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EXTRACTION AND ANALYSIS OF ASPHALT PAVEMENT CORE SAMPLES: DETECTION OF COAL TAR-DERIVED SPECIES USING CHEMICAL AND BIOLOGICAL METHODS

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Abstract.
Epidemiological studies [1,2] have reported elevated cancer incidences and mortality in the Danish mastic asphalt industry, and have associated these elevations with exposure to asphalt fumes. The strength of the causal association depends heavily on the claim that coal tar was not used in the industry after World War II; otherwise, exposure to coal tar pitch volatiles would have seriously confounded study results. Yet, other reports [3,4,5] indicate that coal tar was used until about 1970. To clarify the issue, the Copenhagen Road Institute collected core samples from sites where the history of mastic application was known. Coded samples were extracted, and subjected to HPLC separation, GC-MS, fluorescence fingerprinting and the Diazo test for phenolics. The extracts were also tested in the Modified Ames Assay. The results of the study show that the composition and mutagenicity of the core samples until 1970 were consistent with the presence of coal tar.
Key Words: Asphalt, Coal Tar, PAC, Fluorescence, Modified Ames Test

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INTRODUCTION

A series of epidemiological studies of Danish mastic asphalt workers [1,2] reported elevated mortalities and higher incidences of cancer of the bladder, lung and gastrointestinal tract. The author of the studies attributed these effects to occupational exposure to asphalt (bitumen) fumes. The conclusion rests heavily on her contention that mastic asphalt workers were not exposed to coal tar pitch volatiles, a recognized human carcinogen, during the period following World War II when the men were employed in laying mastic asphalt pavement.

Several lines of information suggest that this assumption may be incorrect. First, records of the Danish Road Authority from the 1950s [3] specify the admixture of coal tar-derived anthracene oil to mastic pavement. Second, an engineer for the Danish Road Administration stated in a letter to the author (AJK) [4] that coal tar was commonly used in mastic pavements until at least 1970. And third, IARC scientists recently concluded that any retrospective epidemiology study of asphalt paving workers in Europe (Denmark was one of eight countries surveyed) would be limited by coal tar confounding up until at least the 1970s [5,6].

In an effort to resolve the issue of coal tar use in mastic asphalt pavements, we obtained asphalt core samples from Copenhagen streets which were paved with mastic asphalt during the time period at issue (i.e. 1950 - 1970). The samples were taken and coded by the Copenhagen Road Institute and shipped to our laboratory. One sample was also sent from 1991 pavement and was known not to contain coal tar. They were then extracted with carbon disulfide to recover the binder and subjected to a variety of physical, chemical and biological characterizations specifically designed to detect the presence of coal tar.

In addition, several core samples were reheated to paving temperatures, and fumes were collected and analyzed for coal tar-derived components. Finally, pulver asphalt (one component of mastic paving) was reformulated using Danish government records [3] from the time period of interest. Fumes generated from the reformulated coal tar-containing asphalt were compared to those from neat asphalt and coal tar from U.S. and European sources.

MATERIALS AND METHODS

Asphalt Pavement Core Samples

Pavement cores were collected and removed in triplicate by the Copenhagen Road Institute. Information on the street location and year of placement of each core can be found in Table 1.

One set of the sample pavement cores was sent directly to Heritage Research Group, Indianapolis, Indiana, USA, where they were photographed and sized. The pulver (bottom layer) and the mastic (top layer) -- both of which are laid by mastic asphalt crews [4] -- were separated using a diamond saw. Both layers from each core were air dried to remove moisture.

Separation of Binder from Aggregate

Mastic paving materials consist of two basic components: the crushed stone (termed "aggregate") and the binder (the asphalt or tar component). In order to conduct analyses on the binder portion of pavement, it was therefore necessary to extract the binder from the core samples using an organic solvent. ASTM D-2172 Method B [7] was used, except carbon disulfide was substituted as the extractant to ensure that any coal tar present would also be solubilized [8]. The carbon disulfide was removed by rotary evaporation at 100°C.

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PAH Analysis

Carbon disulfide extraction residues were prepared for PAH analysis essentially according to the method of Wallcave et al. [9]. In brief, the residues were dissolved in benzene. Then iso-octane was added, followed by pentane to precipitate the pentane-insoluble asphaltenes. The precipitate was removed by filtration, and the resulting solution was concentrated by rotary evaporation. The residue was then dissolved in iso-octane and extracted with DMSO. The DMSO layer was isolated and the aromatics were precipitated by addition of water and then back-extracted into iso-octane.

