

# Formation of organic indoor air pollutants by UV-curing chemistry

T. Salthammer<sup>a,\*</sup>, M. Bednarek<sup>a</sup>, F. Fuhrmann<sup>a</sup>, R. Funaki<sup>b</sup>, S.-I. Tanabe<sup>b</sup>

<sup>a</sup> Fraunhofer-Institut für Holzforschung, Wilhelm-Klauditz-Institut (WKI), Bienroder Weg 54E, D-38108 Braunschweig, Germany

<sup>b</sup> Department of Architecture, Waseda University, 55N701, Okubo 3-4-1, Shinjuku-ku, Tokyo, Japan

Received 12 April 2002; received in revised form 20 May 2002; accepted 20 May 2002

## Abstract

UV-curable systems for manufacturing of furniture and parquet form a major and growing field in radiation curing. Numerous types and combinations of photoinitiators have been developed for crosslinking of acrylated systems and unsaturated polyesters. The properties of the photoinitiators being used in these materials must fulfill requirements like low toxicity, low odor and high reactivity. However, volatile reaction products being produced during the photochemical process contribute to the pollution of indoor air by emission from the surface and may cause strong odor and adverse health effects. Therefore, the release of photoinitiators, fragmentation products and monomers from UV-cured coatings was studied as a function of time under realistic living conditions in emission test chambers and cells. Main components detected in the chamber air were benzaldehyde, cyclohexanone, benzophenone and acrylate monomers. The area-specific emission rates  $SER_A$  were found to be strongly dependent on the climatic conditions.

© 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Photoinitiator; Acrylates; UV-curing; Surface coatings; Degradation product; Emission testing

## 1. Introduction

The exposure to pollutants in the indoor environment may cause adverse health effects on humans. Therefore, this field has received considerable public attention and is of special interest to consumers, administrative bodies, industry and researchers [1]. With regard to pollution of indoor air, the group of so-called volatile organic compounds (VOCs) is of special concern, because most indoor products are known as potential sources of these [2]. For several years, a number of studies have been carried out to determine the spectrum and concentrations of VOCs in indoor air. Hundreds of different substances with indoor concentrations ranging from  $<0.1 \mu\text{g}/\text{m}^3$  to  $>10 \text{mg}/\text{m}^3$  have been reported in the literature [1]. In additional emission tests, the release of VOC from building products and indoor fittings can be determined under controlled conditions. The European standard ENV 13419 part 1–2 defines the performance of emission testing by use of chambers and cells [3,4], where the emission strength is characterized by the area-specific emission rate  $SER_A$  ( $\mu\text{g}/(\text{m}^2 \text{h})$ ).

Classical VOC analysis mainly covers typical solvents like aliphatic and aromatic hydrocarbons, alcohols, ketones and esters. In recent years, indoor studies have increasingly

focused on organic substances, which are known as reactive species or reaction products, as such compounds may also have impact on human health due to low odor thresholds or low irritation levels. The formation of organic indoor pollutants by chemical reaction in indoor air has been extensively studied [5]. Moreover, many building products contain reactive compounds, which decompose under normal living conditions and can be released as secondary emission products [6]. Today it is assumed that so-called “indoor chemistry” contributes to irritation and SBS symptoms [7].

The application of UV-curable systems for coating of furniture and flooring materials like cork [8] and wooden parquet is still a growing field in radiation curing [9–12]. For technical reasons, the photoinitiator is generally added in non-stoichiometric amounts. This triggers uncontrolled reactions during use and may lead to problems in UV-curing technology. It is well known that degradation processes of photoinitiators form a number of volatile reaction products, which contribute to indoor air pollution [13]. In most UV-curing lacquers, the physical and chemical properties are controlled via acrylate monomers or styrene [14]. Airborne monomers also cause manifold problems as they are known as odorous and hazardous compounds. Furthermore, some acrylates undergo hydrolysis under formation of volatile alcohols.

To estimate the contribution of UV-cured lacquers to indoor air pollution, a variety of coating systems for

\* Corresponding author.

E-mail address: salthammer@wki.fhg.de (T. Salthammer).

production of wood-based furniture and flooring materials has been studied for release of VOCs under different climatic conditions by use of test chambers and emission cells. Most experiments were performed in the dark but some samples were also exposed to simulated daylight. Preliminary results of this study have been presented earlier [15].

## 2. Experimental

Samples F1–F9 were selected in cooperation with suppliers of photoinitiators and manufacturers of coating systems. These were then produced under controlled conditions by use of industrial coating machines. UV-lacquers were applied on urea–formaldehyde bonded particle boards coated with beech veneer. The light source for curing was a 280–380 nm UV-radiator with 80 W/cm curve length. Samples F1-B, F7 and F8-B were given only 50% of the required curing time. This was achieved by faster transport through the irradiation zone. Samples F10–F12 were freshly produced pieces of commercial furniture coated with UV-lacquer and were obtained from different manufacturers. Samples P1–P5 were also commercial products (P1–P4: wooden parquet, P5: cork, all coated with UV-cured lacquer). Investigated samples and test conditions are summarized in Table 1. Molecular structures of applied photoinitiators are presented in Fig. 1.

For a test simulating the real indoor environment, emission experiments were carried out in 1 m<sup>3</sup> glass chambers and in the Field and Laboratory Emission Cell (FLEC) in accordance with ENV 13419-1 [3] and ENV 13419-2 [4], respectively. Technical details of the chambers and the FLEC have been described elsewhere [16–18]. The test conditions are also summarized in Table 1. Before each experiment, the test device was heated to reduce memory effects. The effectiveness of thermal cleaning process was controlled by measuring a blank value before chamber loading.

ULTRA-VITALUX UV-lamps were used for artificial production of filtered sunlight. The lamps were placed above the chamber (see Fig. 2) or cell (see Fig. 3). For all chamber tests, a glass filter was used to cut off wavelengths <290 nm. Irradiation was performed for 8 h per day in intervals of 1 h light and 2 h dark to avoid temperature effects. The light intensity in the wavelength region 295–385 nm was measured directly at the sample surface in the center of the chamber using a photoelectric cell made of selenium (Lambrecht). For 8 h per day, the light intensity from 295 to 385 nm was 20–30 W/m<sup>2</sup>. In this wavelength region, the average solar irradiance on the earth's surface in central Europe (latitude 50°N) in May is 24.4 W/m<sup>2</sup> [19]. The total intensity of solar radiation is about 200 W/m<sup>2</sup> [20].

