

OCCUPATIONAL EXPOSURE IN POLISH PAINT AND LACQUER INDUSTRY

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Abstract. Evaluation of occupational exposure to solvent vapours in the production of paints and lacquers is presented. The measurements were carried out in 5 paint and lacquer producing plants of the varied level of technical and technological advancement. Evaluation of exposure was based on determination of all substances identified in the work environment. Analysis was performed by gas chromatography with MSD and FID. Standard mixtures composed of 40 substances were used for calibration. The determined levels of exposure were directly dependent on technical conditions and modernisation status in factories investigated.

Measurements were carried out in the uniform analytical system, which assures comparability of the data from all the factories under study.

INTRODUCTION

Paint and lacquer solvents are complex mixtures of substances representing numerous groups of chemicals. The composition of solvents is frequently changed due to the development of new products and technologies. Consequently, monitoring of hazards induced by those chemicals is associated with numerous analytical and methodological problems. For some years already, the practice of the assessment of occupational exposure during the paint and lacquer production has been subject to much criticism. First of all laboratories responsible for measurements differ considerably in their technical and human capabilities and, the reliability of data presented by them is often disputable. The knowledge of contaminants present in the occupational environment is essential for their successful determinations, and the selection of suitable analytical methods plays a key role.

A comprehensive monitoring system capable of meeting the requirements of measurement compatibility, similar to those used in the USA or West Europe (6,8), has not as yet been implemented in Poland. Such a system is a prerequisite for making the data obtained from individual industrial plants comparable and averaged for general analyses to be presented as reports on exposure in individual industries and sectors (4).

The purpose of this work was to identify, using modern analytical methods, toxic compounds in the work environment of paint and lacquer plants, representative for this branch of industry in Poland, and to evaluate workers' exposure to substances identified.

IDENTIFICATION OF THE WORK ENVIRONMENT POLLUTANTS

Solvent mixtures used in the paint and lacquer industry contain, for example, such chemicals as acetic acid esters, glycols and their alkyl derivatives, glycol acetates and their ethyl and methyl derivatives, styrene, aliphatic alcohols, aliphatic hydrocarbons (components of extraction and painter's naphtha or white spirit). The popular C-9 and C-10 aromatic hydrocarbons, like alkyl derivatives of benzene with nine or ten carbon atoms in the molecule, known under the trade names: Farbasol, Solvesso-100, Solvesso-150 etc., may be also present (Table 1). They also constitute aromatic contamination of white spirit. Unlike in other countries, no limitations for aromatic hydrocarbon content of white spirit are specified in Poland (9). The hygiene-related problems to be considered in the assessment of the occupational exposure, encountered when Polish-made white spirit containing high amounts of aromatic hydrocarbons is used, are quite different if its Western analogues, such as EXXSOL D 40 (Table 2), substantially free of aromatic hydrocarbons, are employed. As a result, interpretation of measurement results becomes more difficult because hygiene standards specifying admissible levels for aromatic hydrocarbon-free replacements of Polish white spirit are not available.

Table 1. Data for aromatic solvents used in Polish paint and lacquer industry

Analysis (tests)*		Jolasol 1000 SOLV	Shellsol A AB		Farbasol	Solvesso 100 150 200		
Density at 15°C	g/cm ³	0.8700	0.8759	0.8930	0.8680	0.8776	0.8988	0.9973
ibp	°C	145	165	182	153	163	186.5	231.5
5% destiled at	°C	—	—	—	—	166	187.5	236
50% destiled at	°C	—	—	—	—	—	190.5	245.5
95% destiled at	°C	—	—	—	160	175	200.5	279
Dry point	°C	190	181	211	—	179	204	290
Aromatic content	% w/w	98	100	99	—	99	99	99
Purveyor/producer		J.L.C Chemie Austria	Shell Nederland Chemie B.V. The Netherlands		Petroche- mia Plock Poland	Exxon Chemical Belgium Belgium		
Country:								
Product code:		2085/3500700	Q7391	Q7493		351007	352005	353003

* data based on quality certificates from petroleum companies

Table 2. Data for aliphatic solvents used in Polish paint and lacquer industry

Analysis (tests)*		Shellsol D 70	Exxsol D 40	White spirit
Density at 15°C	g/cm ³	0.7920	0.7684	0.760–0.870
ibp	°C	> 195	> 152.5	> 126
5% – distilled at	°C	203	–	–
50% – distilled at	°C	215	–	–
95% – distilled at	°C	242	–	200 (94%)
Dry point	°C	246	192	215 (98%)
Aromatic content	% w/w	< 0.03	< 0.25	> 20
Purveyor/producer:		Shell Chemicals	Exxon Chemical	Petrochemia Płock
Country:		Germany	Italy	Poland
Product code:		91/155/EWG	5003	WT-93/MZRIp/50

* data based on quality certificates from petroleum companies

The paint production environment varies remarkably, with respect to both the type of chemicals present and their concentrations. The variability results from the necessity, for technological or economic reasons, to ensure sufficient flexibility in the use of specified solvent, resin and additive formulations. The latter refers, in particular, to complex mixtures of aliphatic and aromatic hydrocarbons marketed under various trade names.

