ASPHALT INSTITUTE
Executive Offices and Research Center
Research Park Drive
P.O. Box 14052
Lexington, KY 40512-4052
USA
Telephone 859-288-4960
FAX No. 859-288-4999

Detection of Coal Tar Materials in Asphalt Pavements Using Chemical and Biological Methods

Gary R. Blackburn PetroLabs Inc. 133 Industrial Drive Ivyland, Pennsylvania 18974	Anthony J. Kriech Heritage Research Group 7901 West Morris Street Indianapolis, Indiana 46231
Joseph T. Kurek Heritage Environmental Services, LLC 7901 West Morris Street Indianapolis, Indiana 46231	Linda V. Osborn Heritage Environmental Services, LLC 7901 West Morris Street Indianapolis, Indiana 46231

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ABSTRACT
Recent reports have linked exposure to asphalt fumes to higher incidences of cancer in workers employed in mastic asphalt pavement operations in Denmark. The conclusion that asphalt fume exposure was responsible for the excess cancers rests heavily on the proper connection for and/or absence of confounding exposures - particularly to coal tar fumes. Coal tar was known to be used in paving in Denmark prior to and during World War II. However, there has been significant debate about when its use was discontinued. This study looked at potential methods for detecting coal tar in historically dated pavements placed in the city of Copenhagen. The study found that there are clear chemical marker compounds and tests which can determine the presence of coal tar materials in an asphalt aggregate mixture. The results of a short term biological test called the Modified Ames Assay also correlated well with the presence or absence of coal tar-derived materials. The results of the study show that coal tar usage in Denmark extended up until at least 1970.

Key Words: Coal Tar, Mastic Asphalt, Pulver Asphalt, Modified Ames Assay, Polynuclear Aromatic Hydrocarbons

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Coal tar was used in road building in Denmark during World War II due to a shortage of asphalt cement. How long its use continued after World War II is less clear. One source *(1,2)* suggests that generally the practice was discontinued at the war's end. The present study was conducted to determine if that premise is correct, and if not, how long after the war its use continued.

Detection of coal tar in historically dated asphalt pavement core samples is possible because of compositions and genotoxicity differences between the coal tar and asphalt.

Puzanauskas and Corbett *(3)* compared coal tar and asphalt cement chemically and found that coal tar's high processing temperatures (>1000°C) produce primarily unsubstituted polynuclear aromatic hydrocarbons (PAHs). A number of these compounds are both animal and human carcinogens *(4)*. Work by Roy et al. *(5)* found that PAH-containing complex mixtures could be evaluated for mutagenicity using a bioassay method called the Modified Ames Test, and that the observed mutagenic potency correlated well with PAC content and carcinogenic potency as determined in animal skin painting studies.

Asphalt, unlike coal tar, contains only low levels of unsubstituted PAHs, primarily because the crude oil from which it is produced has only low levels of these compounds. Also distinct from coal tar, asphalt contains significant amounts of aliphatic *(3)* (straight chain) compounds. Finally, asphalt has much lower levels (ppm) of phenols than does coal tar (>1000 ppm). The German Standards Method *(6)* (DIN Method 52034) developed in the 1920's uses this difference as a means of detecting coal tar in mixtures which also contain asphalt.

MATERIALS

Pavement Core Samples

The Copenhagen Road Institute, which is responsible for quality control and quality assurance for city streets in Copenhagen, identified streets of known age, cored them, and sent the core samples to Heritage Research for analysis. All streets were paved with a special material called mastic asphalt. Such pavement systems included a leveling course called pulver asphalt placed over a concrete base. Once the pulver layer was laid, the same crew poured a semi-fluid, high temperature (250°C) mastic layer. This was trowelled down and then precoated stone chips were spread before rolling. This process should not be confused with Stone Matrix Asphalt (SMA) now being used in the United States. No process similar to mastic asphalt paving exists in the United States.

