HYGIENIC CHARACTERISTICS OF CARBON BLACK USED IN TYRE PRODUCTION

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Abstract. Seven types of carbon black used in type production were subjected to hygienic evaluation. The coal tar pitch volatiles (CTPVs), toluene solubles, were determined by the gravimetric method and benzo/a/pyrene by HPLC with a spectrophotometric detector. Toluene solubles were found to amount to 0.12—0.25% (by weight). Benzo/a/pyrene (1.44—3.07 ppm) was detected in five out of the seven carbon blacks examined.

INTRODUCTION

The carbon black released during the oil-furnace process is widely used in the rubber industry (90% of world production, including 65% for tyre manufacture). Furnace blacks of various types constitute major reinforcing agents in rubber stocks. The use of carbon black in tyre production amounts to 60 weight units per 100 weight units for rubber, which is about 25% of the total tyre weight. Carbon black has been found to produce adverse effects on the respiratory system under conditions of occupational exposure. These effects are manifested by lung function impairment (4, 9, 27), and pneumoconiosis including carbon pneumoconiosis (9, 27). Researchers accept the opinion that carbon black may induce pneumoconiosis; its carcinogenic potential is still controversial. Animal studies reveal that carbon black absorbed through inhalation, intratracheally, orally, or through the skin does not induce neoplasms. However, when benzene and other carbon black extracts were applied as injections or skin smearing, some malignant neoplasms could be observed (1, 3). Taking into account the results of the study, the IARC

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Working Group observed that the carcinogenicity of carbon black was not adequately confirmed whereas, the benzene extracts of carbon black were considered to be carcinogenic. According to epidemiological studies concerning workers in the rubber industry, where the highest quantity of carbon black is used, an icreased risk of cancer was reported (2).

The carcinogenicity of carbon black is associated with the presence of polycyclic aromatic hydrocarbons (PAH), particularly benzo/a/pyrene (BaP) (6, 23). However, these compounds were not detected in industrial carbon black samples examined by chemical methods without solvent extraction (6) or in the samples placed directly in a mass spectrometr. This finding can be explained by a very high adsorption of carbon black particles as PAH (6, 17, 22), and their biological activity initiated by solvent extraction. The study on a possible elution by tissue fluids of PAHs adsorbed from carbon black particles under conditions of occupational exposure did not bring definite conclusions (2, 7, 16, 21, 22).

Among the carcinogenic PAHs it is BaP that was investigated most thoroughly. Therefore, it is regarded as a model compound and a representative of the whole group. The soluble fraction of PAH as coal tar pitch volatiles (CTPV) has been incorporated in the register of carcinogens in Poland.

The literature lacks reports on the quantitative determination of tar extracts or PAHs in domestic carbon blacks (1). The problem is significant, both as regards occupational exposure to PAHs and their chemical impact on the natural environment.

The aim of the present paper is a hygienic evaluation of carbon blacks used in a tyre factory on the basis of the carcinogenisity index i.e. the total content of solvent extracts (CTPVs) and BaP. A specific analytic procedure was developed in order to investigate this problem.

MATERIAL AND METHOD

Samples of seven types of carbon black used in tyre production were examined, including JAS-220, JAS-330, JAS-530 (domestic) and HAF-N-330, SRF-N-762, Durex-0 (imported). The solvents applied included benzene, cyclohexane and toluene. 10—25 mg samples of particular carbon black types were extracted:

1) through direct heating (over reflux condenser) for 2, 3, 4 and 5 hours, with 200 ml benzene or toluene,

2) using the Soxhlet apparatus with 250 toluene for 20 hours, and additionally, 250 ml toluene for 10 hours,

3) shaking of 250 ml cyclohexane, benzene or toluene at room temperature within 18, 24, 48 and 70 hours.

After separation, the extracts were concentrated to the vol. of 10—15 ml at 60°C, placed in test tubes and dried at 40°C by transmitting a stream of nitrogen over the surface of the liquid. The tubes were then weighed and their dry substance masses were determined. Dry extracts were dissolved in cyclohexane and the BaP fraction extracted in a small column (5 cm^3) with silica gel (granulation 0.05—0.2 mm). The mixture was eluted with cyclohexane and 10 ml fractions were collected.

The second portion, with BaP, was evaporated by transmitting a stream of nitrogen over its surface. The dry substance was dissolved in 0.5 ml ethanol and 10 μl of the solution was placed in the HPLC column. Standard solutions were prepared for 0.5—10 μg BaP in 0.5 methanol.

