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DEVELOPMENT OF EFFECT-SPECIFIC LIMIT VALUES (ESLVs) FOR SOLVENT MIXTURES IN PAINTING

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Abstract—This report describes a method for estimating the health-related hazard as a result of exposure to a mixture of organic solvents, with special reference to maintenance painting. Effect-specific exposure indices (EI) with respect to mucous membrane irritation and pre-narcotic effects are calculated. An EI is the sum of the ratios of the air concentration and the corresponding effect-specific limit value (ESLV) for all components of a vapour mixture. ACGIH TLVs are evaluated with respect to the above-mentioned effects. ESLVs are established for substances to which no appropriate TLV or equivalent well-documented standard exists. The merits and limitations of the applied procedure are discussed. An example of evaluating the actual health-related hazard in maintenance painting is given in the appendix.

INTRODUCTION

PAINTERS exposed to vapours of organic solvents are at risk with regard to symptoms of irritation, narcosis and neurotoxicity (AXELSON *et al.*, 1976; HANE *et al.*, 1976; LAJER, 1976). Compliance with TLVs is assumed to protect workers from adverse effects due to their occupation, at least according to most recent knowledge about the toxicology of the compounds in question.

The value of the TLV is limited in cases of exposure to mixtures. The use of individual TLVs is justifiable only if all components of the mixture act on totally different target systems or via totally independent mechanisms. When two or more components act in a more or less identical way on the same target system without potentiation or inhibition, the ACGIH (1983) recommends the use of the summed ratios of the air concentrations of the individual components and their corresponding TLVs. The sum should not exceed 1 and should be kept as low as possible.

The TLVs of different components of a mixture may be based on different criteria (critical effects). For instance, the critical effect of one component may be irritation of

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mucous membranes, whereas that of another may be hepatotoxicity. In order to eliminate some disadvantages of the different origin of the TLVs, it is proposed here to use the method of 'effect-specific weighting'. The introduction of this method was considered necessary to enable us to make a work hygiene survey of maintenance painting in the construction industry in 1980 (see Appendix).

We define an effect-specific exposure index (EI) as the sum of the ratios of the air concentration of individual components and their no-adverse effect-specific limit value (ESLV) derived from TLV documentation (ACGIH, 1971–1983) or other literature. In formula:

$$EI = \frac{C_1}{ESLV_1} + \frac{C_2}{ESLV_2} + \cdots + \frac{C_n}{ESLV_n}.$$

In accordance with the ACGIH method, an EI should not exceed unity and preferably be kept as low as possible.

RESULTS

Hepatotoxicity, kidney dysfunction and neurotoxicity are infrequent 'critical effects' for the determination of TLVs; mostly such effects are reported to occur at exposure levels higher than those at which irritation and pre-narcotic effects occur. Therefore, all components commonly used in painting solvents have been evaluated in this paper, especially for mucous membrane irritation and pre-narcotic effects.

Exposure limits have been adapted primarily from the documentation of the TLVs up to 1983 (ACGIH, 1971–1983). In the case of compounds with unestablished TLVs or TLVs based on effects other than irritation or narcosis, limit values have been deduced from the literature up to 1983. Thus, Table 1 comprises the ESLV with respect to irritation and pre-narcotic effects for 22 commonly used solvents.

White spirit

In maintenance painting the solvent most frequently applied is white spirit. It is commonly used in combination with other aromatic and aliphatic hydrocarbon solvents and less frequently in combination with alcohols, ethers and chlorinated hydrocarbons. The use of one TLV for white spirit is inconvenient, because the white spirit fraction in the workroom air cannot be distinguished from other added hydrocarbon solvents with similar components. Therefore, in maintenance painting the individual components of white spirit should be considered.

Gas chromatographic analysis of 6 white spirits of different origin showed that these contain the same components, although in different ratios (ASTRAND *et al.*, 1975). All white spirits consist of C_8–C_{11} aliphatic and C_7–C_{10} aromatic hydrocarbons. The ACGIH TLVs of the aliphatic solvents were originally established on the basis of the fact that they possessed irritant and narcotic properties. The TLVs were: nonane (C_9) 200, octane (C_8) 300, heptane (C_7) 400, and pentane (C_5) 600 ppm. The 1973 TLV of hexane was 500 ppm, but because of its neurotoxic properties the TLV was reduced to 100 ppm in 1974. These data indicate that the acute toxicity increases with the number of C-atoms. Extrapolating this to decane (C_{10}) results in a TLV of 100 ppm or 600 mg m^{-3}. As the major aliphatic components of white spirit are nonane and decane,

