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Occupational Exposure to Harmful Chemical Substances While Processing Phenol-Formaldehyde Resins

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Air pollutants emitted while processing phenol-formaldehyde resins have been investigated. Gas chromatography-mass-selective detection was used to separate and identify chemical compounds. It was determined that workers were exposed to formaldehyde in all workplaces. Besides, phenol, acetaldehyde, acrylaldehyde, 2-furaldehyde, xylene, ethylbenzene, toluene, tetrachlorethene, ethyl acetate, butyl acetate were found during the production of frictional materials; and 2-furaldehyde, phenol, naphthalene, 2-furan-methanol, polycyclic aromatic hydrocarbons (PAHs) during the production of abrasive materials. Quantitative analyses were performed with gas chromatography and high performance liquid chromatography. Assessment of occupational exposure indicated that chemical compounds emitted during the investigated processes might be dangerous for human health, mainly because of suspected carcinogenic compounds: formaldehyde and PAHs.

phenol-formaldehyde resins   occupational exposure   workplace air
carcinogenic compounds   abrasive materials   frictional materials

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1. INTRODUCTION

Phenol-formaldehyde resins belong to a group of plastics commonly used in various branches of domestic industry for production moulding forms, thermoinsulation materials, glues, lacquers, laminates as well as abrasive and frictional materials in which phenol-formaldehyde resins are used as a bonding agent. The industry is a potential source of occupational exposure to compounds that are mixtures of various chemicals and have various degrees of toxicity.

Tests of the products of the thermal degradation of phenol-formaldehyde resins, which are mentioned in the literature, usually refer to theoretical research carried out in order to study the structure and kinetics of reactions taking place due to temperature (Celler, Jasińska, Malikowska, Otwinowska, & Szczepankowska, 1983; Janio, Czakis-Sulikowska, Radwańska-Doczekalska, 1989; Zowall, 1980; Zowall & Świątecka, 1971). Currently only few studies present the results of research carried out in order to determine the composition of the mixtures of volatile products emitted by the phenol-formaldehyde resins in lower temperatures. Tests performed by Siepmann, Putz, and Swegt (1969) showed that during thermal hardening of moulding sands at a temperature of 220 °C with novolak resin, urotropine, and calcium stearate the following compounds were emitted: carbon monoxide and dioxide, nitrogen, ammonia, phenol, hydrogen cyanide, methane, and hydrogen. According to Hofig (1969) in the process of hardening phenol-formaldehyde resins, which are binding agents of moulding sands, formaldehyde and phenol as well as their derivatives are emitted to a large extent. Kalman (1986) carried out an analysis of volatile compounds emitted by various types of plastics and phenol-formaldehyde resins used in the production of laminate, as a result of high temperature used in the course of their processing. The following were identified among resin thermodestruction products obtained at temperatures of 210–270 °C upon applying gas chromatography technique in conjunction with mass spectrometry: phenol, dimethylbisphenol, aliphatic alcohols, acetone, and formaldehyde.

Phenol-formaldehyde resins and volatile products released while processing them were recognised recently as harmful to human health (Bertazzi, Pesatori, Radice, Zochetti, & Vai, 1986).

Identification of air pollutants emitted while processing phenol-formaldehyde resins and assessment of workers' exposure to chemical compounds were the aim of experimental investigations.

Investigations were carried out in industrial plants during abrasive and frictional materials production. The plants used for the study are the most important of this kind of enterprises in Poland. More than 1,200 workers are employed there and about 800 are exposed to toxic compounds.

2. EXPERIMENTAL

2.1. Apparatus

A Hewlett-Packard (USA) HP 6890 gas chromatograph equipped with a flame ionisation detector and a HP 5972/A mass selective detector; a computer containing Wiley mass spectres' library; a Gynkotek (Germany) GINA 50 HPLC system equipped with a UV 170S spectrophotometer and fluorescence detectors; a laboratory shaker; a Supelco (USA) solid phase extraction-apparatus; personal SKC pumps.