NIOSH Method 5506 [10] using a Waters 600E high pressure gradient pump, (HPLC) a 900 photodiode array detector and a Model 470 fluorescence detector. Separations were performed on a Supelco PAH column using a water-acetonitrile gradient.

TABLE 1. Copenhagen mastic asphalt pavement core samples

Date Placed	Location/Road	Markings	Pavement Type	Percent Binder	Height (mm)
1952	Norre Alle	2NA	Pulver	10.05	33
1952	Norre Alle	2NA	Mastic	10.86	53
1952	Norre Alle	5NA	Pulver	6.67	33
1952	Norre Alle	5NA	Mastic	10.61	56
1957	Hausergade	2HB	Pulver	8.00	41
1957	Hausergade	2HB	Mastic	11.20	64
1957	Hausergade	4HB	Pulver	4.90	25
1957	Hausergade	4HB	Mastic	10.60	81
1963	Ny Carlsberg Vej	1CA	Pulver	5.34	48
1963	Ny Carlsberg Vej	1CA	Mastic	9.93	96
1967	Kalvebod Brygge	3KA	Pulver	4.04	81
1967	Kalvebod Brygge	3KA	Mastic	12.01	81
1970	Eng Vej	1EB1	Pulver	5.65	23
1970	Eng Vej	1EB1	Mastic	9.22	48
1991	Farum Midtpunkt	1FM	Pulver	4.45	---
1991	Farum Midtpunkt	1FM	Mastic	10.43	---

Analysis for Phenols
Coal tar contains significant quantities (> 0.1%) of phenolic compounds, while asphalt binder contains only parts per million levels [11]. The Diazo reaction, DIN Method 52 034 (German Standards Method) [12] was developed in the 1920s specifically to detect the presence of coal tar in bitumen. The method employs a benzene diazonium chloride solution which, under alkaline conditions, turns red in the presence of phenols.

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Fluorescence Assay for PACs
Fingerprint emission spectra were obtained using a Perkin Elmer Luminescence Spectrometer LS50B by scanning from 200-520 nm. Forty scans with an excitation increment of 5 nm, scan speed at 1000 nm/min and slit widths at 3 nm, were collected. Single emission spectra were extracted from this data base.

Modified Ames Test
The Modified Ames Test was performed in accordance with the procedures described in ASTM Standard Method E 1687-95 [13]. In some cases, the quantity of sample available was too small to permit testing at the full number of doses specified.

RESULTS

Core sample analyses
Table 2 shows the results of PAH and Diazo-reaction analyses of extracted bitumen binder.

TABLE 2. Analyses of Danish mastic asphalt pavement core samples

Date	Sample	Pavement Type	Total of 16 PAHs (mg/kg)[1]	Diazo Reaction[2]	Mutagenicity Index
1952	2NA	Pulver	2,573	+	9.8
		Mastic	1,558	SL+	5.4
	5NA	Pulver	7,730	+	23
		Mastic	1,867	+	5.9
1957	2HB	Pulver	5,744	+	27
		Mastic	2,494	+	9.0
	4HB	Pulver	10,340	++	48
		Mastic	1,442	SL+	8.8
1963	1CA	Pulver	9,280	++	50
		Mastic	1,009	SL+	4.4
1967	3KA	Pulver	2,340	+	10
		Mastic	103	SL+	1.5
1970	1EB1	Pulver	333	+	3.1
		Mastic	14	-	1.3
	1EB2	Pulver	233	-	6.3
		Mastic	152	SL+	2.5
	3EB1	Pulver	730	+	3.8
		Mastic	68	-	2.8
	6EB	Pulver	432	SL+	1.1
		Mastic	95	-	0.8
1991	1FM	Pulver	76	-	2.3
		Mastic	77	-	1.1

[1]NIOSH Method 5506 [10]

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[2]Diazo Reaction [22]: + = positive; ++ = strong positive; SL+ = slight positive; - = negative

Also shown are the Mutagenicity Indices (MIs) determined using the Modified Ames Test (discussed below). The data indicate that the levels of unsubstituted PAH in pavements placed from 1952 to 1970 were considerably higher than those in the 1991 sample (factors ranging up to 136-fold). In all cases, the pulver layers showed significantly higher levels of PAH than the corresponding mastic layers. Qualitative responses in the Diazo-reaction for phenols were strongest for those samples with the highest levels of unsubstituted PAHs, and also showed a rough correlation with relative amount of PAH for the lower level samples.

