EMISSIONS OF TERPENES AND ALDEHYDES FROM "BIOPAINTS" -RESULTS OF MEASUREMENTS IN A 1m³-TEST-CHAMBER AND INDOOR MEASUREMENTS IN BUILDINGS

TERPEN- UND ALDEHYDEMISSIONEN VON „BIOFARBEN“ - ERGEBNISSE VON MESSUNGEN AN EINER 1m3 - PRÜFKAMMER UND VON INNENRAUMLUFTMESSUNGEN IN GEBÄUDEN

EMISSIONS DE TERPENES ET D’ALDEHYDES PAR DES "BIO-PEINTURES" - RESULTATS DE METRAGES DANS UNE CHAMBRE D’ESSAI D’ 1m ^{3} ET METRAGES A L’INTERIEUR DE BATIMENTS

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SUMMARY

During the past 10 years so called "biopaints" based on natural resins and plant oils have replaced industrially produced paints for wood preservation or for coloring wooden surfaces. The public generally assumes that naturally grown products are less toxic than industrially manufactured paints. The present paper shows some indoor air concentrations of terpenes and aldehydes emitted by biopaints based on natural resins combined with linseed-oil. The measurements were carried out in a $1m^3$ test-chamber under controlled conditions and additionally compared with real-life indoor air measurements carried out in different flats. It can be shown, that in the first days after the use of biopaints the concentrations of solvents and terpenes are remarkably high. The concentration for volatile organic combinations in the test chamber air reaches 15 to 35 mg/m3 during the first week after the drying period of the paint. The concentration of terpenes in the same period reaches 0,5 to 1 mg/m³, which correlates quite well with the measurements carried out in buildings. After several months a measurable decrease of the emissions of solvents and terpenes was observed. The emission of aldehydes from the examined paint based on linseed-oil was examined till 6 month after the application of the paint. During the first months an almost constant aldehyde (C1 to C9) emission was observed. The aldehyde concentration reaches approx. 1 to 1,5 mg/m³. In a second period 3 to 6 month after the use of the paint, the rate of emission decreased, especially for propanal and hexanal. But the data also shows that the formaldehyde concentrations rise to

a level which are, for a period of one month, significantly higher than the limit value for formaldehyde in indoor-air.

ZUSAMMENFASSUNG

Während der letzten 10 Jahre wurden herkömmliche, lösemittelhaltige Farben zur Holzkonservierung und zum Lackieren von Holzoberflächen durch sogenannte „Biofarben ersetzt, die auf Basis von Naturharzen und Pflanzenölen hergestellt werden. Von der Bevölkerung wird allgemein angenommen, daß Produkte auf Naturbasis weniger toxisch als industriell hergestellte Lacke wären. Die vorliegende Arbeit zeigt einige Innenraumluft-Konzentrationen von Terpenen und Aldehyden, die von Biofarben auf Basis natürlicher Harze und Leinöl emittiert werden. Die Messungen wurden in einer 1 m³ - Prüfkammer unter kontrollierten Bedingungen durchgeführt und zusätzlich mit Innenraumluft-Messungen in verschiedenen Wohnungen verglichen. Es kann gezeigt werden, daß in den ersten Tagen nach Anwendung der Biofarben die Konzentrationen der Lösemittel, Terpenen außerordentlich hoch sind. Die Gehalte an flüchtigen organischen Verbindungen in der Prüfkammer erreichen während der ersten Woche nach der Trocknungsperiode des Lackes Werte von 15 bis 35 mg/m³. Die Gehalte an Terpenen liegen im gleichen Zeitraum bei 0,5 bis 1 mg/m³, was sehr gut mit in Gebäuden durchgeführten Messungen korreliert. Nach einigen Monaten erfolgt eine meßbare Abnahme der Emissionen an Lösemittel und Terpenen. Die Emission von Aldehyden von der verwendeten Farbe auf Leinölbasis wurde über einen Zeitraum von 6 Monaten nach der Applikation verfolgt. Während der ersten Monate erfolgte eine ziemlich konstante Emission von Aldehyden (C_1- C_9); die Aldehyd-Konzentrationen erreichen Werte von 1 bis 1,5 mg/m³. In der zweiten Phase 3 bis 6 Monate nach dem Aufbringen der Farbe sinkt die Emissionsrate, speziell für Propanal und Hexanal. Aber die Daten zeigen auch, daß die Konzentrationen an Formaldehyd eine Höhe erreichen, die über einen Zeitraum von 1 Monat über dem Grenzwert für Formaldehyd in der Innenraumluft liegen.