2.2 Chemicals

Acetone, ethanol, 2,4-dinitrophenylhydrazine, phenol (P.P.H. POCh, Poland); acetonitrile for HPLC, 37% formalin, phenol, 2-furaldehyde, 2-furanmethanol, *o*-, *m*-, *p*-xylene, ethylbenzene, toluene, tetrachlorethene, butyl acetate, ethyl acetate, carbon disulphide—extra-pure (Riedel de Haën, Germany); 2,4-dinitrophenylhydrazones of formaldehyde, acetaldehyde, acrylaldehyde, furaldehyde synthesized by the Organic Industry Institute (Poland); Applied Science Laboratory (UK) silica gel for chromatography 0.25–0.59 mm; polycyclic aromatic hydrocarbons, silica gel coating 1% (m/m) 2,4-dinitrophenylhydrazine and ORBO-43 tubes (Supelco, USA); glass fibre filters of pore diameter 0.8 µm (Supelco, USA). Redistilled water was applied for preparation all solutions.

2.3. Methods

Gas chromatography—mass-selective detection (GC-MSD). The air samples taken from the workplaces were analysed in Hewlett-Packard (USA) HP-1 capillary column (50 m × 0.32 mm × 0.52 µm) cross-linked dimethylpolysiloxane fused silica in programmed temperature from 50 to 280 °C. Helium was used as the carrier gas, with the head pressure of 61 kPa. During the analysis a detector counted ions in the range from 20 to 400 amu. Identification of particular peaks in the obtained chromatograms was carried out by a computer comparison of their mass spectra with the model spectra of the Wiley Library. Identification was confirmed by comparing the retention time and mass spectra of particular compounds with the reference substances.

High performance liquid chromatography (HPLC). This method was used to determine aldehydes after their derivatization to 2,4-dinitrophenylhydrazons and polycyclic aromatic hydrocarbons (PAHs). The separation of hydrazones of aldehydes and the adequate sensitivity of determination were ensured by a Nucleosil (USA) C_{18}/5 (25 m × 4.6 mm) column, acetonitrile and water (55 : 45) mobile phase, 2 ml min^{-1} flow rate, and by a 360 nm wave length UV detector. Separation of PAHs was performed on a Supelcosil™LC-PAH column (Supelco, USA) with a gradient mobile phase of acetonitrile : water (60 : 40/3 min, 100 : 0/6 min, 60 : 40/12 min), 2.5 ml min^{-1} flow rate, and a fluorescence detector programmed in the range 246–300 nm.

Gas chromatography with flame-ionisation (GC-FID). As a result of investigations the following operational conditions for chromatograph work were assumed. They enabled the determination of mixture compounds emitted while processing phenol-formaldehyde resins: an HP-1 capillary column (50 m × 0.32 mm × 0.52 µm) with cross-linked dimethylpolysiloxne, column temperature programmed from 40 °C (4 min) to 280 °C (2 min); temperature increase of 15 °C min^{-1}; detector temperature of 300 °C; injection port temperature of 300 °C; 1.0 ml min^{-1} flow rate of carrier gas (helium); 40.0 ml min^{-1} flow rate of hydrogen, 20 : 1 split ratio.

Air sampling solid sorbents and desorption to the solution were used for adsorption of the compounds from investigated air. Adsorbing tubes consisting of three layers (100 and 50 mg) of silica gel and 200 mg 1% DNFH coating silica gel were used for adsorption of formaldehyde, acetaldehyde, acrylaldehyde, furaldehyde, phenol, furanmethanol, and naphthalene while passing 10–60 L with a flow rate of 150 ml min^{-1} (Anderson, Hallgren, & Levin, 1981; Pośniak & Politowicz, 1998). Acetonitrile for desorption determined compounds was used.

For isolation polycyclic aromatic hydrocarbons glass fibre filters and ORBO-43 tubes were used. The volume of approximately 800 L of air passed with the flow rate below 60 L min^{-1}. After sampling the filters and tubes were stored in the dark at –20 °C. The filters and solid sorbent from ORBO-43 tubes were extracted ultrasonically with dichloromethane (20 ml) for 20 min. The extract was then evaporated nearly to dryness in nitrogen atmosphere. Purification of PAHs was achieved with the use of the solid phase extraction method on a Supelco-SPE Instrument.

Other compounds were adsorbed on active charcoal (100 and 50 mg) while sampling 10–50 L of air with flow rate 150 ml m^{-1}.

The lowest detection limit and relative standard deviations of the methods used to determine these compounds are shown in Table 1.

