Verband der deutschen Lack- und Druckfarbenindustrie e.V.

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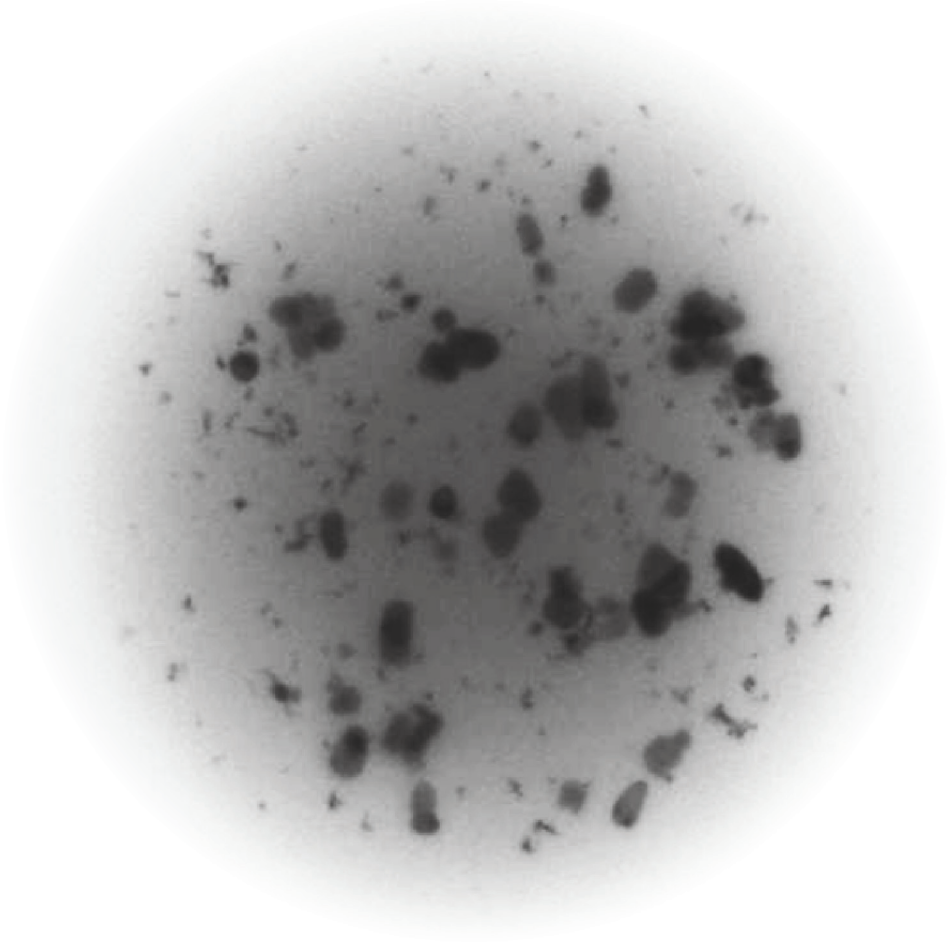
Examinations concerning release and exposure from nanostructured paints and coatings



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Strategy on risk assessment for nanomaterials

Several disperse raw materials of the paint and coating industry like fillers, functional additives or pigments are categorized as nanomaterials according to the nanomaterial definition as recommended by the European Commission (2011)[1]. In contrast to non-nanomaterials, nanomaterials are associated with a higher risk for human health and environment that can be attributed to the ability of individualised nanoparticles to transcend natural protective barriers.

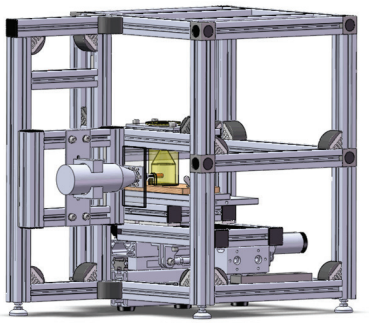
In this context, risk is seen as the probability of a negative impact on human health and environment, which results from the hazard profile of a substance (i.e. toxicity) and the exposure to the substance (i.e. duration, frequency and height of substance dose). Advantageously, toxicity and exposure can be considered and analysed independently from each other during risk assessment.