Working conditions typical of the HPLC chromatograph were as follows:

— HPLC Varian 8500 with a spectrophotometric detector (Variscan) and a recorder,

— a steel column 250×2.1 mm with stationary phase Lichrosorb RP 18.5 μm,

— mobile phase: of methanol and water (96:4) (v/v),

— flow rate: 0.5 ml/min,

— temperature: 21°C,

— analytic wavelength — 384 nm.

RESULTS AND DISCUSSION

In the currently used methods for determining coal tar pitch volatiles (CTPVs) including PAHs, in carbon black, different solvents are used for the extraction: benzene (3, 8, 20, 25), cyclohexane (5, 11, 18), dichloromethane (10, 19), tetrahydrofurane (15), methanol (3, 11), and toluene (26). In our study toluene was applied, for which the cold extraction was found to be twice as efficient as for cyclohexane (Fig. 1 I b/c) while hot extraction, 30% as efficient as for benzene. The data are consistent with those by Taylor et al. (26) (Fig. 1 II a/b).

Depending on the actual solvent used, a different mass for the extracted substance can be obtained from the same carbon black sample (Fig. 1 I and 1 II a/b). Moreover, different values of BaP as a carcinogenicity index can also be found (Fig. 2).

Another essential parameter is the extraction time. The literature data differ considerably, reporting values ranging from 18—100 h (19) for dichloromethane, 20 h (8), 24 h (25) — 250 h (20) for benzene and 24 h (26) for toluene.

In the present study, for toluene extraction in the Soxhlet appara-

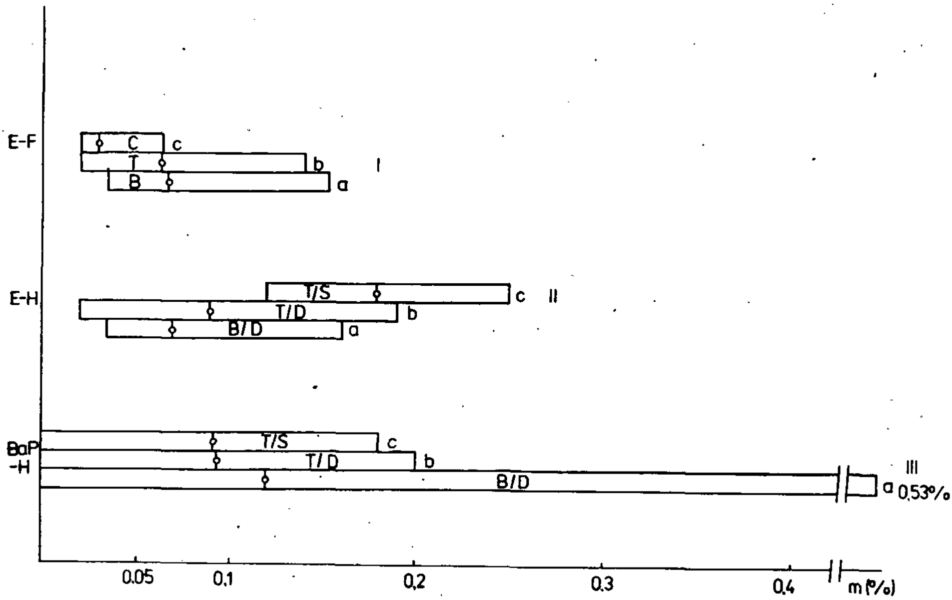

Fig. 1. The influence of the solvent and mode of extraction on the content of CTPVs (solvent soluble fraction and benzo/a/pyrene. Notes: E — solvent extracts (by weight) CTPVs; F — cold extraction; H — hot extraction; T — toluene; B — benzene; C — cyclohexane; S — extraction in the Soxhlet apparatus; D — direct heating.

tus, the extraction time was fixed at 30 h/20 h — for stage I and 10 h for stage II. During stage II no tar substances could be detected regardless of the carbon black examined in 25% of the samples of CTPVs were detected. However, in some of the samples the tar content would exceed 30% of the total extract mass (mean 10%) (Table 1). After 30 hours of extraction the new portion of toluene did reveal fluorescence under ultraviolet.

In order to simplify the analysis, an attempt was made to extract carbon through ultrasounds or heating over the reflux condenser. The former was found to be inappropriate due to the lack of repeatibility of results.