TABLE 1. THRESHOLD LIMIT VALUES AND EFFECT-SPECIFIC LIMIT VALUES (ESLV) ADAPTED FOR THE CALCULATION OF EXPOSURE INDICES

Substance	Irritation of mucous membranes Source	Concentration ($mg\ m^{-3}$)	(ppm)	Pre-narcotic effects Source	Concentration ($mg\ m^{-3}$)	(ppm)
Total C_8–C_{11} alkanes	ESLV	800	150	ESLV	800	150
Toluene	NIOSH (1973)	375	100	Cohr, (1979)*	375	100
Xylene	ACGIH, TLV	435	100	ACGIH, TLV	435	100
Ethyl benzene	ACGIH, TLV	435	100	ESLV	435	100
Isopropyl benzene	ESLV	245	50	ACGIH, TLV	245	50
n-Propyl benzene	ESLV	125	25	ESLV	125	25
Ethyl methyl benzene	ESLV	125	25	ESLV	125	25
Trimethyl benzene	ACGIH, TLV	125	25	ACGIH, TLV	125	25
C_4-benzenes	ESLV	90	15	ESLV	90	15
Turpentine	ACGIH, TLV	560	100	ACGIH, TLV	560	100
Ethyl acetate	ACGIH, TLV	1400	400	—	—	—
Isopropyl acetate	ACGIH, TLV	950	250	—	—	—
n-Butyl acetate	ACGIH, TLV	700	150	—	—	—
Isobutyl acetate	ACGIH, TLV	700	150	—	—	—
Dichloromethane	NIOSH, 1976	360	100	NIOSH, 1976	360	100
Trichloroethylene	—	—	—	ACGIH, TLV	270	50
Tetrachloromethane	ACGIH (1971)	65	10	ACGIH, 1971	65	10
Isobutanol	ACGIH (1971)	300	100	—	—	100
2-Butanone (MEK)	ACGIH, TLV	590	200	—	—	—
Hexone (MIBK)	ACGIH, TLV	410	100	ACGIH, TLV	410	100
2-Ethoxyethanol	ACGIH (1973)	370	100	—	—	—
2-Ethoxyethyl acetate	ACGIH (1971)	540	100	—	—	—

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it was felt that 150 ppm or 800 $mg\ m^{-3}$ as an ESLV for the acute toxicity of C_8–C_{11} aliphatic hydrocarbons in white spirit was a reasonable estimation.

The major aromatic components of white spirit are C_2 and C_3-benzenes, with minor fractions of toluene and C_4-benzenes. The benzene fraction is usually low (less than 0.1%). The TLV-documentations of the ACGIH (1971–1983) mention the pre-narcotic and irritant properties of toluene and xylenes. The properties of ethyl benzene and the C_3 and C_4-benzenes are discussed in the following sections.

Alkylated benzenes

CARPENTER *et al.* (1975; 1977) investigated the effects of two petroleum distillates on the mucous membranes of the eyes, nose and throat and on lacrimation, also the potency of inducing dizziness in a panel of six volunteers. The level at which effects became manifest was 460 $mg\ m^{-3}$ for a mixture of C_2-benzenes. A mixture of 70% C_3 and C_4-benzenes, 20% C_5 and C_6-benzenes and 10% naphthalene plus indane had a lower threshold, namely 150 $mg\ m^{-3}$. From these studies and from the work of GERARDE (1960), it can be concluded that the acute effects (irritation and pre-narcotic effects) increase with an increasing number of aliphatic carbon atoms attached to the aromatic nucleus. Thus, C_4-substituted benzenes should have a lower hygiene standard, with respect to the above-mentioned acute symptoms, than C_3-benzenes and the latter in turn lower than C_2-benzenes.

Ethyl benzene

The ACGIH TLV for ethyl benzene established in 1971 (100 ppm or 435 mg m^{-3}) is based on the relatively strong irritating properties of ethyl benzene, which are more prominent than the narcotic effects. In view of the results of CARPENTER *et al.* (1975) and the structural resemblance to xylenes, we have used this TLV with regard to both the irritative and pre-narcotic properties of ethyl benzene.

