



Size Distribution of Particulate Matter in Indoor Environment During Nanomaterial Paint Application

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Abstract

Due to the increasing production and development of nanoparticles, it has become necessary to control the exposure to ultrafine particles (aerodynamic diameter $< 0.1 \mu\text{m}$) when handling nanopaints. The paper deals with the number and mass distribution of particulate matter (PM) in an indoor environment before, during and after the application of paint Protectam FN containing titanium nanoparticles. The size distribution determination was performed by the electrical low-pressure cascade impactor (ELPI⁺) in the range from $0.006 \mu\text{m}$ to $9.93 \mu\text{m}$. The highest number of particles was observed in the range from 0.006 to $0.0175 \mu\text{m}$. The particulate mass concentration ranging from 0.0175 to $0.0307 \mu\text{m}$ did not represent more than 0.5% of the sum of PM₁₀ during the individual measurements. The particle mass concentration increased in the range of 0.0175 to $0.0307 \mu\text{m}$, after application of the coating nanopaint Protectam FN, but it was observed that the total number of particles has decreased. During the days following the application of the nanopaint, the mass concentration in this grain size class was significantly reduced.

Keywords: nanopaint, indoor environment, particulate matter, nanoparticles, ELPI⁺

Introduction

The indoor air quality can influence decisively human health. People are spending indoor up to 80–90% of the time. The indoor sources of particulate matter (PM) are commonly classified according to the activities of building users. The walking generates a substantial large number of particles larger than $1 \mu\text{m}$. On the other hand, fine-grained particulate matter can be typically generated during a lot of activities as cooking and heating using a fireplace, tobacco smoking, vacuum cleaning and so on (Hussein et al., 2006; Lappalainen et al., 2013; Bo et al., 2017). Emissions from building materials, consumer products, and printers can also be significant sources of PM indoor (Lappalainen et al., 2013). Hussein et al., 2005 investigated the relationship of indoor-to-outdoor PM with the effects of indoor activities on the number size distributions of PM. The particles come from outdoor sources during the absence of indoor sources. The maximum penetration PM was found for particles with diameter $0.1\text{--}0.4 \mu\text{m}$.

The mean value of the indoor/outdoor values was 0.36 for ultrafine particles (diameter $< 0.1 \mu\text{m}$) and 0.60 for PM $> 0.1 \mu\text{m}$ (Hussein et al., 2005). Penetration of particles from outdoor to indoor environment of a building can reach up to 100%. It is most significant for particles of the size from 0.1 to $1 \mu\text{m}$. Particles PM $< 0.1 \mu\text{m}$ a PM $2.5\text{--}10 \mu\text{m}$ usually dominate in indoor environment (Schneider, 2008).

Resuspension of dust particles in an indoor environment of buildings is caused by usual activities (cleaning, walking). It decreases with decreasing particle size, for particles of the size $< 1 \mu\text{m}$ it is not essential. Schneider (2008) reports that resuspension concerns the particles of the size from 2.5 to $10 \mu\text{m}$. In the indoor air (office rooms), mean number of these

particles was 1900 per litre, while the mean number of particles $\geq 5 \mu\text{m}$ was 20 particles per litre (Lappalainen et al., 2013). The number of particles varies from low values ($< 10^3$ particles/cm³) in particularly clean indoor rooms to high values ($> 10^6$ particles/cm³) in the presence of intense sources of PM (Bo et al., 2017). The mass concentration of PM_{2.5} in office rooms ranged between 4.7 and $37.6 \mu\text{g}/\text{m}^3$, the median value was $11.7 \mu\text{g}/\text{m}^3$. The mass concentration of PM_{2.5} varied between 2.6 and $31.2 \mu\text{g}/\text{m}^3$ in the 20 office buildings (Europe) (Szigeti et al., 2017).