The Verband der Chemische Industrie e.V. (VCI) deals among others with the direct determination of exposure in workplaces[2], while the German Paint and Printing Ink Association (VdL) is kept busy with the origin of inhalation exposure since about 10 years. The release of airborne particles is thereby considered as the origin of exposure, based on which the exposure potential of nanostructured paints and coatings in the field of consumer protection and occupational safety can be described.

Differentiation between release and exposure

The starting-point for a particulate exposure by nanomaterials is that pieces of matter (i.e. particles like nanomaterial containing fragments, droplets or agglomerates) are separated from a nanostructured material (i.e. powder, suspension or solid composite) by external forces and are transferred subsequently into the environment. This process is called release or particulate emission. But exposure occurs only if there is also a transport of released particles to the exposure region (e.g. breathing zone). The state of dispersion (i.e. size, form and concentration) within the region of exposure results thus from a complex exposure scenario (cf. Fig. 8) composed of release, transportation and transformation (e.g. coagulation) and requires therefore numerous contextual information[3]. In contrast, the state of dispersion of released objects at the source depends solely on the release process and specific material properties.

Release as measure of the exposure potential



In contrast to the metrological exposure characterisation, release analyses do not require contextual information concerning convective flow conditions or concerning the whereabouts of consumers/workers. Thus, the focus of release is directed solely on the particle source.

Release processes can be simulated independently from the environment in laboratory scale (cf. Fig.1) at optimal measurement conditions that provides a high reproducibility and repeatability for systematic analyses concerning material-specific and process-specific impacts on the release behaviour.

Fig. 1: Operated sanding apparatus with stepping motor driven X-Y-table for the simulation of professional sanding processes in laboratory scale.

1 European Commission. Commission Recommendation of 18 October 2011 on the definition of nanomaterial (2011/696/EU). Official Journal of the European Union, 2011, 54 (L275), 38-40.

2 VCI Strategy Paper. Tiered approach to an exposure measurement and assessment of nanoscale aerosols released from engineered nanomaterials in workplace operation, 2011.

3 Clark K, van Tongeren M, Christensen FM, Brouwer D, Nowack B, Gottschalk F, Micheletti C, Schmid K, Gerritsen R, Aitken R, Vaquero C, Gkanis V, Housiadas C, de Ipina JML, Riediker M. Limitations and information needs for engineered nanomaterial-specific exposure estimation and scenarios: recommendations for improved reporting practices. J. Nanopart. Res., 2012, 14, 970

In close cooperation with VdL, several experimental release studies (Tab. 1) were performed for different release scenarios over the lifecycle of nanostructured paints and coatings. In detail, the experimental release studies dealt with the handling of pigment powders during the production[4], the application of liquid coatings by operation of spray cans and spray guns[5] and with the daily use[6] as well the mechanical processing of cured coatings[7] as well as artificially aged coatings[8].

Tab. 1: Studies on release and exposure from nanostructured paints and coatings supported by VdL.

period	*acronym*	*focus*	*ref.*
2007	TUD-AP1	Release from coatings during daily use treatment 1	[7]
2008	TUD-AP2	Release from coatings during daily use treatment 2	[7]
2008-2009	TUD-AP3	Release from cured coatings during professional sanding	[8]
2009-2010	TUD-AP4	Release from aged coatings during professional sanding 1	[9]
2010-2011	TUD-AP5	Release from aged coatings during professional sanding 2	[9]
2012-2013	TUD-AP6	Release during spray application of liquid coatings	[6]
2013-2015	AIF/NPR	Release during handling of nanostructured powders	[5]
2015-2017	TUD-AP7	Exposure estimation from release data by propagation modelling	[10]

