

Emissions of volatile organic compounds from lacquer coatings used in the furniture industry, modified with nanoparticles of inorganic metal compounds

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Abstract: This study presents results of studies on emissions of volatile organic compounds from lacquer products containing nanoparticles of inorganic metal compounds (SiO_2 , TiO_2 , and Ag). The lacquers selected for analyses were applied on the surface of Scots pine (*Pinus sylvestris* L.) wood. Tests were conducted by gas chromatography coupled with mass spectrometry and thermal desorption. Concentrations of volatile organic compounds (VOCs) released to the air by tested coatings in the first stage of the analyses fell within a very broad range (307–1829 $\mu\text{g}/\text{m}^3$). Analyses of VOC emissions were conducted after 1, 3, 5, 7, 10, 30, 60, and 90 days. After 90 days VOC concentrations were significantly lower, ranging from 42 to 101 $\mu\text{g}/\text{m}^3$. A broad spectrum of compounds, comprising aldehydes, esters, ketones, aliphatic and aromatic hydrocarbons, alcohols, glycols, and terpenes, was identified in the tested air.

Key words: Furniture industry, indoor air, lacquer coatings, nanoparticles, VOC

1. Introduction

Interest in products containing nanomaterials has been observed in the last decade. Nanomaterials are materials containing particles of 1 to 100 nm (EPA, 2007). These materials exhibit novel physical, chemical, and biological properties in comparison to the forms of greater diameters from which they are produced (Sokół, 2012). At present, nanomaterials have been applied in fields such as medicine, cosmetology, electronics, the vehicle industry, and the construction sector. It is estimated that the production of nanomaterials will increase. As reported by Nowack and Bucheli (2007), a total of 2000 t of nanomaterials were produced worldwide in 2004. For the years 2011–2020, production is estimated to reach 58,000 t.

An analysis of the market in 2012 indicates limited application of nanomaterials in furniture products. Nanotechnologies, applied mainly in coatings (Van Broekhuizen, 2012b), contributed to the development of specialist coatings referred to as smart coatings and functional coatings. Using nanotechnology we can produce self-healing coatings, products with molecular memory, products signalling leakage and other failure, and items that respond to changes in temperature or change colour as desired. An important group comprises products with self-cleaning properties, products that neutralise unpleasant odours, or products that possess antibacterial actions. Nanoparticles of certain fillers

enhance mechanical resistance of coatings or protect them against changes caused by external factors, including UV light and water (Van Broekhuizen, 2012a).

Nanomaterials used most commonly in the furniture industry include SiO_2 , TiO_2 , ZnO, CeO_2 , Ag, and CuO (Van Broekhuizen, 2012b). SiO_2 nanoparticles are added to lacquers to provide coatings with enhanced hardness and scratch resistance (Van Broekhuizen, 2012b). Moreover, Zubielewicz (2008) stated that they positively affect rheological properties of lacquers and reduce blistering of coatings as a result of water action. Nanoparticles of SiO_2 may also be added to lacquer products to improve water resistance of the surfaces. Inorganic compounds such as ZnO, TiO_2 , SiO_2 , Al_2O_3 , and CeO_2 have been applied to improve resistance to atmospheric conditions, including light (Hongying et al., 2004; Nowaczyk-Organista, 2008, 2009; Van Broekhuizen, 2012a). In order to obtain surface resistance to bacterial activity, nanosilver is added (Gupta and Silver, 1998; Ruben et al., 2005; Liao et al., 2007; Zhang et al., 2007; Rai et al., 2009; Van Broekhuizen, 2012a).

Although an analysis of the literature on nanotechnology is astounding, the effect of nanoparticles on living organisms and the natural environment has not been fully clarified (Oberdörster et al., 2005; Adams et al., 2006; Borm et al., 2006; Hong et al., 2006; Kreyling et al., 2006; Gwinn and Vallyathan, 2006). Van Broekhuizen

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(2012b) stated that workers in furniture production plants are particularly exposed to nanoparticles, while exposure of end users is slight.

Lacquer products modified with nanoparticles are the latest products launched on the market. Thus, they provide an excellent marketing edge. In general, these products are more expensive than the conventional equivalents, and as a result, furniture manufacturers and their customers may assume they are superior or more eco-friendly and healthier. Van Broekhuizen and Van Broekhuizen (2009) reported that the prefix nano- is considered to be an equivalent to the phrases success, high-quality, and sustainable development.

For these reasons it seems essential to determine the influence of lacquer products containing nanoparticles used to finish surfaces of furniture and other interior design elements on concentrations of volatile organic compounds (VOCs) in indoor air.

The primary objective of the study was to determine the effect of lacquer products containing nanoparticles of inorganic metal compounds used in the furniture industry on emissions of volatile organic compounds. The conducted analyses included qualitative and quantitative analyses of volatile organic compounds released by lacquer coatings applied on pine wood surfaces and the assessment of the dynamics of change in VOC levels in the first 3 months following application (within the first 10 days and after 30, 60, and 90 days).