Particles in indoor rooms can contain contaminants, bacteria, and other harmful substances. Nano-coatings can offer protection from pollutants, bacteria etc. (Koivisto et al., 2018). Nano-coatings are highly transparent layers of metals, ceramics or polymers, with typical size below 100 nm . Photocatalytic materials remove various air pollutants under UV-light illumination. Especially the photoactive materials based on TiO₂ can enable photocatalytic reaction under visible light. These reactions increase the efficiency of photocatalytic oxidation and the using of photocatalytic applications in indoor. Photocatalytic oxidation of materials based on TiO₂ generates free radicals. Due to these properties, photocatalytic surfaces are self-cleaning, antimicrobial, and oxidative for organic pollutants (Koivisto et al., 2018; Haider et al., 2017). Coatings containing nanoparticles (TiO₂ and ZnO) exhibit antibacterial effect for Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa (Hochmannová et al., 2010).

Under wet and dry abrasion of walls protected by the coating containing nanoparticles of TiO₂, submicrometric and micrometric particles were released, but particles with the nanometric diameter (below $0.1 \mu\text{m}$) were not detected.

No free or agglomerated TiO₂ nanoparticles were observed: TiO₂ nanoparticles (~ 30 nm) appear to be embedded in the paint matrix. Agglomerates of matrix particles of about 110 nm are observed. The sizes vary between 100 nm and 300 nm (Golanski et al., 2011).

It was performed determination of the number and mass distributions of dust particles before, during, and after paint because of lack of studies dealing with particles in indoor where paint was containing nano-TiO₂ component. The aim of this work is the determination of the number distribution and mass concentration of particles of the size from 0.006 to 10 µm during application of paint containing nano-TiO₂ and their influence on decreasing of total dust in an indoor environment.

Methods and sampling

Coat of paint containing nanoparticles TiO₂ Protectam FN (nanopaint), was applied on a ceiling in a meeting room with an area of 20 m². The paint consists of water suspension of photoactive titanium oxide with a mixture of inorganic binding materials. The function paint Protectam FN was developed for creating active photocatalytic layers on the wall surfaces. The coats of paint Protectam have nanoparticles of titanium oxide strongly bound in the pore structure of binder that ensures good cohesiveness and adhesiveness to the surface. Without a binding agent, nanoparticles of the photocatalyst are mutually bound solely electrostatically, which is not sufficient under real conditions (J. Heyrovský Institute of Physical Chemistry, Czech Academy of Science, Prague, online: <https://fn-nano.com>).

Measurements of the number and mass concentrations of PM were performed during selected days in December 2017 and January 2018 and lasted 24 hours or 48 hours (Table 1). During sampling, the meeting room was neither used by the staff of an organisation nor was cleaned, to prevent the resuspension of dust particles. The room was during sampling of dust particles visited only by operators of ELPI⁺ instrument.

The sampling of dust particles was performed by electric low-pressure cascade impactor ELPI⁺ manufactured by DEKATI (Dekati Ltd., Tampere, Finland) with air flow 9.88 l/min. ELPI⁺ enables measurement of real-time particle size distribution (in the 14 different stages) in the size range of 6 nm (0.006 µm)–10 µm. Dust particles were caught on individual aluminium foils of 25 mm diameter, on which there was applied the Dekati® collection substrate to prevent particle bounce and blow-off from the impactor stages. The particle number distributions were measured for particles with aerodynamic diameters 0.006, 0.0175, 0.0307, 0.0539, 0.0945, 0.156, 0.258, 0.384, 0.606, 0.952, 1.64, 2.48, 3.67, 5.39, and 9.93 µm in 1 minute intervals using ELP⁺. The gravimetric method was used for mass distribution of PM. Mass concentrations were determined for particles in the range from 0.0175 to 9.93 µm. Samples were repeatedly weighted using ultra-microbalances Mettler Toledo XP6U/M with the capacity of 6100 mg ± 0.1 µg.

Results and discussion

Mass distribution

The values of mass concentration of PM_{2.5} or PM₁₀ in any of the monitored samples did not exceed the permitted hourly

limit of the PM_{2.5} concentrations of 80 µg/m³ or PM₁₀ 150 µg/m³ for the indoor environment as defined by the Decree of the Ministry of Health of the Czech Republic No. 6/2003 Coll. (which sets hygienic limits of chemical, physical and biological indicators for indoor living rooms of some buildings). The highest mass concentration of ΣPM₁₀ was detected the day before application of the nanopaint coating with the value of 117.11 µg/m³. The lowest weight concentration of ΣPM₁₀ was achieved during application of the nanopaint coating (44.13 µg/m³). In the next 2 days after application of the nanopaint coating, a 1.6-fold increase in ΣPM₁₀ concentrations occurred, and almost double the increase during the first control sampling compared to the nanopaint application day (Fig.1). The particles exhibit a unimodal distribution with a peak between 0.606–5.39 µm. Only during the nanopaint coating application, the particle distribution had a non-distinctive bimodal character with peaks in the range of 0.606–1.64 µm and 2.48–9.93 µm.