In the latter method, when the extraction time was shortened to 3 hours, the results were similar to those for the Soxhlet extraction for two types only of carbon blacks, JAS-220 and SRF-N-762. For all the other types the results were 2—6 times lower (Fig. 3).

In the carbon blacks examined, the absolute BaP content was found to be twice as low as in the Soxhlet method, which also refers to the mean extract content (Fig. 1 II b/c). The percentage of BaP in toluene fractions was comparable for both methods (Fig. 1 III b/c).

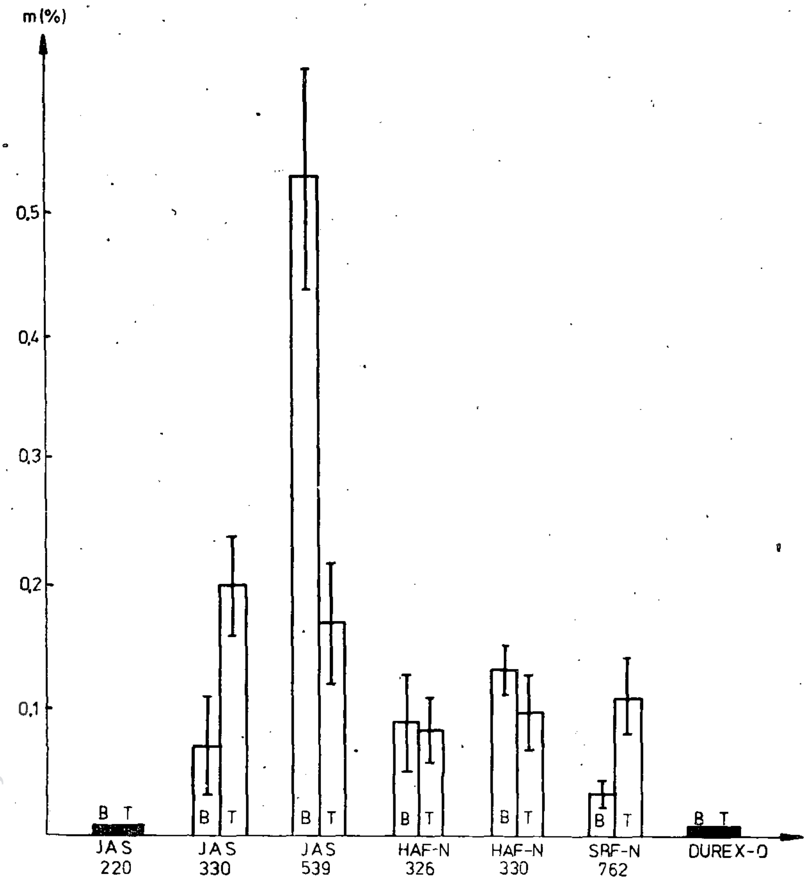

Fig. 2. Percentage (by weight) of BaP in solvent soluble fraction of particular carbon blacks according to the solvent used. B — benzene; T — toluene.

For all the seven types of carbon black the CTPV content in toluene fraction ranged from 0.12—0.25% (by weight) (Durex-0 and JAS-220, respectively). The BaP was not detected in carbon black of two types — — JAS-220 and Durex-0. In the other five types the BaP content ranged from 1.44—3.07 ppm (HAF-N-326, JAS-330, respectively) (Table 2). BaP constituted 0.1—0.2% (by weight) of all the solubles, which is consistent with the results obtained by Taylor et al. (26) and Locatti et al. (20).

The cold extract mass was found to be much lower than in the case of hot extracts, regardless of the solvent used (Fig. 1 I—II a/b). For cold extracts the optimum extraction time was determined at 48 hours, according to the diagram of extraction efficiency as a function of extraction time (within the range of 18—70 hours). (Fig. 4). The content of

TABLE 1. Relationship between Extraction Time and Toluene Soluble Fraction Content in Carbon Black Extracted by the Soxhlet Apparatus

Type of carbon black	No of tests	CTPV content after different extraction times			
		20 h	20—30 h		
		in µg/g carbon black from-to	in µg/g carbon black from-to	percentage (by weight) as related to total mass from-to	mean
JAS-220	2	2067—2480	n.d. — 507	0—20	10
JAS-330	3	1027—1947	n.d. — 167	0— 9.5	6
JAS-530	2	1427—1933	180 — 327	13—14	13.5
HAF-N-326	3	687—1887	n.d. — 407	0—37	14
HAF-N-330	4	1267—2333	n.d. — 680	0—35	13
SRF-N-762	2	1313—2007	n.d. — 40	0— 2	1
DUREX-0	3	453—1320	67 — 380	5—23	14
				total mean	10

