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REPORT ON EMISSIONS FROM ASPHALT HOT MIXES

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I. INTRODUCTION

The most commonly used process to produce asphalt paving mixtures involves mixing petroleum derived asphalt cements at elevated temperatures with mineral aggregates, such as sand, gravel, slag and various crushed rocks. In this manner approximately 350 million tons of paving mixtures are produced annually in about 4,500 hot-mix plants scattered throughout the country.

When a hot asphalt paving mix is discharged from the mixing chamber, a bluish plume frequently arises from the mix. With the increasing concern about matters affecting the environment and the health and safety of workers, The Asphalt Institute initiated an investigation to determine the composition of the air including the emissions, in which measurements were made of the visible and invisible compounds, organic vapors and particulate matter, in the immediate vicinity of the pugmill during the hot mixing process. It was expected that the concentration of such emissions would be the highest at the pugmill, and this was the reason for selecting that area for sampling of emissions. The identification and determination of concentrations of all possible compounds that conceivably could be derived from the asphalt binder was the primary purpose of this investigation. A further purpose was to compare these findings with the emission standards or limits promulgated by the regulatory agencies.

The Asphalt Institute laboratories are not instrumented to perform chemical analyses for various compounds. Thus, the Analytical and Information Division of Exxon Research and Engineering Company, an agency well equipped and experienced for such analyses was retained under a contractual agreement to accomplish the sampling and analyses of the emissions. Institute personnel were responsible for making arrangements for access to the hot-mix plant at which the study was to be made, for sampling and testing materials used in preparing paving mixtures and carrying out tests evaluating the uniformity of materials and the hot-mix process.

Detailed descriptions of experimental procedures and findings of this evaluation are provided in The Asphalt Institute's Research Report 75-1 titled, Asphalt Hot-Mix Emission Study⁽¹⁾.

II. ASPHALT HOT-MIX TEST PLANTS AND EMISSION SAMPLING CONDITIONS

a. Edison, New Jersey Study

The initial sampling of asphalt emissions was carried out at Edison Asphalt Corporation hot-mix plant in Edison, New Jersey. Six complete sets of samplings, two on each of three days, spaced within three months, were obtained at the Edison plant.

The plant shown in Figure 1 was manufactured by McCarter Corporation, Morristown, Pa. It is equipped with a rotary drum-dryer having a burner on each end and a 3-ton capacity pugmill. As shown in Figure 2, the hot asphalt mix was discharged from the mixing chamber into a rail-mounted skip-hoist and transported to the hot storage bins. Figure 3 is a schematic diagram indicating the flow of materials through the plant.

The nominal mixing cycle for each three-ton batch was one minute, approximately 15 seconds being used for weighing and dry mixing of mineral aggregates, and 45 seconds for introduction of asphalt, wet mixing and mixture discharge from the pugmill. However, because of interruptions in the flow of materials or plant operations, the mixing cycle during all three sampling periods varied between approximately 65 and 90 seconds and averaged about 75 seconds. The discharge of mixture from the pugmill into the skip-hoist was timed to be between 7 and 9 seconds. During discharge the hot-mix emissions were visible immediately after the mixture hit the bottom of the skip-hoist and lingered for only a couple of seconds after the discharge was completed.

The skip-hoist arrangement provided several advantages for sampling the hot-mix emissions. It eliminated the frequent passage of transport trucks under the pugmill. Thus, the contamination of asphalt emissions by the truck exhaust gases and by vapors originating from oil used to coat truck beds was avoided. Also, the skip-hoist structure permitted construction of a platform for placement of sampling equipment.

The space between pugmill and skip-hoist was used for sampling asphalt emissions. During the first sampling day (samplings 1 and 2 on September 25, 1973), the space was left unenclosed as is normal in asphalt plant operations. On the other sampling days (samplings 3 and 4 on October 2, 1973 and samplings 5 and 6 on November 20, 1973) the sampling space was substantially enclosed by hanging a polyethylene shroud on all four sides. The resultant enclosed space measured about 3 meters by 3 meters by 1.5 meters high (10 ft x 10 ft x 5 ft). Thus, a total of approximately 14 m^3 (500 ft^3) was enclosed by the shroud. The enclosed sampling space is shown in Figure 4.

Upon completion of the Edison study, The Asphalt Institute's Ad Hoc Technical Committee on Environmental Studies met to review the findings and the needs, if any, for an extension of the study. The analysis indicated an extremely low concentration of chemical compounds which could conceivably have originated from the asphalt cement. It was recognized that the asphalt cements used for the Edison study were typical of those derived from many crude petroleum. It was known, however, that other widely and successfully used asphalt cements had appreciably different physical characteristics. The Committee

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Figure 1.
Edison Asphalt Plant

