EMISSION OF ALDEHYDES FROM PAINTS CONTAINING LINSEED OIL: A FIELD STUDY

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ABSTRACT
Two different workplaces where paints containing linseed oil were used have been studied. Air samples were collected with 2,4-dinitrophenylhydrazin samplers and analysed for aldehydes with liquid chromatography and UV detection. At the first object, the paint was sprayed onto ceilings and parts of the walls. Stationary samplers showed high amounts of formaldehyde, which exceeded the Swedish occupational ceiling value (1.2 mg/m^3), during the first four hours after painting. The amount of aldehydes generally peaked two days after the paint was applied. At the second object, paint was applied by brushing onto woodwork. No limit values were exceeded. The emissions had their maximum at approximately two days after the paint was applied. The emission profile had lower initial values probably due to the absence of paint mist. The large surface area created by spraying the paint causes a burst of emissions due to the accelerated oxidation process.

INDEX TERMS
Paint, Linseed oil, Aldehyde emission, Field study

INTRODUCTION
Since the reintroduction of linseed oil paints in the 80ies, there has been an ongoing discussion in Sweden whether or not this was a good development. From an ecological point of view there are several good aspects, such as the renewable source of raw material and the long lifetime of the paint film. The latter also vouches for a good economy, although the initial cost of applying the paint could be higher than with other paint systems. The cons are of a health and an economical aspect. Earlier laboratory work has shown that while the paint dries, a number of different oxidation products are emitted (Andersson *et al*, 1999). These vary depending on the formulation of the paint (Fjällström *et al*, 2001), but the emissions generally consist of different aldehydes and carboxylic acids. Both these groups of compounds can act as irritants on mucous membranes and have a strong and unpleasant odour (Jensen *et al*, 1995). Aldehydes can be both sensitising and carcinogenic. Due to the gravity of aldehyde effects, this study was limited to study these substances.

Two different workplaces were studied where paints containing linseed oil were used. The first object was a construction site of a university building where emulsion paint was used. At the time of investigation, the paint was sprayed onto ceilings and parts of the walls. The walls were made up of gypsum wallboard and the ceiling was mainly concrete, but the occasional ventilation tube was also sprayed with paint (sheet metal and lagging material). The second object was a historical monument, which was renovated. Walls (lime-mortar) where painted with emulsion paint (containing small amounts of linseed oil) and woodworks were painted

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with a linseed oil paint. At the time of investigation linseed oil paint was applied by brushing on to the woodwork.

METHODS

Air samples where collected using a 2,4-dinitrophenylhydrazin sampler (Sep-Pak, Waters). Air was pumped at 250-500 ml/min with AirChek 2000 pumps (Scantec, Sweden), and the flow was measured with a FlowChek 2000 (Scantec, Sweden). The sampling was performed to determine personal exposure during painting as well as to get an emission profile on the premises. The first type of samples was obtained by mounting two samplers in the breathing area of the painters. Sampling was only maintained during there active time of painting, so the time and air volume varied from sample to sample. The second type of samples was obtained by placing the samplers in the middle of the rooms being painted, by the use of 1.8 m high tripods. Sapling was maintained for 3-4 hours in triplicates. The stationary sampling was performed during a number of days after the application of the paint. As the analysis couldn't be made onsite, the samplers were placed in a freezer, pending the return to the laboratory. Samplers were processed by eluting them with 4 ml of acetonitrile (Rathburn, HPLC Grade S) and diluting the eluate to 5.0 mL. The analysis was performed using a liquid chromatograph (1100 Series, Hewlett-Packard) with a variable wavelength UV detector (VWD). Separation was carried out on a HP hypersil ODS column (5 µm 2.1 × 100 mm), thermostated to 20 ºC. Before use, the column was conditioned with 55% water (A) and 45% AcCN (B) for 45 min. The following binary mobile phase gradient was used for analysis: flow rate 0.5 mL/min, initial concentration 55% (A) and 45% (B) for 10 min, (B) is raised to 75% within 15 min where it was maintained for 10 min, the concentration was then returned to the initial within 5 min giving a total analysis time of 40 min. A signal was recorded at 345 nm. 5µl of each sample were injected. Reference substances were used to identify n-aldehydes (methanal through nonanal). To confirm the structures and identify some of the smaller peaks, some samples were analysed by LC/MS/MS (TSP LC-system and LCQ Duo, ThermoFinnigan). The same column and LC program were used. A library of MS/MS spectra was used to elucidate the structures and the results were compared with the work and findings of Kölliker and Oehme (1998).

RESULTS

At the construction site, the mist created by the sprayed paint posed some problems for the personal samplers, as particles were collected as well as gaseous aldehydes. The stationary samplers showed high amounts of formaldehyde, which during the first four hours after painting exceeded the Swedish occupational ceiling value (1.2 mg/m^3). The following day the amounts had dropped under the threshold limit value (0.6 mg/m^3). Other carbonyls detected were acrolein, ethanal, propanal, pentanal, hexanal and nonanal, with propanal being the most abundant. The amount of these compounds generally peaked two days after the paint was applied. After approximately one week the emission had reached a steady state with levels below 0.1 mg/m^3 for all quantified species.

At the site of renovation, no limit values were exceeded. Approximately the same values where detected during personal and stationary sampling. The emissions had their peak at approximately two days after the paint was applied. Carbonyls detected were the same as in the first investigation, together with cyclohexanone, 2-butanone and 2-butenal.

DISCUSSION

Only the saturated aldehydes were quantified because of the difficulty of correctly doing so with unsaturated aldehydes (Goelen *et al*, 1997). As there was no possibility to process samplers onsite and they could not be placed in a freezer until the end of the day, the risk of

degradation was high. Although uncertain, the levels of the unsaturated species seemed to be low in comparison to the quantified aldehydes. As the odour of the unsaturated aldehydes can be perceived especially irritating (Jensen *et al*, 1995), they could be relevant even in low concentrations, so further investigations should be done.
The fact that the first object showed much higher initial values of formaldehyde (and other aldehydes) is probably due to the paint mist that the spraying generated. The enormous surface area is bound to cause a burst of emissions due to the accelerated oxidation process.

CONCLUSION

The emission process is prolonged and the film can continue to emit oxidation products for months, although the levels drop below ppm within a week. Applying linseed oil based paints by spraying should be avoided if possible. If this method is used, precaution should be taken to ensure the good health of the painters. Forced ventilation can drastically lower the concentrations of oxidation products by simple dilution.

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