PRODUCT MODIFICATION AS RISK MANAGEMENT TOOL: CLASSIFICATIONOF PAINT ACCORDING TO POTENTIAL NEUROTOXICOLOGICAL RISK DURING INDOOR USE D. BROUWER, N. DE PATER, J. VAN HEMMEN

TNO Chemistry, P.O. Box 360, 3700 AJ Zeist, The Netherlands

Introduction

The OAR (Occupational Air Requirement) value represents the quantity of air required to dilute the vapour concentration in the work room resulting from 1 L product to a concentration below the Occupational Exposure Limit (OEL). A simple algorithm with the concentration of solvent in the paint (g/L), the evaporation factor (f), and the OEL of the solvent is used to calculate the OAR (equation 1).

$$OAR = \frac{1000 \text{ x C x F}}{OEL}$$
(1)

Where:

OAR : Occupational Air Requirement (mg/L)

C : Concentration volatile organic compounds (VOC) in product (g/L)

F : Evaporation factor (0, 0.3, 0.7 and 1.0)

OEL : Occupational Exposure Limit (mg/m³)

The OAR approach has been evaluated theoretically and the concept of Occupational Air Requirement (OAR) is considered to have great potential for use in the classification of paints for construction and maintenance applications, i.e. to identify OAR-categories of paints that can be applied without exceeding OELs' with no appreciable room ventilation. An experimental study was conducted and aimed at 1) investigation of the relationship between OAR and exposure during the application of a series of paints, 2) investigation of the ability of the OAR approach to discriminate between low- and high-risk paints, and 3) to explore the relevance of the OAR parameters.

Experimental

A semi-experimental study has been conducted, where exposure was assessed to volatile (organic) solvents during a defined 'standard indoor paint task', i.e. application of 0.5 L of paint by brushing on approximately 6 m² of surface area in an unventilated room of approximately 50.5 m. This standard indoor paint task has been operated by defining an unventilated room as a room with an air exchange rate $< 0.2 \text{ h}^{-1}$, and application of 0.5 L of paints to both sides of a door and a door frame. Fifteen (experimental) paints were prepared by the Dutch Association of Paint Manufacturers (VVVF) according to a designed grid reflecting differences in solvent content (percentage, volatility (three categories), and toxicity (aliphatic, aromatic hydrocarbons) with a target range of OAR levels from 43 to 875 m/L for alkyd resins paints. Two types of paint were included, *i.e.* high solid paints (A-type;n=6), and conventional paints (B-type;n=9). On average the solvent content of the experimental paints was 175 g/L for high solid paints and 350 g/L for conventional paints, respectively. Additionally conventional paints were prepared with solvent contents of approximately 390 g/L and 442 g/L. Based on both the blend data and the results of the chemical analyses, for each paint the OEL (derived for neurotoxicological effects) and the OAR-values were calculated.

Five qualified painters volunteered in the study, each of the subjects conducted several times the 'standard indoor paint task' with different paints, resulting in duplicate exposure data for each type of paint.

Inhalation exposure to solvents during the actual application of the paint was assessed by personal air sampling using an air sampling pump (flow rate approximately 250 mL/min) and a heavy weight (800/200 mg) charcoal adsorption tube over consecutive intervals of 15 min. In addition, real-time air monitoring was performed during the application in the breathing zone of the test subject. A photo ionization detector (PID)-type (Mini-RAE) and a photo-acoustic infrared detection (PAIRD) device (B&K) were used for the measurement of 'total' hydrocarbon-concentration, xylenes and SF6, respectively. Response times were approximately 2 s and 150 s for PID and PAIRD, respectively. After application, but not earlier than 45 min after beginning the application, the painter left the room and personal sampling changed into stationary sampling, i.e. charcoal tube

sampling, and the inlet of the PID and PAIRD devices were placed on a fixed location between the painted surfaces. The sampling period was 60 min. PID and PAIRD responses were expressed as iso-butylene-equivalents

Prior to the start of the painting, a tracer gas (SF6) was generated in the test room and the concentrations were monitored by the PAIRD monitoring device during the experiment to determine the air exchange rate.

Charcoal tubes were extracted and analysed for C8 through C12 n-aliphatic hydrocarbon groups, specified xylenes, aromatic hydrocarbons, and expressed as total aliphatic hydrocarbons, total aromatic hydrocarbons (C9-C11) and xylenes, since these hydrocarbons have different OELs.

Results

Personal air sampling results, i.e. time weighted averages (TWA) over the duration of the task, were expressed as percentage of the nominal concentration of the OEL and ranged from approximately 8% to 93% for high solids, and approximately 38% tot 168% for conventional paints. The B7, B8 and B10 types of conventional paint showed the highest concentrations during and following application. Figure 1 illustrates the TWA-exposure during the task.

In general, the duplicate samples gave similar results (maximum difference < 20%), indicating a slight between-subject and/or within-paint variation.