An accurate qualitative analysis of the monitored environment is a prerequisite for obtaining reliable data.

The toxic substances found in the work environment were identified using Gas Chromatography with Mass Spectrographic Detection (GC-MSD) by analyzing the composition of semi-products and components utilized in the production process and the eluate obtained from the charcoal tube samples, collected in the work environment. The GC-MSD technique is indispensable in testing peak purity, which is essential in the case of complex organic substance mixtures. Errors associated with the application of improper standards are thereby avoided. Although aromatic hydrocarbons content, in aliphatic hydrocarbon mixtures during the product approval procedures, is measured by UV spectrophotometry, the composition of the employed mixture during the work environment monitoring can be assessed only by analyzing disulfide eluate with the aid of the GC-MSD method.

ASSESSMENT OF OCCUPATIONAL EXPOSURE IN SELECTED INDUSTRIAL PLANTS

Sampling locations

The determinations were performed in five plants manufacturing paints and lacquers. Two of these were modern plants provided with completely air-tight mills; the other three plants were rather outdated. The characteristics of individual plants is given below:

No 1 — small plant with rather limited production space, outdated mills, manufacturing small range of products,

No 2 — big, modern, multi-department plant with its own resin manufacturing facility, provided with air-tight mills,

No 3 — small a two-department plant, provided chiefly with ball mills, with outdated resin preparation facility,

No 4 — relatively modern plant, provided with non-air-tight mills and very primitive solvent handling facility,

No 5 — very modern, a multi-department plant provided with its own resin manufacturing facilities, high production volume.

SAMPLING AND ANALYTICAL METHOD

Air sampling strategy

Individual dosimetry method was used for air sampling in all plants. The workers were provided with personal pumps which they carried during all daily routine operations. The duration of the sampling period was always close to the nominal working time, not shorter than 80% of an eight-hour working shift, in accordance with the adopted uniform criteria for the work environment monitoring (7). Workers performing all basic operations associated with the normal production process of a specified production department were represented in the survey. Individual groups of the subjects included people working in direct contact with solvent vapours as well as those performing auxiliary jobs, such as department locksmiths, laboratory employees, transport workers etc.

Air was sampled by passing a known volume of air through charcoal tubes using SKC personal pumps. The absorbed substances were desorbed with carbon disulfide. The eluate was analyzed by gas chromatography.

APPARATUS AND ANALYTICAL METHODS

Apparatus

Two measuring sets, each including a Hewlett Packard Type HP-5890II Chromatograph provided with a HP-MSD-5972 Mass Detector, and a Hewlett-Packard Gas Chromatograph with a Flame-Ionising Detector were used. Both sets were provided with split/splitless injectors, automatic HP-GC-SFC-7673 samplers and identical HP-PONA columns.

Chromatographic conditions

Best conditions of chromatographic separation of the toxic substances present in the work environment air were obtained on a 50 m long 0.2 mm dia. HP-PONA column with 0.5 mm stationary phase film using programmable temperature and pressure values at the column outlet. The values were selected so as to obtain as symmetrical chromatograms as possible on both measuring sets described above.



RESULTS

The chromatographic identification of the desorbed substances was performed using the calibration table comprising 40 most common constituents of paint and lacquer solvents. The identified substances were analysed and their concentrations determined. For commercial aromatic hydrocarbon mixtures (Farbasol, Solvesso etc.) individual component concentrations were determined, since no combined occupational exposure limits (OEL) for these mixtures are established. White spirit concentration was determined from n-alkane peaks, which are easy to identify in the multiple – peak chromatograms. The percentage of n-alkanes in bulk white spirit was determined prior to the analysis of the work environment samples. The n-alkanes content in solvents is presented in Table 3.

