytanium® boards	N/A	Sanding was performed with a random orbital sander operating at 12,000 rpm (100-grit sanding paper). 10 minutes.	Matrix-embedded	Peak concentrations in the breathing zone were 2.9 mg/m^3 for total dust and 1.2 mg/m^3 for respirable dust. Exposures to respirable TiO$_2$ were below detectable limits for all sanding trials m^3 (<0.065 mg/m^3). Particle size distributions during sanding were mostly unaffected by whether the boards were painted or unpainted.
Release from sawing										
Bekker et al.[7]	SiO$_2$	Unknown	Surface protection/coating	N/A	N/A	Synthetic sheets	N/A	Manual sawing of coated synthetic sheets measured with Nanotracer (PBZ measurements). NanoID (near-field), SEM/EDXS. No respirator worn.	N/A	Background concentration of 13081 #/cm^3; PBZ of 15827 #/cm^3 Likelihood of exposure was 'unlikely'

7.1.3 End-of-life

Sandblasting

A single study investigating the removal of nano-enabled paint *via* sandblasting was identified. This study aimed to demonstrate a protocol to detect and quantify free CNTs using UV-vis spectroscopy; sandblasting of a CNT-enabled paint was one of multiple case studies included in the assessment[24]. The protocol involved sandblasting a coated steel panel for a duration of 30-45 seconds, and collecting the removed paint debris for subsequent UV-vis analysis. No free CNT was detected above the limit of detection (1.3 x 10^{-4} wt %). This aligns with that reported by Brame *et al.* above, who saw no free MWCNT release upon Taber abrasion of a weathered-paint [8].

Table 17. Summary of studies investigating release form sandblasting

Ref	NF	NF size (nm)	Functionality	Paint formulation	Concentration of NF in polymers	Substrate	Amount applied	Nature of test	Release characteristics and findings
Anas et al.[24]	CNT	NA	Anticorrosive	N/A	N/A	Steel	N/A	Simulated weathering according to ISO 4892. Econoline sandblasting cabinet; 80 grit media, 90-100 psi, through 1/8" spray gun bore with nozzle, air flow rate of 19-21 cubic feet per minute, and abrasive flow at 110-120 lb/hr. Duration of 30-45 seconds.	When CNT-based anticorrosive paint is removed via sandblasting after its useful lifetime, no free CNTs are present above the detection limit of 1.3 x 10^{-4} wt. %.

7.2 Release scenarios: Environment

Evaluation of environmental release is complex due to the large number of diffusive emission pathways over the life cycle of the engineered nanomaterial and nano-enabled product. For instance, releases can be associated with NF production, their incorporation into nano-enabled products, use of these products and eventual disposal and waste treatment. Alongside this, quantification of nanomaterials in the environment can be difficult due to lack of characterisation techniques and methods to distinguish engineered NFs from background particles[51]. As has been highlighted in a number of the reviewed studies, released materials are often significantly different from their pristine form, or their form inside the product matrix.

A comprehensive review by Gottschalk and Nowack summarised the available information on NF environmental release and the applicability of analytical techniques, experimental methods and models to investigate this[51]. Alongside this, Mitrano *et al.* reviewed nanomaterial aging and transformation through the life-cycle of nano-enabled products to better understand their potential exposure in consumer and environment settings[52]. While neither of these reviews are specific to the paints industry, they provide a useful background and context to the discussion on environmental release of NMs from nano-enabled products.

The reported studies are primarily laboratory simulations and standardised tests. The following release scenario groupings have been used: synthesis and formulation; service life (weathering, abrasion); end-of-life (leaching incineration). In addition, a section on modelling of environmental release is included, as significant work has been carried out in this area.

7.2.1 Synthesis and formulation

No relevant studies were identified that investigate environmental releases from nanomaterial synthesis (specifically for use in nano-enabled paints). However it was noted by Gottschalk *et al.* that this can be difficult to quantify[51]. Most studies carried out in production or occupational settings are performed primarily to determine worker exposure. While useful, the collected data cannot be used directly to quantify airborne release to the environmental as information on parameters such as total air volume, air exchange rates and filtration systems is not available. No relevant studies were also identified that investigated environmental releases from paint formulation.

7.2.2 Service life

Release from weathering

Release from weathering of articles painted with nano-enabled paints is one of the most studied release scenarios in the paints sector. Weathering is a process that takes place outdoors due to a combination of light irradiation, wind, rainfall and temperature fluctuations. Of the six weathering studies identified for nano-enabled paints, three employed natural outdoor weathering conditions; three were carried out in artificial weather systems; and one study made a comparison between these two methods (Table 18).

In artificial weathering experiments climate chambers such as a Suntest XLS+ [8,21] or QPANEL[25] are used to provide the desired test conditions. A number of parameters are reported including UV dose (in MJ/m^2), UV wavelength, condensation, water spraying, and number of wet/dry cycles, freeze-thaw cycles and temperature. Natural conditions provide less control however they allow real-world scenarios to be studied. In these instances, weathering conditions are recorded as they occur including the number of precipitation events

(rain/snow), volume of precipitation and seasonal variations. In some instances, simulated parameters are correlated to real-world conditions, as was done by Scifo *et al.*, noting that their tests corresponded to outdoor weathering of 4 months, 1 year, and 3 years in the south of France[21].

Kaegi *et al.* first reported the release of TiO_2 nanoparticles from new and aged facades, highlighting a release pathway into the aquatic environment from the nano-fraction of white pigment[18]. Released TiO_2 particles were in the range of 20-300 nm with the majority being matrix-embedded. This was supported by results from Azimzada *et al.*, who demonstrated that both natural and artificial weathering caused TiO_2 NPs sized 20-60 nm to leach from painted surfaces, this time utilising a nano-enabled paint (not TiO_2 pigment). The strongest release was associated with wet and cold conditions, particularly when freeze-thaw occurred. Despite this, the overall release of TiO_2 can be concluded as low. Release fractions, expressed as a percentage of the initial amount of NP applied to surface, were 0.001%[16], 0.007%[17] and <1%[18]; albeit using a variety of test conditions and durations.

Ag NPs demonstrated a much higher release, particularly in the initial water-contact events[19]. 80% of the released Ag occurred in the first 8 rain events; with a loss of about 30% of the initially applied Ag. Released particles were <15 nm and attached to the organic binder, however the authors also suggested some transformation from Ag to Ag_2S in the runoff water. This is contrary to that reported by Künniger *et al.* who noted significantly lower releases of Ag in the run-off water (<1% of the initially applied Ag[20]).

CeO_2 was released in both particulate and dissolved forms, with evidence of reductive dissolution (Ce^{IV} to Ce^{III}) during weathering. Incorporation of CeO_2 into the acrylic matrix significantly modified the weathering behaviour, promoting degradation of the stain under UV radiation. SiO_2 was found mostly in the dissolved form after weathering, with 2.3% of the initial quantity being released [53].

Release from abrasion

Alongside weathering, abrasion tests can be used to simulate paint aging during its service life. In contrast to sanding (which has been discussed above under exposure to humans in section 7.1.2), abrasion is a slow, low energy process. Such tests are used to mimic the friction that occurs between the NF matrix and another surface at stress levels applied in a domestic setting, for example during consumer use[54]. In relation to nano-enabled paints, this could represent scenarios where the paint is subject to wear and tear (for example chippings) and environmental factors, such as sand and dirt.
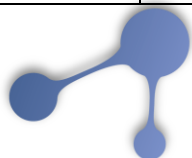
Golanski *et al.* noted low release from both wet and dry abrasion tests when TiO_2 was included in the paint formulation. Releases were solely matrix-embedded with no free TiO_2 particles detected in either dry or wet tests[23]. However, release of free TiO_2 from abrasion was found to be weathering dependent[8,54,55,56].

The formulation of the paint is important. When Morgeneyer *et al.* compared two nano-enabled paints (one consisted of 20 nm sized primary paints, with the other consisting of 7 nm sized particles), only one was shown to be release free TiO_2 NPs[55]. This was attributed to compositional differences, identifying ZnO (which was measured in the paint that emitted TiO_2) as a cause of greater fragility in paints (not indicated if this is in general).
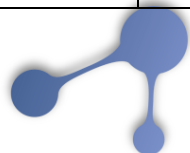
For nano-SiO_2, inclusion in paint formulations was found to improve resistance to abrasion. Fiorentino *et al.* saw a reduction in particle concentrations from 2570 to 1210 $\#/cm^3$ (before weathering) and 5420 to 2600 $\#/cm^3$ (after weathering) upon SiO_2 inclusion. However, free pristine SiO_2 was detected in the releases. This was due to the chemical nature of the matrix; the acrylic copolymer was found to degrade more quickly than styrene-acrylate under UV exposure resulting in a release 2.7 times higher. Interestingly, the inclusion of pigment TiO_2 was found to reduce this release (30,000 to 1200 particles/cm^3) and prevented emission of pristine NPs. This was due to its ability to absorb and reflect light protecting the acrylic copolymer during UV exposure. With less degradation only matrix fragments containing SiO_2 could be observed.