Air samples were collected on silanized glass wool/Tenax TA (1–6 l total volume at a flow rate of 100 ml/min). The analysis of the Tenax tubes was carried out using a GC/MS

Table 1  
Investigated samples and test conditions<sup>a</sup>

Sample	Photoinitiator	Test device	T (°C)	r.h. (%)	Remarks
F1-A	BP/DPAP/TBDPO	1 m <sup>3</sup>	23	45	
F1-B	BP/DPAP/TBDPO	1 m <sup>3</sup>	23	45	50% curing
F2	HMEPP/DAP	1 m <sup>3</sup>	23	45	
F3	HEHMPP/BP	1 m <sup>3</sup>	23	45	
F4	PHMP/BP	FLEC	23	45	
F5	HCPK/BP	1 m <sup>3</sup>	23	45	
F6	HCPK/DTBPPO	1 m <sup>3</sup>	23	45	Pigmented system
F7	HEHMPP/BP	1 m <sup>3</sup>	23	45	50% curing
F8-A	HCPK/BP	FLEC	23	45	
F8-B	HCPK/BP	FLEC	23	45	50% curing
F9-A	HCPK/BP	1 m <sup>3</sup>	20	37	
F9-B	HCPK/BP	1 m <sup>3</sup>	27	70	
F9-C	HCPK/BP	1 m <sup>3</sup>	23	45	Light (with glass filter)
F10 <sup>b</sup>	Not known	1 m <sup>3</sup>	23	45	
F11 <sup>b</sup>	Not known	1 m <sup>3</sup>	23	45	
F12 <sup>b</sup>	Not known	1 m <sup>3</sup>	23	45	
P1-A <sup>b</sup>	Not known	FLEC	23	45	Light (with glass filter)
P1-B <sup>b</sup>	Not known	FLEC	23	45	Light (no glass filter)
P2-A <sup>b</sup>	Not known	FLEC	23	45	Light (with glass filter)
P2-B <sup>b</sup>	Not known	FLEC	23	45	Light (no glass filter)
P3-A <sup>b</sup>	Not known	FLEC	23	45	Light (with glass filter)
P3-B <sup>b</sup>	Not known	FLEC	23	45	Light (no glass filter)
P4-A <sup>b</sup>	Not known	FLEC	23	45	Light (with glass filter)
P4-B <sup>b</sup>	Not known	FLEC	23	45	Light (no glass filter)
P5	Not known	1 m <sup>3</sup>	23	45	Cork product

<sup>a</sup> For all experiments the loading factor was  $L = 1 \text{ m}^2/\text{m}^3$ . The carrier material for UV-coatings was particleboard except sample P5, which was cork. F: furniture coating; P: parquet coating.

<sup>b</sup> Commercial product.

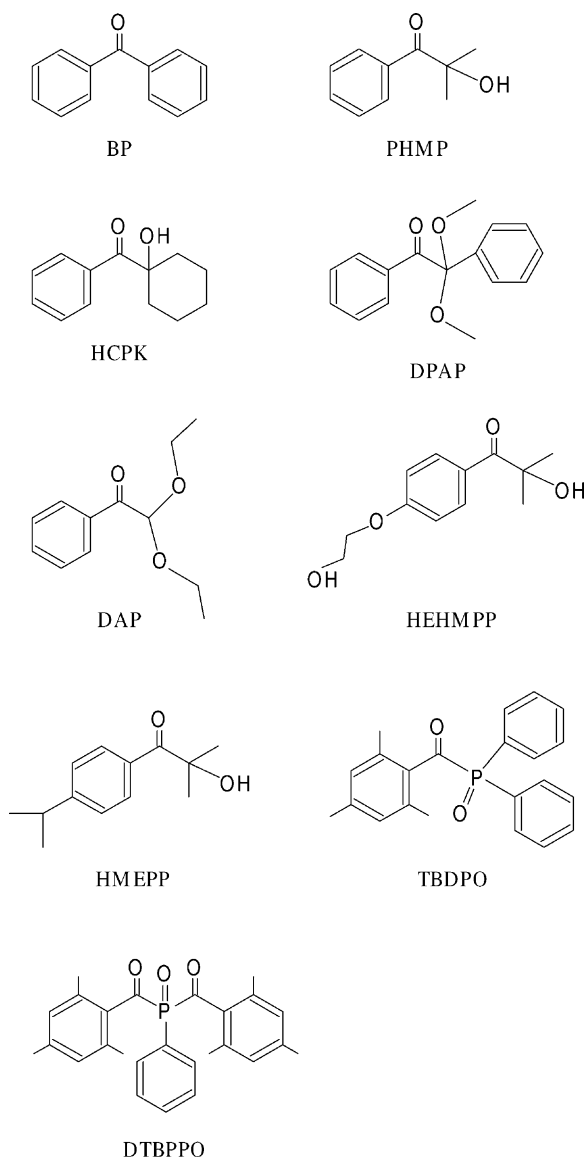


Fig. 1. Molecular structures of photoinitiators and acrylate monomers.

system (Hewlett-Packard 5890A/5870) equipped with a thermal desorber-cold trap injector (Perkin Elmer ATD 400). Identification of the compounds was based on a PBM library search [21]. Moreover, mass spectra and retention data were compared with those of reference compounds. Characteristic mass peaks ( $m/z$ ) of several photoinitiators and fragments have been reported in a previous paper [13]. Area-specific emission rates  $SER_A$  were calculated from chamber concentrations  $C(t)$  by use of the following equation [3]:

$$SER_A(t) = \frac{\Delta C / \Delta t + NC(t)}{L} \quad (1)$$

with  $C(t)$  is the concentration of pollutant in the test chamber ( $\mu\text{g}/\text{m}^3$ ),  $N$  the air exchange rate ( $\text{h}^{-1}$ ) and  $L$  the loading factor ( $\text{m}^2/\text{m}^3$ ). For all experiments in chambers

and cells, the area-specific air flow rate  $Q = N/L$  was  $Q = 1 \text{ m}^3/(\text{m}^2 \text{ h})$ .