In order to consider a broad product range and a large field of application, all experimental release studies were performed by means of nearly identical, industrial prepared sample systems (cf. Fig. 2) based on a functional additive (ZnO, 20 nm, CAS-Nr. 1314-13-2), a transparent pigment (Fe_2O_3, 65 nm, CAS-Nr. 1309-37-1) and a pyrogenic filler (SiO_2, 7 nm, CAS-Nr. 68909-20-6). Up to 3 wt.-% of these nanomaterials were processed within architectural paints and coatings, furniture coatings, parquet lacquers and vehicle coatings.

4 Göhler D, Stintz M. Nanoparticle release quantification during weak and intense dry dispersion of nanostructured powders. J. Phys.: Conf. Ser., 2015, 617, 012029.

5 Göhler D, Stintz M. Granulometric characterization of airborne particulate release during spray application of nanoparticle-doped coatings. J. Nanopart. Res., 2014, 16, 1-15.

6 Vorbau M, Hillemann L, Stintz M. Method for the characterization of the abrasion induced nanoparticle release into air from surface coatings. J. Aerosol Sci., 2009, 40, 209-217.

7 Göhler D, Stintz M, Hillemann L, Vorbau M. Characterization of nanoparticle release from surface coatings by the simulation of a sanding process. Ann. Occup. Hyg., 2010, 54, 615-624.

8 Göhler D, Stintz M, Rommert A. Im Lack und drum herum. Partikelfreisetzung beim Umgang mit nanostrukturierten Materialien. Farbe und Lack, 2016, 122, 52-60.

Fig. 2: Propellant spray can with liquid coating as used for release analyses during spray application.

Number-weighted particle size distributions and concentrations of released particles were determined for each material-process-combination by operating highly sensitive aerosol analytical techniques (i.e. differential electrical mobility analyses, time of flight spectrometry, condensation nuclei counting). Based on the acquired raw data, general valid specific release quantities were deduced by taking into account also the realised analytical conditions. The reported release data distinguish oneself by a high transferability (i.e. scale-up, scale-down) to any process-specific release scenario and provide also a good comparability between results for different release processes and materials.