Table 18. Summary of studies investigating release during weathering and abrasion

Ref	NF	NF size (nm)	Functionality	Paint formulation / components	Concentration of NF in polymers	Substrate	Amount of applied	Nature of test	Form of released NF	Release characteristics and findings
Release from weathering										
Kaegi et al.[18]	TiO$_2$	50-200	White pigment	N/A	N/A	New and aged facade panels (1.3 m^2)	NA	Natural outdoor weathering	Coated in organic binder (20-200 nm)	Ti concentration in the runoff of the new and aged facade panels were 600 µg/Land approximately 350 µg/L
Kaegi et al.[19]	Ag	<15	Antimicrobial	Acrylic binder	6.2 mg/kg	Facade panel (0.8 x 1.75 m)	152 g/m^2 of dry paint	Natural outdoor weathering	Coated in organic binder	After two months and eight rain events, >80 % of the total Ag release was released. The total Ag release was 0.5 mg/m^2 which corresponds to a loss of about 30% of the initially applied Ag. The Ag NMs were attached to the binder. Ionic release was not studied. Pigment TiO$_2$ was released 25,000 mg/m^2

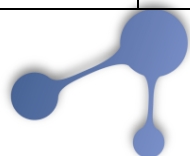| Ref	NF	NF size (nm)	Functionality	Paint formulation / components	Concentration of NF in polymers	Substrate	Amount of applied	Nature of test	Form of released NF	Release characteristics and findings
										which was <1% from initial concentration.
Al-Kattan et al.[17]	TiO_2	20-80	Photocatalytic	Aqueous dispersion with polyacrylate	5 wt %	Fibre cement panels (195 x 75 cm)	N/A	(UV, PE) ETAG 004 (EOTA, 2000)	Matrix-embedded; agglomerated (90-200 nm)	The actual release of Ti over the 113 weathering cycles was only 0.007% (24.5 mg/m^2) of the total Ti, indicating that TiO_2 was strongly bound in the paint. Type of water did not influence the release but type of substrate did.
Künniger et al.[20]	Ag		Antimicrobial	Hydrolysed silane Oily alkyd resin	46 mg/kg 2 mg/kg	Wooden facades	N/A	Natural outdoor weathering (1 year)	Not observed.	Total Ag release: HySilane = 15.7 µg; alkyd resin = 1.7 µg. In both cases this is <1% of the initial coating. No Ag NPs observed in run-off and less the 2% was detected in its ionic form.
Al-Kattan et al.[53]	SiO_2	12	N/A	Aqueous dispersion with polyacrylate	3 wt %	Fibre cement panels (195 x 75 cm)	N/A	(UV, PE) ETAG 004 (EOTA, 2000)	Matrix-embedded; agglomerated (75% >100 nm)	Release was low, about 2% of the SiO_2 contained in the paint over the duration of the study. With a long contact time between paint and water,

Ref	NF	NF size (nm)	Functionality	Paint formulation / components	Concentration of NF in polymers	Substrate	Amount of applied	Nature of test	Form of released NF	Release characteristics and findings
										dissolution of Si is an important process.
Scifo et al.[21]	CeO_2	N/A	Wood-protection	Acrylic stain	4.5 wt %	Larch block	1.5-1.8 mg	Simulated weathering (UV, PE) NF EN 927-6	Transformed	Total Ce release was between 2.8 ± 0.3 - 6.0 ± 2.4 mg/m^2, corresponding to 0.16-0.5 wt% of the initial Ce mass. Release was a consequence of photo-degradation of the stain. Reductive dissolution of CeO_2 (Ce^{IV} to Ce^{III})
Azimzada et al.[16]	TiO_2	131	UV protection and self-cleaning	Water-based acrylic paint	5 wt % i.e. $6.8 \pm 0.1 \times 1015$ NPs per kg-paint	Oak panel (8.4 cm)	400 ± 40 g/m^2 of dry paint	Natural and simulated weathering (UV, PE)	N/A	Natural and simulated weathering indicated TiO_2 release from painted surfaces. Higher leaching in wet and cold conditions.
Release from abrasion										
Vorbau et al.[22]	ZnO	20-700	N/A	Two-pack polyurethane; UV curable clearcoat; White pigmented architectural coating	2.4 wt% 0.9 wt% 2 wt%	fiber board plate; steel panel; fiber cement plate	N/A	Taber abraser 5131 with CS-17 abrasion rolls with 2.5 N normal forces. Three times	Matrix-embedded	Mass loss depends on substrate and type of coating. No significant release observed in particle concentration <100 nm

Ref	NF	NF size (nm)	Functionality	Paint formulation / components	Concentration of NF in polymers	Substrate	Amount of applied	Nature of test	Form of released NF	Release characteristics and findings
								100 revolutions at 60 rpm.		
Golanski et al.[23]	TiO_2	~30	N/A	styrene-acrylic	NA	PVC	N/A	Dry: Taber abraser 5131. (0.15-1 kg; 200-100 cycles) EN ISO 7784-1 (and -2) Wet: Elcometer 1720 abraser (37 cycles/min, 200 cycles). NF ISO 11 998	Matrix-embedded	Standard abrasion conditions in dry and wet environments indicated low release with no free NP present. Released fragments larger than 100 nm.
Shandilya et al.[54]	TiO_2 TiO_2	8 40	Photocatalytic	Water-based	1 vol% 1.1 vol%	Brick	2-4 coatings	Taber abraser 5750 (76 mm, 60 cycles/min, 600 cycles, 10 min).	Matrix-embedded	Coating ability to resist abrasion has significant contribution on the release. Abrasion released airborne copolymer matrix particles embedded with TiO_2 NM.
Release from abrasion of weathered articles										
Fiorentino et al.[57]	SiO_2	19	Rheological properties	Styrene-acrylic or acrylic	13.5 wt%	Wood	0.4 kg/m²	Prior UV exposure was conducted according	Pristine; agglomerated; matrix-embedded.	Addition of SiO_2 reduced number of NPs released during abrasion, before and

Ref	NF	NF size (nm)	Functionality	Paint formulation / components	Concentration of NF in polymers	Substrate	Amount of applied	Nature of test	Form of released NF	Release characteristics and findings
								to ISO 16474-3:2013

Taber Abraser 5131 used conforming to standard ISO 7784-2 (ISO 2006). | | after weathering by a factor of 2.

When pigment TiO_2 was added to the paint formula free SiO_2 particles were not detected. |
| Shandiya et al.[54] | TiO_2 | <8 | Photocatalytic | Poly(methyl methacrylate) | 1.1 wt% | Brick | 4 coatings of 80µm thickness | Simulated weathering according to ISO 16474-1:2012.

Taber abraser 5750 (75 mm, 60 cycles/min, 10 min duration). | Pristine; Matrix-embedded (short weathering periods) | Increased particle release from abrasion tests with increased weathering duration. |
| Truffier-Boutry et al.[56] | TiO_2 | 5 | Photocatalytic | Acrylic-based binder | 2.5 wt% | Aluminium | N/A | Simulated weathering ISO 16474-3:2013

Taber abraser (500g, 100 cycles, 60 | Pristine | Weathered paint released more particles than the non-weathered; these were mostly NPs smaller than 100nm.

Observed degradation of the |

Ref	NF	NF size (nm)	Functionality	Paint formulation / components	Concentration of NF in polymers	Substrate	Amount of applied	Nature of test	Form of released NF	Release characteristics and findings
								rpm) ISO 7784-2		polymer matrix upon weathering (ascribed to the photocatalytic effect of the TiO2 NPs) linked to the emission of high levels of VOCs
Morgeneyer et al.[55]	TiO$_2$	20 7	Photocatalytic	N/A	N/A	Brick	2 coatings	Simulated weathering according to ISO 16474-1:2014. Taber abraser 5750 (75 mm, 60 cycles/min, 10 min duration).	None. Pristine; agglomerates	No free NP/NOAA emissions observed during abrasion before or after weathering on paint with 20 nm TiO$_2$ additive. Free NP/NOAA emission during abrasion after weathering for P2 (appearance of a peak at 21nm and 44nm on SMPS). The difference in emissivity between paints probably related to the great difference in their chemical formulation.
Brame et al.[8]	MWCNTs	Width < 100 nm and lengths of several	Anticorrosive	Contained micron-sized Zn, primer and pigment	N/A	N/A	N/A	Simulated weathering (Atlas Suntest XLS+, simulated continuous	Matrix-embedded	UV weathering prior to abrasion testing increased the nano-size fraction of released material, and the number of MWCNTs

Ref	NF	NF size (nm)	Functionality	Paint formulation / components	Concentration of NF in polymers	Substrate	Amount of applied	Nature of test	Form of released NF	Release characteristics and findings
		hundred nm's						sunlight exposure with a daylight filter (300 –400 nm) for 4 weeks (672 h), with a total dose of 145 MJ/m^2 Custom Taber abrasion process		protruding from the matrix, but did not produce identifiable individual MWCNTs. The increase of nano-size material during weathering is likely due to degradation of the polymer matrix due to UV-exposure.

7.2.3 End-of-life

Literature on the end-of-life processes was limited, partly because the end-of-life of a paint can be extremely varied [58]. For example, in some instances paints will be removed from the surface – through sanding, scraping or sandblasting – to form a paint debris prior to disposal. In other cases, paints are disposed of alongside the material or article they were applied to (e.g. wood, plasterboard, brickwork and machinery). This can lead to a variety of disposal pathways including landfill, incineration and recycling.

Moreover, it is particularly important at later stages in the life-cycle to understand the chemical complexity of released particles. The environmental fate and transport of pristine particles will be different that those which are transformed or matrix-embedded. This has been discussed by Adam *et al.* who systematically assessed the forms in which nanomaterials were released in their life cycle[59].

Leaching

Leaching experiments are used to investigate the release of NPs during prolonged exposure to water. These tests allow investigation of the release of NPs from spent paint debris or discarded painted articles/surfaces, and are particularly relevant for disposal to landfill.

Seven studies on nano-enabled paints were identified. Zuin *et al.* investigated leaching of TiO_2, Ag and SiO_2 from weathered (and abraded) fibre cement panels (according to ISO 11507:2007 and ISO 7784-2:2006, respectively)[25]. Very low concentrations of Ag (detection limit) and Ti (0.00015 wt%) were identified in the leachate; Ti concentrations were 2 orders of magnitude lower than that reported in the weathering studies discussed above[18]. For SiO_2, the cumulative Si loss was about 1.8 wt% and it was present mainly in the form of agglomerates with other particles. Utilising this SiO_2-enabled paint, Zuin and colleagues went on to study the effects of the paint formulation on SiO_2 release[60]. Pigment volume concentration (PVC) was shown to be crucial factor, with higher releases (1.7%) correlated to higher PVC values. Likewise, increasing binder concentrations and less calcite filler lowered release rates (0.35%). In all cases, leached SiO_2 NPs were present as agglomerates. TiO_2 was found to be released as matrix-embedded fragments from milled paint debris exposed to UV[61]. The study demonstrated the difference between the released form and the pristine nano-TiO_2, indicating significant differences in stability in media of different pH and ionic composition. As has been shown by others, prior UV exposure weakened the organic matrix[54,56]. The environmental impact from nano-coatings used in the automotive industry has also been investigated[62]. Testing of 3 nano-pigments (diketopyrrolopyrrole (DPP), Cu-phthalocyanine and iron (III) oxide) did not show significant differences in release behaviour during leaching (0.01-0.06 mg/MJ for all samples). Instead, the polymer matrix was determined as the influential factor.