The pavement cores from the city of Copenhagen are identified in Table 1 by street location and year of placement. A photo of the mastic application process is shown in Figure 1 *(7)*. To insure correct pavement age, cores were only taken in sections which showed no sign or record of repair and were part of the continuous pavement section. Because mastic is somewhat unique in its appearance, it is easy to differentiate between mastic and other paving materials. The 1991 core was known not to contain coal tar and was used as a control. Each core was measured for thickness and photographed. The bottom pulver layer was separated from the top mastic layer using a diamond saw. Both layers from each core were air dried with a fan at ambient temperatures for 48 hours to remove surface moisture.

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COAL TAR AND ASPHALT CEMENT SAMPLES

Asphalt cement was collected from two sources in the United States. Eight single crude asphalts were obtained from the Strategic Highway Research (SHRP) library. These crudes are used to manufacture a large portion of the paving asphalts in the United States. The other four asphalts were obtained through the Asphalt Roofing Manufacturing Association (ARMA) and represent four large commercial sources of roofing asphalt cement.

The coal tar sample is a South Dakota low temperature product. It is similar in processing to the coal tars used in Europe.

METHODS OF ANALYSIS

Binder Content

The binder in the pavement core, if it contains coal tar, cannot be extracted using techniques suitable for asphalt mixtures. Therefore, to ensure the complete extraction of organic matter, carbon disulfide rather than benzene was used as a solvent. To accomplish this, ASTM *(8)* D2172 Method B was used with this solvent. The carbon disulfide was removed using rotary evaporation at 100°C. Carbon disulfide is an extremely dangerous material due both to its biological activity and because of its low autoignition temperature. It should be handled with extreme care in a well ventilated hood.

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, which contains the aromatic fraction, was isolated, and the aromatics were precipitated by addition of water, and then back-extracted into iso-octane.
PAH analyses were performed by means of NIOSH Method 5506 *(10)* using a Waters 600E high pressure gradient pump (HPLC), a Supelco PAH column, a 900 photodiode array detector, and a Model 470 fluorescence detector using a water-acetonitrile gradient.

Analysis of Phenols

Coal tar contains significant quantities (> 0.1%) of phenolic compounds, while asphalt binder contains only parts per million levels. The Diazo reaction, DIN Method 52 034 (German

Standards Method) *(6)* was developed in the 1920's specifically to detect the presence of coal tar in asphalt. Asphalt cement is called bitumen in Europe. The method employs a benzenediazonium chloride solution which, under alkaline conditions, turns red in the presence of phenols.

Modified Ames Assay
The Modified Ames Test was performed in accordance with the procedures described in ASTM Standard Method E 1687-95 (*11)*. In some cases, the quantity of sample available was too small to permit testing at the full number of doses specified. From the test colony counts results, a linear dose response relationship was plotted. The slope of the line relating dose to reverterant is the Mutagenicity Index (MI).

RESULTS

Coal Tar and Asphalt Cement
The analytical tests performed on the twelve U.S. asphalts and one low temperature coal tar are listed in Table 2. Also reported are results of PAH levels in seven European asphalts and a European coal tar as reported by Brandt *(12)*.

These results show that PAH levels in both European and U.S. asphalts are quite low for the sum of 16 PAHs. The U.S. asphalts also tested negative for the presence of phenols by the German DIN method indicating that no coal tar was present. Finally the asphalt cements tested very low for mutagenicity. The mean MI value of 1.07 is in the range associated with little or no carcinogenic response in animal studies *(11)*.

Coal tar, on the other hand, had orders-of-magnitude higher PAH levels, tested strongly positive in the phenol test, and was highly mutagenic in the Modified Ames Test.

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Core Sample Analyses
Table 3 gives the results of PAH, Diazo analysis, and the Modified Ames Test for extracted asphalt binder from the mastic asphalt pavement in Copenhagen. The data indicate that the levels of unsubstituted PAHs 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 PAHs than the corresponding mastic layers. Although only qualitative, the responses in the Diazo-reaction for phenols were strongest for those samples with the highest levels of unsubstituted PAHs.