### 3. Results

#### 3.1. Fragmentation of photoinitiators and acrylates

The photochemistry of most common photoinitiators is predominantly a chemistry of the carbonyl group. In the first step absorption of UV-light in the range 250–350 nm ( $40\,000\text{--}33\,000 \text{ cm}^{-1}$ ) populates an excited singlet state with  $S_1(n\pi^*)$  or  $S_1(\pi\pi^*)$  configuration. As  $n\pi^*$ -transitions are symmetry-forbidden, only low molecular absorbance coefficients  $\epsilon_a$  and therefore low oscillator strengths result. In most aromatic carbonyl compounds, the energy gap between singlet and lowest excited triplet state is small and inter-system-crossing to the  $T_1$  proceeds efficiently. Depending on the individual electronic term energies, the generation of radicals may occur either from the singlet or the triplet state [22]. There are three important fragmentation processes forming radical species. Benzyl ketals (DPAP), hydroxy-acetophenons (PHMP, HCPK, HMEPP, HEHMPP) and phosphine oxides (TBDPO, DTBPPO) (see Table 2 for abbreviations) generate benzoyl radicals via the Norrish-I reaction ( $\alpha$ -cleavage). Dialkoxy-acetophenones (DAP) undergo both Norrish-I ( $\approx 67\%$ ) and Norrish-II ( $\approx 33\%$ ) cleavage. On excitation of benzophenone (BP) in the presence of tertiary amines an electron transfer complex (exciplex) is formed, followed by proton transfer to form a ketyl radical and an aminoalkyl radical.

Table 2

Applied photoinitiators, photofragments, acrylate monomers and degradation products identified by GC/MS in the chamber air and in the material surface

Source	Detected fragments
BP <sup>a</sup>	–
PHMP <sup>b</sup>	Benzaldehyde, benzil, acetone, 1-phenyl-2-methyl-1,2-propanediol, pinacol
HCPK <sup>c</sup>	Benzaldehyde, benzil, cyclohexanone
DPAP <sup>d</sup>	Benzaldehyde, acetophenone, benzil, methylbenzoate, (1-phenyl-1,2-propane-dione)
DAP <sup>e</sup>	Benzaldehyde, 1-phenyl-2-ethoxy-ethane-1-one
HMEPP <sup>f</sup>	4-(1-Methylethyl)-benzaldehyde, 4-(1-methyl-ethyl)-acetophenone
HEHMPP <sup>g</sup>	4-(2-Hydroxyethoxy)-benzoic acid
TBDPO <sup>h</sup>	2,4,6-Trimethyl-benzaldehyde
DTBPPO <sup>i</sup>	2,4,6-Trimethyl-benzaldehyde
<i>n</i> -Butyl acrylate	<i>n</i> -Butanol

<sup>a</sup> Benzophenone.

<sup>b</sup> 1-Phenyl-2-hydroxy-2-methyl-propane-1-one.

<sup>c</sup> 1-Hydroxy-cyclohexyl-phenone.

<sup>d</sup> 2,2-Dimethoxy-2-phenyl-acetophenone.

<sup>e</sup> 2,2-Diethoxy-acetophenone.

<sup>f</sup> 2-Hydroxy-2-methyl-1-(4-(1-methylethyl)-phenyl)-propan-1-one.

<sup>g</sup> 2-Hydroxy-2-methyl-1-(4-(2-hydroxyethoxy)-phenyl)-propan-1-one.

<sup>h</sup> 2,4,6-Trimethyl-benzoyl-diphenyl-phosphine-oxide.

<sup>i</sup> Di-(2,4,6-trimethyl-benzoyl)-phenyl-phosphine-oxide.

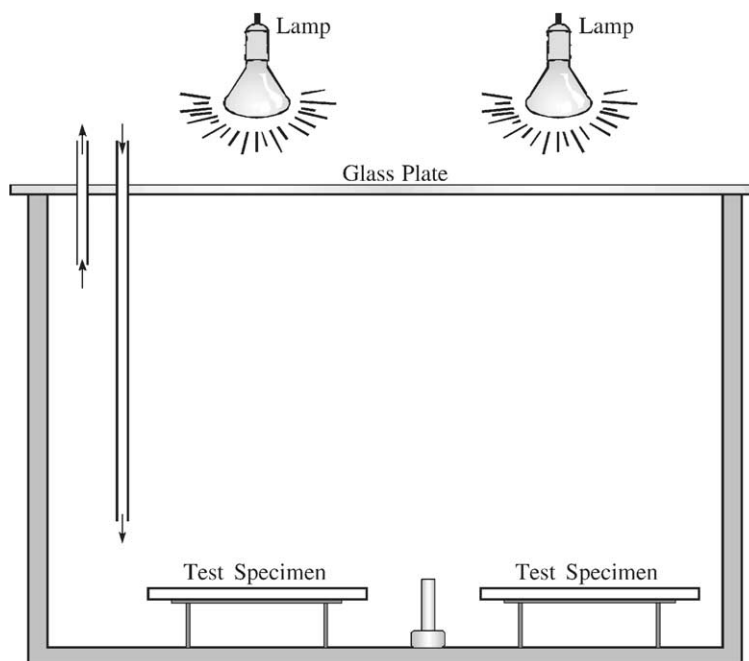


Fig. 2. Schematic view of the 1 m<sup>3</sup> test chamber containing test specimen, photoelectric cell and lamps (experimental setup for test F9-C).

Investigated photoinitiators, acrylates and their detected fragmentation products are compiled in Table 2. Most identified photoinitiator fragments have been described earlier by several authors [23–25]. The reactive benzoyl-, 2,4,6-trimethyl-benzoyl and 4-(1-methyl-ethyl)-benzoyl radicals are directly produced via  $\alpha$ -cleavage. A fast hydrogen abstraction follows to generate benzaldehyde [26], 2,4,6-trimethyl-benzaldehyde and 4-(1-methyl-ethyl)-benzaldehyde. Benzil is formed by dimerization of benzoyl radicals. Methylbenzoate is a secondary product from the thermal decomposition of the dimethoxy-benzyl radical, which is previously formed upon  $\alpha$ -cleavage of DPAP [27]. Acetophenone is a product of the rearrangement of the benzoyl radical and an alkyl radical [28]. Reduction of PHMP leads to 1-phenyl-2-methyl-1,2-propane-diol and acetone, recombination of the 2-hydroxy-propyl radical gives 2,3-dimethyl-2,3-butane-diol (pinacol). Cyclohexanone is produced from the hydroxy-cyclohexyl radical upon  $\alpha$ -cleavage of HCPK, followed by hydrogen abstraction and keto-enol-tautomerization [29]. The main photo-product of HEHMPP is 4-(2-hydroxy-ethoxy)-benzoic acid [30]. In the indoor environment chemical reaction of acrylates is mainly due to hydrolysis. *n*-Butanol is a typical decomposition product of *n*-butyl acrylate.