The above studies were performed using distilled or milli-Q grade water (with the exception of Zuin *et al*), however environmental conditions differ with respect to pH, ionic strength and oxygen content. Adeleye and colleagues considered this, investigating the effect of water salinity on Cu_2O leaching from antifouling paints[26]. Dissolved and particulate Cu species were observed; Cu_2O particles transformed into CuO, while dissolved Cu precipitated as $Cu(OH)_2$ and $CuCl_2$. Release rates increased with increasing salinity and paint drying time. The effect of the substrate was also clearly shown, with higher Cu release observed for oak (1.76%) than aluminium panels (0.21%). In relation to disposal via landfill, the NanoHOUSE project combined their leaching tests with geomembrane lining systems used in typical landfill conditions to prevent contaminants entering the groundwater[27]. These were shown to effectively contain SiO_2- and TiO_2-containing leachates, blocking this as a potential release pathway.

Incineration

One study that investigated the incineration of nano-enabled paint debris was identified[58]. Lab-scale incineration of solid paint waste was conducted at 950°C in an oxidizing atmosphere and the emitted fumes, airborne particulate matter and residue ashes were analysed by gravimetric analysis, ion chromatography ICP-OES (Inductively Coupled Plasma – Optical Emission Spectroscopy) and SEM. No TiO_2 NP release was observed; instead Ti was found to attach to the surfaces of the ash resides. Further analysis by X-ray powder diffraction highlighted that the TiO_2 particles were transformed during incineration to from calcium titanate ($CaTiO_3$), likely due to reaction with the calcium carbonate and talc fillers. However, this was not considered representative of all nano-based paints due to variations in constituents and type of paint. This paper highlighted the low volatilisation of TiO_2 during incineration and indicates that disposal of the solid residues (ashes) is likely the main release scenario for TiO_2 during this processes.
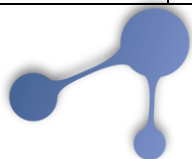
Table 19. Summary of studies investigating release during incineration

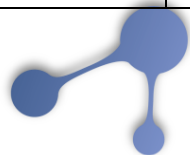| Ref	NF	NF size (nm)	Functionality	Paint formulation	Concentration of NF in paint	Nature of test	Form of released NF	Release characteristics and findings
Release from incineration								
Massari et al.[58]	TiO_2	15	Photocatalytic	Styrene–acrylic polymer	3 wt%	Paint debris (scrapped off plastic panels)	Transformed to $CaTiO_3$	Did not observe a release of TiO_2 nanoparticles into the atmosphere; Ti was attached to the surface of the ash residues.

Table 20. Summary of studies investigating release from leaching experiments

Ref	NF	NF size (nm)	Functionality	Paint formulation	Concentration of NF in paint	Substrate	Amount applied	Nature of test	Form of released NF	Release characteristics and findings
Release from leaching										
Zuin et al.[60]	SiO$_2$	12	Enhance mechanical properties	Styrene-acrylic or acrylic	13.5% of SiO$_2$ suspension of 35 wt %	Polyvinyl chloride panels.	300g of paint debris	Leaching of milled paint debris (EN ISO 12457–3:2002) in deionised water	Agglomerates; matrix-embedded; few single SiO$_2$ particles in 2 of the samples.	Greater release of Si (1.7% of the SiO$_2$ NPs in the paint) for paint formulated with higher PVC value (63%), suggesting that the PVC is a crucial factor for release. A paint sample with the higher amount of binder and less calcite filler exhibited a lower release of Si among the paints with a low PVC value (35%), and no SiO$_2$ particles were detected in leachates

Ref	NF	NF size (nm)	Functionality	Paint formulation	Concentration of NF in paint	Substrate	Amount applied	Nature of test	Form of released NF	Release characteristics and findings
										collected from this paint.
Adeleye et al.[26]	Cu_2O	~220 nm	Antifouling	N/A	47.57%	Oak wood (3x1x1 cm); Aluminium sheet (3 x1 cm)		Leaching for 180 days in water (freshwater, estuary and seawater).	N/A	Maximum Cu released over 180 d was 0.21% from aluminium and 1.76% from wood. Particles in the leachates range in size from the nanoscale to a few microns. The amount of Cu detected in the aqueous phase over 180 d increased with increasing salinity.
Clar et al.[44]	CeO_2	10	UV inhibitor on outdoor surfaces	Milli-Q water or water-based wood stain	6 wt%	Micronized copper azole-treated lumber (MCA) Composite decking	110 mg	Leaching in Milli-Q water (at pH 4.2 by addition of precipitation leaching solution).	Aggregated; transformed	Application matrix affected release characteristics. Evidence of potential release of Ce(III) during leaching tests.
Clar et al.[43]	ZnO	28 ± 23	UV protection	Milli-Q water or water-based wood stain	1.7%	Micronized copper azole-treated lumber (MCA)	295 mg	Leaching in Milli-Q water (at pH 4.2 by addition of precipitation	Aggregated; transformed	Application matrix affected release characteristics. Stain-based application

Ref	NF	NF size (nm)	Functionality	Paint formulation	Concentration of NF in paint	Substrate	Amount applied	Nature of test	Form of released NF	Release characteristics and findings
						Composite decking	187 mg	leaching solution).		resulted in lower release. Most zinc released during leaching is in an ionic form.
Release from leaching of weathered materials										
Al-Kattan et al.[61]	TiO$_2$	Only a few nanometers	Photocatalyst	Styrene-acrylic copolymer binder	5 wt %	Polyvinyl chloride sheets	N/A	Leaching of milled paint debris (in milli-Q water) that has been exposure to UV and milled (according to ISO 11507:2007)	Matrix-embedded; Few single particles were observed in leachate (2-50 nm).	TiO$_2$ concentration in this extract was 580 µg/L, which corresponds to 0.02% of the total TiO$_2$ added to the paint powder. Main aging process was partial degradation of the organic paint matrix by UV light and release of fragments.
Zuin et al.[25]	TiO$_2$; Ag; SiO$_2$	15; 25 (spherical), 80-90 (rods); 19	Photocatalytic; hydrophilic	Water-based, styrene–acrylic copolymer, calcium carbonate extender	1-5 wt %	Fibre cement panels	0.4 kg/m^2	Weathering was conducted according to ISO 11507:2007, followed by Taber abrasion according to	TiO$_2$ and Ag not released; For SiO$_2$, few single particles; agglomerated; matrix-embedded	Low Ti release of between 4-8 ug/l corresponding to around 0.00015%. Ag release concentrations were below the limit of

Ref	NF	NF size (nm)	Functionality	Paint formulation	Concentration of NF in paint	Substrate	Amount applied	Nature of test	Form of released NF	Release characteristics and findings
								ISO 7784-2:2006) Following this, leaching was conducted according to ISO 2812-2:2007		detection. Small Si release with 73 mg/l (120h immersion). Cumulative loss of Si ranged between 0.9-1.8%.
Ruggiero et al.[62]	DPP; Fe_2O_3; Cu-phthalocyanine	42; 9; 17	Pigments	Matrix 1 = alkyd and melamine; Matrix 2 = acrylic and polyester polymers;	3 wt %	Steel test panel	N/A	Leaching in nanopure water and subjected to mechanical simulation via sonication and/or shaking	Matrix-embedded	The polymer matrix was the influential decisive factor for aging and release behaviour. High similarity in release rates (0.01-0.06 mg/MJ) for all samples and nanoforms. The substance, size and coating of the coloristic pigment did not strongly influence the aging resilience of the coating.

7.2.4 Modelling environmental release of NFs

Due to the comparatively low number of studies quantifying environmental release using analytical and experimental methods, there is a limited amount of data available on actual release[51][51]. Thus, mathematical modelling has been an important method to predict NF release and impact into the environment. A number of studies have been reported over the years using a variety of algorithms, input parameters and geographic locations. Input parameters include production volumes, allocation among product categories, releases from different products and forms of released NMs. In many of these the use of NMs in the paints industry is considered, however this is usually alongside a number of other applications and product categories (i.e. studies by Adam et al., 2018[59]; Mueller and Nowack, 2008[63]; O'Brien and Cummings, 2011[64]; O'Brien and Cummings, 2010[65]). The conclusions are therefore more widely applicable than just for the paints industry.

Gottschalk and Nowack published a review summarising the NF models, and in it they highlighted the importance of mathematical modelling and life-cycle considerations[51]. However there are few product-based NF release models.

For the paints and coatings industry, Hincapie *et al.* focused specifically on those used in the construction sector [66]. They were able to estimate the flow of NFs in paints along the life cycle and highlighted recycling as the highest potential release pathway, over landfill and incineration. However, it should be noted that the study focused on construction and waste management within Switzerland and this therefore may vary depending on country specifics.

Song *et al.* designed a stochastic model and applied it to nano-enabled paints across a range of applications (use of TiO_2, SiO_2 and FeO_x in construction, domestic and automotive uses)[67]. The aim of the study was to account for the time-gap between NF production and release. As paints and coatings are in use for years, or even decades, before removal, disposal or demolition, this time-gap can be long and needs to be considered in environmental release modelling. The paper attempted to estimate the releases across manufacturing, application and use and end-of-life, taking into account the increasing 'in stock' quantities. This had a significant effect on release estimates, which were an order of magnitude lower than static studies that assumed emissions occurred linearly.