TABLE 1. Detection Limits of Methods of Determining Chemical Compounds

Compound	Detection Limit (mg m^{-3})	Relative Standard Deviation
Formaldehyde	0.004	0.027
Acetaldehyde	0.002	0.040
Acrylaldehyde	0.002	0.060
2-Furaldehyde	0.800	0.045
2-Furanmethanol	1.000	0.032
Phenol	0.250	0.050
Naphthalene	0.200	0.038
Toluene	0.200	0.030
Ethyl acetate	0.200	0.040
Butyl acetate	0.200	0.052
Tetrachlorethene	0.200	0.040
Ethylbenzene	0.200	0.040
o-, *p*-Xylene	0.400	0.035
m-Xylene	0.200	0.055
PAHs	0.001 (µg m^{-3})	0.062

Notes. PAHs—polycyclic aromatic hydrocarbons.

3. RESULTS

3.1. Identification

Application of the methods described in the previous section (GC-MSD, HPLC) allowed to identify over 20 compounds in the mixtures emitted during three stages of producing abrasive and frictional materials: pulp

TABLE 2. Identified Compounds in Workplace Air During the Production of Friction Linings and Abrasive Materials

Friction Linings		Abrasive Materials	
Compound	**Polish MACs Values (mg m^{-3})**	**Compound**	**Polish MACs Values (mg m^{-3})**
Formaldehyde	0.5	Formaldehyde	0.5
Acetaldehyde	5.0	Acetaldehyde	5.0
Acrylaldehyde	0.2	2-Furaldehyde	10.0
Phenol	10.0	Phenol	10.0
Ethylbenzene	100.0	2-Furanmethanol	30.0
Xylene	100.0	Naphthalene	20.0
Tetrachlorethene	60.0		
Toluene	100.0	Acenaphthene	—
Ethyl acetate	100.0	Fluorene	—
Butyl acetate	100.0	Phenantrene	—
2-Furaldehyde	10.0	Fluoranthene	—
Pentamethylheptane	—	Pyrene	—
Tetradecane*	—	Anthracene**	0.002
Pentadecane*	—	Benzo[a]anthracene**	
Benzothiazole*	—	Chrysene**	
		Benzo[b]fluoranthene**	
		Benzo[k]fluoranthene**	
		Benzo[a]pyrene**	
		Dibenzo[a,h]anthracene**	
		Benzo[g,h,i]perylene**	
		Indeno[1,2,3-c,d,i]pyrene**	

Notes. *—compounds qualified with the library mass spectra, **—compounds included for calculation of polycyclic aromatic hydrocarbons (PAHs) exposure factor, MACs—Maximum Admissible Concentrations.

preparation, moulding, and hardening of manufactured products. A list of compounds identified with GC-MSD and Polish Maximum Admissible Concentrations (MACs) are shown in Table 2. By using the Wiley Library of mass spectra several options were given for each chromatographic signal. To approve the proposed fragmentation scheme, reference substances were analysed. Substances qualified only on the basis of library mass spectra were marked (*).

Investigations carried out with the use of HPLC showed presence of formaldehyde, acetaldehyde, furaldehyde, and acrylaldehyde in the samples obtained where the manufactured products were prepared.

3.2. Assessment of Occupational Exposure to Chemical Substances

Industrial hygienic measurements were carried out during typical production cycles of abrasive disks, clutch facing, and brake lining. In order to assess the health hazard of workers, the concentration of the compounds for which Polish MACs values exist were measured. Personal breathing-zone samples on 24 workplaces were collected during a normal process of producing abrasive and frictional materials according to Polish Standard PN-89/Z-04008/07 (Polski Komitet Normalizacji, Miar i Jakości, 1989).

Tables 3 and 4 present the results of measurements of concentrations of the examined compounds in industrial plants; Tables 5–7 list concentrations of individual PAHs.

TABLE 3. Results of Toxic Compounds Concentration Measurements During the Production of Abrasive Materials at 13 Workplaces

	Range of Exposure Factors (mg m^{-3})		
Compound	Presses Workplaces (4)	Hot Presses Workplaces (4)	Sand-Mill Workplaces (5)
Formaldehyde	0.070–0.197	0.017–0.088	0.048–0.11
Acetaldehyde	trace	trace	trace
Acrylaldehyde	0–0.002	trace	0–0.003
2-Furaldehyde	1.57–4.94	1.13–4.03	0–1.94
2-Furanmethanol	1.68–3.05	0–1.15	0.78*–2.84
Phenol	1.87–3.13	0–0.21*	1.07 –1.72
Naphthalene	0.76–1.69	0.3–0.8	0.57 –1.38
PAHs	0.01–0.33 (µg m^{-3})	0.02–1.3 (µg m^{-3})	0.07–0.3 (µg m^{-})

Notes. *—results below detection limit, PAHs—polycyclic aromatic hydrocarbons.