### 3.2. Release of photoinitiators and fragments

The investigated samples were manufactured by use of different photoinitiators or blends. The main components being released from material surfaces were benzaldehyde, cyclohexanone and benzophenone. Area-specific emission rates measured after 24 and 96 h are shown in

Table 3. Moreover,  $SER_A$ -values for detected monomers are presented.

F1 was an acrylate system with photoinitiators BP/DPAP/TBDPO. For experiment F1-A the curing process met the requirements of the manufacturer. F1-B was given only 50% of the required curing time. This was achieved by faster transport through the irradiation zone. The effect of under-curing is clearly demonstrated in Table 3. In case of F1-B increased  $SER_A$ -values indicated high amounts of non-reacted photoinitiator in the surface. 2,4,6-Trimethyl-benzaldehyde, a degradation product of TBDPO, could be detected in the surface layer of F1-A but not in the gas phase. 1,6-Hexanediol-diacrylate (HDDA), a frequently applied bifunctional monomer, was released from sample F1-B. Samples F7 with HEHMPP/BP and F8-B with HCPK/BP were also given 50% curing. Here, increased emissions of the acrylate monomer tripropyleneglycol-diacrylate (TPGDA) in the chamber air were evident. The effect of non-sufficient curing is also demonstrated in Fig. 4. Time-dependent measurements clearly show increased  $SER_A$ -values for benzaldehyde and benzophenone (F8-B) in comparison to full curing (F8-A).

Samples F5 and F9 also contained HCPK in combination with benzophenone. As for samples F8-A and F8-B, benzaldehyde and cyclohexanone were mainly detected as cleavage products in the chamber air, where cyclohexanone can only be produced from HCPK (see Section 3.1). Vice versa, the appearance of the combination benzaldehyde/cyclohexanone always indicates the application of HCPK. The pigmented sample F6 was produced by use of HCPK/DTBPPO. Again, benzaldehyde and cyclohexanone were identified in the chamber air, while 2,4,6-tri-

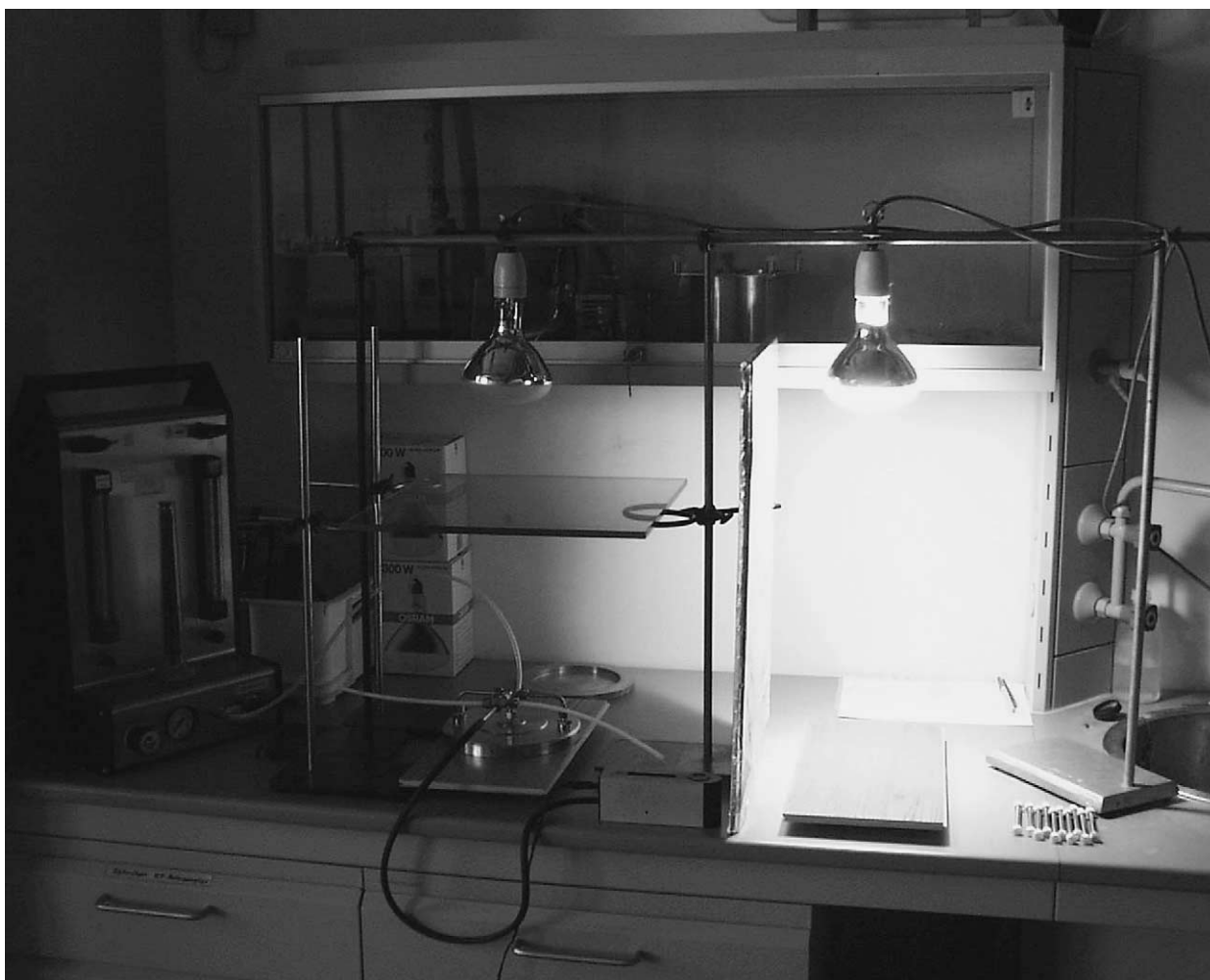


Fig. 3. Experimental setup for testing the influence of irradiation on VOC emission from UV-cured lacquer by use of the FLEC.

methyl-benzaldehyde, a degradation product of DTBPPO, was only found in the material surface.