8. 3D printing Literature Review

8.1 Release scenarios: Human

8.1.1 Filament production

One study has been identified for potential exposure to nanomaterials in filaments. The potential release of embedded Carbon Nanotubes (CNTs) in a Polylactic acid (PLA) filament during 3D printing has been investigated using UV-Vis spectroscopy. Anas *et al.* filed commercially available CNT-PLA coated filaments using a standard 6th steel file and measured CNT released[24]. No free CNTs were detected from filing above the detection limit (2.5 x 10^{-2} wt. %) in 0.1g of debris.

Table 21. Summary of studies investigating release during filament production

Ref	NF	NF size (nm)	Functionality	Matrix	Concentration of NF in paint	Nature of test	Form of released NF	Release characteristics and findings
Anas et al.[24]	CNTs	30-50	Filament for printing	Styrene–acrylic polymer	1,2 and 4 wt%	Filing (abrading study)	Free CNTs	No free CNTs detected above the LOD

8.1.2 Pre-processing activities

One study that measured potential release of NFs during pre-printing activities was identified. Stefaniak *et al.* assessed the potential of release of carbon nanotubes in Acrylonitrile Butadiene Styrene (ABS), PLA and Polycarbonate (PC) matrices[28]. During pre-printing, no evidence was obtained for carbon nanotubes being present on the filament surface.

NIOSH have identified that pre-printing activities have a high exposure risk [68] for inhalation and dermal exposure in printing with filaments and metal powders[69]. Cleaning printer heads/nozzles and heating nozzles have been highlighted as potential high exposure risk activities, as have sieving powders and manually loading powders into the machine when printing with metal powders. No information on release rates and/or masses are presented in these guidance posters (no references are provided in the posters).

Table 22. Summary of studies investigating release during pre-processing activities

Ref	NF	NF size (nm)	Functionality	Matrix	Concentration of NF in paint	Nature of test	Form of released NF	Release characteristics and findings
Stefaniak et al.[28]	CNTs	N/A	Filament for printing	ABS, PLA and PLC	1.5 -5 5.2 wt%	FE-SEM	Free CNTs	No free CNTs detected on the surface of the filament

A number of studies have also measured release pre-printing. Some have only performed background measurements whilst others have assessed pre-printing processes such as the warming up of the printer (which are more relevant in terms of exposure). These are summarised in Table 23.

Table 23. Summary of studies investigating background levels

Ref	NF	Technology	Matrix	RMM	Nature of test	Release characteristics and findings
Mendes et al.[70]	N/A	ME	ABS, PLA	Performed in a chamber; High Efficiency Particulate Air (HEPA) filter	Background (before printing)	Particle number concentration of ~ 300 particles per cm^{-3} (# cm^{-3})
Stephens et al. [29]	N/A	Molten Polymer Deposition (MPD)	ABS, PLA		Background (before printing)	UFP: 9684 (248) mean # cm^{-3} Highest level for particle size 36.5 nm: mean of 2025 (76) # cm^{-3}
Yi et al.[71]	N/A		ABS, PLA	Chamber	Pre-operating	Particle number concentration ~ 500 particles/cm^3 before printing
Kim et al.[72]	N/A	FDM	ABS, PLA	HEPA filter, charcoal absorbent bed	Before printing	ABS: 5021 ea/cm^3 Count Median Diameter (CMD) 67.9 nm PLA1: 1997 ea/cm^3; CMD 44.46 PLA2: 2174 ea/cm^3 CMD 84.44 nm
Alberts et al.[73]	Copper and tungsten	FFF	ABS, PLA	Inside particle collection chamber	Warm up of printer	PLA 220 ºC: 15.7 ± 1.4 nm (median diameter) PLA Cu 220 ºC: 16.9 ± 0.5 nm (median diameter) ABS 240 ºC: 14.1 ± 0.1 nm (median diameter) ABS W 240 ºC: 16.7 ± 0.6 nm (median diameter) ABS W 290 ºC: 20.0 ± 0.6 nm (median diameter)

8.1.3 Printing (Additive Manufacturing)

The majority of studies concerning release of NFs have been performed during the printing process. The release of process generated NMs is of the most concern, as highlighted by Graff et al[33] and Mellin et al[32], where the unintentionally generated nano-objects produced during metal AM process is highlighted as a risk. NIOSH have also identified a high exposure risk from using a 3D printer in the general office work area, working near the printer, and also going to a printer immediately after printing failures and during start-up[68].

The release scenarios during printing are affected by the NF, filament composition, printer type and also printing temperatures. These parameters can either increase or lower exposure.

Binder jetting

No studies were identified for release scenarios for binder jetting. One study has been identified by Petretta *et al.* which discussed the general risk from binding jetting. Using the binder jetting process can result in potential inhalation exposure, skin exposure (skin contact) and damages to the respiratory tract, circulatory, lymphatic and nervous systems[74]. To reduce the potential health a number of recommended risk management measures are recommended: use of an enclosed system, having restricted access, using a ventilation air system, using a HEPA (300 nm) filter with activated carbon, performing exposure evaluation and environmental monitoring, performing periodic cleaning, training personnel and having standard operating procedures, and using personal protective equipment.

Directed Energy Deposition

No studies were identified for release scenarios for directed energy deposition.

Material extrusion

Material extrusion is the most common 3D printer type and includes a number of desktop printers. Material extrusion includes the following technologies: Fused Filament Fabrication (FFF) and Fused Deposition Modelling (FDM). Studies that describe release scenarios for material extrusion are discussed in this section and a summary is presented in Table 24.

Väisänen et al. measured released concentrations for dust and VOCs during material extrusion[31]. This process involved a solid plastic filament being extracted through a heated nozzle layer by layer. During material extrusion, a slight increase was observed in VOC concentrations. For the filament, the carbon based filament emitted the lowest particles with the ABSpro filament emitting the highest number of particles (mean of 2070 #/cm^3 versus 81,890 #/cm^3).

Five studies were identified for FFF printing. Alberts *et al.* investigated the effect of doping ABS and PLA printing feedstock with metal additives (copper and tungsten; not nanoparticles)[73]. Doping the polymeric feedstocks with metal additives resulted in increased emission profiles, even when the temperature remained the same. For example, at an extruder temperature of 220 °C, PLA had a mean emission factor of $7.20 \pm 0.3 \times 10^6$ compared to $5.58 \pm 0.21 \times 10^7$ with the addition of Cu at the same temperature. At an extruder temperature of 230 °C, the mean emission factor for ABS only was $2.66 \pm 0.19 \times 10^7$ compared with $1.07 \pm 0.04 \times 10^9$ with the addition of tungsten.

Emissions from FlashForge Creator, Dremel 3D Idea Builder, XYZ printing da Vinci 1.0, Lulzbot Mini and MakerBot Replicator 2X desktop printers which use Fused Filament Fabrication (FFF) technology have been assessed by Azimi et al[75]. Printing of a 10 x 10 x 1 cm sample was performed inside a 3.6 m^3 stainless steel chamber with a small stainless steel mixing fan. The printing duration varied from 2 hours 38 minutes to 3 hours and 42 minutes, with bed temperatures of RT- 110 °C and extruder temperatures between 190-270 °C used dependent on the filament and printer used. Emission rates varied depending on the temperature, printing time, 3D printer used and filament used. Typically, ultrafine particle emissions rapidly increased once printing commenced for 10-20 minutes and then decreased to a lower level (higher than the background levels). For each filament type, a primary VOC was emitted. For ABS and High Impact Polystyrene (HIPS) filaments, styrene was emitted; for nylon, Plasticised Copolyamide TPE (PCTPE), laybrick and the laywood filaments caprolactam was the primary VOC emitted; and lactide was the primary VOC emitted for the PLA filament used. Emissions of UFPs and VOCs in a small office have been simulated based on the results by the authors. Assuming a worst case scenario for 3D printing in a small office (45 m^3 well-mixed furnished and conditioned office space), ~58,000 cm^{-3} of UFPs can be emitted, ~244 µg/m^3 for caprolactum emission, ~150 µg/m^3 for emissions of styrene and ~6 µg/m^3 for lactide emission during printer operation. The authors conclude that caution should be employed for printing particularly when using styrene-based and nylon-based filaments.

Gu et al evaluated the 3D printer, Model M200 (Zortrax)[76]. The study has looked at a number of process including printing with various filaments (i.e. ABA, Acrylic Styrene Acrylonitrile (ASA) and Polyethylene Terephthalate Glycol (PETG) in a 3 m^3 stainless steel chamber. Incoming air was filtered and cleaned. During printing operations, high particle number concentrations were observed during 3D printing in 5.6- 560 nm range for FMPS. The particle count mean diameter (CMD) was below 30 nm for the majority of filaments, however the CMD was 59 nm and 89 nm for the two PETG based filaments and 41 nm for the HIPS filament. Particle emission rates varied from 2.0 × 10(9) #/min (GLASS, a PETG-based filament) to 1.7 × 10(11) #/min (ASA filament). The major VOC emitted during printing was styrene. Growth in the particle size was observed at the beginning of the printing process. The initial particle number size distribution peaked at 11 nm for ABS, increased to ~30 nm within 20 minutes and then remained stable until 3rd printing hour. Similar for ASA, ESD, PCABS, HIPS, PETG and GLASS. The particle count medium was ~<30 nm for most filaments/printing jobs except for PETG (59 nm), GLASS (82 nm) and HIPS (41 nm).