RESUME

Au cours des dix dernières années, les "bio-peintures" basées sur des résines naturelles ou des huiles végétales ont remplacé les peintures industrielles dans le domaine de la préservation et la coloration du bois. Le public suppose généralement que les produits à base naturelle sont moins toxiques que les peintures fabriquées industriellement. Ce rapport présente les résultats de métrages sur la concentration dans l’air intérieur en terpènes et aldéhydes émis par des "bio-peintures" à base de résines naturelles et d’huile de lin. Les métrages

ont été exécutés dans une chambre d'essai d'1m ^{3} sous des conditions contrôlées et comparés avec les métrages effectués sur l'air à l'intérieur de différents appartements. Il peut être montré, que dans les premiers jours après l'application de "bio-peintures" les concentrations en solvants et en terpènes sont remarquablement élevées. Dans l'air de la chambre d'essai, la concentration des combinaisons organiques volatiles atteint des valeurs de 15 à 35 mg/m3 pendant la première semaine après la période de séchage de la peinture. La concentration en terpènes durant la même période atteint 0,5 à 1 mg/m^3, ce qui correspond assez bien aux métrages exécutés dans des bâtiments. Après plusieurs de mois une diminution mesurable des émissions de solvants et terpènes peut être constatée. L'émission d'aldéhydes de la peinture à base d'huile de lin examinée a été suivie durant une période de 6 mois après l'application de la peinture. Pendant les premiers mois, une émission quasi-constante d'aldéhydes (C1 à C9) a été observée; la concentration en aldéhydes atteint des valeurs de 1 à 1,5 mg/m^3. Dans une deuxième période 3 à 6 mois après l'application de la peinture les émissions diminuent, surtout pour le propanal et l'hexanal. Mais les données montrent également que la concentration en formaldéhyde atteint pendant un mois un niveau nettement supérieur à la valeur limite pour la concentration en formaldéhyde dans l'air intérieur.

1 INTRODUCTION

During the past 10 years so called "biopaints" based on natural resins and plant oils substituted industrially produced paints for wood preservation or for coloring wooden surfaces. The public generally assumes that naturally grown products are less toxic than industrially manufactured paints. Those alternative products are normally based on natural resins such as turpentine oils and plant oils like linseed oil. Some of the paints contain only one of both possible ingredients. Aliphatic hydrocarbons are frequently used as solvents for those paints. In order to improve the scent, different lemon-oils are usually added. Turpentine oils normally contain volatile terpenes such as α-pinene, β-pinene, limonene and Δ-3-carene. The boiling points of the terpenes can be compared to boiling points of other cyclic and/or aromatic hydrocarbons. This leads to the situation that most terpenes should be vaporized parallel to the solvent during the drying phase of the painting, thus the highest concentrations of terpenes in indoor air can be expected immediately after the use of those colors. Due to the surface constitutions of the varnish, the diffusion of volatile compounds in air can be reduced, so the concentration of terpenes in indoor air can be on a higher level over a longer period [7]. Measurements in so-called "alternative houses" show that, compared to usually constructed buildings, significantly higher concentrations of terpenes in indoor air can be detected. Table 1 gives a survey about those differences [1].

Tab. 1: Comparison of terpene-concentrations in indoor air of normal and alternative buildings

Building No.	Terpinene [µg/m³]	alpha-pinene [µg/m³]	beta-pinene [µg/m³]	limonene [µg/m³]
K 1	4,5	9,3	1,2	3,0
K 2	53	129	4,0	22
K 3	--	1,2	--	0,9
K 4	90	291	14	35
K 5	--	--	1,8	11
A 1	105	256	26	18
A 2	85	358	13	30
A 3	265	660	61	72
A 4	217	480	22	44
A 5	239	66	4,6	41

The average concentrations of terpenes (see table 2) in the indoor air in German households were examined in 1986/87 by a study in which the concentrations of volatile organic compounds in nearly 500 buildings were determined [2]. The medium concentrations and the 95. percentile (reference value) of terpenes in indoor air according to this study are:

Tab. 2 : Average concentrations of terpenes in indoor air in german households.

	alpha-pinene	beta-pinene	limonene	Δ-3-caren *	sum of terpenes
Medium Concentration	6,8	0,7	13,2	2,3	27,3
95. Percentile	26,6	4,3	103,3	4,3	132,7

*data from [3]:

Measurements in alternative houses showed that a series of different aldehydes are detectable in the indoor-air. Mainly hexanal, heptanal and octanal are detectable when alternative paints are used in a building. It is well known that plant oils normally consist of unsaturated fatty acids, which can decompose with oxygen. One class of the decomposition products are aldehydes. Therefore the emission of aldehydes was additionally observed during the experiments.