Samples F9 (A–C) were measured to study the influence of climatic parameters on the emission behavior. Test F9-A was carried out at a temperature of 20 °C and a relative humidity of 37%. During the first week, emission rates of the acrylate monomer TPGDA were about 20–30  $\mu\text{g}/(\text{m}^2 \text{h})$ . In comparison to test F9-A, the recorded emission rates were significantly higher at a temperature of 27 °C and a relative humidity of 70% (F9-B). Test F9-C was carried out at 23 °C, a relative humidity of 50% and with simulated solar radiation. The effect of radiation is evident from the results shown in Table 3 and in Fig. 5. In contrast to tests (A) and (B), the main component in the chamber air after 24 h was benzaldehyde with an emission rate of 234  $\mu\text{g}/(\text{m}^2 \text{h})$ . Furthermore, the concentration of cyclohexanone was also considerably higher with 110  $\mu\text{g}/(\text{m}^2 \text{h})$  (24 h). The decrease of the benzaldehyde emission was fast and only 134  $\mu\text{g}/(\text{m}^2 \text{h})$  could be recorded after 120 h. Surprisingly, the decay of the more volatile cyclohexanone was much slower with 100  $\mu\text{g}/(\text{m}^2 \text{h})$  after 120 h. The effects clearly originate from the formation

of both components by  $\alpha$ -cleavage of non-reacted HCPK on irradiation. In comparison to tests F9-A and F9-B, the chamber concentration of benzophenone was lower in test F9-C. Benzophenone does not undergo  $\alpha$ -cleavage and reacts via electron transfer. No benzaldehyde can be produced by this type of photoprocess. However, the lower chamber values indicate a reaction in the surface. The results have shown that simulated daylight has a strong influence on the emission behavior of UV-cured furniture coatings. This may cause increased concentrations of photoproducts in indoor air during use.

Sample F10, which was a commercial type, emitted considerable amounts of PHMP (326  $\mu\text{g}/(\text{m}^2 \text{h})$  after 24 h). In addition, the appearance of styrene in the chamber air indicated the application of this compound as reactive solvent. 2-Ethyl-hexyl-acrylate (EHA), a volatile and odorous monomer, was released from F12.

Samples P1–P4 were exposed to simulated indoor daylight by use of an ULTRA-VITALUX UV-lamp with (A) and without (B) glass filter. The light intensity was again measured directly at the sample surface and was the same

Table 3

Area-specific emission rates ( $SER_A$ ) of benzaldehyde, cyclohexanone, benzophenone and some monomers after 24 and 96 h testing time (HDDA = 1, 6-hexanediol-diacrylate, EHA = 2-ethyl-hexyl-acrylate, TPGDA = tripropyleneglycol-diacrylate)

Sample	$SER_A$ ( $\mu\text{g}/(\text{m}^2 \text{h})$ )								
	Benzaldehyde		Cyclohexanone		Benzophenone		Monomers		Compound
	24 h	96 h	24 h	96 h	24 h	96 h	24 h	96 h	
F1-A	31	18			62	43			
F1-B	51	35			328	275	51	22	HDDA
F2	25	15							
F3									
F4	137	124							
F5	68	54	43	31					
F6	53	22	53	27					
F7					46	23	60	73	TPGDA
F8-A	39	31	20	14	3	2			
F8-B	116	58	65	24	97	92	53	9	TPGDA
F9-A	53	32 <sup>a</sup>	30	19 <sup>a</sup>	36	16 <sup>a</sup>	30	18 <sup>a</sup>	TPGDA
F9-B	126	46 <sup>a</sup>	71	33 <sup>a</sup>	42	22 <sup>a</sup>	41	24 <sup>a</sup>	TPGDA
F9-C	234	134 <sup>a</sup>	110	100 <sup>a</sup>	21	4 <sup>a</sup>	37	15 <sup>a</sup>	TPGDA
F10	156	125	44	35			36	18	Styrene
F11	100	90							
F12							20	15	EHA
P1-A	10	4	7	6					
P1-B	<1	<1	9	5					
P2-A	7	3	<1	<1			82	16	<i>n</i> -Butyl acrylate
P2-B	6	2	<1	<1			53	10	<i>n</i> -Butyl acrylate
P3-A	95	17	46	24	5	<1			
P3-B	16	3	37	18	2	<1			
P4-A	12	4	14	13			9	13	TPGDA
P4-B	2	<1	11	15			4	20	TPGDA
P5	4	2	4	3	20	139			

<sup>a</sup> Measured after 120 h (no data available for 96 h).

for experiments A and B. The FLEC was applied for determination of  $SER_A$  instead of the  $1 \text{ m}^3$  chamber. For each experiment, the test specimen was cut from one piece and investigated in parallel [31]. The first measurement at  $t = 0$  was carried out in the dark. Before each successive sampling, the surface was irradiated for 4 h. Fig. 6 demonstrates the effect on *n*-butyl acrylate and *n*-butanol for sample P2. *n*-Butanol is an odorous compound and formed from *n*-butyl acrylate by hydrolysis. Light exposure stimulates a sudden increase of emission (5 h), followed by a fast decay, which indicates progressive curing in the surface. There was no significant influence of the glass filter. In contrast, there was a clear effect on the release of benzaldehyde. As is demonstrated in Fig. 7 for sample P1, the emission is considerably

higher when the sample surface is irradiated with filtered light (experiment A;  $\lambda > 290 \text{ nm}$ ). This is also obvious from Table 4, where the total amounts of benzaldehyde, emitted in the time range from 0 to 106, 5 h, are summarized. In comparison, there were no distinct differences of  $SER_A$ -values in case of cyclohexanone (see Fig. 7). Benzaldehyde shows strong absorption in the wavelength range 260–280 nm and the effect might result from direct photolysis.

#### 4. Discussion

For reasons of human health, safety and comfort, the release of hazardous and odorous VOCs from materials for indoor use should be minimized. Optimization of manufacturing processes for UV-curing surface coatings may result in products with low emission levels, which help to improve indoor air quality.