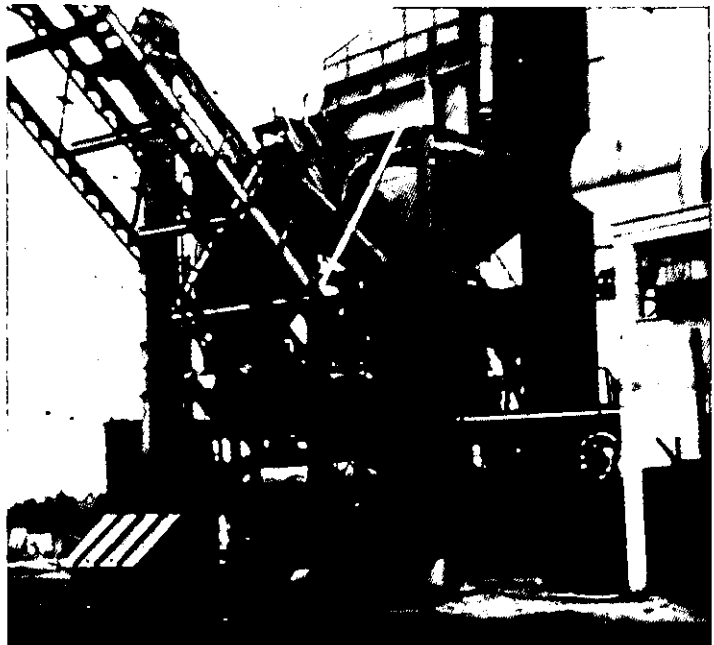


Figure 2. Discharge of Paving Mixture to Skip-Hoist

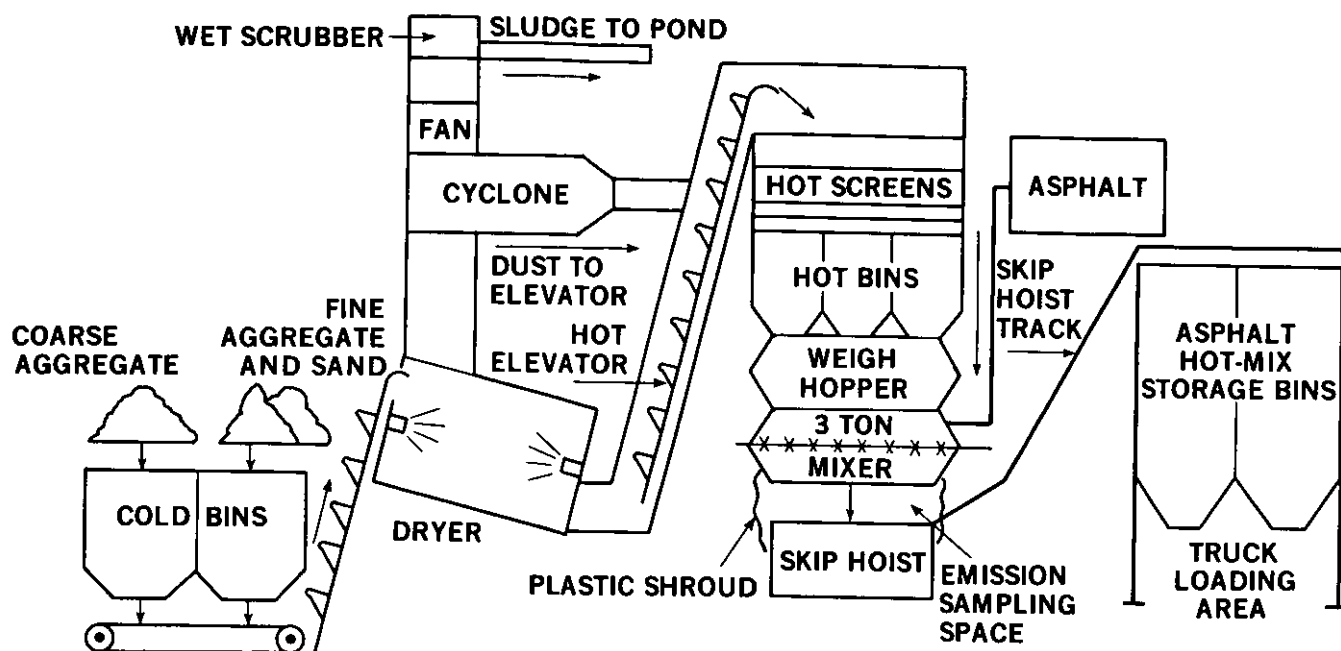


Figure 3. Edison Plant Materials Flow Chart

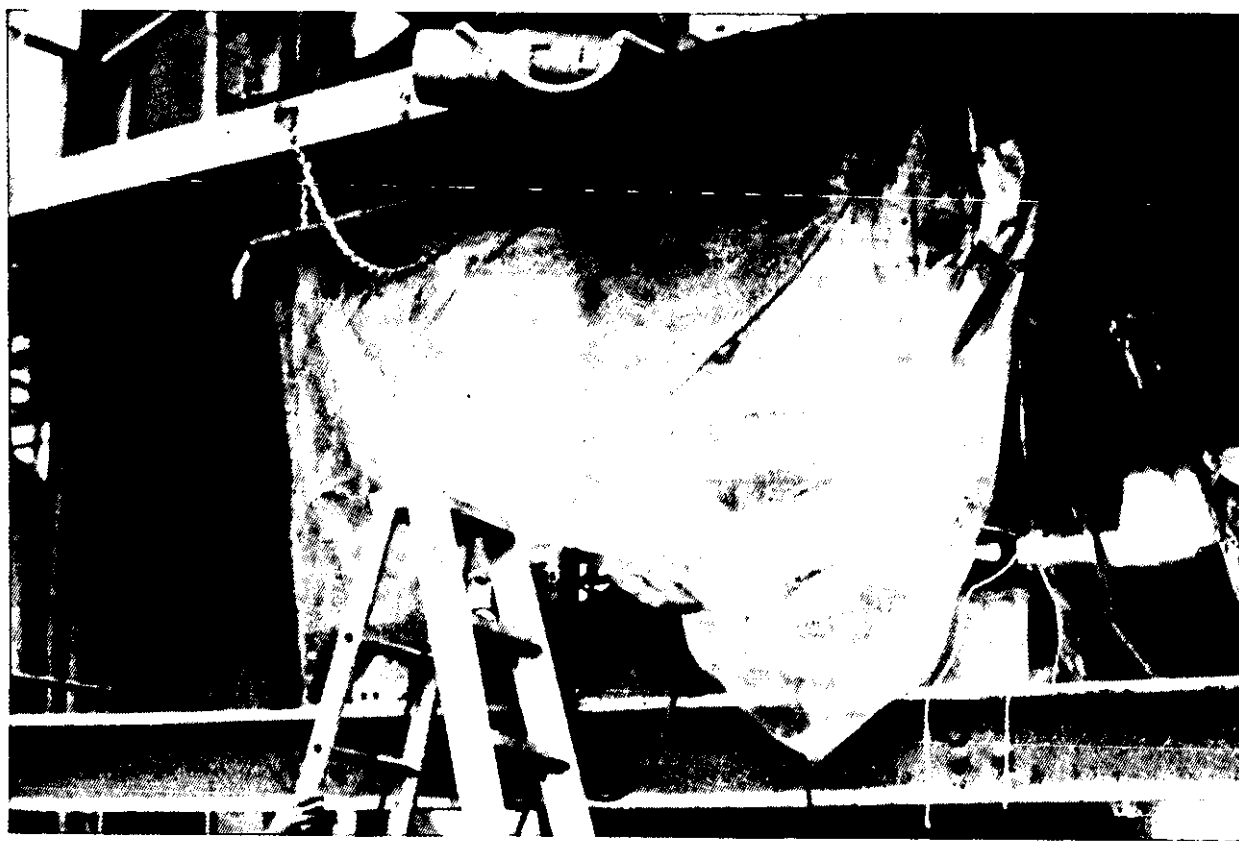


Figure 4. Enclosed Sampling Space

concluded that the study should be extended to include an asphalt cement with these different characteristics, in order that the results of the study would truly represent all the asphalt types commonly used in the United States.

b. Greensboro, N. C. Study

A Thompson-Arthur Company hot-mix asphalt plant located at Greensboro, N. C. was selected for an extension of the study because at this plant asphalt cements having the desired properties were in normal use. This plant also had a 3-ton pugmill capacity. The mix was discharged from the pugmill into a hopper, and was then transported for a short distance by a screw-type conveyor, in an enclosed trough, to the foot of a bucket elevator. The mix was then carried to hot storage bins by the bucket elevator. These plant facilities are more fully described and illustrated in Figure 5, with the flow of materials through the plant schematically illustrated in Figure 6.

The one minute mixing cycle for each individual batch in this plant was sub-divided as follows: twelve seconds for charging the mixer with aggregates; two to three seconds for dry mixing and thirty-eight seconds for introducing hot asphalt cement and wet mixing. The remaining seven to eight seconds were required for discharge of the finished mixture.

Emissions evolving from hot-mixture when discharged into the second receiving hopper were sampled for analysis. The space surrounding the hopper was approximately 2.4 meters high, 2.1 meters long and 1.8 meters wide (8 ft x 7 ft x 6 ft), which was enclosed by a polyethylene sheet during the emission sampling period. This formed an enclosure about 9.6 m^3 (340 ft^3) which was sufficient to accommodate two high-volume samplers and various other sampling devices. The enclosed sampling space is shown in Figure 7.

In Greensboro two sets of asphalt hot-mix emission samples (Nos. 7 and 8) were obtained on a single day (June 19, 1974).

c. Tests and Conditions During Emission Sampling

During emission sampling in Edison and Greensboro, wind velocity, ambient temperatures, humidity and weather conditions, were observed and recorded. Individual batches were counted and timed and temperature of each batch was measured with an IR Con Company infrared thermometer Model CJ 346. These measurements were made by aiming the thermometer at the mix during discharge from the pugmill. Occasionally, the infrared temperatures were checked with bi-metallic dial thermometers and good agreement between the two measurements generally was observed.

