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Release of volatile organic compounds from UV-radiation curing furniture coatings

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Summary: *The paper presents results of studies on the type and amounts of volatile organic compounds (VOC) from UV-radiation cured coatings. Two lacquer products were selected for analyses: based on unsaturated acrylic ester and unsaturated polyesters applied on three wood species: pine, zebrawood and wenge. It was found that lacquer coatings cured with UV radiation were characterised by low levels of VOC emissions ranging from 54 to 259 µg/m^3 after 24h sample exposure in the chamber. Moreover, it was found that the greatest VOC amounts were released to the air by coatings applied on pine wood, which additionally released terpene compounds.*

Key words: VOC, UV-cured lacquers, furniture coatings

INTRODUCTION

The application of ultraviolet radiation to cure lacquer coatings is a dynamically developing method (Allen 1996). Increased interest in UV-radiation cured lacquer systems is connected first of all with its advantages. Curing of coatings by UV radiation makes it possible to shorten the entire technological process of element finishing, as it facilitates almost instantaneous further working and application of successive layers. In comparison to traditional drying and curing methods, requiring considerable amounts of labour and energy, the UV technology promotes increased production efficiency at a lower consumption of lacquer and energy (Salthammer 1996, Lee 2006, Bongiovanni et al. 2002, Müller et al. 2008). This technology also guarantees excellent performance parameters of coatings, their high chemical resistance and mechanical strength (Garrat 1996) as well as lower emissions of volatile organic compounds (VOC) (Lee et al. 2006).

UV-cured coatings typically contain four main components: oligomers, monomers, photoinitiators and various additives (Lee et al. 2006). Photoinitiators are important components of UV-cured systems, required for the formation of active forms, which will initiate the chain reaction (Decker 2002). Analyses showed that as a result of photoinitiator fragmentation processes new compounds may be formed (e.g. Norrish type I and II reactions and intermolecular proton transfer), which in turn may contribute to pollution of indoor air (Salthammer 1996, Pluschke 2004, Lee et al. 2006).

Studies on emissions of volatile organic compounds from UV-radiation cured lacquer products have been conducted e.g. by Salthammer (1997), Salthammer et al. (1999, 2002), Uhde and Salthammer (2007) and Kagi et al. (2009).

In order to provide better understanding and more detailed information on characteristics of volatile organic compounds potentially released by coatings of UV-cured systems, analyses were conducted on lacquer coatings cured using UV radiation, applied on three wood species, i.e. pine and two exotic species, zebrawood and wenge.

MATERIALS AND METHODS

Analyses were conducted on three wood species: pine (*Pinus sylvestris* L.), zebrawood (*Microberlinia brazzavillensis* A. Chev.) and wenge (*Millettia laurentii* Wild.) wood. Samples of 280 x 200 x 16 mm were prepared under production conditions. Pine wood was dried in a drying kiln (Hamech SK 55, Hajnówka) equipped with software by Automatex. In turn, it was difficult to obtain reliable information on the time of storage and drying conditions of exotic wood. This wood was purchased from Polish wood processing plants.

Samples for analyses were collected from strips of 100 mm in width, glued with polyacetate vinyl adhesive. The wood surface was sanded with sandpaper of 180 and 220 grits. The moisture content of the samples determined by the gravimetric method fell within the range of 7.5 – 8.5%.

The samples of the selected wood species were covered on both sides with two types of UV-cured products, whose characteristics are presented in Table 1.

Table 1. Technical parameters of UV-curing lacquer systems

Parameters	Lacquers	
	K/UV1	**K/UV2**
Film-forming substance	unsaturated acrylic esters and unsaturated polyesters	
	with the addition of low-molecular mono-, di- and tetra-acrylates	-
Photoinitiator*r*	benzofenon	
Dilutant	-	
Solid content [%]	99 ± 1	99 ± 1
Specific gravity [kg/cm^3]	1140 ± 30	1210 ± 30
Commercial viscosity [s]	910	1450
Application viscosity	delivered	

Lacquering products were applied on the wood surfaces by means of a pneumatic spray gun (nozzle diameter – 1.4 mm). The application amount of the lacquering product applied was 110 ± 5 g/m^2.