For several paint types, i.e. A2, A4, B2, B4, some of the periods observed during the task showed VOC-concentrations up to 140% OEL, while the overall period revealed concentrations below OEL. During experiments with paint type B7 en B10 short time exposure exceeded two to three times the nominal concentration of the OEL.



Figure 1 Plot of the average VOC exposure during the task, expressed as %OEL. A and B indicates results of high solid and conventional types of paint, respectively.

Vapour emission profiles, resulting from PID and PAIRD real-time air monitoring, show a strong increase of the vapour concentration during the actual application, a slight increase during the first period after the painter left the experimental room followed by a slight decrease. These profiles indicate that the highest vapour concentration occurred after the actual application when the painter had left the room. Total hydrocarbon measurements during experiments with high solid paints by PAIRD revealed similar results compared to PID-detection. The exposure profiles also show a (statistically significant) higher increase of vapour concentrations of the paints containing the most volatile solvents (evaporation factor (f) =1) compared to other paint types with lower fvalues. Moreover, the same sequence of evaporation factor for equilibrium concentrations was observed. In a combined plot of the average hydrocarbons concentration determined by charcoal tube sampling of each individual experiment over different time periods and the real-time monitoring a remarkable good fit between the two measurement methods can be observed (Figure 2).



Figure 2 Concentration profiles for high solid paints with different evaporation factors (f). The left y-axis indicates the results of real time monitoring (PAIRD), the right y-axis shows the PAS results (solid rectangles in corresponding colours).

Linear regression analysis revealed a strong relation between the OAR-value of the paints and the TWA-concentration (%OEL) during the task. For all alkyd paint types 73% of the differences in exposure could be explained by the differences in OAR-values.

Discussion

The influence of the evaporation factor (f) was demonstrated clearly for the high solid paints, where pure categories of evaporation could be distinguished. Both the slope of the concentration-time profiles and the level of the TWA-concentration following application were significantly different for all three categories of f-factors (Figure 2). In addition, the

differences between the classes of evaporation were demonstrated by the results of the different PAS-samples over the period of application.

The concentration of VOC in the paint has been demonstrated to affect the exposure. In the experiments the B types of paint (conventional paints) contained at least twice the concentration of VOC compared to the high solid types (A). Application of the B-types resulted in higher exposure compared to the corresponding A-types of paints (identical indices) (Figure 1).

The type of VOC determines both the evaporation category (f) and the OEL. Within the same class of f-factor, the presence or absence of aromatic hydrocarbons affects the OEL of the mixture (and thus the OAR of the paint product) strongly. This can be illustrated most clearly for the high solid paints. Substitution of approximately 20% of the aliphatic hydrocarbons by aromatic hydrocarbons resulted in a decrease of the OEL (and an increase of the OAR of the paint) by 50%, 33% and 42% for A2 compared to A1, A4 compared to A3, and A6 compared to A5. During the application of the paints containing aromatic hydrocarbons an increase of exposure (%OEL) was observed compared to the comparable non-aromatic paint types of 45%, 37% and 37%, respectively. It should be noticed that in practice aromatic hydrocarbons will be substituted by aliphatic hydrocarbons to result in a higher OEL for the mixture.

The use of concentration limits equal to 8-hours TWA threshold limit values as OELvalues in the calculation of the OAR implies that the OAR is a conservative surrogate of risk, i.e. the ratio of exposure and OEL. Actual duration of tasks will be less than 8 hours. Implicitly the 8-hr TWA threshold limit value has been adopted as a surrogate ceiling value. In addition, the OAR approach results in conservative estimates of exposure/risk since in the conceptual model the ventilation necessary to prevent from exposure above the OEL is approximately 25 times the actual ventilation during the application of those paints that result in exposures just below 100% OEL, i.e. A2 and B2.

Conclusions and recommendations

It is concluded that the results indicate that all OAR parameters, i.e. evaporation factor (f), the concentration VOC in the paint, and the OEL, are relevant and OAR values calculated according to the OAR algorithm related to exposure during application of the

paints. For the specific 'standard paint task' the relation between exposure and OAR can be considered as a task- specific risk parameter that makes it possible to derive a 'cut off' OAR-value. This relation is illustrated in Figure 3 by the regression line and the 95% confidence interval which upper- and lower limits are illustrated by the dotted lines.



Figure 3 Task-specific, product-independent 'risk parameter' derived from the relation between OAR value and exposure. This parameter is illustrated as regression line and 95% confidence interval.

If an acceptable level of exposure (in terms of %OEL) has been set, the relationship enables to establish a cut-off or limit value of OAR. For the specific task paint products that have lower OAR-values could be applied safely with a confidence of 95%. For the conditions of the experiments, the OAR approach showed to be a useful tool for the classification of paints according to neurotoxicological risks. The approach might be transposed to other products that are used in quit similar scenarios', i.e. similar application techniques and application rates, and VOC exposure resulting from similar evaporation processes (film layers on substrates). However, the risk parameter for all (specific) tasks that are distinguished should be known.