Table I summarizes all pertinent information regarding sampling conditions at both the Edison and Greensboro tests. As this table indicates, there were appreciable variations in the duration of the individual samplings, the amount of mixture produced during each sampling, the mix temperature and other factors. While these variations probably influenced emission test results to some degree, an accurate assessment of the effects of such variations was neither possible nor intended. The variations as indicated in Table I are not unusual and should be considered as representative of normal plant operation procedures.



Figure 5. General View of Greensboro Plant

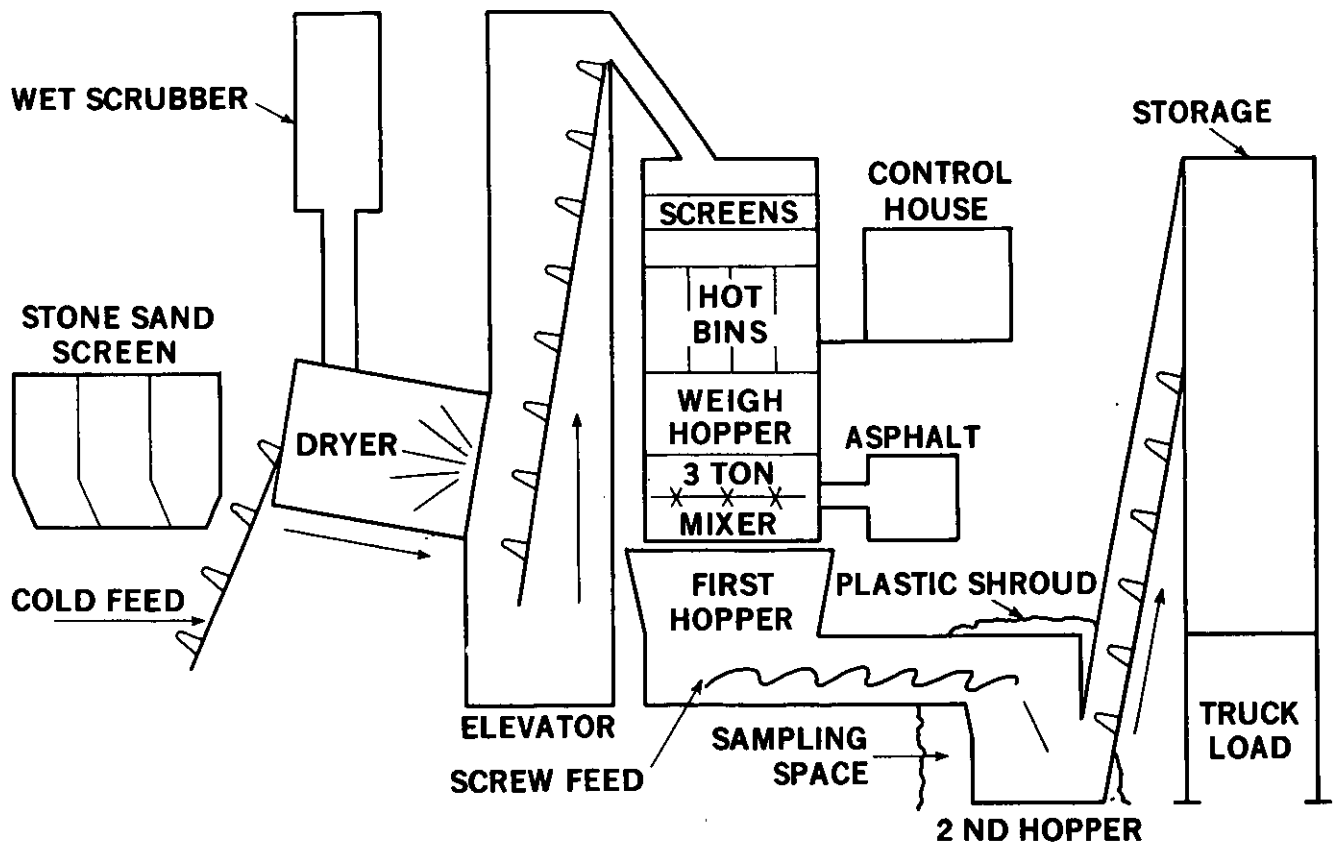


Figure 6. Greensboro Plant Materials Flow Chart



Figure 7. Shrouded Sampling Area

TABLE I - EMISSION SAMPLING CONDITIONS

SAMPLING NO.	1	2	3	4	5	6	7	8
SAMPLING SITE	EDISON, NEW JERSEY						GREENSBORO, N.C.	
DATE	September 25, 1973		October 2, 1973		November 20, 1974		June 19, 1974	
TIME	7:53 AM - 10:00 AM	10:10 AM - 12:28 PM	7:30 AM - 8:40 AM	8:47 AM - 9:44 AM	12:01 PM - 1:07 PM	1:24 PM - 2:44 PM	8:06 AM - 9:58 AM	4:24 PM - 6:28 PM
TEST DURATION	127	138	70	57	66	80	112	124
NUMBER OF BATCHES	96	90	60	50	60	60	112	125
TONNAGE OF MIX	279	270	180	150	180	180	336	375
ASPHALT CEMENT (AC-20)	Exxon	Exxon	Chevron	Chevron	Chevron	Chevron	Amoco	Amoco
MIXTURE TEMP., °F	280-336	250-312	295-312	297-305	300-326	301-342	247-336	290-335
AMBIENT TEMP., °F	60	62	66	65	50	51	69	75
WEATHER CONDITIONS	Partly Cloudy	Partly Cloudy	Overcast	Overcast- Misty	Sunny	Sunny	Clear	Partly Cloudy
WIND VELOCITY, mph	3 to 8.5	Approx. 3.0	Approx. 3.0	Calm	Gusty	Gusty	Calm	Gusty
SAMPLING SPACE	Open	Open	Partially Enclosed	Partially Enclosed	Partially Enclosed	Partially Enclosed	Shrouded	Shrouded

The EPA has promulgated a standard (6) for asphalt concrete plant limiting particulate matter emissions to 20% opacity without identifying the testing procedure. During the Greensboro test an attempt was made to estimate the opacity of the visible asphalt emissions during and immediately after the discharge of paving mixture from the pugmill. A Spectra Brightness Spot Meter (Photo Research, Div. of Kollmorgen Corp., Burbank, Ca.) was used for these measurements with the readings ranging from 2 to 18 percent opacity. Because these measurements included water vapor which contributed to the opacity, its true opacity would be substantially lower than that found.

III. MATERIALS

a. Asphalts

