Field Study

Determination of Pollutants in the Air of Textile Industries

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Abstract: Determination of Pollutants in the Air of Textile Industries: Valentino RIMATORI, *et al.* Institute of Occupational Medicine, Catholic University

In order to investigate the pollution degree in three weaving and dyeing and in two clothing factories, the authors measured the indigo, oil mist, hydrogen sulfide (H₂S), sulfur dioxide (SO₂) and total particulate matter (TP), as well as the biphenyl, o-phenylphenol and p-phenyldiamine (PPDA) concentrations. H₂S ranged from <0.01 to 1.85 mg/m³; indigo from <0.001 to 0.042 mg/m³; TP from 0.58 to 3.65 mg/m³; biphenyl and o-phenylphenol from 0.2 to 15.5 mg/m³. SO₂ and PPDA concentrations were lower than 0.2 ppm and 5 µg/m³ respectively. Higher concentrations were recorded during specific operations. The oil mist concentrations in different factories at different heights in the air, ranged from 0.2 to 15.5 mg/m³. Up to date, neither the TLV nor the maximum allowable concentration for indigo and o-phenylphenol have been established, and there are no studies on the health effects of long term exposure, so the risk for the concentrations listed above cannot be assessed. The PPDA concentration in our study was much lower than the ACGIH TLV for 1993-1994. Biphenyl concentration sometimes exceeded the TLV, suggesting the need for closer controls in the workplace. Oil mist concentration in weaving rooms fell within the TLV, except in the weaving rooms where air forcing and air extraction systems were at a higher level: here the concentration of oil mist exceeded this limit.

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Key words: Pollutants, Textile industries, Indigo, p-phenyldiamine, Oil mist, Hydrogen sulfide, Sulfur dioxide, Total particulate matter

Nowadays the textile industry is one of the largest industries in the world. A vast occupational population is employed in this industry, to supply a rapidly increasing demand for textiles. Numerous chemical compounds are used to give textiles the

desired properties; for example dyes are utilized to obtain different shades of colour. During textile production, these chemical compounds and oil mists are dispersed into the air of the workplace as pollutants. Sampling and analytical methods for measuring these pollutants have been in operation for many years. Little is known about the hygienic and environmental problems involved in indigo dyeing processes^{1,2}, about the use of carriers such as biphenyl and o-phenylphenol which transport the dye into the fibers, or about mineral oil mist. Natural indigo has been used as a textile dye for over 4,000 years, and synthetic indigo has been developed and used for more than 100 years, but there are few research reports on the adverse effects and toxicity of indigo. Until now it was widely believed that indigo was a compound of low toxicity^{3,4}. Synthetic indigo was, however, strongly mutagenic towards TA1538 and TA98⁵. U. Rannug, *et al.* reported that technical grade or 98% pure synthetic indigo showed mutagenic effects. Further purification to 99.5% reduced mutagenicity⁶. Oral administration of complex indigo powder at a daily dose of 0.5 g/kg raised the leukocyte count in rats⁹ showing that indigo can still be a potential health risk as a non-genotoxic carcinogen.

p-Phenyldiamine (PPDA) is an aromatic diamine which is suitable for the preparation of dyeing materials. PPDA, or its N-substituted derivative, was the main ingredient in "acid" or "basic" phenothiazinic and quinonimanic dyes and also in other classes of dyes. Nowadays their importance has diminished since they have been replaced by azoic and other dyes. They are used in some grades and their adverse effects are little known.

Biphenyl and o-phenylphenol are considered low toxicity compounds⁸. Intradermal injection in guinea pigs caused local necrosis and some evidence of allergenic response⁹. Inhalation by rats of biphenyl dust produced irritation of nasal mucosa, labored breathing with bronchopulmonary lesions, and slight toxic effects on the liver and kidneys at a concentration of 300 mg/m³, 7 hours/day for 64

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days⁸⁾.