In other work, it was shown that the curing rate is dependent on the photoinitiator concentration up to an optimum concentration [32]. Surplus amounts stimulate increased emission of photofragments and monomers from UV-cured surfaces, which may have a negative influence on human well-being in the indoor environment. Many aldehydes are very odor-intensive. With sensitive persons

Table 4

Emitted amounts of benzaldehyde from 0 to 106.5 h (total testing time) for samples P1–P4 (parquet coating)

Sample	Benzaldehyde (emitted amount in $\mu\text{g}$ , 0–106.5 h)	
	With glass filter (A)	No glass filter (B)
P1	850	118
P2	594	500
P3	7622	1393
P4	1026	224

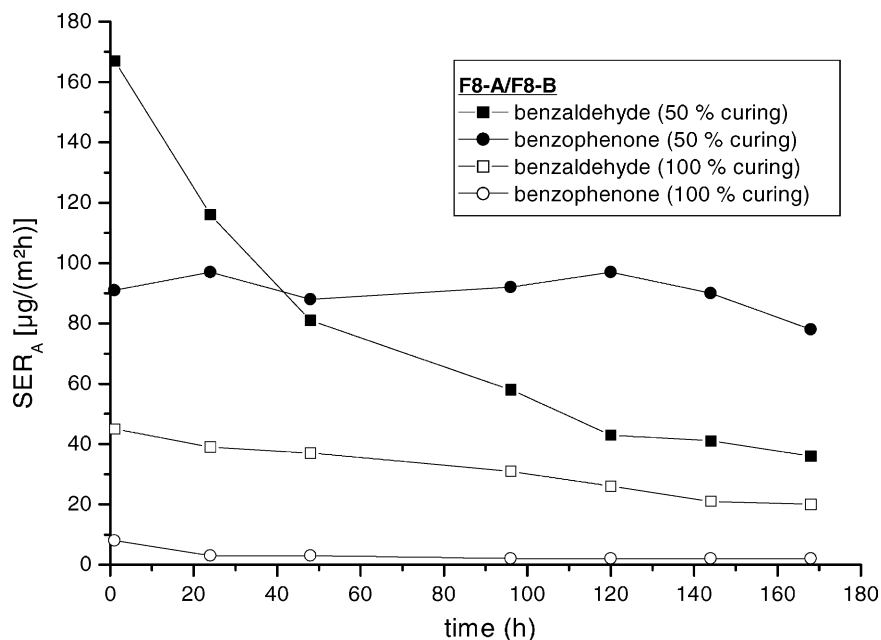


Fig. 4. Time versus concentration profiles for the emission of benzaldehyde and benzophenone with 100% curing (F8-A) and 50% curing (F8-B).

or in high concentrations the perception of aldehydes can cause nausea. The maximum emission rates of benzaldehyde, cyclohexanone and benzophenone measured after 24 h were 234  $\mu\text{g}/(\text{m}^2\text{h})$  (F9-C), 110  $\mu\text{g}/(\text{m}^2\text{h})$  (F9-C) and 328  $\mu\text{g}/(\text{m}^2\text{h})$  (F1-B), respectively. With known  $\text{SER}_A$  it is possible to estimate indoor concentrations from Eq. (1). In the steady state with  $\Delta C = 0$ , Eq. (1) reduces to  $C =$

$\text{SER}_A(L/N)$ . For emission from floor coverings, a typical indoor scenario is  $N = 0.5\text{h}^{-1}$  and  $L = 0.4\text{m}^2/\text{m}^3$  [3]. The odor threshold (OT) of benzaldehyde covers a range of  $\text{OT}_{(\text{benzaldehyde})} = 0.8\text{--}182\ \mu\text{g}/\text{m}^3$ , the odor is generally described as “pleasant” and “bitter” [33].

Problems may also arise from free acrylate monomers as they cause irritations to the eyes and mucous membranes.

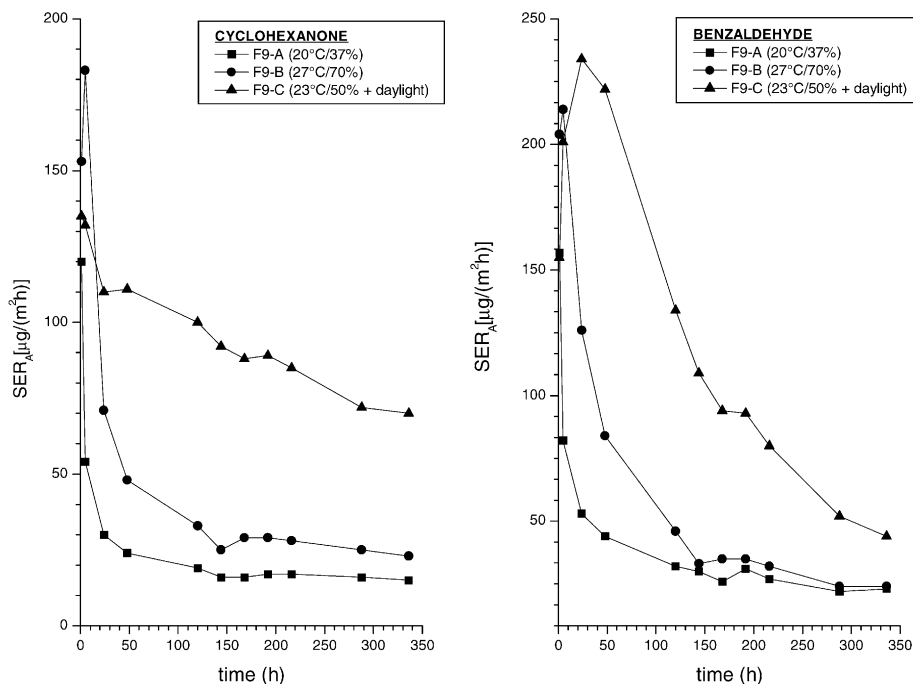


Fig. 5. Time versus concentration profiles for the emission of cyclohexanone and benzaldehyde as a function of climatic parameters (F9A–F9C).