TABLE 4. Results of Toxic Compounds Concentration Measurements During the Production of Friction Linings at 11 Workplaces

	Range of Exposure Factors (mg m^{-3})	
Compound	Presses Workplaces (8)	Other Workplaces (3)
Formaldehyde	0.028—0.100	0.004–0.11
Acetaldehyde	trace	trace
Acrylaldehyde	0.002–0.004	0.002–0.010
2-Furaldehyde	0.000–0.970	0.230*–1.070
Phenol	0.350–6.730	0.410–1.030
Tetrachlorethene	0.000–7.400	0.000–5.450
Ethylbenzene	0.000–0.840	0.000–0.410
Xylene	1.990–7.840	0.000–2.830
Toluene	0.000–0.220	0.000–0.730
Ethyl acetate	0.000–1.900	0.000–0.130
Butyl acetate	0.000–0.770	0.000–0.690

Notes. *—results below detection limit.

TABLE 5. Results of PAHs Concentration Measurements at the Hot Presses Making of Abrasive Materials Workplaces

	Concentration at Workplaces (μg m^{-3})			
Compound	Press Operator 1	Press Operator 2	Press Operator 1's Assistant	Press Operator 2's Assistant
Acenaphthene + fluorene	58.74	20.90	73.79	13.81
Phenantrene	—	5.83	—	1.44
Anthracene	1.70	1.07	2.05	0.15
Fluoranthene	3.08	0.68	3.64	0.40
Pyrene	2.46	0.37	3.25	0.32
Benzo[a]anthracene	0.23	0.21	0.67	—
Chrysene	0.18	0.24	0.58	0.07
Benzo[b]fluoranthene	0.05	0.03	0.13	0.01
Benzo[k]fluoranthene	0.03	0.03	0.08	0.01
Benzo[a]pyrene	0.05	0.06	0.07	0.01
Dibenzo[a,h]anthracene	0.02	0.01	0.23	—
Benzo[g,h,i]perylene	6.39	0.08	1.05	0.02

TABLE 6. Results of PAHs Concentration Measurements at the Cold Presses Making of Abrasive Materials Workplaces

Compound	Concentration at Workplaces (μg m^{-3})			
	Press Operator 1 (Abrasive Materials ∅ = 115 mm)	**Press Operator 2 (Abrasive Materials ∅ = 300 mm)**	**Press Operator 3 (Abrasive Materials ∅ = 230 mm)**	**Press Operator 4 (Abrasive Materials ∅ = 305 mm)**
Acenaphthene + fluorene	0.280	0.280	—	27.330
Phenantrene	—	—	—	1.400
Anthracene	0.002	0.002	0.530	0.540
Fluoranthene	—	0.004	0.310	0.560
Pyrene	—	—	0.130	0.460
Benzo[a]anthracene	0.002	0.003	0.020	0.002
Chrysene	—	—	0.020	0.070
Benzo[b]fluoranthene	—	—	0.010	0.003
Benzo[k]fluorantene	—	—	0.004	0.005
Benzo[a]pyrene	—	—	0.010	0.010
Dibenzo[a,h]anthracene	—	—	—	—
Benzo[g,h,i]perylene	—	—	0.010	0.040

TABLE 7. Results of PAHs Concentration Measurements at Bolting of Moulding Composition Workplace and Sand-Mill Workplaces

	Concentration at Workplaces (μg m^{-3})				
	Batching of Sand-Mill				Bolting of Moulding Composition
Compound	1	2	3	4	
Acenaphtene + fluorene	0.010	—	—	20.81	—
Phenantrene	—	—	—	0.32	—
Anthracene	0.002	1.300	1.400	0.47	0.530
Fluoranthene	0.001	0.900	1.250	1.05	0.310
Pyrene	—	0.550	0.670	0.86	0.130
Benzo[a]anthracene	0.002	0.090	0.260	0.11	0.020
Chrysene	—	0.050	0.220	0.19	0.020
Benzo[b]fluoranthene	0.004	0.010	0.050	0.04	0.009
Benzo[k]fluoranthene	—	0.060	0.040	0.18	0.005
Benzo[a]pyrene	—	0.010	0.070	0.04	0.002
Dibenzo[a,h]anthracene	—	0.010	0.010	0.05	—
Benzo[g,h,i]perylene	—	0.020	0.040	0.05	0.010
Indeno[1,2,3-c,d,i]pyrene	—	0.010	0.009	—	—

Notes. PAHs—polycyclic aromatic hydrocarbons.