COMPARISON OF CORE SAMPLES WITH U.S. AND EUROPEAN ASPHALT AND COAL TARS
When comparing Table 2 with Table 3 it is clear that all the pulver and mastic layers up until 1970 contained coal tar in both layers. All of the 1970 pulver layers also show evidence of coal tar usage. However, the levels of coal tar in mastic layers in the 1970 samples appeared to be much lower, suggesting that coal tar was either not used, or used at a much reduced level. The sample from 1991 was confirmed by the City of Copenhagen not to contain coal tar and the tests verified that none was present. Also considered were PAHs from other possible sources such as oil dripping from vehicles. However if vehicles were a significant source, then the mastic should have been higher than the pulver layer which is under the mastic layer.

COMPARISON OF DIN METHOD FOR PHENOLS WITH THE CORE SAMPLES
The results in Table 3 show that the DIN Method (Diazo-reaction) detected the presence of coal tar in all core samples prior to 1970 and in half the 1970 samples. No coal tar was detected in

the 1991 cores. The 1970 core analysis found some pavement layers did not contain measurable amounts of coal tar. However, all cores found indications of coal tar present in either the pulver or mastic layer, suggesting that exposure by the paving crew could have occurred.

COMPARISON OF MODIFIED AMES TEST RESULTS

Table 3 provides the Mutagenicity Indices (MIs) of binder extracted from the core samples. Extensive experience in Modified Ames testing *(13)* 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 all pulver samples except 1991 contained coal tar-derived material. The association of the higher MIs with coal tar is further substantiated by the high correlation ($r^2 = 0.94$) between MI and the levels of 16 PAHs. For these samples a plot is shown in Figure 2. This result suggests that these unsubstituted PAHs are responsible for the mutagenic activity and that coal tar is the likely source.

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DISCUSSION

Upon completion of this study, a letter was written to the Danish Road Directorate asking if our findings were consistent with known government records. A response (*14)* from the chief engineer verified that coal tar was widely used in pulver asphalt and the precoated chips used in the mastic layer well into the 1970's in Denmark. Coal tar was produced from coal gasification plants in Denmark. Records from the Danish Road Directorate indicate a general decrease in tar usage on roadways between 1948 and 1970. Coal tar was used as an effective adhesion promoter on the difficult-to-coat granite used in these pavements. The Danish Road Directorate indicated that after 1970 the use of amine based adhesion promoters increased. Denmark's climate is characterized by high humidity and significant rainfall during some seasons. Therefore good adhesion is required on high silica aggregates. Formulations obtained through the Danish Road Directorate found that pulver asphalt used tar oils (anthracene oil) up to 20% of the binder in 1950-1960. Whereas, mastic used coal tar pitch primarily in the precoated chips which represents 2-5% of the binder.

CONCLUSIONS

1. This study found that it is possible to determine the presence of coal tar mixed with asphalt cement in paving mixtures. The chemical and biological differences between coal tar and asphalt allow at least qualitative differentiation based on unsubstituted PAH analysis, phenol assay, and mutagenicity testing.
2. The results of the study found a strong correlation ($r^2 = 0.94$) between PAH level and Mutagenicity Index (MI), which taken together with tar production and formulation records from the Danish Road Directorate suggests that unsubstituted PAHs from coal tar are most likely responsible for the mutagenic activity found in these pavements. This conclusion was supported by the fact that the 1991 sample, which had low values for all end points, was known not to contain coal tar.
3. Pavements between 1970 and 1991 were not tested so it is not known specifically when coal tar usage was discontinued in Danish mastic pavements.