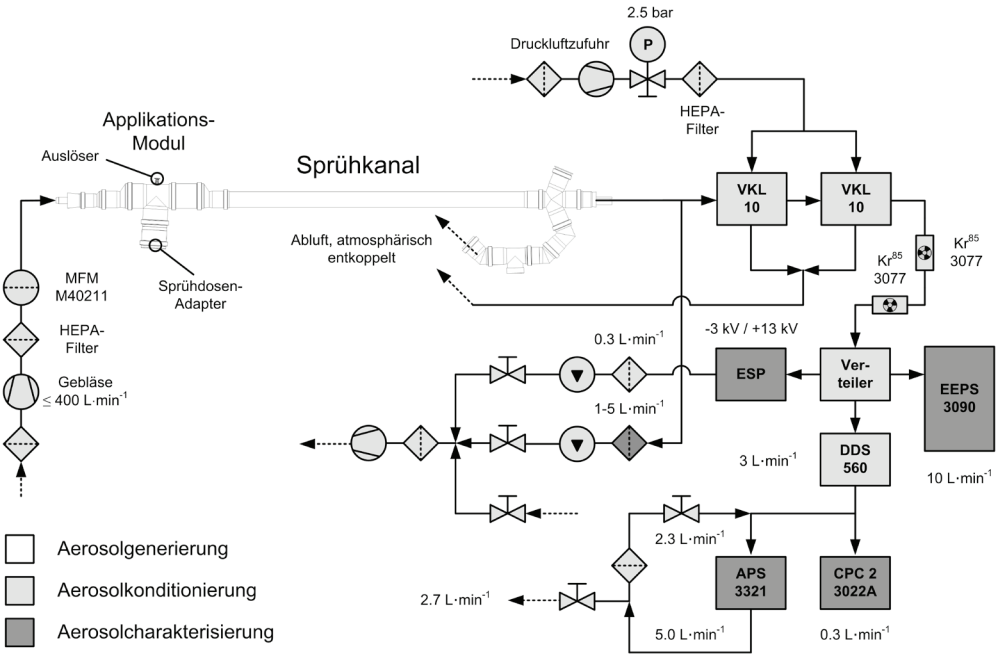


Fig. 3: Schematic illustration[9] of the experimental setup used for the release characterisation during spray application of liquid coatings (APS = time-of-flight spectrometer, CPC = condensation nuclei counter, EEPS = fast measuring electrical mobility spectrometer, VKL/DDS ... dilution units, ESP ... electrostatic precipitator for subsequent electron microscopy).

In general, no significant differences in the specific release quantities were determined between the analysed nanostructured paints and coatings and their non-nanostructured counterparts. Nevertheless, quantities between 10^{06} and 10^{12} particles per gram (#/g) stressed, ejected or abraded material were released into air across all the studies and samples. The least release (10^{07} #/g resp. 10^{05} #/m²) and thus the lowest exposure potential was determined for the cured coatings in daily use, followed from their mechanical processing (10^{09} #/g resp. 10^{10} #/m²). Artificially aged coatings showed during mechanical processing a higher release (10^{10} #/g resp. 10^{11} #/m²) than their non-aged counterparts. Furthermore, it could be observed that the addition of nanostructured materials in coatings accompanied with a lower aging-induced release increase as determined for the non-nanostructured reference coatings. The application of liquid coatings by a professional manual gravity spray gun (10^{09} #/g resp. 10^{08} #/s) led to a lower release in comparison to the operation of propellant spray cans (10^{10} #/g resp. 10^{10} #/s) from the DIY section.

9 Göhler D, Stintz M, Rommert A, Eichstädt D. Was geht denn da in die Luft? Farbe und Lack, 2015, 121, 142-149.

Extensive analyses on released particles after electrostatic precipitation by scanning electron microscopy and transmission electron microscopy in combination with energy dispersive X-ray spectroscopy showed that the nanoparticles of the nanomaterials were embedded firmly within the coating matrices (cf. Fig. 4-6).

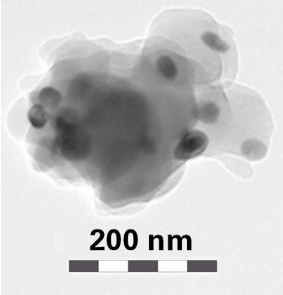


Fig. 4: TEM-image of a 350 nm furniture coating particle with firmly embedded nanoscaled ZnO additive particles, released during sanding.

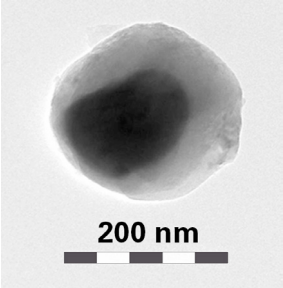


Fig. 5: TEM-image of a 200 nm sanding aerosol particle, where a single TiO_2 pigment particle is sheathed completely by the matrix material.

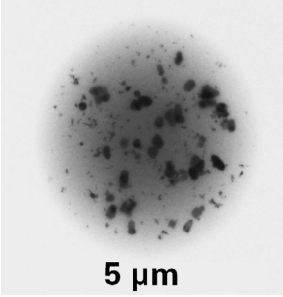


Fig. 6: TEM-image of a dried acrylate spray droplet from a propellant spray can with embedded nanoscaled ZnO additive particles and non-nanoscaled TiO_2 pigment particles.

Exposure modelling based on release data

For worst case consideration (i.e. accidents, misuse), the release data of the above mentioned studies can be equalised with exposure ones if a meaningful definition of the release scenarios is preceded. But in the reality if at all, only a fractional amount of the released material will reach the region of exposure due to propagation-caused dilution and flow-induced emigration.