2 EXPERIMENTAL DATA

2.1 General testing conditions

The present paper shows the results obtained with a biopaint containing natural resin, linseed-oil, orange-oil and aliphatic hydrocarbons as solvent. A wooden plate (size 1 m^2) was treated with about 0,1 l of the chosen product. After drying for 48 h under normal conditions the plate was put in a 1 m^3 test chamber and stored there under defined conditions. The air exchange rate was fixed to 0,65/h. The temperature inside the test chamber was registered and varried from 18 to 22 °C. The humidity of the test chamber atmosphere was not influenced and generally determined by the surrounding atmosphere. The blind values of terpenes and aldehydes in outside air were determined as well as the blind values for those substances in the test chamber air with and without the untreated wooden plate.

The test chamber we used is a simple glass container with a volume of 1 m^3 and a ground area of 1 m^2. The air exchange rate is assured by an exhaust pump and the exhausted volume is measured.

The results for terpenes obtained in different kindergartens in Baden Württemberg, reported in this paper, were mainly achieved by thermal desorption technique.

2.2 Air sampling

The air was collected on three different sampling systems. For the determination of solvents and terpenes two systems were used. One of them is the classical way of trapping hydrocarbons on activated charcoal (ORBO 32, sampled volume 100 to 200 l; desorption with CS_2.) The other chosen possibility was the use of a thermal desorption technique, which has the advantage that the sampling volume is reduced to 1 to 2 l.

The sampling for aldehydes was carried out with DNPH-tubes (ORBO LPD DNPH cartridge; sampling volume 50 to 150 l; Method: US EPA TO11).

2.3 Detection methods

Gaschromatography- low resolution mass-spectrometry (GC/MS LR; Varian Saturn II) was used to determine terpenes and aliphatic hydrocarbons after thermal desorption from charcoal tubes. Due to the concentration range in the test chamber atmosphere it was possible to use nuclear magnetic resonance-spectrometry (NMR; Bruker Avance DPX 300) to determine terpenes and aliphatic hydrocarbons after desorption from charcoal with CS2.

The determination of aldehydes was carried out with HPLC after desorption with acetonitrile from the DNPH-tubes

3 RESULTS

3.1 Emissions of hydrocarbons and terpenes.

3.1.1 Results of the test chamber experiment

The paint used for these experiments contains aliphatic hydrocarbons as solvent, limonene as terpenes and unsaturated triglycerides (probably linseed-oil). Aldehydes cannot be found in the liquid phase of the paint. All samples taken from the test chamber atmosphere in the first two days after starting the test chamber experiment were collected on thermal desorption tubes.

It can be shown that hydrocarbons and limonene are part of the test chamber atmosphere. The concentrations of all substances in the test chamber air are too high to be detected by thermal desorption technique. Using the GC/MS in combination with thermal desorption it is only possible to give an estimation of the total amount of volatile organic compounds (VOC) in the chamber air during the first week.

Total-VOC in test chamber air (after 3 days) 34,5 mg/m³
Total-VOC in test chamber air (after 5 days) 32,5 mg/m³

After this period another sampling and detection system was chosen. The air was collected on activated charcoal, desorbed with CS_2 and the obtained solution measured with NMR with this system the following results can be achieved.

Tab. 3: Emissions of terpenes, aliphatic hydrocarbons and aldehydes from biopaint during the first twelve days (air-exchange-rate 0,67/h; temperature 18 to 22 °C; humidity 35 - 60 % rel.)

Days after installing the dried wooden plate in the test chamber	test chamber air contents, detectable with NMR concentrations in mg/m³		
	aliphatic hydrocarbons	limonen	sum of aldehydes (calculated as hexanal)
7 days	19,2	0,64	0,06
10 days	14,3	0,46	0,14
11 days	10,3	0,31	0,07
12 days	11,2	0,38	0,18

3.1.2 Terpenes in indoor air of buildings

In a kindergarten the teachers and children complained about irritative effects in the nose and eye area and dermal irritations. The newly built kindergarten had opened a few weeks before, in January. The construction of the kindergarten was made of building materials on natural basis; for example much wood was used.

The indoor-air-measurements, carried out by the Forschungs- und Materialprüfungsanstalt Baden-Württemberg, gave the following indoor air concentrations of terpenic substances during normal kindergarten activities:

[µg/m³]	Room 1	Room 2	Room 3	Room 4
alpha-pinene	150	140	180	260
beta-pinene	15	12	39	48
camphene	< 1	< 1	< 1	< 1
limonene	40	25	36	48
delta-3-carene	49	38	59	93
alpha-terpinene	< 1	< 1	< 1	< 1
gamma-terpinene	< 1	< 1	< 1	< 1
sum of terpenes	254	215	314	449

The cause of the increased indoor air concentrations of terpenes were the used building-materials like paints, lacquers and adhesives. The data sheets of the used materials showed that most of these products contain natural oils or natural resins, which, depending on their origin, comprise various amounts of terpenes.