2. Materials and testing methods

2.1. Sample preparation

The experimental material comprised wood samples of Scots pine (*Pinus sylvestris* L.). Samples of 280 × 200 × 16 mm were prepared under industrial conditions. They were produced from strips 100 mm wide that were dried in a chamber drier (Hamech SK 55, Hajnówka, software by Automatem) and then glued with polyvinyl acetate

adhesive. The wood surface was polished with sandpaper (180 and 220 grit). Mean moisture content of samples, determined by the drier-gravimetric method according to the standard PN-77/D-04100, was 7.5%. Density, determined by the stoichiometric method according to the standard PN-77/D-04101, was 569 kg/m³.

Then prepared pine wood samples were coated with lacquer coatings. Analyses of VOC emissions from lacquer coatings containing nanotechnological solutions included tests of four commercially available products (nano1, nano2, nano3, nano4). The selected products were transparent lacquers used in finishing surfaces of wood materials, for indoor use, produced from various wood species, in accordance with recommendations of the manufacturers. They were multilayer lacquers applied as basecoats and topcoats. Tested products came from various producers.

Lacquer products were applied to pine wood surfaces with a brush, while oil was rubbed into the wood using a rag. The products were applied at approximately 110 g/m². According to the manufacturer, optimal surface protection of the flame retardant is provided by the application of approximately 250–300 g/m². For this reason, nano4 was applied at 250 g/m².

Detailed information concerning the physicochemical properties of the lacquer products tested is presented in Table 1.

According to the manufacturer, lacquer nano1 containing SiO₂ nanoparticles is recommended for painting elements produced from various wood species for use indoors and where there is exposure to water or other aggressive agents. It is recommended for use in hospitals, nurseries, kindergartens, schools, and housing facilities, i.e. locations in which enhanced mechanical resistance and hardness of lacquer coatings as well as extended performance life are required. It is advertised as a hypoallergenic product.

Table 1. Technical parameters of commercial lacquer products containing nanoparticles of inorganic metal compounds (based on data supplied by the manufacturer).

Parameters	Lacquer			
	nano1	nano2	nano3	nano4
Binding agents	Acrylic resin	Polyurethane- acrylic resin	Vegetable oil, alkylic resin	Amine resin
Curing agent [parts per volume]	-	Aliphatic polyisocyanate 20	-	-
Diluent	Water	Esters, aromatic hydrocarbons	-	Water
Solids contents [%]	32	38	70	60
Density [g/cm ³]	1.0 – 1.05	1.35	0.9	1.3
Type of applied nanoparticles	SiO ₂	Ag	TiO ₂	Information classified by the manufacturer

Lacquer nano2, containing Ag nanoparticles, is recommended for lacquering furniture and elements from different wood species used in public buildings, hospitals, clinics, waiting rooms, schools, and kindergartens. According to the producer, it exhibits enhanced resistance to light and provides long-term protection of the surface against colonisation and development of bacteria and fungi.

Solvent oil nano3 containing TiO₂ nanoparticles is recommended to protect hardwood elements, including wood of exotic species. It provides enhanced resistance to water and sunlight.

The product nano4, expanding flame retardant lacquer, effectively protects surfaces of wood elements and wood-based materials against fire and serves as decorative lacquer. It is recommended for indoor applications, particularly in public buildings, ships, railway carriages, and aircraft.

2.2. Chamber tests

Tests were conducted in a 0.225 m³ glass chamber under the following conditions: temperature = 23 °C ± 1 °C, relative humidity = 45 ± 1%, air exchange rate n = 1 h⁻¹, and loading factor = 1 m²/1 m³.

Air samples were collected by Tenax TA after 24, 72, 120, 168, and 240 h and after 30, 60, and 90 days (for measurements between 30 and 90 days, ±3 days) starting from the time of finishing with lacquer products. In each case three simultaneous air samples of 1000 mL were collected at a rate of 100 mL/min; air constituting the chamber background was collected with a FLEC pump (Chematec ApS).

2.3. TD/GC/MS analyses

The chromatographic analyses of adsorbed analytes were performed on a gas chromatograph coupled with a mass spectrometer and a thermal desorber under conditions specified in Table 2.

Table 2. Parameters of the TD/GC/MS analytical system.

Elements of measuring system	System working conditions
Injector	Thermal desorber connected to sorption microtrap; purging gas: argon at 20 m ³ min ⁻¹ ; purge time: 5 min.
Microtrap	Desorption temperature: 250 °C; sorbent: 80 mg Tenax TA/30 mg Carbosieve III; desorption temperature: 250 °C for 90 s.
Gas chromatograph	TRACE GC, Thermo Finnigan
Column	RTX – 624 Restek Corporation, 60 m × 0.32 mm ID.
Detector	D _i – 1.8 μm: 6% cyanopropylphenyl, 94% dimethylpolyoxosilane. Mass spectrometer (SCAN: 10 – 350).
Carrier gas	Helium: 100 kPa, ~2 cm ³ min ⁻¹ .
Temperature settings	40 °C for 2 min, 7 °C min ⁻¹ to 200 °C, 10 °C min ⁻¹ to 230 °C, 230 °C for 20 min.