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FIGURE 2 City of Copenhagen Asphalt Pavement Core Samples

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	---

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TABLE 2 Analytical comparison of selected core samples with standard asphalt and coal tar products

Material	Total of 16 PAHs (ppm)	Diazo Reaction[a]	Mutagenicity Index
Mean of seven European asphalt cements[b]	10	NA	NA
Mean of twelve US asphalt cements	24	-	1.07
Average Pulver Layer	4000	+	
Average mastic	900	SL+	
European coal tar[a]	152,647	NA	NA
Low temperature US coal tar	63,160	++	1020

[a] Diazo Reaction: + = positive; ++ = strong positive; SL+ = slight positive; - = negative
NA = Not Available for Testing
[b] Brandt *(12)*

TABLE 3 Analyses of Danish mastic asphalt pavement core samples

Date	Sample	Pavement Type	Total of 16 PAHs (mg/kg)[a]	Diazo Reaction[b]	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

[a]NIOSH Method 5506

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

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FIGURE 1 Mastic Asphalt Paving in Copenhagen (1953)

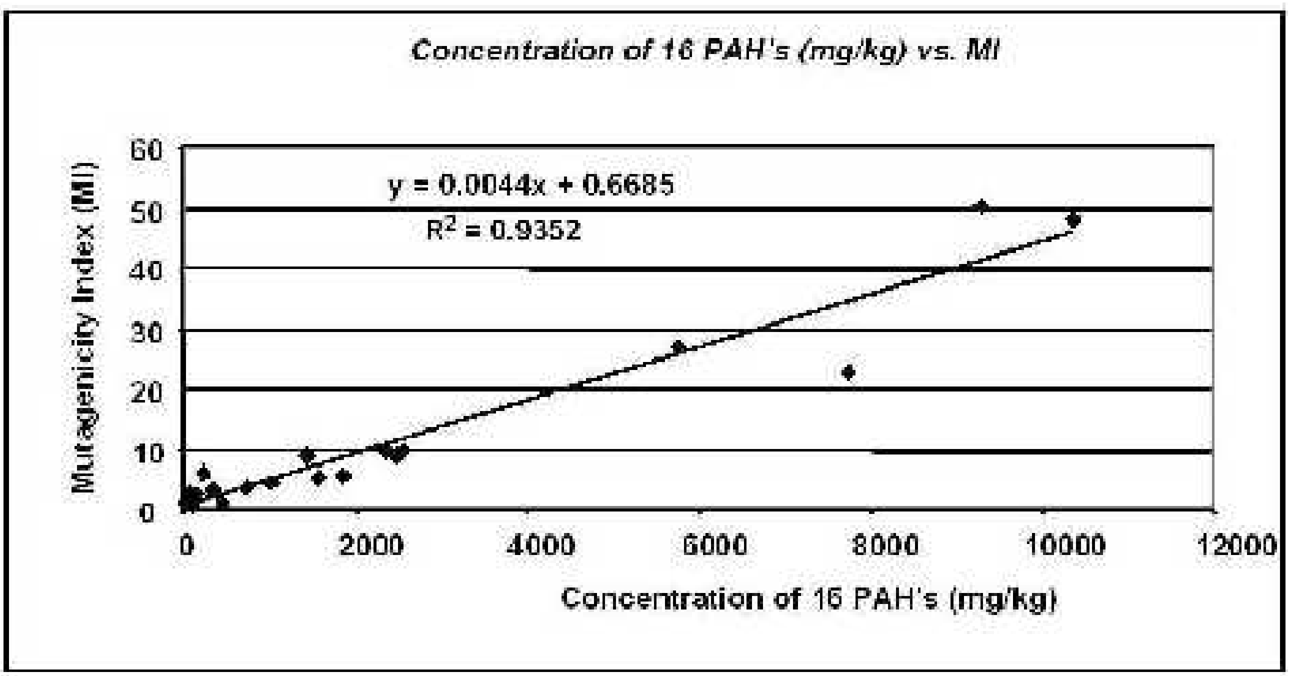

FIGURE 2 City of Copenhagen Asphalt Pavement Core Samples

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