Isopropyl benzene (cumene)

In 1975, the ACGIH established the TLV of isopropyl benzene at 50 ppm (245 mg m^{-3}) to prevent narcotic effects. This was based on the advice of GERARDE (1960). As no other results are known, this TLV is also used as an ESLV for irritation.

n-*Propyl benzene, ethyl methyl benzene and C_4-benzenes*

The ESLVs of *n*-propyl benzene and ethyl methyl benzene are considered to be the same as the TLV for trimethyl benzene, namely 25 ppm (125 mg m^{-3}). Subsequently, the ESLV of C_4-benzenes has been chosen as between that of *p*-*t*-butyl toluene (10 ppm) and the C_3-substituted benzenes (25 ppm) resulting in 15 ppm (90 mg m^{-3}).

Chlorinated hydrocarbon solvents

In 1976, NIOSH proposed a 'recommended standard' for dichloromethane of 75 ppm (265 mg m^{-3}) to prevent pre-narcotic effects, mucous membrane irritation and undesirably high carbon monoxide levels in blood.

The TLV tetrachloromethane is based on its chronic hepatotoxic properties. In 1971, the ACGIH TLV was estanlished at 10 ppm (65 mg m^{-3}) because of mucous membrane irritation and depression of the CNS. This value has been used in calculating the EI.

The TLV of trichloroethylene is based on its narcotic effects, with symptoms such as headache and abnormal fatigue. In 1971, the ACGIH-TLV was established at 100 ppm (535 mg m^{-3}), but for a better protection against the effects mentioned it was reduced to 50 ppm (270 mg m^{-3}) in 1982.

Other hydrocarbon solvents

Besides white spirit and related solvents, other organic solvents are used in maintenance painting, although in relatively small quantities. The TLVs of ethyl, propyl and butyl acetates and those of turpentine and MEK are based on the irritative properties of these solvents. The TLV for MIBK is established on the basis of the fact that it is both an irritant and a narcotic compound. Pre-narcotic effects of the other solvents are either not considered in the TLV documentations (ACGIH, 1971–1983) or occur at much higher concentrations than does irritation, with the exception of turpentine.

Pre-narcotic effects of turpentine are manifest at vapour concentrations not much higher than 100 ppm (560 mg m^{-3}). Thus, for turpentine, we use a pre-narcotic ESLV of 100 ppm in establishing EIs.

The TLV of butanol is based on vertigo and irreversible hearing loss. The ACGIH-TLV of 1971 for *n*-butanol and isobutanol (100 ppm) was based on eye irritation. This value and not the reduced TLV of 1981 (50 ppm or 150 mg m^{-3}) has been used in the calculation of EIs.

In 1973, TLVs of 2-ethoxyethanol and 2-ethoxyethylacetate were both 100 ppm (370 and 540 mg m^{-3}, respectively) to prevent eye and nose irritation. In 1980 these values were reduced to 50 ppm (185 and 270 mg m^{-3}, respectively) to prevent hematological changes and in 1983 again reduced to 5 ppm (18 and 27 mg m^{-3}, respectively) to prevent testicular effects. Thus, for 2-ethoxyethanol and 2-ethoxyethylacetate we have used an ESLV for irritation of 100 ppm.

DISCUSSION

Because many solvents act on the same target tissue, it is too coarse an approximation to apply individual TLVs as indices of exposure. On the other hand, individual TLVs often protect against different effects, so that the use of the crude summed ratio over-estimates the risk, therefore, the use of effect-specific exposure indices may be a more accurate method of estimating risks.

A major handicap in establishing exposure indices is the fact that, in the case of insufficiently documented standards, new standards with regard to the specific effects have to be established, sometimes even by means of extrapolation procedures. In spite of these limitations, we have used exposure indices for irritation and pre-narcotic effects as hygienic standards in maintenance painting. It was observed that painters with exposure indices exceeding 2 had complaints of reduced appetite and increased somnolence in the evening (see Appendix). This may be an indication that, in the case of solvent exposure, exposure indices may provide useful criteria for acute toxic symptoms.

ESLVs should be used preferably in combination with individual TLVs, because a specific TLV (e.g. based on hepatotoxicity as in the case of carbon tetrachloride) may be lower than the corresponding ESLV for irritation.

It should be emphasized, however, that further investigations on the validity of exposure indices as well as on the possible kinds of interactions when a subject is simultaneously exposed to a variety of organic solvents have to be carried out.