Individual compounds were identified by comparing the obtained mass spectra with the spectra stored at the NIST MS search library (program version 1.7) and were confirmed by juxtaposing mass spectra and retention times of the identified compounds with the spectra and retention times of appropriate standards.

Quantitative analyses of VOCs emitted from the examined wood surfaces were carried out by adding the 4-bromofluorobenzene standard (Supelco).

3. Results

In order to provide more detailed characteristics of the wood material used in the analyses and to determine the source of identified compounds, VOC emissions from pine wood were determined prior to the finishing processes. Results of these tests are given in Table 3.

Table 3. Concentrations of VOCs from pine wood with no lacquer coatings.

Compound	Concentration (μg/m ³)	
	24 h	72 h
Acetone	31.6	21.2
Pentanal	12.8	8.7
Hexanal	36.2	27.6
Furfural	31.2	22.8
α-Pinene	169.8	98.2
Camphene	12.9	7.2
3-Carene	36.3	12.8
Limonene	46.2	16.2
TVOCs:*	377	215

*TVOCs (total volatile organic compounds).

After 24 h of storage, the tested, unfinished pine wood in the chamber released volatile organic compounds to the air at 377 $\mu\text{g}/\text{m}^3$. During 72 h of exposure the amount of released compounds decreased to 215 $\mu\text{g}/\text{m}^3$. Compounds identified in the tested air included both monocyclic monoterpenes (α -pinene, delta-3-carene, camphene) and bicyclic monoterpenes (limonene) as well as aldehydes and ketones. The dominant group of compounds released by pine wood comprised terpenes. After 24 h they accounted

for over 70% of total emissions and after 72 h over 62%. α -Pinene was released in the greatest amounts. In the first stage of analysis the concentration of this compound was 169.8 $\mu\text{g}/\text{m}^3$, while in the other it was lower by 71.6 $\mu\text{g}/\text{m}^3$.

Finishing of wood samples with selected lacquer coatings caused changes in both the type and amount of released compounds. Results of tests on emissions of volatile substances released by lacquer coatings containing nanoparticles are given in Tables 4–7.

Table 4. Concentrations of VOCs emitted from lacquer coating nano1 on pine wood over 90 days.

No.	Compound	Concentration ($\mu\text{g}/\text{m}^3$)							
		24	72	120	168	240	30	60	90
		Hours				Days			
1	Acetone	22.5	18.6	12.5	4.3	3.4	-	-	-
2	1-Butanol	276.9	182.5	125.4	100.6	66.6	20.5	18.3	12.5
3	Toluene	214.9	152.7	100.2	77.5	42.5	12.5	8.3	6.6
4	n-Butyl acetate	145.5	98.2	65.4	45.8	36.5	20.5	8.2	7.7
5	Hexanal	49.5	36.2	38.2	36.2	33.2	16.2	12.1	10.5
6	o-Xylene	23.9	19.2	18.5	16.5	8.6	2.2	2.1	2.5
7	α -Pinene	84.6	62.4	53.2	42.8	44.1	5.2	3.2	4.8
8	2-Butoxyethanol	835.1	631.2	535.4	436.8	336.5	125.5	44.2	21.5
9	1-Butoxy-2-propanol	115.2	85.4	75.4	68.2	45.2	12.5	8.8	8.8
10	3-Carene	16.6	12.2	12.8	10.5	9.9	3.3	3.2	-
11	Unidentified	44.5	32.5	25.4	21.2	16.5	3.3	2.3	-
TVOCs:		1829	1331	1062	860	643	222	111	75

Table 5. Concentrations of VOCs emitted from lacquer coating nano2 on pine wood over 90 days.

No.	Compound	Concentration ($\mu\text{g}/\text{m}^3$)							
		24	7	120	168	240	30	60	90
		Hours				Days			
1	Acetone	52.5	32.5	25.6	16.8	12.5	-	-	-
2	1-Butanol	105.9	79.2	65.2	45.2	30.5	5.2	<1	-
3	Pentanal	89.2	62.5	42.5	32.5	20.5	8.2	6.6	-
4	Toluene	321.5	211.5	136.5	85.4	60.1	20.1	8.2	10.2
5	n-Butyl acetate	215.2	132.5	91.9	84.3	58.2	36.2	30.1	7.2
6	Hexanal	62.5	55.2	36.6	31.5	26.2	16.5	18.2	14.3
7	Ethylbenzene	62.7	42.5	32.5	25.9	20.5	5.2	3.2	2.2
8	m-, p-Xylene	162.5	100.1	52.4	45.2	26.3	12.2	5.2	3.6
9	o-Xylene	42.5	23.2	18.2	13.8	7.3	-	-	-
10	α -Pinene	72.5	61.5	58.4	49.5	30.5	26.2	20.1	20.3
11	3-Carene	16.5	14.2	11.5	10.5	6.2	2.5	-	-
12	Limonene	42.5	30.1	26.8	20.5	12.5	3.3	<1	-
13	n-Butyl acrylate	97.5	132.5	125.8	110.6	116.5	88.5	72.5	38.5
14	Unidentified	115.2	82.5	61.7	50.5	30.1	12.5	6.3	4.9
TVOCs:		1459	1060	786	622	458	237	170	101

Table 6. Concentrations of VOCs emitted from lacquer coating nano3 on pine wood over 90 days.