Table II lists all pertinent properties of asphalt cements used in preparing paving mixtures during eight samplings of asphalt emissions. Asphalts A, B and B¹ were used in the Edison hot-mix plant and Asphalt C was used in the Greensboro plant. All asphalts were AC-20 grade materials complying with Table 1 or 2 requirements of the American Association of State Highway and Transportation Officials (AASHTO) Specification M 226 and corresponding ASTM specifications. Asphalt A was prepared by Exxon Co. (U.S.A.) from Venezuelan and domestic crude oils. Asphalts B and B¹ was prepared by Chevron Asphalt Co. from Middle East and Venezuelan crudes. Asphalt C was prepared by Amoco Oil Co. using Venezuelan crude. Although crude oil origins for the three sources differed, the physical properties were typical for grade AC-20. As indicated in Table II, Asphalt C used in Greensboro had appreciably lower flash point and higher volatility than materials in the Edison study. The Greensboro asphalt had a Cleveland-Open-Cup Flash Point about 44°C (80°F) lower than three asphalts used in Edison. Also, weight loss during the Thin Film Oven Test heating for 5 hours at 163°C (235°F) indicates that the Greensboro asphalt contained relatively more volatile compounds than the three asphalts used at Edison.

b. Mineral Aggregates

Table III summarizes properties of all mineral aggregates used for preparation of paving mixes at the Edison and Greensboro plants. Samples of these materials were taken either from stockpiles or from cold-bins during each sampling day. Mineral aggregate gradation, specific gravity and water absorption values shown in this table are averages of multiple samples obtained at each location during emissions sampling periods.

In Edison, four types of mineral aggregates were used to prepare either base or surface course mixtures, complying either with Pennsylvania Turnpike Authority or New Jersey Highway Department requirements. The coarse aggregate for the base course was crushed granite-gneiss from a Glen Gardner, N. J. quarry. The coarse aggregate for the surface course mixtures was crushed basaltic trap rock from a Bound Brook, N. J. quarry. Granite-gneiss screenings from Glen Gardner quarry and quartzitic sand from South Amboy constituted the fine aggregate for both base and surface course paving mixtures. No mineral filler, a material passing 74 μ m (74 micron) mesh (U.S. Std. Sieve No. 200), was added to either mix because the stone screenings and sand contained a sufficient amount of fines to comply with filler and gradation requirements of these paving mixes.