Comparison of Core Samples with U.S. and European Asphalts and Coal Tars
To confirm that levels of unsubstituted PAHs and Diazo reactivities seen in Table 2 were uncharacteristic of coal tar-free asphalt binder, the comparisons in Table 3 were drawn between selected core samples and typical asphalt binder products. The core samples had PAH levels from 0.06 to 6% of the neat European coal tar, while the corresponding levels for neat asphalt ranged from 0.006 (European) to 0.01% (U.S.). Diazo reactivity followed PAH concentrations.

TABLE 3. Analytical comparison of selected core samples with standard asphalt and coal tar products

Material	Total of 16 PAHs (ppm)	Diazo Reaction
Mean of seven European bitumens[1]	10	N/A
Mean of twelve US bitumens	24	-
Mastic sample 2NA (pulver layer) (1952)	2,573	+
Mastic sample 4HB (mastic layer) (1957)	1,442	SL+
Mastic sample 1CA (pulver layer) (1963)	9,280	++
Mastic sample 1EB (mastic layer) (1970)	95	-
European coal tar[1]	152,647	N/A
Low temperature US coal tar	63,160	++

[1]Brandt [9]
NA = Not Available for Testing

The lower than expected levels of PAH (even assuming that Danish mastic asphalt was blended with 15% or less of coal tar) probably reflects the fact that the samples in question were fumed at the time of original pavement application resulting in a loss of PAHs. This conclusion is supported by data from pulver layer reformulation and refuming experiments described below.

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Analysis of Refumed Mastic Asphalt Pavement Samples
Portions of two core samples (2HB and 1FM from Table 1) were refumed at the temperature used in the original mastic asphalt placement (250ºC). As Table 4 shows, measurable quantities of four of the sixteen PAHs determined using NIOSH Method 5506 (fluoranthene, pyrene, benzo[a]anthracene and chrysene) were detected in the fumes from sample 2HB, laid in 1957, while no PAH was detected in those from sample 1 FM, laid in 1991. Again, levels of PAH in the 1957 sample were relatively low, since significant quantities of PAH were undoubtedly lost to the fume during the original mastic placement.

TABLE 4. Fume PAH composition of reheated Danish mastic asphalt pavement samples

PAH	Concentration (ug/m^3) Sample 2HB (1957)	Sample 1FM (1991)
Fluoranthene	6.3	BDL[1]
Pyrene	3.3	BDL
Benzo(a)anthracene	1.3	BDL
Chrysene	2.0	BDL

[1]Below Detection Limit <0.1 ug/m^3

Analyses of Reformulated Pulver Binder and Fumes: Comparison to the Coal Tar Distillate Oils and Asphalt Used in the Reformulation

Pulver binder containing coal tar distillate oils was reformulated using procedures outlined in a Danish Road Institute publication [3]. Table 5 presents compositional analyses of the reformulated pulver, fumes generated from it, and the residue after fuming. For comparison purposes, the same data are presented for the neat asphalt binder used in reformulation. Also presented is the PAH content of the coal tar distillate oils added to the simulated pulver mixture.

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TABLE 5. Compositional analyses of reformulated Danish pulver asphalt and its components

Material	Total of 16 PAHs (ppm)	Wt. % Fumes	Diazo Reaction
Pulver Binder	6,709		+
Pulver Fumes	50,000	3.2	+
Pulver Residue	5,320		+
Coal Tar Oils	44,678		+
Bitumen	16		-
Bitumen Fumes	75	0.9	-
Bitumen Residue	13		-

TABLE 6. Comparison of reformulated pulver residue with Danish samples

Material	Total of 16 PAHs (ppm)
Pulver Residue	5,320
Mean 1952 Pulver	5,152
Mean 1957 Pulver	8,042
1963 1CA Pulver	9,820
1967 3KA Pulver	2,340
Mean 1970 Pulver	349

Levels of sixteen unsubstituted PAH in pulver were more than 400-times higher than those in neat asphalt, while the corresponding fumes showed a difference of well over 600-fold. The residues from fuming in each case showed similar trends. That the differences were attributable to the presence of coal tar-derived material was demonstrated by the analysis of the coal tar distillate oils, which had a PAH level of 44,678 ppm. The Diazo reaction for phenols tracked with the presence of coal tar. The quantity of fumes collected from the reformulated pulver was almost four-times higher than that from the neat asphalt used in the reformulation.

Comparison of Reformulated Pulver Residue with Danish Mastic Core Samples

The degree of similarity between the PAH contents of pulver binder reformulated using Danish Road Institute specifications from the 1950s and the actual core samples from the same and later times is shown in Table 6. The reformulation sample used for the comparisons is the residue from fuming, since it would be expected to be most similar to the core samples as it had already undergone one fuming at the time of analysis.