No.	Compound	Concentration ($\mu\text{g}/\text{m}^3$)							
		24	72	120	168	240	30	60	90
		Hours					Days		
1	Acetone	10.5	6.3	2.2	-	-	-	-	-
2	Acetic acid	12.5	10.5	6.3	1.1	-	-	-	-
3	Pentanal	198.2	152.4	136.2	106.5	89.2	60.5	25.4	9.2
4	Toluene	8.9	7.3	6.5	4.1	3.3	3.6	2.6	2.2
5	Hexanal	112.6	105.2	77.5	60.5	39.5	30.5	27.6	18.2
6	α -Pinene	105.6	92.2	85.2	70.3	60.5	30.2	26.3	30.1
7	2,2,4,6,6- Pentamethylheptane	336.2	263.2	183.3	105.2	86.6	40.8	25.6	15.1
8	3-Carene	12.5	8.3	8.1	7.2	5.2	1.6	2.2	<1
9	Limonene	25.2	16.3	15.5	16.3	12.5	8.3	5.5	7.2
10	1,3,5-Trimethylbenzene	12.5	8.2	5.4	2.6	2.5	2.8	-	-
11	2,2,4,4-Tetramethyloctane	26.9	16.3	13.2	13.1	5	<1	-	-
12	n-Undecane	70.6	50.9	36.3	14.2	5.1	2.9	2.2	2.1
13	Unidentified	36.5	21.5	15.2	14.6	10.1	5.2	4.4	4.3
	TVOCs:	969	759	591	416	320	186	122	88

Table 7. Concentrations of VOCs emitted from lacquer coating nano4 on pine wood in the period of 90 days.

No.	Compound	Concentration ($\mu\text{g}/\text{m}^3$)							
		24	72	120	168	240	30	60	90
		Hours					Days		
1	1-Butanal	36.2	26.5	20.5	15.3	13.2	4.3	-	-
2	3-Hydroxy-2-butanone	28.5	32.5	25.5	19.2	17.3	5.2	<1	-
3	α -Pinene	22.5	27.5	20.1	18.2	18.9	16.3	12.1	12.6
4	2-Butoxyethanol	69.2	45.2	31.2	26.5	23.6	15.5	6.8	7.2
5	3-Carene	8.6	8.5	6.6	6.8	6.3	5.2	5.4	4.1
6	Limonene	12.1	10.2	10.1	9.6	8.8	5.2	4.3	4.8
7	Ethylene glycol	93.5	72.5	55.2	33.5	28.6	20.5	12.1	10.2
8	Unidentified	36.2	31.5	23.9	15.5	14.3	8.6	4.3	3.4
	TVOCs:	307	254	193	145	131	81	45	42

Analyses of products containing nanoparticles showed that emission of volatile substances from coatings may change within a very broad range of values. After 24 h VOC concentration in the air of the chamber containing pine wood samples coated with nano1 amounted to 1828 $\mu\text{g}/$

m^3 . In the case of lacquer coating with nano2 it was lower, amounting to 1459 $\mu\text{g}/\text{m}^3$. Samples coated with the nano3 oil emitted volatile substances at 969 $\mu\text{g}/\text{m}^3$, while those coated with the flame retardant nano4 emitted 307 $\mu\text{g}/\text{m}^3$.

As far as the composition of volatile substances

emitted by tested coatings is concerned, similar differences were reported. Lacquer coatings of nano1 released the greatest amount of alcohols, glycols, esters, and aromatic hydrocarbons. The dominant components of emissions were 1-butanol, toluene, butyl acetic acid ester, 2-butoxyethanol, and 1-butoxy-2-propanol.

Lacquer coatings of nano2 also emitted large amounts of alcohols, aromatic hydrocarbons, and esters. The tested air contained considerable amounts of 1-butanol, toluene, butyl acetic acid ester, ethylbenzene, xylene isomers, and n-butyl acrylate.

Volatile substances released by wood finished with the nano3 oil containing ZnO nanoparticles were composed mainly of aldehydes and aliphatic hydrocarbons. Moreover, a small amount of aromatic hydrocarbons was also detected. Samples refined with the nano3 oil released the greatest amount of pentanal, hexanal, 2,2,4,6,6-pentamethylheptane, and n-undecane.