First rough estimations concerning exposure levels to be expected were performed contemporaneous with the release studies by the means of simplified calculations based on ideal and lossless mixing of released particles within defined model volumes (e.g. air column, model room). The thus determined particle number concentrations varied in the dependence of the material-process-combination and perception between negligible values of < 1 #/cm³ for cured coatings in daily use and up to a magnitude of order of $4 \cdot 10^{04}$ #/cm³ for spraying or sanding.

One has to internalise that aerosol propagation as well as exposure are transient/unsteady phenomena. In order to estimate exposure levels under conditions closer to reality, an in-silico study[10] was performed, wherein the experimental received release data were combined with propagation modelling. Therefore, different release scenarios (wiping, sanding and spraying) and varying ventilation scenarios (natural ventilation by door slit infiltration at 0.5 hr^{-1}, natural ventilation by an opened pivot-hung window at 1.5 hr^{-1}, technical ventilation at 8.0 hr^{-1}) were simulated within one model room.

10 Göhler D, Gritzki R, Stintz M, Rösler M, Felsmann C. Propagation modelling based on airborne particle release data from nanostructured materials for exposure estimation and prediction. J. Phys.: Conf. Ser., 2017, 838, 012010.

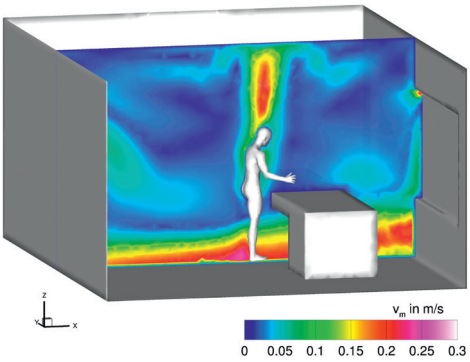


Fig. 7: Visualisation of the mean steady-state flow velocity through the working area in case of natural ventilation by opened pivot-hung window (air exchange rate 1.5 h-1, temperature specifications: 5°C inlet air, 20°C mean room temperature via floor heating, 26°C clothing surface, 30°C hand surfaces, 35°C head surface).

Despite a lot of assumptions and extensive specifications for modelling, the simulated exposure scenarios showed impressive that the exposure level depends fundamentally on the release scenario, the ventilation scenario and the whereabouts of the consumer/worker. The ratio between the number of released particles to the number of inhaled particles varied during nearfield considerations (distance of around 0.6 m between particle source and region of exposure) between $4 \cdot 10^2$ and $1.5 \cdot 10^7$ over all analysed exposure scenarios. It could be shown, that the highest levels of exposure arise immediately during resp. short after nearfield release. Furthermore, it could be observed that convective flows caused by person heat can lead to particle availability in the breathing zone (cf. Fig. 7).

All simulated exposure scenarios for the release scenario wiping, which relies on experimental release data for cured coatings under daily use, show quasi no inhalation exposure (i.e. less than one particle is inhaled). On the other hand, the highest exposure level with a concentration peak of $1.6 \cdot 10^4$ #/cm³ (130 µg/m³) was determined for the spraying release scenario for almost undisturbed aerosol propagation (i.e. natural ventilation by door slit infiltration), whereby around one billion particles with a mass of 9 µg were inhaled during and after a 60 s lasting spray application. It should be noted here, that in the case of the spray example a high amount of inhaled particles will also be exhaled (> 73 wt.-% resp. > 78 number-%).