The data in Table 6 show that the levels of NIOSH Method 5506 PAH for core samples of pavements laid in 1952, 1957, 1963 and 1967 are quite comparable to those from the reformulated pulver. The mean level for the 1970s samples was more than ten-times lower, possibly indicating a lower use of coal tar in mastic pavement at this site.

Fluorescence Emission Spectra of Coal Tar, 1963 Pulver and 1970 Pulver
Figure 1 shows emission spectra of a coal tar standard, together with those of 1963 and 1970 Pulver binders. The similarity between 1963 pulver binder and coal tar is evident. The 1970 sample, however, shows no such similarity.

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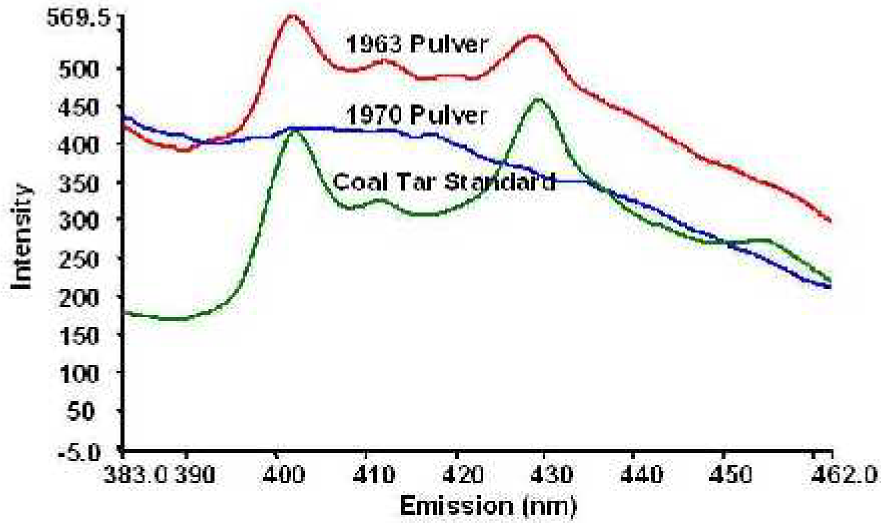

1 These graphs show fluorescence spectra after excitation of 310 nm

FIGURE 1. Comparison of the Fluorescence Emission Spectra of Coal Tar, 1963 and 1970 Pulver Binders

Comparison of Modified Ames Test Mutagenicity Indices for the Eleven Core Samples
Table 2 provides the Mutagenicity Indices (MIs) of binder extracted from the core samples. Extensive experience in Modified Ames testing [14] has shown that MIs of uncracked petroleum oils seldom exceed a value of about 20. Coal tar samples, on the other hand, generally have MIs ranging from about 300 to well over 1000. It is clear, therefore, that pulver samples 4HB, 1CA, 2HB, and 5NA all contained significant quantities of coal tar-derived material. The association of the high MIs with coal tar is further substantiated by the correlation between MI and the levels of 16 PAH and Diazo reactivity for these samples. For the other samples with relatively high MIs (those over 3.0, all placed prior to 1970), MI tracks relatively well with the other indications of coal tar modification.

Previous studies [14] have shown that MI has a high correlation in predicting dermal carcinogenicity of PAC-containing materials in animal studies. From the relationships established in those studies, it seems likely that the binders from all but one of the core samples placed before 1970 (Mastic 3KA) would be carcinogenic in the mouse skin-painting bioassay.

Based on the same relationships, the pulver and mastic binders used in 1970 (1EB1) would be expected to be weakly carcinogenic, and those from 1991 (1FM) noncarcinogenic.

DISCUSSION

The results of this study clearly demonstrate that:

(1) Coal tar was present in all core samples up to and including that taken from mastic asphalt pavement laid in 1970. Data from PAH analysis, the Diazo reaction for phenolics, the Modified Ames Test, and fluorimetry were all consistent with this conclusion.

(2) The fumes from mastic paving operations using coal tar-modified asphalt must have contained significant concentrations of unalkylated PAHs, some of which are carcinogenic.

(3) Fumes from coal tar-free asphalt contain little or no unsubstituted 4-6 ring PAHs and no phenolics.

(4) The mutagenic potency (MI) of the coal tar-containing core samples is consistent with potent carcinogenicity, even though significant quantities of PAC were undoubtedly lost from the coal tar during the original application of pavement.

Because of the high carcinogenic potency of coal tar fume and its clear use in mastic paving during the post-war period, the conclusions regarding the etiology of the cancers seen in the mastic asphalt cohort bear careful reexamination.

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