Among the tested products containing nanoparticles the smallest amount of volatile substances was released to the air by the flame retardant lacquer coatings. These coatings also released the smallest spectrum of volatile compounds. The main emission components included 2-butoxyethanol and ethylene glycol. Moreover, they emitted slight amounts of 1-butanol and 3-hydroxy-2-butane.

In the tested air samples, compounds coming from wood, mainly terpenes, aldehydes, and ketones, were also detected. Samples covered with coatings of nano1 released smaller amounts of terpenes and acetone, while the amounts of hexanal were greater than those from unfinished wood. Coatings of nano2 also reduced emissions of terpenes from wood, but caused an increase in the amount of acetone in the air. In turn, the nano3 oil reduced emissions of acetone and terpenes, while it constituted an additional source of emission for hexanal and other aldehydes. The greatest limitation of emissions of volatile substances from the wood interior was provided by the flame retardant. Coatings of nano4 definitely limited emissions of most compounds released by wood. This was probably due to the amount of lacquer applied to the wood surface, which was over 2-fold greater than in the case of the other products.

When analysing concentrations of individual compounds emitted by tested coatings it was found that most of these emissions decreased within the first 72 h. In some cases only a slight increase in hexanal emission was observed.

Total concentration of emitted volatile substances from the nano1 coating decreased by 27% within the first 72 h of sample exposure in the chamber. After 240 h of exposure concentrations of these compounds were even lower. The decrease in the amounts of released volatile substances was

65% in relation to the concentrations measured after 24 h. In the case of the nano2 coatings the degree of reduction of released compounds was similar; 27% after 72 h and 69% after 240 h. Emissions of volatile substances from the layers of the nano3 oil after 72 h exposure were reduced by 22%; after 240 h, by 67%. The decrease in the amounts of compounds released by the flame retardant coatings, which had the lowest emissions after 24 h, was the smallest. After 72 h it amounted to 17%, while after 240 h it was 57%.

After 30 days, the concentrations of all compounds emitted by the tested surfaces ranged from 81 to 237 $\mu\text{g}/\text{m}^3$, depending on the type of applied lacquer, while within the next 90 days it changed to 42–101 $\mu\text{g}/\text{m}^3$.

The dynamics of change in the 90-day period for concentrations of volatile organic compounds from lacquer coatings containing nanoparticles are presented in the Figure.

4. Discussion

At present, studies on lacquer products dedicated to finishing furniture surfaces and containing nanoparticles of inorganic metal focus mainly on analysis of their physicomechanical, optical, and thermal properties. Results of such analyses have been presented in numerous publications (Bauer et al., 2009; Sow et al., 2010, 2011; Cristea et al., 2011; Salleh et al., 2013). The effect of products containing nanoparticles on the indoor microclimate and the health of occupants has not been described. It is essential to analyse volatile emissions from lacquer products, since numerous studies show that volatile organic compounds may have a significant effect on human health (Brinke et al., 1998; Hunter and Oyama, 2000; Mølhave, 2003; Katz et al., 2006). However, Saber et al. (2012a, 2012b) showed that there may be a significant difference between exposure to pure nanomaterials and exposure to nanomaterials embedded in a coating. Analyses of emissions of volatile organic compounds from conventional lacquer products, with no nanoparticles added, applied in the furniture industry have been conducted for several years (Salthammer, 1996, 1997;

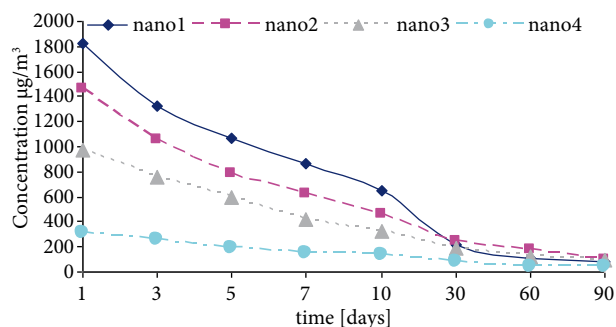


Figure. Dynamics of changes in concentrations of VOCs from lacquer coatings containing nanoparticles over 90 days.

Salthammer et al., 1998; Dziewanowska-Pudliszak, 2007; Uhde and Salthammer, 2007).

Analyses of VOC emissions from coatings of conventional waterborne lacquers, based in acrylic resin and containing no nanoparticles, were presented by Dziewanowska-Pudliszak (2007), Salthammer (1999), Stachowiak-Wencek and Prądkowski (2011), and Stachowiak-Wencek et al. (2014). A study by Dziewanowska-Pudliszak (2007) on coatings of waterborne acrylic lacquer applied to different wood species showed that VOC emission from coatings on pine wood amounted to 1584 $\mu\text{g}/\text{m}^3$ after 24 h of exposure, while emissions from coatings on larch, oak, and beech wood were lower, ranging from 122 to 829 $\mu\text{g}/\text{m}^3$. Stachowiak-Wencek and Prądkowski (2011) reported that concentrations of volatile substances from waterborne lacquer coatings applied to an oak wood surface after 24 h of exposure ranged from 388 to 1794 $\mu\text{g}/\text{m}^3$. In turn, a study by Salthammer (1999) showed that emissions of volatile organic compounds from UV-cured lacquer coatings may be around 296 $\mu\text{g}/\text{m}^3$.