Lubricating oil was thought to have a very low order of toxicity. If inhaled in sufficiently high concentrations, oil mist may cause irritation of the lungs¹⁰⁾.

As indigo was considered to be a compound with a low level of toxicity, no threshold limit value (TLV) or maximum allowable concentration (MAC) was established and no measurements were made of the indigo concentration in the workplace. In order to investigate the degree of pollution in the workplace due to indigo and oil mist¹¹⁾, we measured the concentrations of indigo, oil mist, hydrogen sulfide (H₂S), sulfur dioxide (SO₂) and total particulate matter (TP), as well as the biphenyl and o-phenylphenol concentrations and PPDA in the environmental air of different workshops in five textile factories. After this investigation, we will do clo tests on exposed workers to ascertain any eventual adverse effects of these pollutants on workers' health.

The five textile factories included three weaving and dyeing factories and two clothing factories. In the dyeing workshop of factories A and C (Table 1), the workers were exposed to Biphenyl, and o-phenylphenol. In the dyeing workshop of factory B, the workers were exposed to indigo, H₂S and

SO₂. The workers employed in the weaving workshop were also exposed to oil mist. The weaving workshops were equipped with forced air intake quota and different air extraction systems. When we made the first investigation, factory A was equipped with air extraction in quota and factories B and C were equipped with air extraction equipment at floor level. On our advice, factory A has changed its air extraction system to air extraction at floor level. In factories D and E, the workers were exposed to dyes that may contain PPDA.

Materials and Methods

Sampling was carried out in the five factories for research purposes and was aimed at the effective manufacturing processes. The distribution of sampling points, the number of samples and pollutants collected are listed in Table 1.

The H₂S in the air during the indigo dyeing process was collected by active and passive samplers, using a small glass tube filled with lead acetate, a solution of zinc acetate or a glass fiber filter (with a solution of salts) in the dyeing workshop during the dye-bathing process. Analysis was carried out by a spectrophotometric method after derivatization to methylene blue with a Perkin Elmer Lamde 5 spectrophotometer. SO₂ was collected with active and

Table 1. Exposed workers and samples of pollutants in five textile factories

Factory	Workshop	Exposed workers	Samples of pollutants			
			Biphenyl o-phenylphenol	Indigo H ₂ S, SO ₂	Oil mist	PPDA
A	dyeing	12	15			
	weaving	110			77	
B	dyeing	10		20		
	weaving	120		30	57	
C	dyeing	20	22			
	weaving	80			36	
D	cutting, sewing and ironing	200				40
E	cutting, sewing and ironing	70				15

Table 2. Concentrations (mg/m³) of indigo (IN), hydrogen sulfide (H₂S) and total particulate matter (TP) in the air of textile factories

Sampling position	IN	H ₂ S	TP	IN/TP (%)
Weaving room				
among looms	0.041-0.07	<0.01	2.72-3.65	1.5-1.92
near looms	0.021-0.032	<0.01	1.53-1.72	1.37-1.86
Dyeing room				
breast dyeing	<0.001	0.09-0.38		
dyeing area	<0.001	0.07-1.85		
beam	<0.01	0.01	0.58-1.4	
dye preparation area	<0.01	<0.01	0.47-2.42	

passive Draeger tubes. TP was collected with cellulose nitrate filters, and analysed by the gravimetric method. Indigo was sampled by environmental air filtering through a glass fiber filter, extracted at equilibrium with dimethylformamide (DMF) and analyzed by reverse phase HPLC. Operative conditions were: RP-18 5μ 12, $5\text{ cm} \times 1/4''$ column; acetonitrile/water 70% at 2 ml/min as the mobile phase; detection λ 610 nm; $k' = 0.9$ $rt' = 1.5'$.

PPDA was analysed by HPLC. Air samples were collected both in fixed positions and in the breathing area of workers doing the same jobs in different departments of the factory.