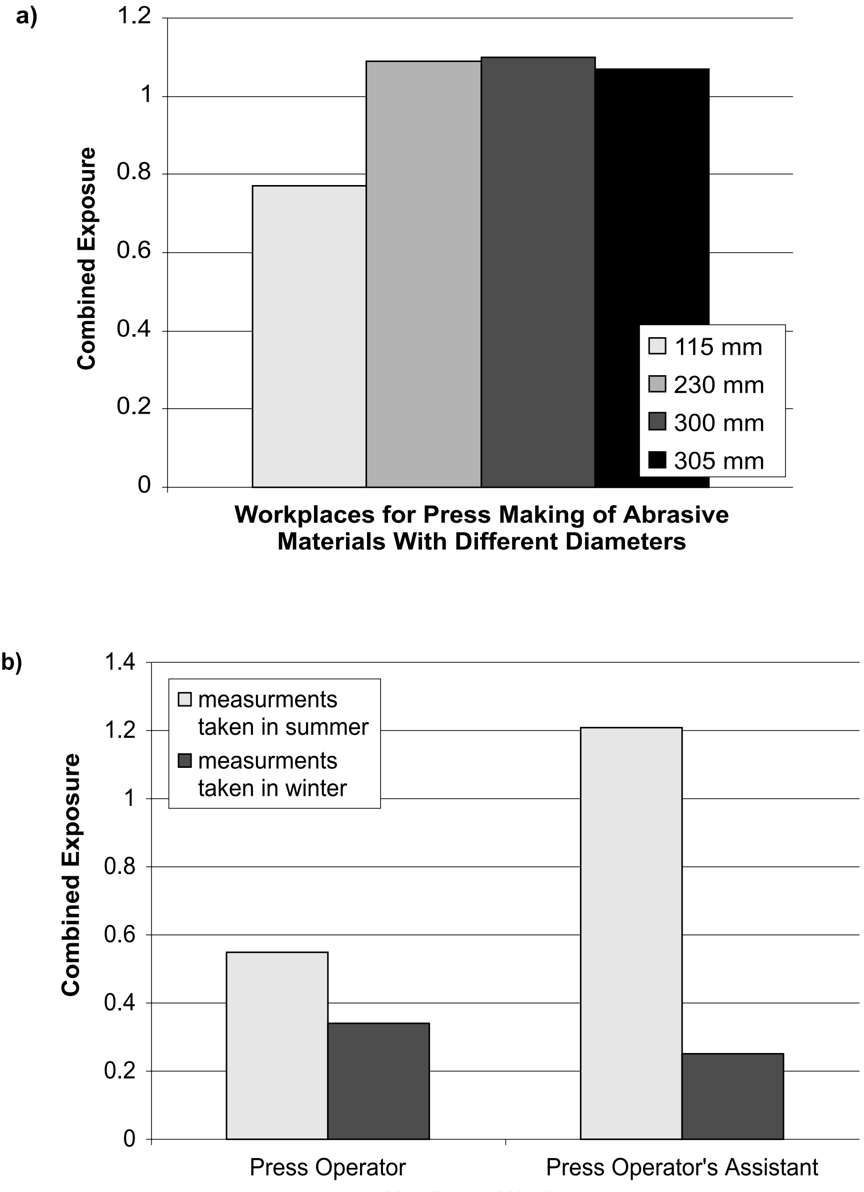
4. DISCUSSION

The results of the identification of chemical substances emitted in processes of producing abrasive and frictional materials have shown that toxic compounds are present in workplace air in three stages of these processes. About 20 chemical compounds representing different classes of organic products were found among the volatile compounds emitted from hardening manufactured products. Because of their suspected cancerogenicity, formaldehyde and PAHs were the most dangerous compounds.

The calculation of the added effects (combined exposure) of air chemical impurities was very difficult because there were no hygienic standards available for several compounds either in Poland or abroad. The difficulties in measuring all substances in workplace air routinely are another problem. It is thus practical to choose some typical products from an emitted mixture and measure them to assess occupational exposure. The chosen substances can be used as indicator substances in hygienic measurements. The result of this study indicated that it is sufficient to measure formaldehyde, acetaldehyde, 2-furaldehyde, 2-furanmethanol, phenol, naphthalene, and PAHs to get a hygienic picture of the production process of abrasive materials.