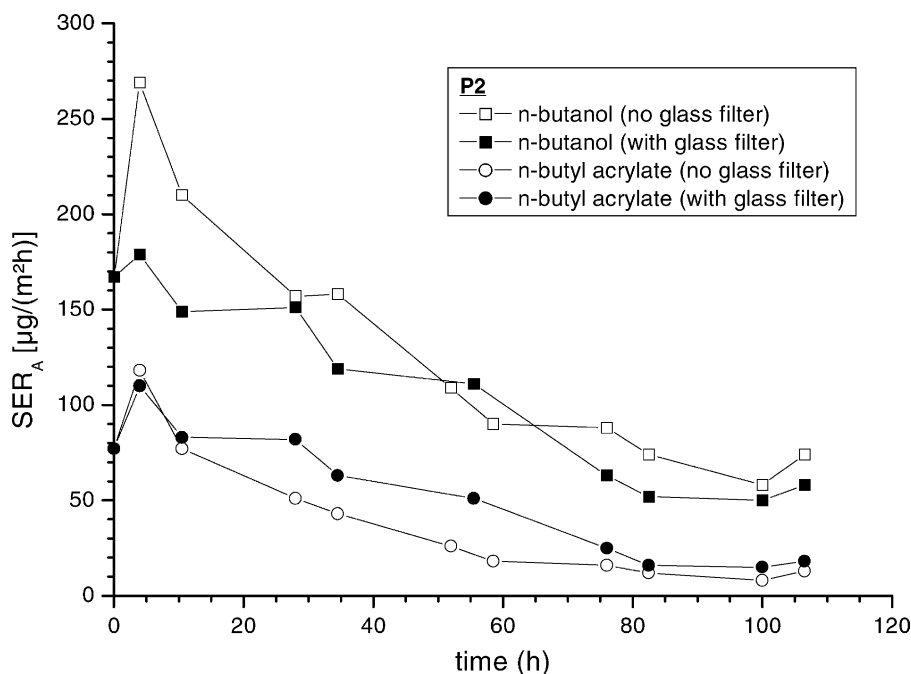


Fig. 6. Time versus concentration profiles for the emission of *n*-butanol and *n*-butyl-acrylate from P2.

Direct contact with acrylate monomers remaining in surfaces can lead to skin irritation and dermal burns [34]. The odor of butyl-acrylate with  $OT_{(\text{butyl-acrylate})} = 11\text{--}66 \mu\text{g}/\text{m}^3$  is classified as “sweet” and “musty” [33]. The non-acrylic monomer styrene is still used as a reactive solvent in the polymerization of coating systems on the basis of unsatu-

rated polyesters. Styrene has a penetrating and unpleasant odor and a strong irritant effect. The highest emission was  $36 \mu\text{g}/(\text{m}^2 \text{h})$  (F10) after 24 h. In earlier investigations chamber concentrations up to  $614 \mu\text{g}/\text{m}^3$  (24 h) were found [6]. In Germany, the recommended guideline value for styrene in indoor air is  $<30 \mu\text{g}/\text{m}^3$  [35].

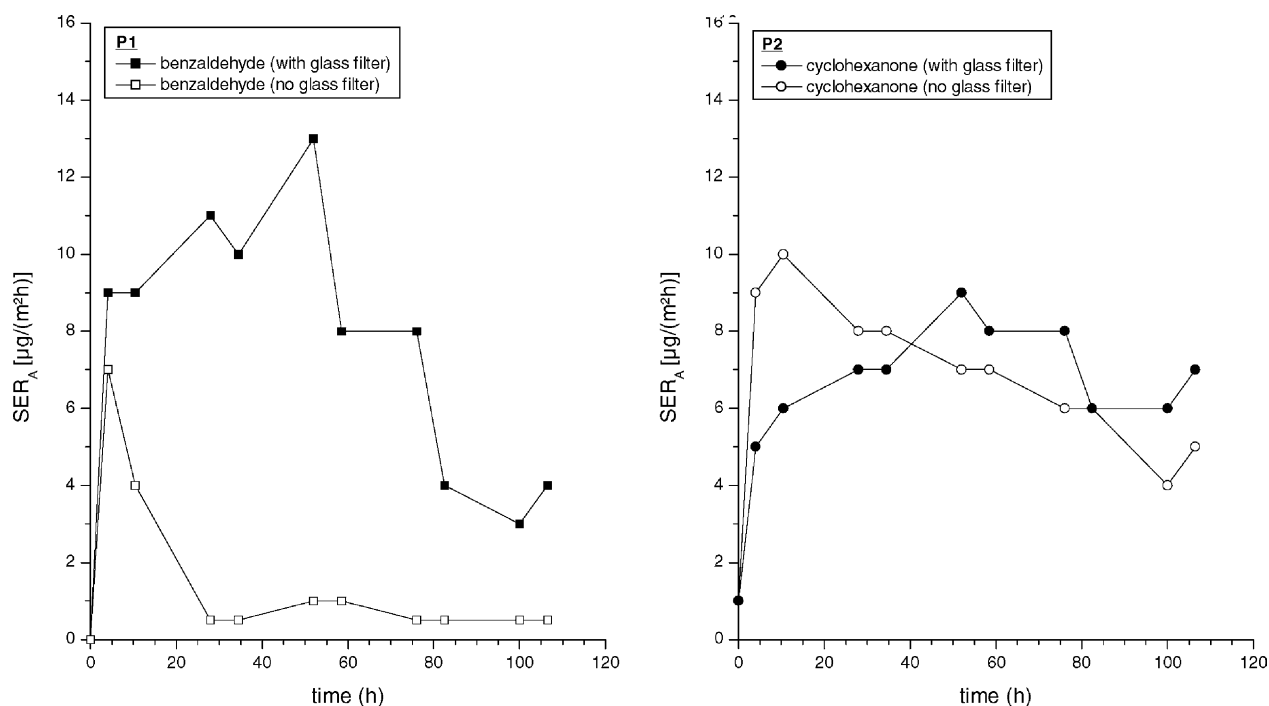


Fig. 7. Time versus concentration profiles for the emission of benzaldehyde from P1 and cyclohexanone from P2.



## 5. Conclusion

UV-cured surface coatings were tested in 1 m<sup>3</sup> chambers and the Field and Laboratory Emission Cell (FLEC) to characterize the emission of VOCs as a function of the test conditions. The results have shown that climatic parameters have a strong influence on the emission behavior of UV-cured surface coatings. This may cause increased emission and therefore increased concentrations of photoproducts in indoor air during use. The release of photoinitiators, photofragments and monomers is a problem in UV-curing, as such compounds may affect humans due to low odor thresholds and low irritation levels. However, UV-curing coating technology has a number of benefits and these problems can be avoided by optimization of lacquer recipes and the manufacturing process. New types of photoinitiators with less volatile fragmentation products are under development. A possibility to reduce VOC emissions might be co-reactive systems with acrylated photoinitiator [11].