Since PPDA could be present in the form of both aerosol and vapour, the air was filtered through a glass fiber filter and, downstream of it, through a sampling tube containing silica gel as an adsorbent. The flow rate ranges between 0.2 and 0.8 l/min depending on the silica gel content and sampling duration.

The filter and the silica gel were separately extracted, at equilibrium, by methanol after refrigerator storage in the dark. An aliquot of the extract, was concentrated, after centrifugation, with nitrogen. Extraction yields were $92 \pm 4\%$ from the filter, and $87 \pm 5\%$ from the silica gel. Extraction at slightly alkaline pH was also carried out in order to check whether PPDA was present as salt, but this extraction yielded negative results.

Analysis was performed by HPLC. A HS 5 C18 column was used in order to improve the method. A mixture of methanol in water with or without PIC B6 was used as the mobile phase. The detection limit at 241 nm is about 2 ng.

Biphenyl and o-phenylphenol vapors in the environmental air were collected on porous polymer, extracted with a mixture of cyclohexane-methylacetate and analyzed by gas chromatography. The sampling glass tubes 0.5 cm in diameter were

filled with two fractions of Porapak Q 80–100 mesh. Analysis parameters were: $1.8\text{ m} \times 1/8''$ column with Apiezon L 3%, phosphorous acid 0.1%, Carbowax 20 M 0.2% on chromosorb W HP 80–100 mesh. T column 160°C , Flow 20 ml/min (Nitrogen UPP), rt Biphenyl = 8', rt o-phenylphenol = 14'.

The oil mist was collected by means of MFS glass fiber filters, diameter 20 mm (filtering surface 1.3 cm^2 ; air speed 12.5 cm/sec), at a flow rate of 1 l/min. The sampling filters were extracted with 2 ml n-Hexane. Oil mist recovery was 96%. The samples were analyzed by uV absorption and differential refractometry. Refractometric determinations were carried out by means of Reodyne sample loop injection valves injecting a known volume of standard solution and filter extraction solution in a $5 \times 0.5\text{ cm}$, 60–70 mesh glass beads column in a Perkin Elmer series 3 HPLC equipped with a differential refractometric detector R 401 Waters Associates. A Perkin Elmer LC 55-B scanner spectrophotometer may also be used as the HPLC detector. The wavelength was selected (200, 220, 235 or 265 nm) according to the interferences. The spectrum of the oil peak in the stop-flow mode may also be used. The detection limit for a lubricating oil (Basestock medium heavy paraffinic) is 5 ng at 0.02 A full scale. Analysis was also performed without HPLC by using a double beam Perkin Elmer Lambda 5 spectrophotometer equipped with first and second derivatives. The spectrum was recorded between 190 and 330 nm. Absorption peaks fall at different wavelengths according to the solvent used: n-Hexane has a cut-off at about 200 nm and it is possible to use the analytical bands at 200, 220, 235 and 265 nm.

Results

The concentrations of H_2S , indigo and TP found

Table 3. Concentrations (mg/m^3) of oil mist in the air of weaving rooms with air forcing in quota and air extraction in quota or at floor level

	Air extraction in quota		Air extraction at floor level	
	1st survey		2nd survey	
Factory	A	A	B	C
Height of sampling	1.6 m	1.6 m		
N	30	16	33	20
Mean	10	2.11	0.79	4
Range	7–15.5	0.7–6.3	0.23–4.4	3.5–4.5
Height of sampling	2.5 m	2.5 m		
N	22	9	24	16
Mean	4	1.56	0.57	4
Range	3.5–4.5	0.5–4.6	0.2–1.35	3.5–4.5

in textile factories are listed in Table 2. Concentrations of SO_2 were lower than 0.2 ppm (TLV=2 ppm).

Concentrations of PPDA were lower than $5 \mu\text{g}/\text{m}^3$.