UK Health and Safety Executive (HSE) investigated particulate and volatile emission from FFF/FDM desktop 3D printers in a lab-based study[77]. Various filaments were investigated including the use of (non-nano) copper, brass and bronze in filaments. Two exposure scenarios were used: printing with the same filament on different printers and printing with different filament materials on the same printers. Particle emission rates varied from 1.12 x 10(11) – 8.03 x 10(11) particles/min^{-1} for printing with ABS filament when the nozzle temperature range was between 245-260 °C. The average particle size did not increase above 10 nm. For printing with the PLA filament and a nozzle temperature of 220-240 °C, the particle emission rates were from 3.26 x 10(9) - 8.23 x 10(10) particles/min^{-1} with an average particle size between 24 nm and 69 nm. The particle emission rates are in the size range in which they could enter the airways and lungs. It is also worth noting that as the nozzle temperature increased, the particle emission rates increased with a decrease in the average particle size. Some of the filaments also released styrene and isocyanates and there were very small metal particles in the emissions from filaments that contained embedded metals (Copper FLEX, brassFill, BronzeFill filaments).

Mendes et al. Investigated nanoparticle emissions were assessed when using the miniFactory Oy, model 3 Education Edition Single Extruder which is based on ME technology[70]. Two release scenarios were utilised for the printing stage:

- Printing in a 0.18 cm^3 chamber with a HEPA filter
- Printing in a room of a conventional building with a floor area of 27 m^2 and a volume of approximately 81 m. This room was well-ventilated with 5 air exchanges an hour and two table top fans at opposite ends for the convective mixing of room air

For the first exposure scenario (printing in a chamber), a burst of nanoparticles occurred when the extruder temperature reached that of the filament material melting point. For printing in the room with an ABS filament, the particle concentration reached greater than 10(4) # cm^{-1}. The Geometric Mean Diameter (GMD) for printing with an ABS filament was between 7.6 nm and 14 nm for standard temperature (230 °C for extruder and 90 °C for bed) and high temperature. The GMD for PLA printing was 26.4 nm for standard temperature (200 °C for extruder and 80 °C for bed) and 7.6 nm for high temperature (230 °C for extruder and 80 °C for bed). The study concluded that printing with an ABS filament results in a significant amount of nanoparticle emissions, whilst printing with the PLA filament results in nanoparticle emissions not being of a significant amount. A preventative approach should be used. The use of multiple printers for a prolonged period may result in the 8-hour TWA indicative value of 4·10(4) # cm^{-3} being exceeded.

Six studies used FDM technology. Potter et al. studied emissions from two commercially available 3D printer filaments (ABS based) and subjected them to simulated FDM thermal conditions (230 °C for printing temperature; 200 and 300 °C for degradation experiments)[78]. The addition of carbon nanotubes to the ABS matrix reduced emissions of VOCs slightly, particularly styrene (most dominant VOC). The nanotubes may have been acting as a sink for certain VOCs. Some of the VOC emissions were as a result of polymer degradation; however some emissions were as a result of the carbon nanotubes possibly necessitated a different polymer formation.

Stefaniak et al. evaluated the emissions of printing using PLA and ABS filaments[28]. Detectable levels of organic chemicals were observed during printing. Personal exposure to Total Volatile Organic Compounds (TVOCs) were below 15,000 µg/m^3 of air on all days. Printing with PLA filament, the concentration of particles with sizes from 300 nm to greater than 20 µm did not exceed 100 particles per cm^3 of air. Particle concentrations reached 275,000 particles/cm^3 at one location. After installing printer covers and doors, the particle number concentration decreased, however began to rise again after 60 minutes. This is because initially the emitted particles would be deposited on the covers and doors. Using a ventilated enclosure, there was a 98.4% reduction in particle concentration inside the enclosure. Stefaniak et al. also assessed the potential of nanomaterial exposure from polymer filaments that contained carbon nanotubes (CNTs) using a Desktop FSM printer (Fused Deposition Modelling)[79]. The measured average diameters of the CNTs on surfaces of the as-received filaments was 16±3 nm (ABS+CNT), 19±4 nm (PLA+CNT), and 21±6 nm (PC+CNT). Pre-printing, there was no evidence of CNTs on the surface of the filaments. During printing, there was some emission of CNT-containing polymer particles in the submicron to micron scale size. There was release of up to 1010 ultrafine particles per gram printed (diameter < 100 nm) and also the emission of 106-108 respirable particles per gram printed (diameter of ~0.5-2 µm). In the emitted respirable fraction, 1% of the particles contained carbon nanotubes.

Kim et al., using ABS and PLA filaments for printing 14.52g-18.58g, measured increased concentrations of particulate and gaseous materials during printing, this differed dependent on the cartridge type and manufacturer[72]. The ABS cartridge had higher particle concentration and emissions rate than the PLA cartridge. Nanosized particles were emitted at high concentrations, this was not dependent on the filament. In another study using ABS (extruder temperature of 230 °C, baseplate temperature of 110 °C) and PLA (extruder temperature of 215 °C, baseplate heater off) filaments for a Replicator 2x® (MakerBot Industries) printer were assessed for particulate emissions[71]. Risk management measures used for printing included using a printer cover and a two piece high efficiency particulate air filter for filtering the incoming air into the chamber. During printing, a rapid increase in the particle concentration was observed (3.5 x 10^5/cm^3) for a couple of minutes which reduced to the background levels approximately 100 minutes after printing had finished. The average geometric mean electrical mobility diameter was similar for the first printer operation of printing a comb (34.7 nm) to 32.2 nm for the second printed comb. Emissions from the ABS filament varied depending on the filament colour, with the blue ABS filament emitting particles x1.7 greater than the black ABS filament. The geometric mean mobility diameters varied for the PLA coloured filaments, from 28 nm for red PLA to 37 nm for army green. The authors were not able to discern a clear and consistent relationship between filament type and emissions from the data.

Stephens *et al.* compared printing with PLA thermoplastic feedstock and with ABS thermoplastic feedstock in a 45 m^2 furnished and conditioned office space. Desktop 3D printers commonly use molten polymer deposition (MPD) technology[29]. The authors broke the measurements down to the following activities with the only RMM used being the doors to the room being closed:

- Two PLA thermoplastic feedstock printers operating for a period of twenty minutes. The conditions for printing was 200 °C for the extruder temperature and 18 °C for the baseplate temperature
- Two PLA feedstock printers and three ABS feedstock printers operating. For the PLA printers, the temperatures used were 200 °C for the extruder temperature and 18 °C for the baseplate temperature. For the ABS-filament printers, the extruder temperature was 220 °C and the baseplate temperature was 118 °C.

Using PLA feedstock resulted in an increased concentration of particles greater than 20 nm. Differences were observed between using PLA feedstock and ABS feedstock. ABS printers had total UFP emission rates of nearly a magnitude higher then lower temperature PLA printers (1.8-2.0 x 10(11) # min^{-1} versus 1.9-2.0 x 10(10) # min^{-1} respectively). Peak emissions for PLA feedstock were in the 48-65 nm range, whilst for ABS feedstock the peak emissions were in the 15-49 nm range. When the two PLA printers and three ABS printers were used in the same period, the peak UFP concentrations for when all five printers were operating was ~142,200 cm^{-3}, which was nearly five times higher than the two PLA printers operating only and nearly 15 times higher than the background.

Table 24. Summary of studies investigating release for material extrusion

Ref	Matrix	Technology	Temp (ºC)	RMM	Particle release characteristics and findings	VOC Release findings
Väisänen et al. [31]	ABS	ME	N/A	LEV for EOS	Dust concentrations low for all the filaments (0.01-0.03 mg/m^3) and below LOD when measured with IOM samplers. The carbon filament emitted the lowest amount of particles (mean of 2070 #/cm3) and the ABSpro filament the highest (mean of 81,890 #/cm^3).	Low VOC concentrations, but did increase slightly during printing (108 µg/m^3 and 48 µg/m^3). Formaldehyde detected in low concentrations for all printing processes
Alberts et al. [73]	ABS and PLA	FFF	220- 290	N/A	Mean emission factor (#/g): PLA 220 ºC $(1.64 \pm 0.06) \times 10^6$ $(7.20 \pm 0.3) \times 10^6$; PLA Cu 220 ºC $(4.43 \pm 0.17) \times 10^7$ $(5.58 \pm 0.21) \times 10^7$; ABS 240 ºC $(2.06 \pm 0.07) \times 10^7$ $(2.66 \pm 0.09) \times 10^7$; ABS W 240 ºC $(3.05 \pm 0.11) \times 10^8$ $(1.07 \pm 0.04) \times 10^9$; ABS W 290 ºC $(1.62 \pm 0.55) \times 10^9$ $(2.17 \pm 0.07) \times 10^9$; Median particle diameter by number concentration during printing was greatest for neat PLA (57.2 nm), with PLA-Cu (22.7 nm), ABS (29.7), and ABS-W (26.7) significantly lower.	
Azimi et al. [75]	ABS, HIPS, laybrick, laywood, PC,PCTPEM TGlase	FFF	Bed: RT-110 Extruder: 190-270	Stainless Steel chamber and mixing fan	Highest UFP rates for ABS filaments (~2 x 10(10) to ~9 x 10(10) min^{-1}). Lowest UFP rates for PLA filaments (median of ~10(8) min^{-1}). Printer type, filaments and temperatures affected emission rates.	Primary VOCs emitted were styrene and lactide. Levels of UFPs, styrene and lactide emitted higher than recommended levels.
Gu et al.[76]	ABA, ASA, HIPS, PETG, PCABS	FFF	N/A	Stainless Steel chamber	Median PNCs of 5.6-560 nm. Mean particle emissions of 4.7 ± 1.1 x 10(10) for ABS. Observed particle SERs in 5.6-560 nm range were from 2.0 x 10(9) for GLASS to 1.7 x 10(11) for ASA #/min. Most prominent VOC emitted was styrene. Decrease in particle size and number concentrations with increasing temperatures.	Most prominent VOC emitted was styrene.