TABLE II - PROPERTIES OF ASPHALT CEMENTS

<u>SAMPLING NUMBER</u>	<u>1 & 2</u>	<u>3 & 4</u>	<u>5 & 6</u>	<u>7 & 8</u>
<u>SAMPLING SITE</u>	<u>Edison, N.J.</u>			<u>Greensboro, N. C.</u>
<u>ORIGINAL ASPHALT</u>	<u>A</u>	<u>B</u>	<u>B¹</u>	<u>C</u>
<u>VISCOSITY</u>				
140°F, poises	2000	1678	1849	2206
275°F, cS	394	387	409	360
77°F, mP @ 0.05 sec ⁻¹	1.60	1.65	1.60	1.45
<u>DUCTILITY</u>				
77°F (5 cm/min), cm	150+	150+	150+	150+
39.2°F (1 cm/min), cm	12.75	7.75	11.10	70.0
<u>PENETRATION, 0.1 mm</u> (77°F, 5s, 100g)	72	70	69	70
<u>FLASH POINT, COC, °F</u>	610	605	605	525
<u>SOLUBILITY</u>				
Trichloroethylene, percent	99.99	99.94	99.95	99.94
<u>SPECIFIC GRAVITY, 77°F</u>	1.019	1.022	1.026	1.027
<u>THIN FILM OVEN TEST</u>				
<u>WEIGHT LOSS, PERCENT</u>	0.104	0.056	0.053	0.50
<u>VISCOSITY</u>				
140°F, poises	4454	3660	4253	5733
275°F, cS	565	531	607	574
<u>DUCTILITY, cm</u>				
77°F, 5cm/min	150+	150+	150+	150+
<u>PENETRATION, 0.1 mm</u> (77°F, 5s, 100g)	45	46	43	41
<u>ELEMENTAL ANALYSIS</u>				
CARBON, percent	86.2	85.6	--	85.7
HYDROGEN, percent	9.7	9.5	--	9.9
SULFUR, percent	3.2	4.6	--	3.5
IRON, ppm	30	--	--	18
NICKEL, ppm	78	--	--	115
VANADIUM, ppm	620	--	--	405
LEAD, ppm	0.6	0.1		0.4
CADMIUM, ppm	<0.6	<0.1		<0.1

TABLE III - PROPERTIES OF MINERAL AGGREGATES (1)

SAMPLING SITE	EDISON, NEW JERSEY				GREENSBORO, N. C.			
AGGREGATE TYPE	Coarse	Coarse ⁽²⁾	Screenings	Sand	Coarse	Coarse	Screenings	Sand
SOURCE OR QUARRY	Glen Gardner	Bound Brook	Glen Gardner	South Amboy	Pamona	Pamona	Jamestown	Candor
MINERAL TYPE	Granite-Gneiss	Basaltic Trap Rock	Granite Gneiss	Quartzite	Granite	Granite	Granite	Quartzite
SPECIFIC GRAVITY								
APPARENT	2.804	3.015	2.839	2.660	2.765	2.776	2.711	2.656
BULK	2.741	2.882	2.805	2.627	2.733	2.726	2.700	2.617
WATER ABSORPTION	0.8	1.5	0.5	0.5	0.4	0.7	0.3	0.6
pH (3)	8.5				9.3			
GRADATION	PERCENT PASSING							
SIEVE SIZE								
1 inch	100.0				100.0			
3/4 inch	78.9				96.2			
1/2 inch	33.8	100.0			35.7	100.0		
3/8 inch	12.6	95.6	100.0		11.6	95.5	100.0	
No. 4	4.3	40.8	93.4	100.0	2.3	24.9	97.5	100.0
No. 8	3.0	13.5	70.3	98.6	1.3	4.9	84.0	99.7
No. 30	2.3	5.6	35.0	88.1	0.6	1.5	47.7	76.4
No. 100	1.5	4.2	14.6	11.2	0.4	0.9	22.2	14.2
No. 200	1.1	3.5	9.5	4.9	0.3	0.7	15.8	6.8

NOTES: (1) Values in this table are averages for samples taken during all emissions sampling periods at respective test site.
(2) Used for surface course mixtures only.
(3) Mineral fines (<74 microns) in water slurry.

TABLE IV - SUMMARY OF SAMPLING AND ANALYTICAL METHODS

SUBSTANCE	SAMPLING METHOD	METHOD OF ANALYSIS
Air	Grab samples in evacuated 300 ml stainless steel bomb.	Mass spectrometer, ASTM 2650-68T
Hydrocarbons (C ₁ -C ₆)	Fast or slow filling of evacuated 10-liter stainless steel pressure vessel	Gas chromatography on two types of columns
Hydrocarbons (C ₇ -C ₁₄)	Impingers (300 ml) filled with chilled CCl ₄	Infrared spectrometer, Gas chromatography-mass spectrometry
Carbon Monoxide	Same as for (C ₁ -C ₆) Hydrocarbons	Non-dispersive infrared analyzer
Volatile Sulfur Compounds	Grab sample in evacuated glass (250 ml) gas sampling tubes	Gas chromatography, flame photometric or microcolorimetric detector
Nitrogen Dioxide	Absorption in azo dye forming reagent bubbler	Visual comparison with color standards, ASTM D 1607
Aldehydes	Absorption in 2, 4 dinitrophenyl-hydrazine bubbler	Ultraviolet absorption
Phenols	Absorption in 10 percent sodium hydroxide bubbler	Differential ultraviolet spectrometry
Ozone	Absorption in alkaline potassium iodide on bubbler	Spectrophotometric absorption, ASTM D 1609-60
Total Particulates	High volume sampler, glass fibre filter, EPA	Gravimetric method, EPA
Benzene Soluble Particulates	Extraction with benzene	Gravimetric method
Hydrocarbons in Benzene Solubles		Gas chromatography and mass spectrometry. Also, UV and IR spectrophotometry
PNA's in Benzene Solubles	Benzene solubles variously treated in preparation for PNA analysis	Gas chromatography, UV spectrophotometry and radioisotope measurements
Nickel, Vanadium		Atomic absorption
Cadmium, Lead		Optical emission spectrography