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APPENDIX

ACTUAL HEALTH-RELATED HAZARD FROM SOLVENTS TO MAINTENANCE PAINTERS

THE EXPOSURE to solvent vapours and the actual health-related hazard was investigated in a small random sample of 45 maintenance painters at 23 different job locations spread over 12 projects (Table 1A). Among these painters was a group of 20 house painters only applying alkyd resins by brush and roller. To estimate the health hazards associated with painting, not only are the concentrations of solvent vapours compared with the individual limit values, but also effect-specific exposure indices with regard to irritation and narcosis, as established in the accompanying paper, were applied to the results of personal air sampling. The investigation included also a comparison of two methods of personal air sampling of which the results have already been published (VAN DER WAL and MOERKERKEN, 1984). Air samples from the breathing zone of 45 painters were obtained by use of a NIOSH-approved charcoal adsorption tube. The methods of sample preparation, gas chromatography and calibration were identical to the methods of VAN DER WAL and MOERKERKEN (1984).

The distribution of exposure data obtained from several days are generally log-normally distributed (LEIDEL *et al.*, 1977). They are consequently characterized by the geometric mean (GM) and standard deviation (GSD). The distribution of the summed concentrations from personal air sampling and the exposure indices were tested for log-normality with a method for small (< 50) samples (SHAPIRO and WILK, 1965). 95% tolerance limits (TL) with 95% confidence were estimated for those distributions for which log-normality could not be rejected at the 5% level. The GM, GSD and the tolerance factor, k_7 (DOCUMENTA GEIGY, 1980), for extrapolating the sample TL to the population level were used in the formula:

$$TL = GM \times (GSD)_{\pm k_7}.$$

TABLE A1. SUMMARY OF THE INVESTIGATED PROJECT LOCATIONS

Type of object	Number of painters*	Types of paint	Remarks
1 Apartment building	6	Chlororubber paint	
2 Ambassador's house	4 H	Synthetic wall paint, prime colour varnish	
3 Telephone district centre	3 H	Alkyd resin, latex wall paint, synthetic wall paint	
4 Brewery	4	Synthetic wall paint, 2-component epoxy resin	
5 Furniture showroom	6 H	Alkyd resin	Spraying by 1 painter
6 Canteen	4	Structure wall paint, alkyd resin	Spraying by 1 painter assisted by 1 colleague
7 Room of regents in Lower House residence	4	Turpentine paint	Only 2 painters were sampled
8 Garage	5 H	Latex wall paint, synthetic wall paint, 2-component varnish	
9 Pumping station	4	Chlororubber paint	During only a few minutes were protective clothes with air refreshment worn
10 Laboratory	2 H	Synthetic wall paint	
11 Laboratory	3 H	Varnish, alkyd resin	
12 Distributing station	2	2-component polyurethane lacquer	Spray-painting was performed during several minutes

* H indicates that house-painters were working at these objects. House painters were defined as painters applying alkyd resins by brush and/or roller, while they performed no spray-painting or were not working near a spray-painter.

Table A2. Personal air sampling for 45 painters at 12 different projects and the 8-h time-weighted averages (mg/m^3)* of solvent concentrations

Object No.	C_8-C_{11} alkanes	Benzene	Toluene	Substituted benzenes C_2-	C_3-	Isopropyl-	C_4-	Other solvents						Number of painters	EI_{lit} (means ± S.D.)	EI_{aarc}
1	—	—	—	13(8-18)	25(16-33)	—	—	Carbon tetrachloride <0.5			Ethyl acetate 7(4-11)			6	0.24 ± 0.06	0.23 ± 0.06
2	88(55-140)	—	0.3(0-1)	8(6-9)	26(15-41)	—	—							3	0.34 ± 0.17	0.34 ± 0.17
3	12(5-19)	—	—	3(2-4)	5(4-6)	—	—							3	0.06 ± 0.02	0.06 ± 0.02
4	75(5-200)	—	1(0-4)	82(10-135)	13(2-31)	0.3(0-1)	—	2-Ethoxyethanol 6-11						3	0.41 ± 0.13	0.39 ± 0.14
5	68(25-160)	—	1.3(1-3)	8(2-19)	22(8-71)	0.3(0-1)	—							6	0.28 ± 0.27	0.28 ± 0.27
6	228(190-340)	—	—	6(4-7)	35(26-49)	1.3(1-2)	—							4	0.62 ± 0.16	0.62 ± 0.16
7	20	—	—	1	2.3(1-3)	—	—	Terpenes 91(56-162)	Methylene chloride 9(1-24)					4	0.24 ± 0.10	0.24 ± 0.10
8	48(35-95)	0.08(0-0.2)	1.4(0-2)	9(4-13)	9(5-13)	0.2(0-1)	—	Ethyl acetate 1‡	Butyl acetate 6‡	2-Ethoxyethyl acetate 3‡	Ethoxy ethanol 19‡	MEK 5‡	Trichloro-ethylene 3‡	5	0.19 ± 0.10	0.19 ± 0.10
9	9(8-10)	—	30(23-43)	415(336-457)	72(65-88)	0.8(0-2)	10(9-12)	6(4-7)	2.3(2-3)	Carbon tetrachloride 14(10-17)		2.5(2-4)	—	4	1.97 ± 0.27	1.95 ± 0.27
10	15-32	0.1-0.2	1	1-4	5-9	—	—	—					—	2	0.09 ± 0.04	0.09 ± 0.04
11	63(50-75)	—	—	7(5-10)	11(9-13)	—	—	—					—	3	0.18 ± 0.04	0.18 ± 0.04
12	—	—	2	108-129	107-142	3-4	4-5	2-3 Isopropyl acetate 22-28	Butyl acetate 54-65	2-Ethoxyethyl acetate 28-34	Isobutanol 7	MIBK 14-21	2-6	2	1.58 ± 0.28	1.39 ± 0.25