The highest weight concentrations were found for particles with an aerodynamic diameter of 1.64–2.48 µm (22–24% of ΣPM₁₀) and the lowest concentrations (0.03–0.5%) for 0.0175–0.0307 µm particles (Figure 2) before and after application of the nanopaint coating. During nanopaint application, the highest concentration for particles of 2.48–3.67 µm (22% of ΣPM₁₀) was found. The lowest concentration was found for particles 0.0175–0.0307 µm (0.012% of ΣPM₁₀) before and after coating application. The most extensive particle weight loss approximately one month (control sampling 2) after coating application can be observed in the grain-size class of 1–2.5 µm (about 50%), and in the grain-size class of 2.5–10 µm (about 60%). The smallest effect was observed for nanoparticles (up to 0.1 µm).

Number distribution

In the case of the particle number distribution in the individual grain-size classes in ΣPM₁₀, the opposite dependence applies to the mass concentrations (Figure 3). The highest number of particles in the grain-size class < 0.1 µm class is also confirmed by Kelly and Fussell (2012). Ultrafine particles (UFPs) dominate the number concentration of dust particles, but they represent only a negligible mass of total PM. The highest percentage of particle counts in ΣPM₁₀ (before application, during application of the nanopaint coating and control sampling I and II) was found for particles of 0.006–0.0175 µm (18 to 35% of ΣPM₁₀). An exception was the results obtained after application of the nanopaint coating, where the highest number of particles was found for 0.156–0.258 µm particles (17% of ΣPM₁₀). After the application of the coating, a temporary short-term (48 h) reduction of the 0.006–0.0175 µm dust particles occurred.

Before and during paint application, the highest number of particles in the grain-size class of 0.006–0.0175 µm was identified. The lowest number of particles was found for particles > 0.952 µm and above. The same tendency was also observed for the maximum particle count (Figure 4). After application of the nanopaint coating, the tendency of the number distribution of dust particles changed. The average number of particles decreased two to four times as compared to the nanopaint coating application. The mean particle count was the lowest at PM > 0.952 µm.

Fig 1. Scheme of sampling
Rys. 1 Schemat pobierania próbek

Date of sampling	Time interval of sampling	Process name	ΣPM_{10} ($\mu\text{g}/\text{m}^3$)	
30.11.-1.12.2017	24 h	Before application of nanopaint	117.11	working day
1.12.-2.12.2017	24 h	During application of nanopaint	44.13	working day/ non-working day
2.12.-4.12.2017	48 h	After application of nanopaint	87.64	non-working day
4.12.-6.12.2017	48 h	Control sampling I	69.38	working day
15.1.-17.1.2018	48 h	Control sampling II	60.81	working day

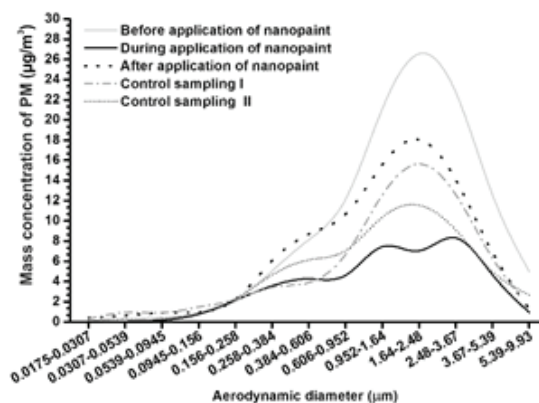


Fig. 2. Mass concentrations of particles before, during, and after application of paint including two control samplings
Rys. 2. Masowe stężenia cząstek przed, w trakcie i po nałożeniu farby, w tym dwie próbki kontrolne