Table 3. Concentrations of n-alkanes in white spirits (WS) from different paint shops (% w/w)

Compound	WS-1	WS-2	WS-3	WS-4	WS-5	WS-6	WS-7	WS-8
n-HEPTANE	0.06	0.00	0.04	0.04	0.13	0.06	0.07	0.22
n-OCTANE	0.32	0.93	0.29	0.29	0.34	0.10	0.87	1.97
n-NONANE	1.96	5.90	1.84	1.93	2.27	12.10	9.28	8.43
n-DEKANE	11.82	13.40	11.80	11.96	10.47	8.07	8.54	11.85
n-UNDEKANE	8.46	11.12	8.47	8.66	9.69	2.18	5.66	8.15
SUM (%) = >	22.6	31.4	22.4	22.9	22.9	22.5	24.4	30.6
MULTIPLICATOR = >	4.4	3.2	4.5	4.4	4.4	4.4	4.1	3.3

Concentrations of the main toxic substances found in the work environment in five plants manufacturing paint and lacquer products are presented in Table 4. The table specifies the values for: substance concentration geometric mean, its percentage in total exposure and coefficient of additive exposure (calculated as sum of fraction of respective OEL values). The data for the whole population of the measurement results in all five plants, supplemented with geometric (GM) and arithmetic mean (AM) values are also presented in the table. The detection limit of the analytical method was 0.04 mg/m³ for each of the analysed substances. However, concentrations lower than 0.05 mg/m³ were reported as "0" in the table, to simplify the presentation.

Synthetic data for the total exposure in the individual plants are given in Table 5. Data in Table 5 were calculated as sums of quotients of concentrations of individual compounds by respective OEL values. Geometric and arithmetic means from all time weighted average concentrations are presented as well as maximum and minimum values determined in particular plants.

Data on total exposure to organic solvents of different occupational groups or during different work tasks are presented in Table 6.



Table 4. Solvent vapour concentration measured in paint shops

Paint and lacquer shop = >		1	2	3	4	5	All shops		
No	Name	CAS	GM mg/m ³	GM %	GM mg/m ³	GM %	GM mg/m ³	GM %	n
1	Methanol	67-56-1	0.1	0.2	0.2	1.1	0.1	0.5	0.1
2	Ethanol	64-17-5	0.1	0.2	0.1	0.4	0.1	0.3	0.0
3	Acetone	67-64-1	0.2	0.2	0.2	0.8	0.1	0.5	0.1
4	Isopropanol (2-propanol)	67-63-0	0.0	0.1	0.1	0.4	0.2	0.6	0.1
5	n-Pentane	109-66-0	0.1	0.1	0.1	0.5	0.1	0.2	0.0
6	Methyl ethyl ketone (2-Butanone)	78-93-3	0.1	0.1	0.1	0.3	0.0	0.2	0.0
7	Ethyl acetate	141-78-6	0.0	0.1	0.0	0.2	0.6	2.2	0.1
8	n-Hexane	110-54-3	0.0	0.1	0.1	0.3	0.0	0.2	0.0
9	Isobutanol								
10	(2-Methyl-1-Propanol)	78-83-1	0.1	0.1	0.1	0.4	0.1	0.2	0.1
11	n-Butanol	71-36-3	0.1	0.1	0.5	2.6	0.3	1.0	0.1
12	Benzene	71-43-2	0.0	0.1	0.0	0.2	0.0	0.2	0.0
13	2-Ethoxyethanol (Cellosolve)	110-80-5	0.1	0.1	0.1	0.6	0.1	0.5	0.1
14	n-Heptane	142-82-5	0.1	0.1	0.1	0.3	0.0	0.2	0.0
15	Isobutyl methyl ketone (4-Methyl-2-pentan)	108-10-1	0.1	0.1	0.1	0.4	0.7	2.7	0.1
16	Toluene	108-88-3	2.8	3.8	0.5	2.4	2.0	7.9	5.2
17	n-Butyl acetate	123-86-4	2.3	3.0	0.1	0.4	1.0	3.7	2.1
18	n-Octane	111-65-9	0.1	0.2	0.1	0.5	0.1	0.5	0.3
19	2-Methoxyethyl acetate (Methylcellosolve)	110-49-6	0.0	0.1	0.1	0.3	0.1	0.3	0.1
20	2-Methoxypropyl acetate (Dovanol)	108-65-6	nd	nd	0.1	0.6	nd	nd	nd