* Values are means with ranges in parentheses. In the case of two observed persons, ranges are presented.
† Means ± S.D.
‡ Results from one subject.

TABLE A3. EXPOSURE CHARACTERISTICS OBSERVED IN MAINTENANCE PAINTERS

Parameter	Painter group	Number of painters (n)	Tolerance factor k_7*	Log normality P†	Geom. mean GM‡ (mg m^{-3})	Geom. stand GSD§	95% limits* 2. 5% LC‖ (mg m^{-3})	97. 5% UC¶ (mg m^{-3})
Summed concentrations	House painters	20	2.752	0.85	58.66	2.086	8	444
	Total group	45	2.408	0.38	100.9	2.673	9.4	1076
Exposure index for irritation (EI_{irr})	House painters	20	2.752	0.50	0.15	1.936	0.02	0.94
	Total group	45	2.408	0.04**	0.28	2.648	—**	—**

* According to DOCUMENTA GEIGY (1980).
† According to SHAPIRO and WILK (1965).
‡ $GM = \exp[1/n\ \Sigma \ln \alpha]$.
§ $GSD = \exp\{[(1/n-1)\ \Sigma\ (\ln \alpha_i - \ln GM)^2]^{\frac{1}{2}}\}$.
‖ Lower concentration (LC) $= GM \times GSD^{-k_7}$.
¶ Upper concentration (UC) $= GM \times GSD^{+k_7}$.
** Null hypothesis for log-normality rejected ($P<0.05$).

RESULTS

The results of personal air sampling for 45 exposed painters are summarized in Table A2.

At two projects, 1 and 9, carbon tetrachloride was detected in ambient air samples. At location 9, 3 out of 4 painters were exposed to concentrations exceeding the present Dutch MAC value (2 ppm = 12.6 mg m^{-3}). In The Netherlands, carbon tetrachloride is no longer a paint solvent, but it is still a constituent of chlororubber binders. House painters were not exposed to this compound. Concentrations of 2-ethoxyethanol and 2-ethoxyethylacetate, measured at two non-housepainting projects (8 and 12), are in compliance with the TLV 1980 and the Dutch MAC but *not* with the 1982 TLVs. All other concentration measurements of individual compounds were in compliance with the limit values (TLV, Dutch MAC).

Six of 45 painters had an EI_{irr} and EI_{narc} exceeding 1 and 6 had indices between 0.5 and 1. At project 9, where EI-values of about 2 were observed, the painters had symptoms of pre-narcotic effects and complained of reduced appetite and somnolence in the late afternoon. For 35 painters, including all house painters, the EI_{irr} and the EI_{narc} were identical and for 10 the EI_{irr} was higher than the EI_{narc}, but they differed by a maximum of 0.14.

GM, GSD and the tolerance limits of the summed concentrations and the EI_{irr} values from the house-painter and the total painter group are listed in Table A3. Log-normality of the distribution of EI_{irr} values in the total painter group was rejected. Thus, tolerance limits were not calculated.

The data have been adapted from a report by the authors T.M.L. S. and F.J. J. (in Dutch) published by the *Stichting Bedrijfsgezondheidsdienst voor de Bouwnijverheid* (*BGBouw*).

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