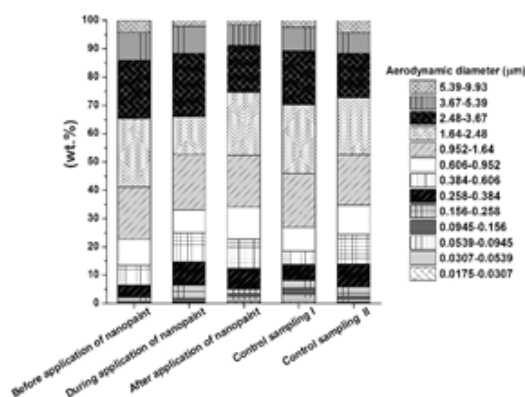


Fig. 3. Percentage of the mass concentration of individual grain size classes in ΣPM_{10}
Rys. 3. Procent stężenia masy poszczególnych klas wielkości ziarna w ΣPM_{10}

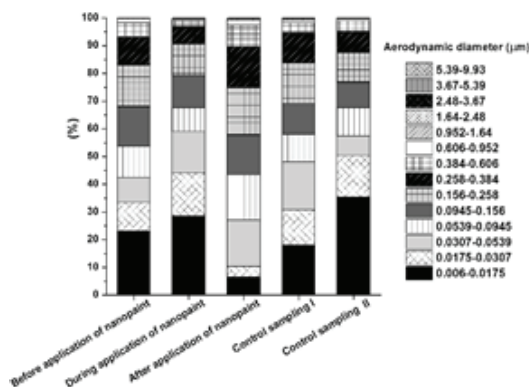


Fig. 4. The number of particles in individual grain size classes in ΣPM_{10} expressed in %
Rys. 4. Liczba cząstek w poszczególnych klasach wielkości ziarna w ΣPM_{10} wyrażona w%

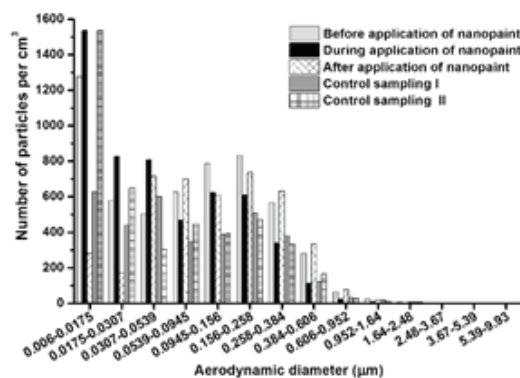


Fig. 5. Average number of particles in individual particle size classes of PM
 Rys. 5. Średnia liczba cząstek w poszczególnych klasach wielkości cząstek PM

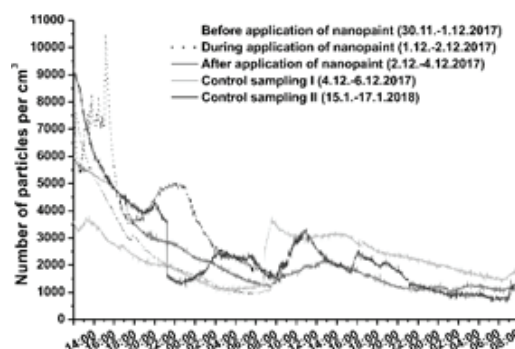


Fig. 6. Number of particles in dependence on the time interval of measurement
 Rys. 6. Liczba cząstek w zależności od przedziału czasu pomiaru

With the application of the nanopaint coating, the highest number of particles was found in the grain-size class of 0.006–0.0175 μm , at the same time there was a significant increase in the number of particles in the grain-size classes of 0.0175–0.0307 μm and 0.0307–0.0539 μm . During coating application, nanoparticles release particles within the range of 0.0175–0.0539 μm .