A similar volatile organic compound emission level from coatings of UV-cured lacquers based on unsaturated acrylic oligomers was reported by Stachowiak-Wencek et al. (2014). The concentration of volatile substances from tested coatings was 251–557 $\mu\text{g}/\text{m}^3$. A significant role was played by the lacquer product composition as well as the type of surface to which the coatings were applied. Similar to Dziewanowska-Pudliszak (2007), Stachowiak-Wencek et al. (2014) stated that the greatest amounts of volatile substances were released by the coatings on pine wood.

Emissions of volatile substances from coatings of waterborne lacquer modified with SiO_2 nanoparticles (nano1) were relatively high compared with the results presented in the literature for conventional products. However, it should be stressed that the contribution of lacquered furniture to air pollution depends not only on the chemical composition of the lacquer product and its solvent content, but also the thickness of the coating and coating application, curing, and drying conditions.

In turn, lacquer coatings based on polyurethane-acrylic resin modified with silver nanoparticles (nano2) were characterised by relatively low emissions in comparison to literature data (Salthammer, 1999; Dziewanowska-Pudliszak, 2007; Stachowiak-Wencek and Prądkowski, 2012). Literature data indicate that concentrations of volatile organic compounds emitted by coatings of conventional polyurethane lacquers may fall within a wide range of values from 1130 to 9472 $\mu\text{g}/\text{m}^3$. Polyurethane lacquer coatings tested by Stachowiak-Wencek (2012) released volatile substances to the air in amounts ranging from 1130 to 4870 $\mu\text{g}/\text{m}^3$. In turn, coatings tested by Dziewanowska-Pudliszak (2007) emitted even greater amounts of volatile substances to the air, ranging from 4304

to 6886 $\mu\text{g}/\text{m}^3$, depending on the wood species to which they were applied. The highest values for polyurethane lacquer coatings were recorded by Salthammer (1999) at 9472 $\mu\text{g}/\text{m}^3$.

Tests of wood products finished with natural oils were conducted by Guo and Murray (2001), Hansen (2001), and Kirkeskov et al. (2009). Guo and Murray (2001) tested three typical furniture polishes. One was an aerosol spray, one was an emulsion polish, and one was a solvent polish. Those products contained natural oils and waxes as their main ingredients. The maximum total volatile organic compounds (TVOCs) concentration from the emulsion polish was 4520 $\mu\text{g}/\text{m}^3$ and from the solvent furniture polish it increased rapidly to a maximum value of 584 $\mu\text{g}/\text{m}^3$. The health effects of elements produced from exotic wood covered with oils were assessed by Kirkeskov et al. (2009), who tested five commercial products. Total amounts of emitted volatile compounds ranged from 10 to 6445 $\mu\text{g}/\text{kg}$. Results of analyses concerning emission of aldehydes and aromatic hydrocarbons from beech wood coated with linseed oil products were presented by Hansen (2001). Aldehyde emission from these products in the first stage of analyses (after 4 days) ranged from 300 to 550 $\mu\text{g}/\text{m}^2/\text{h}$. In turn, emission of aromatic hydrocarbons was higher, amounting to 2100–6000 $\mu\text{g}/\text{m}^2/\text{h}$.

Results of analyses presented in this study confirm the need to investigate VOC emission from lacquer products modified with nanoparticles, which are the most advanced commercial products available and considered the future products of choice. Studies determining VOC emissions from lacquer products used in surface finishing of furniture and other interior design elements are a necessary precondition for prospective actions aimed at improved hygienic standards in housing and public facilities.

5. Conclusions

1. Testing results indicate that lacquer products modified with inorganic metal compounds may contribute to air contamination with volatile organic compounds. Concentrations of these compounds released from tested coatings varied. Average TVOC ranged from 307 to 1829 $\mu\text{g}/\text{m}^3$ after 24 h of exposure in the chamber.
2. The spectrum of identified compounds was consistent with previous analyses of VOCs in indoor air. The tested air contained aldehydes, esters, ketones, aliphatic, and aromatic hydrocarbons, alcohols, glycols, and terpenes. The composition of emissions was dependent on the type of lacquer used.
3. We found a significant time effect on contents of volatile organic compounds in the testing chamber. The greatest reduction of emissions was recorded during the first 7 days (168 h) from sample preparation. If

producers want to launch wood products finished with lacquer coatings that are safe for user health and meet hygienic standards they should subject them to at least 7-day conditioning.