Four stockpiles of mineral aggregates were available at the Greensboro plant. Two were coarse aggregates differing in maximum particle size and both were highly angular crushed granite from the Pamona quarry located in the vicinity of Greensboro. A third stockpile was siliceous sand of medium angularity obtained from Candor, N. C. located about 80 miles from Greensboro. Granite type screenings originated from a quarry at Jamestown, N. C. was the fourth stockpile. Again, as in the case of the Edison plant, no added mineral filler was necessary to comply with the state specification requirements for surface course paving.

c. Paving Mixes

In order to verify the uniformity of plant operations, multiple random samples of the paving mixes were taken immediately after discharge of the batch from the pugmill during all four emission sampling days. With each mix sample, the asphalt cement and mineral aggregate were later separated in the laboratory by a standard extraction procedure.

Variation in test properties of the original aggregate materials and of finished asphalt mixtures at both plants may be considered as typical of those found in asphalt hot mix plant operations. Thus, the conditions for emission sampling and test results of these samples should be considered as representative and indicative of conditions and results to be expected at other hot-mix asphalt plants using similar asphalt cements and mineral aggregates.

IV. EXPERIMENTAL PROCEDURES - SAMPLING AND ANALYSIS OF ASPHALT EMISSIONS

A variety of sampling and analytical techniques and procedures were used in order to achieve the objective of this investigation. Commonly used methods, including ASTM standards plus those approved by the Environmental Protection Agency and procedures developed and used by the Analytical and Information Division of Exxon Research and Engineering Company, were used for sampling and analysis of all emission components. Table IV lists substances for which analyses were performed and provides an abbreviated summary of the sampling and analytical techniques involved.

To obtain samples of asphalt emissions two basic techniques, namely grab sampling and continuous sampling, were used. Grab samples were obtained in evacuated stainless steel and glass sampling tubes. These containers were held in the immediate area of the paving mix being discharged, with the stopcocks opened at the height of the visible plume. Glass containers were used for grab sampling when testing for volatile surface compounds.

Continuous sampling was accomplished by passing emission samples at variable rates through impingers, bubblers or sampling trains containing various reagents for absorption of different components of the emission. Normally, more than one sample of an emission was collected during a given sampling period. Chilled carbon tetrachloride impingers were used to collect samples of C₇ - C₁₄ hydrocarbon vapors, which subsequently were measured by infrared technique.

Continuous sampling was used to collect samples of particulate matter. High-volume samplers were used drawing air at the rate of 1.13 to 1.70 m³/min (40 to 60 ft³/min) through a glass fiber filter. These samplers were placed as close as possible to the discharged mixture and were operated for periods of one to two hours to obtain a single sample of particulates. In some cases, samples were collected by two samplers in order to obtain sufficient amounts of particulates for analysis.

No attempt will be made in this report to describe the commonly used analytical techniques, as this may be found in Reference (1). However, analytical techniques employed for measurement of polynuclear aromatic (PNA) hydrocarbons in benzene soluble particulates merit a brief description.

Soxlet extraction using benzene was used for the separation of organic substances from inorganic mineral particulates. A sample of benzene solubles was spiked with a known quantity of carbon-14 labeled benz(a)anthracene (BaA) and benzo(a)pyrene (BaP). The sample was placed in a 100 ml beaker and was evaporated to dryness under nitrogen on a steam bath. The residue dissolved in cyclohexane was treated with caustic to remove some acidic components. PNA hydrocarbon concentrate was then obtained by solvent elution off a column of partially deactivated alumina using cyclohexane, cyclohexane-benzene, benzene and benzene-methanol as successive eluates. The fraction containing PNA hydrocarbons was reduced to a small volume by evaporation on a steam bath. An aliquot of this sample was injected into a gas chromatograph and fractions were collected for measurement by UV and, in the case of BaA and BaP peaks, also for carbon-14 activity. These activities, compared with the known, originally added concentrations, provided factors to relate the concentration of each PNA hydrocarbon to its total weight in the sample. This method is described in greater detail in Reference (2).

V. TEST RESULTS AND DISCUSSION

a. General

Table V summarizes the test results on six sets of asphalt hot-mix emission samples collected at the Edison plant on three days, and two sets of samples in a single day at the Greensboro plant. The quantities shown in the second and third column of this table are either ranges or maximum values found for the indicated substance. Generally, all compounds listed in Table V are at extremely low concentrations, even though the sampling was accomplished under exaggerated conditions, namely in an enclosed space. This is not at all surprising if it is considered that in preparation of asphaltic paving mixes only moderate temperatures, generally lower than 160°C (325°F), are utilized.