20 Ethylbenzene	100-41-4	10.7	14.4	2.2	11.8	3.0	11.6	2.9	6.6	2.5	8.4	95.1	0.1	7.0	3.2	10.9	179
21 m,p-Xylen	1330-20-7	25.9	20.3	6.0	21.1	8.2	21.2	10.4	15.6	11.4	25.1	314.1	0.4	21.6	11.2	23.6	179
22 2-Ethoxyethyl acetate (Cellosolve acetate)	111-15-9	0.1	0.1	0.3	1.3	0.1	0.4	0.1	0.3	0.1	0.3	16.3	0.0	0.3	0.1	0.4	179
23 Styrene (Vinylbenzene)	100-42-5	nd	nd	0.4	2.1	nd	nd	nd	nd	nd	nd	5.3	0.0	1.7	0.4	1.3	6
24 2-Butoxyethanol (Butyl glycol)	111-76-2	0.4	0.5	0.3	1.4	0.2	0.9	0.3	0.8	0.1	0.3	6.9	0.0	0.5	0.2	0.6	179
25 n-Nonane	111-84-2	0.5	0.6	0.4	1.9	0.3	1.3	1.0	2.2	0.2	0.6	16.4	0.0	1.1	0.3	1.0	179
26 Isopropylbenzene (Cumene)	98-82-8	1.1	1.5	0.1	0.7	0.2	0.8	0.3	0.6	0.1	0.4	5.3	0.0	0.5	0.3	0.9	179
27 n-Propylbenzene	103-65-1	2.5	3.4	0.2	1.1	0.3	1.1	0.6	1.4	0.2	0.7	14.3	0.0	1.5	0.6	2.0	104
28 3-Ethyltoluene	620-14-4	5.9	7.9	0.2	1.2	0.4	1.4	1.3	2.9	0.6	1.9	40.1	0.0	2.6	0.9	3.2	179
29 4-Ethyltoluene	622-96-8	3.4	4.5	0.2	1.2	0.3	1.2	0.8	1.8	0.4	1.3	18.8	0.0	2.0	0.7	2.4	104
30 1,3,5-Trimethylbenzene (Mesitylene)	108-67-8	2.4	3.2	0.3	1.5	0.3	1.2	1.0	2.2	0.3	0.9	17.7	0.0	1.4	0.6	2.1	179
31 2-Ethyltoluene	611-14-3	2.0	2.7	0.3	1.4	0.2	0.8	0.7	1.7	0.1	0.5	13.8	0.0	1.4	0.6	1.9	104
32 1,2,4-Trimethylbenzene (Pseudocumene)	95-63-6	6.6	8.8	0.4	2.1	0.5	2.1	1.8	4.1	0.7	2.4	54.3	0.0	3.2	1.2	4.1	179
33 n-Decane	124-18-5	0.6	0.8	0.4	2.3	0.6	2.1	1.3	2.9	0.2	0.8	35.6	0.0	1.7	0.4	1.4	179
34 1,2,3-Trimethylbenzene (Hemellitol)	526-73-8	1.1	1.4	0.3	1.6	0.3	1.2	0.6	1.4	0.2	0.8	16.4	0.0	1.0	0.4	1.2	179
35 1,3-Diethylbenzene	141-93-5	0.4	0.5	0.1	0.4	0.2	0.6	0.2	0.4	0.1	0.2	5.4	0.0	0.3	0.1	0.4	179
36 1,4-Diethylbenzene	105-05-5	0.4	0.6	0.1	0.6	0.2	0.9	0.3	0.6	0.2	0.7	8.9	0.0	0.5	0.2	0.8	179
37 n-Undecane	1120-21-4	0.1	0.1	0.1	0.6	0.2	0.7	0.6	1.3	0.1	0.5	17.1	0.0	1.0	0.2	0.6	104
38 1,2,4,5-Tetramethylbenzene (Durene)	95-93-2	0.0	0.0	0.1	0.3	0.1	0.3	0.1	0.2	nd	nd	11.4	0.0	0.4	0.1	0.2	104
39 1,2,3,5-Tetramethylbenzene (Izodurene)	527-53-7	0.0	0.1	0.1	0.3	0.1	0.5	0.1	0.3	nd	nd	3.9	0.0	0.2	0.1	0.3	104
40 Aromatic hydrocarbons C-9		25.0	33.5	2.3	12.0	3.0	11.5	7.4	16.7	3.7	12.7	174	0.2	11.9	4.9	16.6	179
41 White spirit		5.8	7.8	5.1	26.8	5.8	22.5	14.9	33.4	2.4	8.0	274	0.15	16.9	4.5	15.2	179
43 Total exposure		0.77		0.34		0.47		0.61		0.43		4.94	0.1	0.65	0.47		179

% - percent of all measurements
 nd - not determined

GM - Geometric mean
 AM - Arithmetic mean

Table 5. Mean exposure to sum of organic solvents* during all operations in five Polish lacquer and paint plants (by ascending geometric mean)