The drying and curing process consisted of three parts. The first part was a flash-off-period – 10 min at a temperature of 23-25°C. The second part was the proper drying period - 15 min at a temperature of 60°C. The third part was the ultraviolet curing with a UV unit equipped with a Mercury lamp and an eliptical (focused) reflector. The power of the UV lamp was characterised as 120 W/cm. The speed of the conveyor during the drying and curing process was 10 m/min.

Chamber tests and TD/GC/MS analyses

All the experiments were carried out in a 0.225 m^3 glass chamber under the following conditions: temperature: 23 ± 2°C, relative humidity: 45 ± 5%, air exchange rate: 1 h^{-1} and loading factor: 1.0 m^2/m^3. Air samples were collected on a Tenax TA (35/60mesh, Alltech Company) at a 1l total volume and at a flow rate of 100 ml/min. Analytes adsorbed on the Tenax TA were analysed using a GC/MS apparatus, equipped with a thermal desorber, according to the procedure presented in Table 2.

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 then confirmed by juxtaposing the 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).

Table 2. Operating conditions of TD/GC/MS

Elements of measuring system	System's working conditions
Injector	Thermal desorber connected to sorption microtrap; Purging gas: argon at 20 m^3min^{-1}; Purge time: 5 min. Desorption temperature: 250°C
Microtrap	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, 60m x 0.32mm ID; D_f – 1.8 µm: 6% cyanopropylphenyl, 94% dimethylpolyoxosilane
Detector	Mass spectrometer (SCAN: 10 – 350)
Carrier gas	Helium: 100 kPa, ~2 cm^3min^{-1}.
Temperature settings	40°C for 2min, 7°C min^{-1} to 200°C, 10°C min^{-1} to 230°C, 230°C for 20 min.

RESULTS

Results are given in tables 3 - 4. They indicate that coatings of UV-radiation cured lacquers based on unsaturated acrylic esters and unsaturated polyesters emitted to air relatively small amounts of volatile substances. This may be connected with high contents of solid substances, in these products amounting to 99 ± 1%.

Concentrations of volatile organic compounds emitted from tested coatings after 24 h ranged from 54 to 259 µg/m^3. Coatings of K/UV1 lacquer applied onto the wood surface of pine and exotic species after 24 h emitted volatile substances ranging from 35 to 259 µg/m^3. Coatings of K/UV2 lacquer emitted smaller amounts of volatile substances, from 54 to 137 µg/m^3. In both lacquer systems the highest concentrations of volatile substances were recorded for coatings applied onto the surface of pine wood.

Table 3. Concentration of volatile organic compounds released from K/UV1 lacquer coating in the period of 240 h

Compound	Concentration [µg/m^3]								
	Pine			**Zebrawood**			**Wenge**		
	24h	72h	240h	24h	72h	240h	24h	72h	240h
acetone	15,3	11,3	6,8	6,3	4,1	2,4	13,0	8,2	4,4
pentanal	-	-	-	7,9	6,9	4,2	12,1	8,9	5,4
hexanal	15,2	16,3	13,1	3,8	3,5	1,8	8,4	7,7	4,0
1,6-hexanediol diacrylate	48,3	30,5	12,5	42,8	29,7	12,2	39,3	26,5	10,5
butyl acrylate	26,3	18,7	10,5	19,3	16,1	8,1	18,7	15,4	7,2
α-pinene	85,3	63,2	25,1	-	-	-	-	-	-
3-carene	12,1	8,7	6,6	-	-	-	-	-	-
limonene	20,4	13,3	7	-	-	-	-	-	-
other	36,3	20,5	8,7	14,5	13,3	5,2	16,9	11,9	3,8
TVOC:	**259**	**183**	**90**	**95**	**74**	**34**	**108**	**79**	**35**

Table 4. Concentrations of volatile organic compounds released from K/UV2 lacquer coating in the period of 240 h