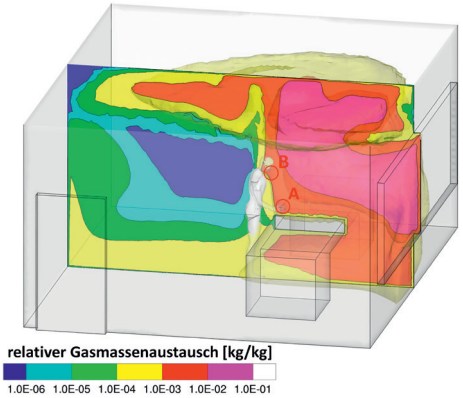


Fig. 8: Calculated aerosol propagation 75 s after spray application of a liquid coating by a propellant spray can within a 5 m x 6 m x 3 m = 90 m³ model room ventilated by an opened pivot-hung window (air exchange rate 1.5 h-1) and closed door; A = region of release, B = region of exposure (breathing zone).

Both the results on exposure of the simplified calculations (provided in the context of each release study) and the ones based on propagation modelling correlate comparatively well among each other. A look on metrological determined exposure data based on daily life situations should help to classify the above mentioned exposure data. Particle number concentrations of around $1.5 \cdot 10^4$ #/cm³ can be found for example in offices[11]. Moreover, field measurements[12] have shown that vacuum cleaning leads to concentration peaks up to $1.4 \cdot 10^4$ #/cm³ (> 5 µg/m³). Significantly higher particle number/mass concentrations arise typically during cooking activities. For toasting and boiling concentration peaks of $1.0 \cdot 10^5$ #/cm³ (> 20 µg/m³) were determined, while frying and barbecuing led to values of $1.4 \cdot 10^5$ #/cm³ (> 700 µg/m³). According to the mentioned examples, it will be obviously that a direct correlation between number and mass concentrations is per se not possible due to large differences between release-caused particle size distributions.

11 Lonati G, Ozgen S, Luraghi T, Giugliano M. Particle number concentration at urban microenvironments. Chemical Engineering Transactions, 2010, 22, 137-142

12 He C, Morawska L, Hitchins J, Gilbert D. Contribution from indoor sources to particle number and mass concentrations in residential houses. Atmos. Environ., 2004, 38, 3405 – 3415.

Synopsis/Summary

The performed release studies initiated by VdL have received a high international acceptance[13]. The developed methodical approach to deduce quantitative release data is currently in national and international standardisation[14], while the designed test devices and experimental setups (cf. Fig. 1 resp. Fig. 3) are also operated for release characterisation from nanostructured materials of different other industrial sectors[15].

Especially for the paint industry, the nanomaterial release behaviour was analysed for nearly the whole life cycle of nanostructured paints and coatings. In this context, no significant differences in quantities and sizes of released particles could be observed by comparing nanostructured sample materials and corresponding non-nanostructured reference systems. In the cases of liquid, cured and aged coatings, nanoparticles of the admixed nanomaterials were solely recovered firmly embedded within matrix material particles (i.e. within abraded fragments or dried droplets). Furthermore, it could be shown that aging of coatings goes along with an increase in the number of released particles during mechanical processing.

In comparison to exposure data, quantitative release data have a more general nature and could be determined more reliable. Release data are also a measure for the exposure potential of nanostructured materials. Thus, release data become more and more important with regard to the regulatory context. Furthermore, it could be shown that propagation modelling in combination with experimentally determined release data can be a useful and economic tool for non-metrological exposure estimation of variable exposure scenarios.

In summary, VdL has made with its studies concerning release and exposure a significant contribution to the nanomaterial risk assessment.

13 Koivisto AJ, Jensen ACO, Kling KI, Nørgaard A, Brinch A, Christensen F, Jensen KA. Quantitative material releases from products and articles containing manufactured nanomaterials: Towards a release library. NanoImpact, 2017, 5, 119-132

14 Stintz M, Göhler D. International standardization in particle characterization for quality and safety assessment in particle technology. Procedia Engineering, 2015, 102, 233 - 239.

15 Göhler D, Nogowski A, Fiala P, Stintz M. Nanoparticle release from nanocomposites due to mechanical treatment at two stages of the life-cycle. J. Phys.: Conf. Ser., 2013b, 429, 012045.

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