Number of ship	Max	Min	AM	GM	n
2	0.82	0.10	0.49	0.34	23
5	1.63	0.12	0.53	0.43	75
3	2.51	0.10	0.69	0.47	26
4	4.94	0.12	1.00	0.61	27
1	1.89	0.32	0.86	0.77	28
All shops:	4.94	0.1	0.65	0.47	179

GM – Geometric mean

AM – Arithmetic mean

* – calculated as the sum of the quotient of individual component concentrations by corresponding values

Table 6. Values of total exposure to chemicals measured during different work tasks

Occupational groups	Max	Min	AM	GM	n
Resin synthesis workers	0.90	0.11	0.31	0.26	14
Foremen	1.28	0.10	0.49	0.33	11
Dry components mixer workers	1.60	0.13	0.53	0.43	19
Packers of final products	3.50	0.11	0.64	0.47	65
Laboratory workers	0.99	0.19	0.54	0.48	11
Mill operators	3.22	0.20	0.78	0.58	35
Colorists	1.63	0.31	0.77	0.69	13

DISCUSSION

Measurements for exposure evaluation were made in five plants, typical for the paint and lacquer industry in Poland. The plants and operations varied in the advancement of manufacturing techniques. The measurements were performed during a relatively short test period, from April to October, during the most intense operation of the plants due to increased demand for their products. The use of the same analytical instruments and methods as well as the performance of chromatographic analysis of all collected air samples under identical conditions with an automatic sampler and the same standard mixtures facilitated the comparison of the results, without any doubt as to their compatibility. Possible analytical errors are identical for samples collected in each of the plants. Therefore, the comparison procedure and the comparison of the results itself, with all the measurement data population remain unaffected.

As shown in Table 4, workers in all 5 plants were exposed to as many as almost 40 organic solvents, the most significant exposure may be attributed to ethylbenzene, xylenes and C-9 aromatic hydrocarbons (trimethylbenzenes, ethyltoluenes). Since all of the determined solvents exhibit similar toxicological effects (narcotic action), the counting of additive effects as the sum of quotients of concentrations and corresponding OEL values is justified. Additive exposure values (Tables 4 and 5) indicate that geometric means (calculated from all individual time weighted average concentrations) fall below 1 in all 5 plants. The coefficients of additive exposure in the modern plants (No 2 and No 5) are lower than the average for all test plants.



In plant No 1, where production equipment is outdated and production space limited, the results are poorest in terms of exposure.

Where the job function is concerned (Table 6), employees of the resin synthesis department belong to the group of the lowest occupational exposure to organic solvent vapours. The highest exposure levels were detected in the colorists and mill operators and this is inherently associated with their job. Quite surprising is high exposure of the laboratory workers and packers of final products, which can be explained only by their reluctance to observe fundamental health and safety rules.

Excessive exposure (coefficient of total exposure to organic solvent vapours exceeding 1) was found in 13.4% of workers, the highest percentage (25%) being determined in plant No 1.

The observation of working conditions in the plants resulted in a conclusion that skin absorption of solvents should be rather excluded as a possible route of entry. It should be, however, confirmed by biological monitoring although only limited number of quantitative exposure tests for all organic solvents used is available.

In Poland paints and lacquers are produced in 12 plants employing about 5,200 workers, 50% of them being exposed to organic solvents. The results of measurements in 5 plants employing 1,700 workers (over 1,000 exposed to solvents) may therefore be considered as representative for the paint and lacquer industry in Poland.

CONCLUSIONS

On the basis of the measurement results from 5 plants, representative for the paint and lacquer industry in Poland, the following conclusions can be drawn:

1. Approximately 40 organic solvents were identified in the workroom atmosphere;
2. Among identified solvents ethylbenzene, xylenes and C-9 aromatic hydrocarbons were predominant;
3. Similar toxicological effects of identified substances justify the calculation of coefficients of total workers' exposure to organic solvent vapours. The geometric mean exposure to organic solvents, calculated from individual exposure data in all 5 plants, was 0.47;
4. Significant differences resulting from varied advancement of the employed manufacturing techniques were detected between the individual plants;
5. About 13.4% of workers were employed under conditions of excessive exposure, the most exposed groups being colorists and dispenser operators;
6. The complexity of solvents in the paint and lacquer industry indicates the necessity to use gas chromatography with mass detection for qualitative and quantitative assessment of work environment;
7. Although dermal exposure to organic solvents seemed to be not significant, biological monitoring of workers in paint and lacquer producing plants is recommended.

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