Compound	Concentration [µg/m^3]								
	Pine			Zebrawood			Wenge		
	24h	72h	240h	24h	72h	240h	24h	72h	240h
acetone	7,5	5,6	3,3	7,2	5,3	1,9	14,6	10,2	4,5
pentanal	-	-	-	8,6	7,9	5,1	13,1	9,8	5,8
hexanal	7,5	8,0	6,4	7,8	6,2	2,0	9,1	7,6	4,2
α-pinene	67,6	50,1	25,2	-	-	-	-	-	-
3-carene	7,2	5,2	3,2	-	-	-	-	-	-
limonene	10,6	7,3	3,7	-	-	-	-	-	-
1-methyl-2-pyrrolidinone	19,3	16,3	10,3	20,5	16,2	7,7	22,1	16,3	7,7
other	17,9	10,1	4,3	10,2	13,5	5,3	18,9	12,5	4,7
TVOC:	**137**	**102**	**57**	**54**	**49**	**22**	**78**	**56**	**27**

After 72 h concentration of all compounds released from K/UV1 coatings on pine wood decreased and amounted to 183 µg/m^3, while it was 74 – 79 µg/m^3 from coatings refining the surfaces of exotic species. Similarly to the situation after 24 h, amounts of compounds released by coatings of K/UV2 lacquer after 72h sample exposure were lower than those released by samples covered with K/UV1. Coatings of K/UV2 lacquer on pine wood after 72 h emitted volatile compounds at 102 µg/m^3, while on wood of exotic species emissions ranged from 49 to 56 µg/m^3. In the next stage of the study a further decrease was observed in the amounts of compounds released by the tested coatings. After 10 days (240 h) it was 65 – 68% for K/UV1 lacquer coating and 58 – 65% for K/UV2 lacquer coating.

Coatings from K/UV1 and K/UV2 lacquers emitted a limited spectrum of compounds. Characteristic components of emissions from K/UV1 coating included 1,6-hexanediol diacrylate and butyl acrylate. The concentration of 1,6-hexanediol diacrylate 24 h after the samples were placed in the chamber ranged from 39.3 to 48.3 µg/m^3, depending on the type of finished surface. The concentration of butyl acrylate was lower, ranging from 18.7 to 26.3 µg/m^3. In contrast, samples coated with K/UV2 lacquer released only 1-methyl-2-pyrrolidinone. The concentration of 1-methyl-2-pyrrolidinone in the air inside the chamber ranged from 19.3 to 22.1 µg/m^3. Moreover, analysed air was found to contain small amounts of compounds released by wood, i.e. pentanal, hexanal, acetone and terpenes. As a result of the presence of terpene compounds, α-pinene, 3-carene and limonene, recorded in the case of pine wood the concentrations of volatile organic compounds emitted from pine wood finished with UV-cured coatings were highest among the tested wood species.

ODSUMOWANIE

1. Samples prepared under production conditions were characterised by low emissions of volatile substances. Coatings analysed in the first stage of the study, i.e. after 24h exposure in the chamber, released to air volatile organic substances at 54 up to 259 µg/m^3. This confirms reports published in available literature (Lee et al. 2006), concerning low VOC emissions from UV-cured products.
2. VOC emissions from K/UV1 lacquer coating containing not only unsaturated acrylic esters and unsaturated polyesters, but also additions of low-molecular mono-, di- and tetra-acrylates, were higher than from K/UV2 lacquer coating, containing only unsaturated acrylic esters and unsaturated polyesters.
3. Studies on emissions of volatile organic compounds from coatings applied on various wood species, including increasingly popular exotic wood, showed the effect of the

type of surface on levels of released compounds. It was found that among wood species selected for analyses the highest emission levels were found for coatings applied onto pine wood.

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Streszczenie: *Wydzielania się lotnych związków organicznych z powłok meblarskich utwardzanych promieniowaniem UV*. Streszczenie: W pracy przedstawiono wyniki badań rodzaju i ilości lotnych związków organicznych z powłok systemów utwardzanych promieniami UV. Do badań wytypowano dwa wyroby lakierowe na bazie nienasyconych estrów akrylowych i poliestrowych, które nanoszono na trzy gatunki drewna, sosnę, zebrano i wenge. Stwierdzono, że powłoki lakierowe utwardzane promieniowaniem UV charakteryzowały się niskim poziomem emisji VOC, wynoszącym od 54 do 259 $\mu g/m^3$ po 24h ekspozycji prób w komorze. Ponadto stwierdzono, że największe ilości VOC wydzielały do powietrza powłoki na drewnie sosny, które to, dodatkowo uwalniało związki terpenowe.