Notes: n.d. — not detectable

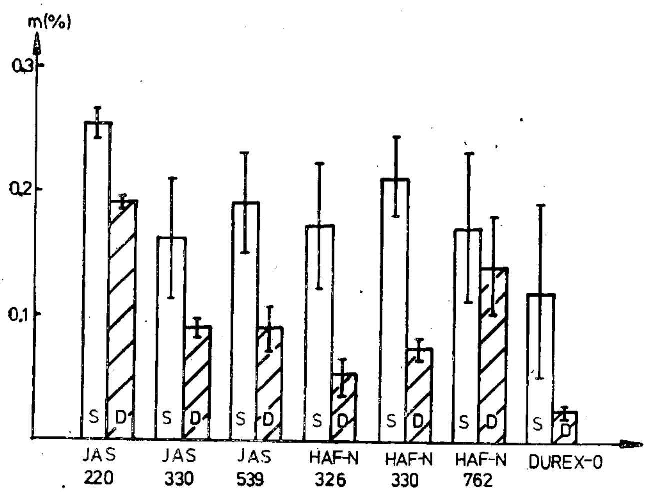

Fig. 3. CTPV percentage (by weight) (toluene soluble fraction) of carbon blacks according to the mode of hot extraction. S — Soxhlet extraction; D — direct heating.

cold toluene extracts varied from 0.02—0.14% (by weight), thus being much lower than the content of the hot extracts (Fig. 2). According to Wettir (24), cold extraction is more appriopriate for eluting PAHs from carbon black particles by body fluids in the human system. Hence, in some reports, the cold extract content is also considered.

As revealed by the results of hygienic evaluation, domestic carbon

TABLE 2. Content of Coal Tar Pitch Volatiles and Benzo/a/pyrene in The Carbon Blacks Examined Data Represent Means (X) and their Ranges (R). If not otherwice stated n = 2

Type of carbon black	Toluene solubles, in percentage (by weight)				BaP ppm (after hot extraction with toluene)	
	cold extracts		hot extracts			
	X	R	X	R	X	R
JAS-220 (D)	0.14	0.003	0.25	0.009	n.d.	—
JAS-330 (D)	0.038	0.018	0.16[A]	0.083	3.07	0.32
JAS-539 (D)	0.059	0.025	0.19	0.065	2.98	0.79
HAF-N-326 (I)	0.074	0.023	0.17[B]	0.090	1.44[E]	0.21
HAF-N-330 (I)	0.048	0.006	0.21[C]	0.080	2.03	0.06
SRF-N-762 (I)	0.058	0.019	0.17	0.073	2.13	0.66
DUREX-0 (I)	0.021	0.002	0.12[D]	0.115	n.d.	—

Notes: (D) — domestic products
(I) — imported products
n d. — not detectable
A — n = 3, S = 0.049
B — n = 3, S = 0.053
C — n = 4, S = 0.039
D — n = 3, S = 0.068
E — n = 3, S = 0.12

X — arythmetic mean
R — range, $S = \frac{R}{d_n}$
S — standard deviation
d_n — parameter of R distribution

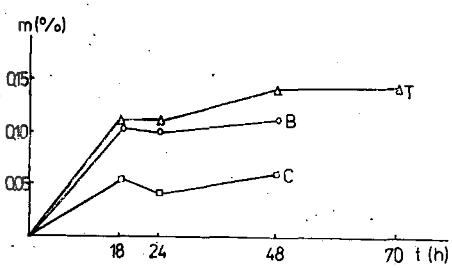

Fig. 4. The influence of extraction time (t) and type of solvent on total extractables (m) content for cold extraction. T — toluene; B — benzene; C — cyclohexane.

blacks were found to be of worse quality than the imported ones, which was reflected by higher indices of dry toluene extracts (hot and cold) and of the BaP.

CONCLUSIONS

In the developed method (gravimetry combined with HPLC), toluene was used to determine CTPVs (including PAH) and the BaP content in carbon blacks. For all the seven types of carbon black the toluene solubles were found to amount to 0.12—0.25% (by weight).

BaP at the level of 1.44—3.07 ppm was detected in five out of seven carbon blacks.

The use of the carbon black under study in tyre production may bring about contamination of the working environment with PAHs and consequently lead to an increased risk of neoplastic diseases.

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