In another kindergarten, investigations about the continuance of emission from the terpene-containing sources were made. The indoor air was examined after a renovation procedure because of a wood preservation problem. During the renovation the wood materials in this kindergarten were painted with an "alternative" paint containing terpene. Several weeks after the reopening of the kindergarten after this renovation, the teachers complained about skin and eye irritations. The measurements on indoorair caried out thereupon were made under worst case conditions (closed room for at least 12 hours). Only the sum of terpenes was determined, yielding the following result:

Sum of terpenes [µg/m³], Room A	526

The only possibility to reduce these high concentrations of terpenes in the indoor air beside the removal of the painted wood was to increase the ventilation of the concerned rooms.

After one year the indoor air in the kindergarten was measured once more in order to check the effect of time and ventilation on the continuance of the emission sources. The results for particular terpenes of this second measurement after one year are shown in table 5.

Tab. 5: Terpenes concentrations in indoor air one year after the renovation (conditions: worst case, closed for at least 12 hours)

Room A	[µg/m³]
alpha-pinene	36
beta-pinene	4
camphene	6
limonene	48
delta-3-carene	< 1
alpha-terpinene	< 1
gamma-terpinene	< 1
sum of terpenes	94

The results of this second measurement indicate that the emission process of terpenes used in natural paints needs more time to decrease in comparison to the solvents used in normal paints.

3.2 Emission of aldehydes

As mentioned before, a number of aldehydes, especially hexanal, heptanal and octanal can be found in indoor air after "alternative" paints were used. The following results give a survey over the development of the aldehyde concentrations in air after using a paint based on unsaturated triglycerides.

Parallel to the determination of terpenes and solvents (see table 3) the concentration of various aldehydes were determined. The used sampling system based on DNPH-cartridges allows to collect and determine all aldehydes from C1 to C 9 in a single step. The possibility of determining aldehydes by NMR (see table 3) after sampling the air contents with activated charcoal allowed to validate the chosen method.

In order to give a survey about the importance of the detected concentration ranges, it was necessary to determine the aldehyde concentrations in the surrounding atmosphere, as well as inside the test chamber filled with the untreated wooden plate. The results of this measurements are given in table 6. Additionally the medium concentrations for some of the aldehydes are mentioned in table 6.

Tab. 6: Blind values of the test-chamber, aldehyde-concentrations in outside air (temperature 16 to 22 °C, humidity 30 to 75 % rel.) and medium aldehyde concentrations in indoor air [2].

Aldehyde concentration in µg/m³	test-chamber air with untreated wooden plate	outside air (rural area)	outside air (urban area)	medium concentrations in indoor air in german households
formaldehyde (C_1)	8	1	2	55
acetaldehyde (C_2)	5	5	<2	
propionaldehyde (propanal), (C_3)	<2	<2	<2	
butyraldehyde (butanal), (C_4)	<2	<2	<2	
valeraldehyde (pentanal), (C_5)	2	<2	<2	
caproaldehyde (hexanal), (C_6)	5	<2	<2	< 1
enanthaldehyde (heptanal), (C_7)	6	<2	<2	
caprylaldehyde (octanal), (C_8)	8	<2	<2	
nonylaldehyde (nonanal), (C_9)	13	3	5	

Due to the fact that aldehydes are not detectable in the paint, it must be assumed that the aldehydes are generated during the decomposition of unsaturated fatty acids. Therefore, the observation period for aldehydes in the test chamber air differed from the observation period for terpenes and solvents. The first sampling, especially for aldehydes, was carried out 8 days after storing the treated and dried plate in the test chamber. The development of the aldehyde concentration in test chamber air during the first month can be seen in table 7.

Tab. 7 : Development of the aldehydes concentrations in test chamber air during the first month after treating a wooden plate with an "alternative" paint. (air exchange rate 0,67/h; temperature 18 to 22 °C; humidity 35 to 60 % rel.)