During the assessment of occupational exposure at workplaces for the production of friction linings, the following compounds should be determined: formaldehyde, acetaldehyde, 2-furaldehyde, phenol, xylene, ethylbenzene, toluene, tetrachlorethene, ethyl, and butyl acetate.

Exposure factors (time-weighted average concentrations) calculated on the basis of determined concentrations of particular compounds in workers'



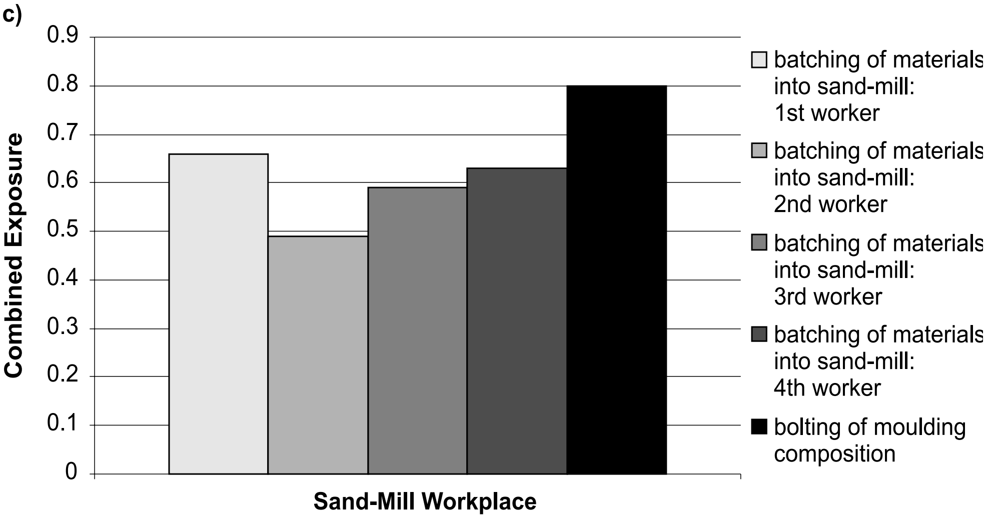


Figure 1. Combined exposure factors for workplaces for the production of abrasive materials.

breathing-zone air did not exceed Polish MACs values. The results of occupational exposure assessment indicated that the combined exposure factors ranged from 0.2 to 1.2 during the production of abrasive materials (Figure 1) and from 0.24 to 0.88 during the production of frictional linings (Figure 2). Emission of toxic compounds during the processing of phenol-

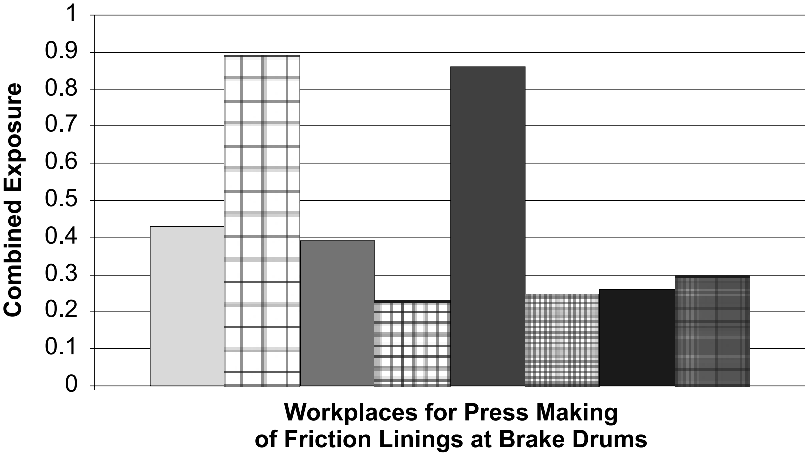


Figure 2. Combined exposure factors for workplaces for the production of friction linings.

formaldehyde resins might be especially dangerous for human health at hot press workplaces for the production of abrasive materials.

The data summarised in this article appears to be the most comprehensive report of occupational exposure to toxic compounds emitted while phenol-formaldehyde resins processing and should constitute significant help in future hygiene studies of this group of workers.

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