- The study confirmed the need to study the qualitative and quantitative characteristics of harmful substances emitted by nanoparticle-modified lacquer products. The level of VOC emissions from these products should be supervised by sanitary monitoring units similar to those used in conventional products, since they have only recently been introduced and are advertised as

new generation products. Studies showed that among such products we may find some with low and some with high emission levels. Appropriate selection of a product for refining furniture surfaces makes it possible to reduce the emission of volatile substances, particularly in the initial period of their use.

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References

- Adams LK, Lyon DY, Alvarez PJJ (2006). Comparative eco-toxicity of nanoscale TiO₂, SiO₂ and ZnO water suspensions. *Water Res* 40: 3527–3532.
- Bauer F, Decker U, Czihal K, Mehnert R, Riedel C, Riemschneider M, Schubert R, Buchmeiser MR (2009). UV curing and matting of acrylate nanocomposite coatings by 172 nm excimer irradiation. *Prog Org Coat* 64: 474–481.
- Borm PJA, Robbins D, Haubold S, Kuhlbusch T, Fissan H, Donaldson K, Schins R, Stone V, Kreyling W, Lademann J et al. (2006). The potential risks of nanomaterials: a review carried out for ECETOC. *Part Fibre Toxicol* 3: 1–35.
- Brinke J, Kelvin S, Hodgson AT, Fisk WJ, Mendell MJ, Koshland CP, Daisey JM (1998). Development of new volatile organic compound (VOC) exposure metrics and their relationship to “sick building syndrome” symptoms. *Indoor Air* 8: 140–152.
- Cristea MV, Riedl B, Blanchet P (2011). Effect of addition of nanosized UV absorbers on the physico-mechanical and thermal properties of an exterior waterborne stain for wood. *Prog Org Coat* 72: 755–762.
- Dziewanowska-Pudliszak A (2007). Emisja lotnych związków organicznych z powłok lakierów naniesionych na drewno lite. (Emissions of volatile organic compounds from coatings applied onto the solid wood). *Technologia drewna—Wczoraj, Dziś, Jutro. Studia i szkice na Jubileusz Profesora Ryszarda Babickiego (Wood Technology—Yesterday, Today, Tomorrow. Studies and drafts for the Jubilee Professor Richard Babicki)*. Poznań, Poland: Wood Technology Institute, pp. 295–306.
- EPA (2007). Nanotechnology White Paper. US Environmental Protection Agency Report EPA 100/B-07/001, Washington DC 20460, USA.
- Guo H, Murray F (2001). Determination of total volatile organic compounds emissions from furniture polishes. *Clean Prod Process* 3: 42–48.
- Gupta A, Silver S (1998). Molecular genetics: silver as a biocide. Will resistance become a problem? *Nat Biotechnol* 16: 888.
- Gwinn MR, Vallyathan V (2006). Nanoparticles: health effects—pros and cons. *Environ Health Persp* 114: 1818–1825.
- Hansen MK (2001). Health evaluation of volatile organic compounds (VOC) emissions from wood and wood-based materials. *Arch Environ Health* 5: 419–432.
- Hong R, Pan T, Qian J, Li H (2006). Synthesis and surface modification of ZnO nanoparticles. *Chem Eng J* 119: 71–81.
- Hongying Y, Sukang Z, Ning P (2004). Studying the mechanisms of titanium dioxide as ultraviolet-blocking additive for films and fabrics by an improved scheme. *J Appl Polym Sci* 92: 3201–3210.
- Hunter P, Oyama ST (2000). Control of Volatile Organic Compound Emissions, Conventional and Emerging Technologies. New York, NY, USA: John Wiley and Sons.
- Katz NB, Katz O, Mandel S (2006). Neurotoxicity of chemicals commonly used in agriculture. In: Messenger JE, editor. *Agricultural Medicine. A Practical Guide*. New York, NY, USA: Springer, pp. 300–323.
- Kirkeskov L, Witterseh T, Funch LW, Kristiansen E, Mølhav L, Hansen MK, Kundsen BB (2009). Health evaluation of volatile organic compounds (VOC) emission from exotic wood products. *Indoor Air* 19: 45–57.
- Kreyling W, Semmler-Behnke M, Möller W (2006). Health implications of nanoparticles. *J Nanopart Res* 8: 543–562.
- Liau SY, Read DC, Pugh WJ, Furr JR, Russell AD (2007). Interaction of silver nitrate with readily identifiable groups: relationship to the antibacterial action of silver ions. *Lett Appl Microbiol* 25: 279–283.
- Mølhav L (2003). Organic compounds as indicators of air pollution. *Indoor Air* 13: 12–19.
- Nowack B, Bucheli TD (2007). Occurrence, behavior and effects of nanoparticles in the environment. *Environ Pollut* 150: 5–22.
- Nowaczyk-Organista M (2008). Zabezpieczenie drewna brzozy przed działaniem światła przez zastosowanie mikrotonizowanej bieli tytanowej w lakierze wodorozcieńczalnym. (Protection of birch wood against light using ultra-fine titanium dioxide in the water-based lacquer). *Drewno* 51: 45–60.
- Nowaczyk-Organista M (2009). Protection of birch and walnut wood colour from the effect of exposure to light using ultra-fine zinc white. *Drewno* 52: 19–40.