Aldehyde Concentrations in µg/m³	test-chamber air 8 d after test start	test-chamber air 10 d after test start	test-chamber air 11 d after test start	test-chamber air 12 d after test start	test-chamber air 28 d after test start
formaldehyde	35	54	33	39	93
acetaldehyde	220	250	155	200	180
propanal	480	560	290	410	250
butanal	15	15	14	22	45
pentanal	71	56	38	51	100
hexanal	440	410	250	320	320
heptanal	21	23	24	34	140
octanal	34	35	33	38	170
nonanal	39	35	32	38	110
sum of aldehydes C_1 to C_9	1414	1493	920	1220	1408

After 28 days the plate was removed from the test chamber and stored outside for further 2 months. After this interruption the plate was reinstalled in the cleaned test chamber and the aldehyde emission registered for further 3 months. The first sample was taken 24 h after reinstalling the plate in the test chamber. The emission characteristics for this period can be seen in table 8.

Tab. 8: Development of the aldehydes concentrations in test chamber air 3 to 6 months after treating a wooden plate with an "alternative" paint. The plate was stored 2 months outside the test chamber and then reinstalled (air exchange rate 0,67/h; temperature 18 to 22 °C; humidity 35 to 60 % rel.)
The first sample was taken 24 h after reinstalling the plate in the test chamber.

Aldehyde concentration in µg/m^3	test-chamber air 24 h after reinstalling	test-chamber air 25 d after reinstalling	test-chamber air 35 d after reinstalling	test-chamber air 60 d after reinstalling
formaldehyde	47	240	168	89
acetaldehyde	5	110	58	17
propanal	17	141	47	26
butanal	20	8	7	3
pentanal	4	19	12	7
hexanal	6	53	27	16
heptanal	17	45	29	22
octanal	18	67	55	25
nonanal	38	99	76	5
sum of aldehydes C_1 to C_9	172	782	479	210

4 DISCUSSION

The test chamber results for the emission of volatile hydrocarbons and aldehydes show that remarkable amounts of both substances are emitted during the first month from so-called "biopaints". The emission of aliphatic hydrocarbons during the first months results in concentrations which might cause health effects. Englert et al. [4] point out that indoor-air-concentrations of hydrocarbons above 0,2 mg/m³ could result in discomfort and disturbances of well-being. Above 3,0 mg/m³ total VOC headaches and sickness could occur as indoor-air related symptoms. The medium concentration of VOC`s in indoor-air is about 0,33 mg/m³.

In the first months after using paints containing terpene in the interior, high terpene-and solvent concentrations in the indoor air can be expected, depending on the amount of used color, the painted surface and the air exchange rates. After a certain time, which is generally longer than the corresponding period for normal paints containing solvents, the rate of emission of the terpene-sources decreases and the indoor air concentrations approach the normal concentrations. The existing data and studies offer only inadequate evaluations about the health effects of indoor terpene exposures. Only delta-3-carene it known to have a strong irritative potential and to possibly be the trigger of an allergic contact-dermatitis. Taking into consideration the fact that the indoor-air-measurements were made several months after the opening of the kindergarten, it can be supposed that, shortly after the reopening, the terpene concentrations were far higher. Informations from the investigation center for environmental toxicology.(Kiel, Dr. Heinzow) indicate that concentrations of about 600 µg terpenes / m³ can result in skin irritations and healthy effects [5]. This could be the explication for the aforementioned health-problems of the teachers and children in the investigated kindergarten.

While the concentration range for hydrocarbons and terpenes decreases within the first month, the concentrations for aldehydes remain on a high level.

The present results show, that for example formaldehyde is emitted in a steadily increasing amount over aperiod of half a year after using such biopaints to preserve wood. In this period, the amount of aldehydes like propanal and hexanal decreases, while the amount of formaldehyde constantly increases. It can be proved that, during the second testing period, formaldehyde concentrations are reached which are higher than the limit value for formaldehyde in indoor air. The contamination of indoor air with aldehydes seems to be a serious problem after using biopaints based upon plant oils. Some toxicologist are discussing a limit for health effects for aldehydes in the range of 20 $\mu g/m^3$ [6]. The aldehyde concentration range in the test chamber air are at least ten times higher. The obtained test chamber results for terpene show that the presented results can easily be compared with results obtained by indoor-air measurements in buildings. Therefore it can be expected that the aldehyde concentrations in indoor air reach the same level than inside the test chamber.

In general, it can be stated that the label "biopaint" is not an indicator for paints to be less toxic than other products. The chosen biopaint shows a remarkably high rate of emission for hydrocarbons, terpenes and aldehydes during the first six months. The results presented in this paper also show that the emission of aldehydes and terpenes will continue. The emission will run on a lower level but the concentration is expected to be high enough to exceed the discussed level of 20 $\mu g/m^3$. The influence of these products on indoor air has to be regarded as carefully as the influence of other wood preservatives or paints.

5 LITERATURE

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