HSE[77]	ABS, PLA, HIPS Nylon, NinjaTek, bronzeFILL, brassFILL, Copper FLEX	FFF	Nozzle temp: 220-260	Enclosed Hood, HEPA filter, fan	Emission rates: 1.12 x10(11) – 8.3 x 10(11)/min^{-1} for ABS; average particle size <10 nm; For PLA: Emission rates of 3.26 x 10(9) – 8.23 x 10(10)/min^{-1}; average particle size 24 nm- 69 nm. Emissions of very small metal particles for filaments containing embedded metals. Some release of styrene and isocyanates	
Mendes et al.[70]	ABS and PLA	FFF	200-230 for extruder; 80-90 for bed	HEPA filter, chamber	Particle concentration >10(4) #cm^{-1} in the room with ABS. Mean particle size of 7.8 nm -10.5 nm. Effected by temperature and polymer (PLA less release of NPs). Trace amounts of some VOCs.	
Potter et al.[78]	ABS	FDM	200 ºC and 300 ºC	N/A		Release of degradation products from the polymer and number of VOCs. Addition of CNTs reduced VOC emissions slightly; reduced styrene emissions (most prevalent VOC)
Stefaniak et al.[28]	ABS and PLA	FDM	235 ºC	Ventilated enclosure	Detectable levels of organic chemicals emitted; Number of particles 10 printers [0.3 to >20 µm], #/cm3 10 (3 ABS/7 PLA) 100 (10 PLA) Number of particles [20 to 1000 nm], #/cm3 80,000 (3 ABS/7 PLA) 200,000 (10 PLA) Size: 48 nm (3 ABS/7 PLA) 44 nm (10 PLA)	
Stefaniak et al.[79]	ABS, PLA, PC	FDM	N/A	Air filtering (HEPA and carbon filters)	No free CNT in air or on surfaces of filaments; emitted polymer particles in submicron-microscale size	
Kim et al.[72]	ABS, PLA	FDM	ABS: 250 ºC; PLA: 210-220 ºC	HEPA filter and charcoal absorbent bed	For ABS, the size during printing was 33 (1.11) nm for ABS, 28 (1.14) nm for PLA 1 and 188 (1.26) nm for PLA 2. GM (GSD) number concentration for the ABS cartridge, by SMPS was 1 731 578 (1.47) particles/cm^3 and the values for the PLA1 and PLA2 cartridges were 52 252 (1.98) particles/cm^3 and 45 690 (2.50), respectively. GMs (GSD) of the particles emitted for each cartridge were: ABS; 63.74 (1.10) μg/m^3, PLA1; 31.89 (1.01) μg/m^3 and PLA2; 153.20 (1.69) μg/m^3 during printing.	Increase in formaldehyde, acetaldehyde and isovaleraldehyde

| Yi et al.[71] | ABS, PLA | FDM | ABS (extruder temperature of 230 ºC, baseplate temperature of 110 ºC) and PLA (extruder temperature of 215 ºC, baseplate heater off | Printer cover, air filter | Rapid increase in the particle concentration was observed (3.5 x 10^5/cm^3) for a couple of minutes at start of printing. Blue ABS filament emitted particles x1.7 greater than the black ABS filament. GM mobility diameters varied for the PLA coloured filaments, from 28nm for red PLA to 37 nm for army green | |
| Stephens et al.[29] | ABS, PLA | FDM (MPD) | ABS: 200 (extruder), 18 (baseplate) PLA: 220 (extruder), 118 (baseplate) | Closed doors | ABS feedstock: Total UFP emission of 1.8-2.0 x 10(11) # min^{-1}. Peak emissions in the 15-49 nm range PLA feedstock: Total UFP emission of 1.9-2.0 x 10(10) # min-^{1}. Peak emissions in 48-65 nm range. | |

Material jetting

One study was identified for material jetting in which VOCs were released (isopropanol, propylene and toluene)[30]. No information is supplied for the measurements of nano release.

Powder bed fusion

Powder bed fusion includes the following technologies: Direct Metal Laser Sintering (DMLS), Electron Beam Melting (EBM), Selective Heat Sintering (SHS), Selective Laser Melting (SLM) and Selective Laser Sintering (SLS).

One study was identified for powder bed fusion. High particle concentrations were measured (mean of 0.4 mg/m^3 from DustTrak, 5.2 mg/m^3 for stationary IOM sampler and 9.1 mg/m^3 for personal IOM sampler) and a mean particle concentration of 16900 #/cm^3 was measured during printing with an ABS filament[31].

Two studies were identified for SLM, which concerned printing with metal powders. Graff *et al.* used IN (Inconel) 939 alloy (15-45 μm in size) for printing, which resulted in nanoparticles (>300 nm) being generated[33]. However, Mellin *et al.* measured particles of 1-2 μm being generated during printing using IN939 alloy[32]. No temperatures are provided in either study for the printing operations. No information is supplied in these studies for primary particle sizes.

No relevant studies were identified for DMLS, EBM, SHS and SLS for release during printing.

Table 25. Summary of studies investigating release for powder bed fusion

Ref	NF	NF size (nm)	Technology	Matrix	Particle release characteristics and findings	VOC release findings
Väisänen et al.[31]	Easywood and carbon (not stated if nano)	N/A	Powder bed fusion	ABS	High particle concentrations during printing ((mean of 0.4 mg/m^3 from DustTrak and 5.2 mg/m^3 for stationary IOM sampler and 9.1 mg/m^3 for personal IOM sampler).	PBF had highest levels of formaldehyde
Graff et al.[33]	IN939 (not nano)	15-45 µm	Selective laser sintering	N/A	Increased levels of chromium, nickel and cobalt in the air in the additive manufacturing area. For particles >300 nm, the highest peaks were found in in the additive manufacturing area.	N/A
Mellin et al.[32]	IN939	1 µm and above	Selective laser sintering	N/A	Produced small round metal particles of 1-2 µm during printing.	N/A

Sheet lamination

Sheet lamination also includes Ultrasonic Additive Manufacturing (UAM) and Laminated Object Manufacturing (LOM). No relevant studies for release scenarios were identified for sheet lamination.

Vat Photopolymerisation

Two studies measured potential result during vat photopolymerisation. Väisänen et al.[31] measured dust concentrations, whereas Zissok *et al.* reports on VOC emissions during vat photopolymerisation[30]. Dust concentrations between 0.01 and 0.12 mg/m^3 for measuring with DustTrack and below the LOD when measuring using an IOM sampler. The released particle concentrations were dependent on the printer used; no increase using Formalabs Form 2 was observed whilst printing using a BEGO Varseo machine resulted in a mean particle concentration of 8020 #/cm^3. Zisook *et al.* measured fluorine (6.6 ppb and <5.2 ppb respectively) and also emissions of acetone (245 ppbv) and isopropanol (560 ppbv).

Table 26. Summary of studies investigating release for powder bed fusion

Ref	Technology	Matrix	RMM	Particle release characteristics and findings	VOC characteristics and findings
Väisänen et al.[31]	Vat photopolymerization	Verseo WAX CAS/Cast; Formlabs Grey and Castable	BEGO: natural; Formlabs: mechanical ventilation	Dust concentrations between 0.01 and 0.12 mg/m^3 Mean particle concentration of 8020 #/cm^3 for BEGO Varseo.	Low VOC concentrations (113-317 µg/m^3).
Zisook et al.[30]	Vat photopolymerization	Curable liquid photopolymer	General dilution ventilation		Fluorine measured above LOD; 245 ppbv acetone and 560 ppbv (parts per billion by volume) isopropanol measured

8.1.4 Post-processing activities

Post-processing activities identified by the SAbyNA industrial partner for after printing include powder cleaning, powder recovery, resin cleaning, curing, support removal, abrasion and part cutting. Other post-processing activities identified from the literature include sandblasting, shot peening and cleaning and maintenance.

NIOSH discuss a number of activities for 3D printing using filaments [68]. These are:

- Post-printing. The removal of support structures with solvents or other chemicals and post-processing actions such as with filaments containing nanomaterials are identified as high risk activities;
- Cleaning and maintenance. Cleaning the printer head/build plate with solvents is identified as a potential high risk for exposure

The inhalation and dermal routes are identified as potential exposure routes; no levels of exposure are presented. For 3D printing with metal powders, NIOSH identify the following activities for inhalation and dermal exposure [69]:

- Post-printing. Removal of the powder or the printed object from the printer and also from moving the powder/printed object around the work area are identified as higher exposure risks.
- Cleaning and maintenance. Preventative maintenance and also either removal or installing HEPA filters are identified as having higher potential exposures.

The use of solvents during post-processing activities is also a risk, for example Tijing et al identify that exposure to alcohols and propylene carbonate during Digital Light Processing (DLP) and stereolithography (SLA) post-processing is a human and environmental risk[80].

A number of studies also include post-printing as a release scenario; however no measurements are discussed (e.g. Alberts *et al.*). Studies in which measurements have been performed for post-processing are described in the following sections. A summary of post-processing activities in the literature is discussed in Table 27.

Table 27Injection Moulding

Stefaniak *et al*. measured the particle number concentration and the release of VOCs during injection moulding of ABS thermoplastic FDM printed objects [28]. During the warm-up of the injection moulding machine, the particle number concentration increased from 3,400 particles/cm^3 to >134,000 particles/cm^3. During injection moulding, particle number concentrations from 20,000-26,000 particles/cm^3 during the activity. A number of VOCs were also detected during the activity including ethylbenzene, styrene, m,p-xylene and o-xylene.

Processing and cleaning of printed parts

One study (Zisook *et al*.) investigated the release during the cleaning and processing of 3D-printed parts for powder bed fusion and material jetting [30]. The printed objects from powder bed fusion were first removed and then cleaned using compressed air and abrasive beads inside a complete glovebox enclosure; powders were also transferred to re-use the uncured powder. In this activity, similar dust concentrations to that presented by Väisänen et al (2019) were obtained (0.4 mg/m^3). The measured concentrations were below the recommended 8 hour ACGIH (The American Conference of Governmental Industrial Hygienists) guidance values. For material jetting printed parts, these were washed in a rinsing cabined with soapy water, with both acetone and isopropanol levels being above the LOD.