- Oberdörster G, Ferin J, Lehnert BE (1994). Correlation between particle size, in vivo particle persistence, and lung injury. *Environ Health Persp* 102: 173–179.
- Oberdörster G, Oberdörster E, Oberdörster J (2005). Nanotoxicology: an emerging discipline evolving from studies of ultrafine particles. *Environ Health Persp* 113: 823–839.
- Rai M, Yadav A, Gade A (2009). Silver nanoparticles as a new generation of antimicrobials. *Biotechnol Adv* 27: 76–83.
- Ruben JM, Luis JE, Alejandra C, Katherine H, Juan BK, Tapia JR, Miguel Jose Y (2005). The bactericidal effect of silver nanoparticles. *Nanotechnology* 16: 2346.
- Saber AT, Jensen KA, Jacobsen NR, Birkedal R, Mikkelsen L, Møller P, Loft S, Wallin H, Vogel U (2012a). Inflammatory and genotoxic effects of nanoparticles designed for inclusion in paints and lacquers. *Nanotoxicology* 6: 453–471.
- Saber AT, Koponen IK, Jensen KA, Jacobsen NR, Mikkelsen L, Møller P, Loft S, Vogel U, Wallin H (2012b). Inflammatory and genotoxic effects of sanding dust generated from nanoparticle-containing paints and lacquers. *Nanotoxicology* 6: 776–788.
- Salleh NGN, Alias MS, Gläsel HJ, Mehnert R (2013). High performance radiation curable hybrid coatings. *Radiat Phys Chem* 84: 70–73.
- Salthammer T (1996). Release of photoinitiator fragments from UV-cured furniture coatings. *J Coating Tech* 68: 41–48.
- Salthammer T (1997). Emissions of volatile organic compounds from furniture coatings. *Indoor Air* 7: 189–197.
- Salthammer T (1999). *Organic Indoor Air Pollutants: Occurrence, Measurement, Evaluation*. Weinheim, Germany: Wiley-VCH.
- Salthammer T, Schwarz A, Fuhrmann F (1998). Emissions of reactive compounds and secondary products from wood-based furniture coatings. *Atmos Environ* 33: 75–84.
- Sokół JL (2012). Nanotechnologia w życiu człowieka (Nanotechnology in human life). *Ekonomia i zarządzanie (Economics and management)* 4: 18–29.
- Sow C, Riedl B, Blanche P (2010). Kinetic studies of UV-waterborne nanocomposite formulations with nanoalumina and nanosilica. *Prog Org Coat* 67: 188–194.
- Sow C, Riedl B, Blanche P (2011). UV-waterborne polyurethane-acrylate nanocomposite coatings containing alumina and silica nanoparticles for wood: mechanical, optical, and thermal properties assessment. *J Coat Technol Res* 8: 211–221.
- Stachowiak-Wencek A (2012). Emission of volatile organic compounds (VOC) from polyurethane lacquers used in furniture production. Physico-chemical analysis of lignocellulosic materials. Part II. WULS-SGGW Press: 44–54.
- Stachowiak-Wencek A, Prądzynski W (2011). Emission of volatile organic compounds (VOC) from waterborne lacquers with different content of solids. *Drewno* 54: 51–63.
- Stachowiak-Wencek A, Prądzynski W, Mateńko-Nożewnik M (2014). Emission of volatile organic compounds (VOC) from UV-cured water-based lacquer products. *Drewno* 57: 87–97.
- Uhde E, Salthammer T (2007). Impact of reaction products from building materials and furnishings on indoor air quality—a review of recent advances in indoor chemistry. *Atmos Environ* 41: 3111–3128.
- Van Broekhuizen FA (2012a). Nano in furniture—state of the art 2012. Research Report No. VS/2011/0134-SI2-596685. IVAM Uv BV, Amsterdam, NL.
- Van Broekhuizen FA (2012b). Nano in furniture—state of the art 2012. Executive Summary. Research Report No. VS/2011/0134-SI2-596685. IVAM Uv BV, Amsterdam, NL.
- Van Broekhuizen FA, Van Broekhuizen JC (2009). Nano-products in the European construction industry—state of the art 2009. Executive Summary. Research Report No. VS/2008/0500-SI2-512656. IVAM Uv BV, Amsterdam, Netherlands.
- Zhang W, Qiao X, Chen J (2007). Synthesis of silver nanoparticles—effects of concerned parameters in water/oil microemulsion. *Mater Sci Eng B* 142: 1–15.
- Zubielewicz M (2008). Wpływ nanocząstek SiO₂ na właściwości lakierów i powłok lakierowych (Effect of SiO₂ nanoparticles on the properties of paints and coatings). *Ochrona przed korozją (Protection against corrosion)* 12: 462–464.