The concentrations of biphenyl and o-phenylphenol found in factory A (with the better aspiration systems) ranged from 0.2 to $0.8 \text{ mg}/\text{m}^3$ during specific operations (6 samples) and from 0.01 to $0.4 \text{ mg}/\text{m}^3$ during the normal shift (9 samples). The concentrations of biphenyl and o-phenylphenol found in textile factory C ranged from 0.2 to $4.6 \text{ mg}/\text{m}^3$ and from 0.01 to $0.7 \text{ mg}/\text{m}^3$. During the normal work shift, in 19 out of 22 samples taken in the workplace, we found concentrations below $1.3 \text{ mg}/\text{m}^3$. Higher concentrations (up to $4.6 \text{ mg}/\text{m}^3$ for biphenyl) were recorded during specific operations. In samples taken during carrier mixing and the opening of dyeing tanks, concentrations reached $7 \text{ mg}/\text{m}^3$ for biphenyl and $1.5 \text{ mg}/\text{m}^3$ for o-phenylphenol.

The oil mist concentrations measured in different factories at different heights in the air of weaving rooms equipped with various types of ventilation, are listed in Table 3. From Table 3, we can see that when factory A was equipped with air extraction in quota, its oil mist concentration in the respiratory zone of workers was higher than that in factories B and C, and also above the TLV. After it was re-equipped with air extraction at floor level, the oil mist concentration decreased significantly.

Discussion

In order to make a hygienic evaluation, we compared the concentrations found in the air of textile factories with the threshold limit value TLV (1993–1994) of the American Conference of Governmental Industrial Hygienists (ACGIH). Up to now, neither the TLV nor the maximum allowable concentration for indigo in the air of the workplace has been established, so we cannot tell the hygienic significance of the concentrations listed above. Since there are no studies on the health effects of long term exposure to indigo, we cannot assess the risk resulting from these concentrations. We will therefore study the effect of long term exposure to indigo on workers' health so as to provide scientific data that can be used as a basis for the establishment of the TLV.

The concentrations of PPDA found in our study were below $5 \mu\text{g}/\text{m}^3$, which is much lower than the $100 \mu\text{g}/\text{m}^3$ listed in the ACGIH TLV for 1993–1994.

A few cases of occupational biphenyl poisoning have been reported, with transient nausea, vomiting,

and bronchitis in workers exposed to biphenyl vapors during paper impregnation¹²⁾. When air concentrations of biphenyl were below $1 \text{ mg}/\text{m}^3$, no differences were detected between exposed and unexposed workers in blood pressure, pulmonary function tests, serum creatinine values, urinary protein levels, and standard blood cell counts¹³⁾. The time weighted average-threshold limit value (TLV-TWA) for biphenyl recommended by the Occupational Safety Health Administration (OSHA) is $1 \text{ mg}/\text{m}^3$, and the value recommended by the ACGIH is $1.3 \text{ mg}/\text{m}^3$. No TLV has been established for o-phenylphenol. In our study, the biphenyl concentration in factory C sometimes exceeded the TLV indicating that biphenyl pollution in the air of the workplace still needs to be controlled. We recommend investigating workers' symptoms and complaints related to biphenyl exposure in the factories where we sampled pollutant concentrations.

The current TLV for oil mist adopted by ACGIH is $5 \text{ mg}/\text{m}^3$. In 1993–1994 the ACGIH proposed a TLV of $5 \text{ mg}/\text{m}^3$ for highly refined mineral oil and $0.2 \text{ mg}/\text{m}^3$ for medium refined mineral oil. The limit depends on difference in the amount of polynuclear aromatic hydrocarbons contained (PAHs). We measured the amount of PAH in our samples which may be considered as highly refined. The concentration of PAHs in the air of weaving rooms is lower than that in the air of the city of Rome²⁾.

For some time it was thought that long term exposure to oil mist would lead to an increased risk of lung or digestive tract cancer, but later studies found no evidence to support this hypothesis^{14, 15)}.

In our study, the oil mist concentration in weaving rooms fell within the TLV, but in weaving rooms where air forcing and air extraction occurred at a high level, it exceeded this limit.

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