Sanding

Stefaniak *et al*. measured the release of particles during sanding of ABS thermoplastic FDM printed objects[28]. During this activity, the particle concentration in air increased from a background concentration of 7,200 particles/cm^3 to levels between 11,000-15,000 particles/cm^3. The released particles were in the order of several micrometers.

Printers off ('decay')

A number of studies discuss printers off after printing as a scenario, however only one study present measurements. Kim *et al*. measured a rapid decrease in the particle number concentration after printing using FDM technology[72]. Using an ABS filament, the geometric measured mean was 6373 #/cm^3 with a count median diameter of 50.49 nm; for PLA1 filament, the geometric measured mean was 1374 #/cm^3 with a count median diameter of 43.37 nm; and for the PLA2 filament, geometric measured mean was 1583 #/cm^3 with a count median diameter of 82.90 nm. Stephens *et al*.[29] during the printers off period for molten polymer deposition measured a lumped loss rate of 2.5 h^{-1} – 5.6 h^{-1} with a total Ultra Fine Particle (UFP) loss of 3 h^{-1}. Lumped loss rates use the estimated total loss rate of each particle size and total UFPs that fit a straight line on a log-linear plot.

Cleaning and maintenance

The use of solvents during post-processing activities presents a potential risk, for example Tijing et al identify that potential exposure to solvents (which can be toxic to the environment) such as propylene carbonate and alcohols during post processing activities for DLP and SLA as a potential emission source to the environment[80].

One study has compared cleaning articles for three different technologies (vat photopolymerisation, powder bed fusion and multi jet fusion)[31]. The printed objects from vat photopolymerisation were washed with isopropanol over a household sink; the printed objects from powder bed fusion were unloaded and washed inside an airtight chamber with depressurised air; and the printed objects from multi jet fusion were washed in a similar manner

in a fume hood. Dust concentrations for cleaning was highest for the printed objects from powder bed fusion, with a mean dust concentration of 0.4 mg/m^3. This was followed by objects printed by multi jet fusion, with a mean dust concentration of 0.19 mg/m^3. VOCs were detected during cleaning for multi jet fusion and significant levels were detected for cleaning vat photopolymerisation printed objects (Total VOC concentration of 11,084 µg/m^3. Graff *et al.* measured a peak particle concentration measurement of 16,000 p/cm^3 from metal powder printing (IN939) using selective laser melting. During powder handling, particle emissions were in the 300 nm interval [33].

Table 27. Summary of studies investigating release during post-processing activities

Ref	NF	NF size (nm)	Matrix	Technology	Nature of test	Particle release characteristics and findings	VOC release findings
Graff et al.[33]	IN939	15-45 μm	N/A	Selective Laser Melting	Machine cleaning	Peak particle measurement of 16,000 p/cm^3 during cleaning	
Kim et al.[72]	N/A	N/A	ABS, PLA	Fused Deposition Modelling	Post-printing	ABS filament: 6373 #/cm^3 GM with a CMD of 50.49 nm; PLA-1 filament: the geometric measured mean was 1374 #/cm^3 GM with CMD of 43.37 nm; PLA2 filament: 1583 #/cm^3 GM with CMD of 82.90 nm.	
Stephens et al.[29]	N/A		ABS, PLA	Molten Polymer Deposition	Printer off	Lumped losses rates of 2.5 h^{-1} – 5.6 h^{-1}; total UFP loss of 3 h^{-1}	
				Selective Laser Melting	Powder handling	Particle emissions in 300 nm interval	
Stefaniak et al.[28]	N/A	N/A	ABS	Fused Deposition Modelling	Injection moulding	Particle number concentration of 20,000 particles/cm^3 – 26,000 particles/cm^3	Presence of VOCs (ethylbenzene, styrene, m,p-xylene and o-xylene)
					Sanding	Increase from a background concentration of 7,200 particles/cm^3 to levels between 11,000-15,000 particles/cm^3	
Väisänen et al.[31]	N/A	N/A	ABS	Vat Photopolymerisation	Cleaning		Significant source of VOCs (>20 times that during printing);

Ref	NF	NF size (nm)	Matrix	Technology	Nature of test	Particle release characteristics and findings	VOC release findings
							TVOC concentration 11,084 $\mu g/m^3$
				Powder bed fusion	Cleaning	DustTrak DRX: 0.1-2.57 mg/m^3 (mean 0.4 mg/m^3); stationary IOM sampler: 5.2 mg/m^3 and 9.1 mg/m^3 for personal IOM sampler. Particle concentrate 15 050-22 300 $\#/cm^3$ (mean 16 900 $\#/cm^3$)	
				Multi Jet fusion	Cleaning	Dust levels: Mean 0.19 mg/m^3 (DustTrak DRX), 1.4 mg/m^3 (stationary IOM sampler), 2.4 mg/m^3 (personal IOM sampler)	Elevated VOCs: isobornyl acrylate (1233 $\mu g/m^3$), butylated hydroxytoluene (225 $\mu g/m^3$) and p-xylene (76 $\mu g/m^3$)
Zisook et al.[30]	N/A	N/A	Liquid photopolymer, nylon, ABS	Powder bed fusion	Post-processing (cleaning/processing parts)	Similar dust concentration results as Väisänen et al (2019): 0.4 mg/m^{-3}; below 8-hr ACGIH guidance values for respirable and total particles	Isopropanol above LOD
				Material Jetting	Post-processing (cleaning/processing parts)		Acetone and isopropanol above LOD

From the retrieved studies, there is very limited information on releases to the environment from 3D printing. Tijing et al. identified potential exposure to solvents (which can be toxic to the environment) such as propylene carbonate and alcohols during post processing activities for DLP and SLA as a potential emission source to the environment. The authors also identified the importance of using Life Cycle Assessment (LCAs) for 3D printing processes to identify environmental burdens. Furthermore, the environmental impacts from 3D printing are dominated by the energy demands of the printing processes[80].

9. Deviations from the workplan

No deviations to be reported. The outputs of this task will be further expanded and updated by other work packages over the course of the SAbyNA project.

The literature review will also be updated on a regular basis during the course of the project (by use of an internal database) and updates communicated to WP2-WP6.

10. Conclusion

A systematic literature review has been performed alongside interviews with WP7 industrial partners and questionnaires to associations and companies in order to identify sector-specific practices and relevant nanosafety alerts in the paints and 3D printing sectors. Relevant nanosafety alerts include the potential for release of NFs during spray painting/spray applications in paint, the release of NFs during the weathering and abrasion of paints and the release of NFs during printing for 3D printing. Nanosafety alerts for the paint and 3D printing sector are summarised in Annex 3.

For the paints sector, interviews were held with Nouryon and ALLIOS to identify practices in paint manufacturing and identify release scenarios. Nouryon manufacture colloidal silica which can be used as part of paint formulation, whereas ALLIOS are a paint manufacturer. For Nouryon, the manufacture of colloidal silica involves six steps (from producing a sodium silicate solution in step 1 through to filling drums in step 6). Release and exposure are thought to be low as these steps are in solution and fully enclosed. For ALLIOS, seven steps are involved in the manufacture of paints (from producing a slurry solution in step 1 to filling and canning in step 7) with the most important step being stage 6 which involves manufacturing the paint. There may be possible exposure in step 1, which involves dry powder handling. ALLIOS also typically use micro-sized TiO_2, with nano TiO_2 only used at an R&D scale.

The literature review for paints identified 52 studies relevant for the paints sector. Commonly used nanomaterials reported in paints include TiO_2, SiO_2 (these two are also used by the industrial WP partners) and ZnO. Other common nanomaterials used include Fe_2O_3, multi walled carbon nanotubes and Ag. Commonly used matrix materials in paints include acrylic-based matrices. Activities for the life cycle of paints have been identified. The processes are formulation (including nanomaterial synthesis and paint formulation), service life (i.e. spray painting, drying, sanding and weathering) and end of life (i.e. sandblasting, incineration and leaching). The release potential is influenced by a number of factors depending on the process. This includes paint either being water-borne or solvent-borne, manual or automated processes, amount/volume of material, matrix

properties (such as embedded, photo degradation and formulation), activity performed during service life and over-spraying (for spray applications).

From the review process, there are gaps in the literature for release during the life cycle of paints. Only one study was identified for release during nanoform synthesis which could be explored further. No studies have been identified for release during paint formulation using SiO_2 with three identified for TiO_2 and one identified for MWCNTs. For dermal contact during paint service life, only three studies were identified. For mechanical treatment (sawing) only one study has been identified which was for SiO_2 which is a knowledge gap. End-of-life studies are very limited in the literature with only one study identified for sandblasting using CNT-based paint. Environmental data during formulation is lacking, lacking for some aspects of the service life such as paint rolling and spray painting) and also lacking for end-of-life apart from leaching.

For the 3D printing sector, interviews were held with LATI and LEITAT-3D Hub to identify practices within the sector and identify release scenarios. LATI manufacture the filaments (SWCNT or silver nano enabled) to be used in printing, whereas LEITAT-3D Hub perform the additive manufacturing and will use filaments from LATI. In the process from the filament production to printing, there are eight steps. The first five steps involve filament production (from step 1 weighing to filament production in stage 5) with steps 6-8 involving printing operations (step 7 is the printing stage using different technologies). For printing, non-nanomaterials are commonly used, such as metal powders. Exposure is possible during weighing and mixing in the filament production.