The particle size distribution of the pooled classes from 0.006 to 0.0945 μm ($< 0.1 \mu\text{m}$) with minute intervals for individual sampling (before, during, after coating application and control sampling I and II) is shown in Figure 5. The highest particle counts were found during the first two hours of measurement between 10:00 and 12:00, followed by a decrease in the number of particles. This is due to the fact that at the beginning of the measurement, 2 or 3 persons were operating the ELPI⁺ apparatus in the room. Figure 5 shows the values after achieving the equilibrium (after re-settling of the particulate matter 2 hours after the start of the measurement). After reaching the equilibrium state of the environment, the day before application of the nanopaint coating, a maximum value of 8,219 particles/cm³ was determined. Nanoparticles (with a maximum value of 10,500 particles/cm³) were temporarily increased during the application of the coating (on 1 December 2017), which was taking place from 12 a.m. to 2 p.m., but the number of particles was generally lower than the day before nanopaint application. During the day when the nanopaint coating was applied, there was a slight increase in nanoparticles ($< 0.1 \mu\text{m}$) between 5 p.m. and 12 p.m. The following days after coating application, nanoparticles decreased after

application of the nanopaint coating (after equilibration of the environment) with a maximum value of 6,002 particles/cm³, and for the control sampling I of 3,785 particles/cm³. The control sampling II performed one month later showed that the number of nanoparticles in the room is the same as before the coating application with a maximum value of 9,264 particles/cm³.

The day before and during the application of the coating, the average number of ΣPM_{10} particles was almost comparable and was (5,562 and 5,363 particles per cm³). The average number of ΣPM_{10} particles (4,281 particles/cm³) was slightly reduced over the next two days after coating application. During the third and fourth day after application (control sampling I), the decrease in the average number of particles was even more pronounced (3,471 particles/cm³). By control sampling II in January 2018, it was found that the average number of ΣPM_{10} particles (4,343 particles/cm³) was comparable to the results obtained after applying the nanopaint coating.

Conclusions

During all monitored sampling, the highest number of particles was identified in the grain-size class of 0.006–0.0175 μm . Particles had the lowest weight concentration. In all ΣPM_{10} samples, the mass concentration of the 0.0175–0.0307 μm particles was less than 0.5%. During application of the nanopaint coating, particles are especially released in the range of 0.0175–0.0539 μm . On the day after coating application, the highest mass concentration was for the 0.0175–

0.0307 μm particles. At the same time, there was a total decrease in the number of particles. Although the total particle drop was detected immediately after application of nano-TiO₂ paints, one month after coating application, the number of particles was comparable to the conditions before application. During application of the nano-TiO₂ coating, nanoparticles (< 0.1 μm) are not released, and their number does not pose a risk to workers applying the coating. The importance of nanopaint application does not consist in the decrease in the particles, but especially in the effective removal of poly-

cyclic aromatic hydrocarbon pollutants and the minimization of microbial activity (the antibacterial effect).

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Rozkład wielkości cząstek stałych w środowisku wewnętrznym podczas nakładania farby nanomateriałowej

W związku z rosnącą produkcją i rozwojem nanocząstek konieczne stało się kontrolowanie ekspozycji na ultradrobne cząstki (średnica aerodynamiczna <0,1 μm) gdy wykorzystuje się farby zawierające nanocząsteczki (nanopaint). Artykuł dotyczy liczby i rozkładu masowego cząstek stałych (PM) w środowisku wewnętrznym przed, w trakcie i po zastosowaniu farby Protectam FN zawierającej nanocząstki tytanu. Określenie rozkładu wielkości przeprowadzono za pomocą elektrycznego impaktora kaskadowego (ELPI+) w zakresie od 0,006 μm do 9,93 μm. Największą liczbę cząstek zaobserwowano w klasie ziarnowej od 0,006 do 0,0175 μm. Udział masowy cząstek w zakresie od 0,0175 do 0,0307 μm nie stanowił więcej niż 0,5% sumy PM10 podczas poszczególnych pomiarów. Stężenie cząstek wzrosło w zakresie od 0,0175 do 0,0307 μm, po nałożeniu powłoki nanopaint Protectam FN, ale zaobserwowano, że całkowita liczba cząstek zmniejszyła się. Z upływem czasu od nałożenia nanopaint, udział tej klasy ziarnowej spadał.

Słowa kluczowe: nanopaint, środowisko wewnętrzne, cząstki stałe, nanocząstki, ELPI+