## Acknowledgements

Part of this work was financially supported by Stiftung Industrieforschung, Cologne via Verein für Technische Holzfragen (VTH), Braunschweig. We are grateful to Dr. Klaus Suhling, ICSTM, London, for valuable comments and careful revision of the manuscript.

## References

- [1] J.D. Spengler, J.M. Samet, J.F. McCarthy, *Indoor Air Quality Handbook*, McGraw-Hill, New York, 2001.
- [2] T. Salthammer (Ed.), *Organic Indoor Air Pollutants*, Wiley-VCH, Weinheim, 1999.
- [3] *Building Products, Determination of the Emission of Volatile Organic compounds, Part 1: Emission Test Chamber Method*, ENV 13419-1, Beuth, Berlin, 1999.
- [4] *Building Products, Determination of the Emission of Volatile Organic compounds, Part 2: Emission Test Cell Method*, ENV 13419-2, Beuth, Berlin, 1999.
- [5] C.J. Weschler, H.C. Shields, *Atmos. Environ.* 31 (1997) 3487.
- [6] T. Salthammer, A. Schwarz, F. Fuhrmann, *Atmos. Environ.* 33 (1999) 75.
- [7] P. Wolkoff, P.A. Clausen, B. Jensen, G.D. Nielsen, C.K. Wilkins, *Indoor Air* 7 (1997) 92.
- [8] W. Horn, D. Ullrich, B. Seifert, *Indoor Air* 8 (1998) 39.
- [9] J.-P. Fousassier, *Photoinitiation, Photopolymerization and Photocuring*, Hanser, Munich, 1995.
- [10] N.S. Allen, *J. Photochem. Photobiol. A* 100 (1996) 101.
- [11] N.S. Allen, M.C. Marin, M. Edge, D.W. Davies, J. Garrett, F. Jones, S. Navaratnam, B.J. Parsons, *J. Photochem. Photobiol. A* 126 (1999) 135.
- [12] R.S. Davidson, *Exploring the Science, Technology and Applications of UV and EB Curing*, SITA Technology Ltd., London, 1999.
- [13] T. Salthammer, *J. Coat. Technol.* 68 (1996) 41.
- [14] G. Webster, *Chemistry and Technology of UV and EB Formulation for Coatings, Inks and Paints, Vol. II: Prepolymers and Reactive Diluents*, Wiley, Chichester, 1997.
- [15] T. Salthammer, M. Bednarek, F. Fuhrmann, in: *Proceedings of the Eighth International Conference on Indoor Air and Climate, Vol. 5*, Edinburgh, UK, 1999, p. 99.
- [16] M. Wensing, in: T. Salthammer (Ed.), *Organic Indoor Air Pollutants*, Wiley-VCH, Weinheim, 1999, p. 129.
- [17] H. Gustafsson, in: T. Salthammer (Ed.), *Organic Indoor Air Pollutants*, Wiley-VCH, Weinheim, 1999, p. 143.
- [18] E. Uhde, A. Borgschulte, T. Salthammer, *Atmos. Environ.* 32 (1998) 773.
- [19] R. Frank, P. Klöpffer, *Chemosphere* 17 (1988) 985.
- [20] T.E. Graedel, P.J. Crutzen, *Chemie der Atmosphäre, Spektrum Akademischer Verlag, Heidelberg*, 1994.
- [21] F.W. McLafferty, F. Turecek, *Interpretation of Mass Spectra*, University Science Books, Mill Valley, 1993.
- [22] N. Turro, *Modern Molecular Photochemistry*, Benjamin/Cummings Publ. Co., Menlo Park, 1978.
- [23] H.J. Hagemann, in: N.S. Allen (Ed.), *Photopolymerization and Photoimaging Science and Technology*, Elsevier, Crown House, 1989, p. 1.
- [24] C.-H. Chang, A. Mar, A. Tiefenthaler, D. Wostratzky, in: L.J. Calbo (Ed.), *Handbook of Coatings Additives, Vol. 2*, Marcel Dekker, New York, 1992.
- [25] J.V. Crivello, K. Dietliker, *Photoinitiators for free radical, cationic and anionic photopolymerisation*, in: G. Bradley (Ed.), *Chemistry and Technology of UV and EB Formulation for Coatings, Inks and Paints, Vol. III*, Wiley, Chichester, 1998.
- [26] J.E. Baxter, R.S. Davidson, H.J. Hagemann, T. Overeem, *Makromol. Chem.* 189 (1988) 2769.
- [27] J.T. Banks, J.C. Scaiano, W. Adam, R. Schulte-Oestrich, *J. Am. Chem. Soc.* 115 (1993) 2473.
- [28] M.R. Sandner, C.L. Osborn, *Tetrahedron Lett.* (1974) 415.
- [29] X.T. Phan, *J. Radiat. Curing* 13 (1986) 11.
- [30] M. Köhler, *Eur. Coat. J.* 12/97 (1997) 1118.
- [31] T. Salthammer, R. Meininghaus, E. Uhde, in: P. Wolkoff (Ed.), *Proceedings of the Second International FLEC Symposium*, Copenhagen, Denmark, 2001, p. 34.
- [32] R.S. Davidson, H.J. Hagemann, S.P. Lewis, *J. Photochem. Photobiol. A* 118 (1998) 183.
- [33] J.H. Ruth, *Am Ind. Hyg. Assoc. J.* 47 (1986) A-142.
- [34] T. Ohara, T. Sato, N. Shimizu, G. Prescher, H. Schwind, H. Weiberg, K. Marten, *Acrylic Acid and Derivatives*, Ullmann's Encyclopedia of Industrial Chemistry, Vol. A1, VCH, Weinheim, 1985, p. 161.
- [35] Ad-hoc Arbeitsgruppe aus Mitgliedern der Innenraumlufthygiene-Kommission (IRK) des Umweltbundesamtes und des Ausschusses für Umwelthygiene der AGLMB, *Bundesgesundheitsblatt*, 41 (1998) 392.