The literature review identified 28 relevant studies, although some of these studies were general reviews or guidelines for users. Commonly used nanomaterials in filaments identified in the literature include carbon nanotubes (relevant for SAbyNA) and graphene nanoplatelets. Commonly used polymeric matrix materials include acrylonitrile butadiene styrene (ABS), polylactic acid (PLA) and polycarbonate (used by industrial WP partner). Activities in the 3D printing life cycle have been identified. The processes are filament production (i.e. weighing, mixing and extrusion), pre-processing (i.e. powder handling, resin filling and sieving), additive manufacturing (printing process) which is divided into the seven technologies defined in American Society for Testing and Materials (ASTM) 52900:2015), post-processing (i.e. support removal and curing), cleaning and maintenance and end of life. The release potential is influenced by a number of factors. This includes printing temperatures, filament matrix materials used, automated/manual process and the use of solvents. An important finding from the literature review is the potential of release of nanoparticles during printing, even when the filaments are not nanoenabled. Micro-sized particles and the release of volatile organic compounds also occur during printing.

From the review process, there are gaps in the literature for release during the 3D printing life cycle. No studies were identified for end of life studies on filaments and printed objects. There is a lack of studies measuring release using nanoenabled filaments with the literature focussed on printing with non-nanoenabled filaments. It is known from the literature that particles (in the nano range) and also VOCs are released, however more investigation is needed for using nanoenabled filaments and their effect on release. There is also a severe lack of information for environmental release scenarios which needs to be developed throughout the life cycle. In terms of printing technologies, some are covered in more depth than others in the literature (i.e. material extrusion is covered in a number of studies, whereas binder jetting is not). There is also a new FDM printing technology which is based on printing pellets without a spool. No relevant exposure/release scenarios have been identified, however the literature can be monitored for developments.

The information collected during this task can be used by the experimental WPs (WPs 2-4) in planning the experiments to be performed on the case study materials, the most relevant methods to be used, to improve prediction of release and to identify redesign opportunities to minimise exposure. The data collected from the literature review can also be used to establish default parameters for the relevant scenarios and entered into common templates for release and exposure. Potential activities which could be performed based on the identified gaps include:

- For paint activities:
  - o Human exposure for paints: Measurements during mechanical treatment, measurements during spray painting, dermal simulation activities for painted articles, abiotic aging and weathering (no studies were identified) and end of life activities (i.e. leaching);
  - o Environmental exposure for paints: Measurements during the service life of the paints, particularly for paint applications by hand (i.e. spray painting and paint rolling) and end of life activities;
  - o Paint formulations: Measurements could be performed on different matrix materials on paint formulations, as some studies find the inclusion of NFs into the matrix can result in release rates of NFs being generally unaffected;
  - o Mesocosm testing for both medium and long term nature-like aging could be performed on paint formulations;
  - o Using the list of common NFs for benchmark testing.
- For 3D printing:
  - o Measurements could performed comparing nanoenabled filaments and non nanoenabled filament to compare the release as there is limited information available. This could also involve comparing different nanoenabled filaments to compare differences in release;
  - o Performing measurements for VOCs and the effect of using nanoenabled filaments. This is an identified issue which requires further investigation;
  - o Investigate the effect of changing the matrix materials in nanoenabled filaments
  - o Environmental exposure activities such as leaching could be performed;
  - o Post-printing activities could be identified (i.e. abrasion). The effect of printing with nanoenabled filaments and non nanoenabled filaments and changing the matrix materials could be investigated for potential release during these activities;
  - o Environmental exposure needs to be investigated throughout the life cycle i.e. emissions during printing, effect of different NFs/matrices, post processing activities and end of life
  - o Using the list of common NFs for benchmark testing.

11. Annex 1- Literature review search terms

11.1 Paint sector

The search terms used were:

("nanomaterial" OR "nanocomposite") AND "exposure" AND ("paint" OR "lacquer" OR "binder" OR "resin" OR "pigment" OR "additive" OR "dye" OR "paste") AND (search term), with the following used for (search term):

- Processing: "handling", "fluid dosing", "suction", "fluid dosing", "suction", "charging", "weighing", "polishing", "spray", "spraying", "sanding", "mixing", "dispersion", "dispersing", "blending", "milling", "ball milling", "mill base", "sol-gel", "emulsion"
- Workers: "maintenance", "cleaning", "let down", "thinning", "tinting", "shading", "filling", "filtering", "grinding", "turning", "painting", "spray painting", "shot blasting", "spreading", "flow coating", "electrode position", "air drying", "roller coating", "spray booth"
- Environmental: "weathering", "leaching", "aging", "degradation", "waste", "emission", "abrasion", "stripping"

11.2 3D printing

The search terms used were:

("nanomaterial" OR "nanocomposite") AND "exposure" AND (search term), with the following used for (search term):

- 3D printing technology: "additive manufacturing", "3D printing", "3D printer", "three dimensional printing", "fused deposition modelling", "fused deposition modelling", "FDM", "selective laser melting", "SLM", "multi jet fusion", "MJF", "VAT photopolymerization", "VAT photo-polymerisation", "SLA", "stereolithography", "direct light processing", "DLP"
- Filament production: "extrusion", "extruder", "filament", "filament manufacturing", "modified filament", "melting"
- Process steps: "sandblaster", "sandblasting", "blaster", "graphite blaster", "polishing", "vibrational polishing", "curing", "curing oven", "shot peening", "drying", post-processing"

12. Annex 2 – Exposure Routes Summary

The following tables are a summary of the literature review for the route of exposure, the activities and the materials used from the literature review.

Table 28. Materials used and exposure routes from literature review for human exposure

Route of exposure	Process	Activity	Release potential	NF used	Matrices
Paints					
Inhalation	Formulation	Synthesis	Low	SiO_2, TiO_2, MWCNT, α-Fe_2O_3, FeO(OH), Fe_3O_4, $CaCO_3$,	Water-based
	Service Life	Paint brushing, Paint rolling	Low	SiO_2, TiO_2, MWCNTs	Water-borne acylic, solvent-borne alkyd, water suspension
		Drying	Low	Carbon black	Water-borne acrylic, solvent-borne
		Spray painting, spray applications	High	ZnO, Fe_2O_3, SiO_2, ZnO	Polyurethane, acrylate, water based, aqueous
		Sanding	High	TiO_2, carbon black, ZnO, Fe_2O_3, SiO_2, kaolin	Polyurethane, polyvinyl acetate, acryl binder, lacquer, water, proplylene glycol, Uradil AZ XO 601Z44
		Sawing	Low	SiO_2	N/A
	End of Life	Sandblasting	Low	CNT	N/A
Dermal	Service Life	Weathering	Release	CeO_2, ZnO, CuO	Water-based
		Sanding	Release	CuO, TiO_2	acrylic
3D printing					
Inhalation	Filament production	Weighing and Mixing	High potential	CNTs (and other NPs used)	
		Extrusion	Potential	CNTs	e.g. ABS, PLA, PC etc.
	Pre-processing	Filling, handling and sieving	High potential	CNTs	ABS, PLA, PLC
	AM	Binder jetting, directed energy deposition, material extrusion, material jetting, powder bed fusion, sheet lamination, Vat polymerisation	High potential (NPs and VOCs)	CNTs Metal powders: IN939	ABS, PLA, HIPS, alybrick, laywood, PC, PCTPEM, TGlase, ABA, ASA, HIPS, PETG, PCABS, liquid photopolymer, plus filament trade names
	Post-processing	Injection moulding, part cutting, support removal, sandblasting, sanding, curing, abrasion/polishing, handling	Potential for release	CNTs Metal powders: IN939	ABS, PLA, liquid photopolymer, nylon; Solvents used
	Cleaning and maintenance	Cleaning, maintenance	High potential	CNTs Metal powders: IN939 Solvents	Polymer used in filament composition; Solvents used

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Dermal	Pre-processing	Filling, handling and sieving	Potential		
	Post-processing	Injection moulding, part cutting, support removal, sandblasting, sanding, curing, abrasion/polishing, handling	Potential		Use of solvents
	Cleaning and maintenance	Cleaning, maintenance	Potential		Use of solvents

Table 29. Materials used and exposure routes from literature review for environmental exposure

Process	Activity	Release potential	NF used	Matrices
Paints				
Formulation	Synthesis	No studies identified		
Service Life	Weathering	Potential	TiO_2, Ag, SiO_2, CeO_2	Acrylic binder, aqueous dispersion, hydrolysed silane, oily alkyd resin, water-based acrylic
	Abrasion	Potential	ZnO, TiO_2, SiO_2, MWCNTs	Polyurethane, styrene-acrylic, water-based, acrylic, poly(methyl methacrylate)
End of life	Incineration	Transformed	TiO_2	Styrene-acrylic
	Leaching	Potential	SiO_2, Cu_2O, CeO_2, ZnO, TiO_2, DPP, Fe_2O_3, Cu-phthalocyanine	Styrene-acrylic, acrylic, water-based, alkyd and melamine, acrylic and polyester
3D printing				
Filament production	Weighing and Mixing	No studies identified		
	Extrusion			
Pre-processing	Filling, handling and sieving	No studies identified		
AM	Binder jetting, directed energy deposition, material extrusion, material jetting, powder bed fusion, sheet lamination, Vat polymerisation	No studies identified		
Post-processing	Injection moulding, part cutting, support removal, sandblasting, sanding, curing, abrasion/polishing, handling	No studies identified		

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Cleaning and maintenance	Cleaning, maintenance	No studies identified

13. Annex 3- Nanosafety alerts

Table 30. 3D printing practices and nanosafety alerts

Practice	Nanosafety alerts	Other alerts	Route of exposure
Paints			
Formulation	Handling of NFs (dependent on formulation and synthesis)		Human
Service Life	Release of NFs particularly during spray painting/spray applications and sanding (high release potential)		Human
	Release of NFs during weathering and abrasion (high release potential)		Environment
End of Life	Potential release of NFs during sandblasting, leaching and landfill (low potential)		Human and environmental
3D printing			
Pre-processing and filament manufacturing	Handling of NFs for filament production	Handling of metal powders	Human
Additive Manufacturing	Release of NFs during the process	Release of VOCs	Human
Post-processing	Release of NFs during treatment of printed objects and post AM operations	Release of VOCs; use of solvents	Human and environmental
Cleaning and maintenance		Release of VOCs; use of solvents	Human and environmental

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