Table V indicates that the range for non-visible gaseous components is quite similar for samples collected at both plants. The "less than" values shown for the majority of the components indicate the sensitivity of the sampling or testing procedure used. Thus, the "less than" compounds were either completely absent or, if present, the concentrations for such compounds were below the indicated value. Values shown for methane and carbon monoxide are

TABLE V - COMPOSITION OF ASPHALT HOT-MIX EMISSIONS

Sample Location	Edison, N.J.	Greensboro, N.C.
Number of Samples	6	2
<u>Non-Visible Components (ppm)</u>		
Carbon monoxide (CO)	4-6	3-4
Nitrogen dioxide (NO ₂)	<0.1	0.05-0.08
Sulfur dioxide (SO ₂)	<2	<0.05
Hydrogen sulfide (H ₂ S)	<0.2-1.5	<0.2
Carbonyl sulfide (COS)	<0.2	<0.2
Mercaptan (RSH)	<0.2	<0.2
Aldehydes (RCHO)	<0.1	0.3-0.4
Phenol (jOH)	<1	<1
Ozone (O ₃)	<0.1	---
Methane (CH ₄)	2-3	2-3
Non-methane Hydrocarbons (C ₂ -C ₆)	<1	<1
Volatile organic compounds (C ₇ -C ₁₄)	0.5-1.5	0.5-1.0
<u>Particulates (mg/m³)</u>		
Total particulates	2.6-7.2	0.5-5.7
Benzene solubles	0.3-2.8	0.2-5.4
Polynuclear aromatics (total), max.	0.00034	0.00016
Nickel (Ni), max.	0.000005	0.00004
Vanadium (V), max.	0.00008	<0.0001
Cadmium (Cd)	---	<0.00005
Lead (Pb)	---	<0.00005

NOTE: Where the less than (<) values are indicated, the numbers represent the sensitivity of the sampling or testing procedure used. If the component is present at all, it is below the value shown.

comparable to concentrations normally found for ambient air. Mass spectrometric analyses of gas samples obtained in an enclosed space by the evacuated bomb technique indicated that 99.9 percent of this gas was air (N_2 , O_2 , H_2O), the remaining 0.1 percent as CO_2 . Since such measurements are sensitive to 0.1 percent of the individual hydrocarbon and other organics, the measurement provides additional qualitative confirmation that gaseous emissions do not contain a major amount of any contaminant.

Table V indicates rather low quantities of total particulate matter collected in a shrouded sampling space in either the Edison or Greensboro plants. The amount of benzene soluble fraction of particulates from the Greensboro plant was found to be somewhat higher than in samples from the Edison plant. This may be associated with lower flash point or higher volatility of asphalt used at Greensboro.

Table V also shows extremely low concentrations, if present at all, of vanadium, nickel, lead and cadmium. This is not surprising since these metals are normally associated with the non-volatile, high-molecular weight components of asphalt, thus residing in the asphalt mix and not in the emission.

b. Polynuclear Aromatic Compounds in Particulates

Table V indicates that the amounts of polynuclear aromatic (PNA) compounds in the benzene soluble fraction of particulates found in the Edison plant samplings were somewhat higher than in Greensboro. However, extremely low concentrations were found at both sites. The concentration ranges and averages for the individual PNA's are listed in Table VI for both test sites. This table indicates that by far the largest portion of total PNA's found in Edison and Greensboro is pyrene, a rather harmless, biologically inactive substance.

Table VII compares the appropriate amounts of benzo(a)pyrene, a biologically active carcinogenic PNA emitted from several industrial and other sources (3). The amount of 13 micrograms of 1000 m^3 of emitted gas shown for asphalt hot-mixing is the average value for all eight samplings. Again, this low quantity could be explained on the basis that the process of preparation of hot paving mixtures does not involve combustion of materials as do all the other processes listed. Temperature of hot paving mixture seldom exceeds 160°C (325°F) which is considerably lower than the boiling range of all polynuclear aromatic hydrocarbons involved.

c. Comparison of Asphalt Emission with Regulatory Standards

Several regulatory standards issued by a number of agencies were compared with the findings of this study, including the following:

1. Standards for air contaminants promulgated by the Occupational Safety and Health Administration (OSHA) for workroom conditions (4).
2. National Primary and Secondary Ambient Air Quality Standards issued by the Environmental Protection Agency (EPA), (5).

TABLE VI - POLYNUCLEAR AROMATIC COMPOUNDS IN PARTICULATES

<u>SAMPLING SITE</u>	<u>EDISON, N. J.</u>		<u>GREENSBORO, N.C.</u>	
<u>NUMBER OF SAMPLES</u>	6		2	
<u>COMPOUND: $\mu\text{g}/1000 \text{ m}^3$</u>	<u>Range</u>	<u>Ave</u>	<u>Range</u>	<u>Ave</u>
Pyrene	44 - 240	107		96
Benz(a)anthracene	5 - 24	11	32 - 38	35
Benzo(a)pyrene	3 - 20	11	14 - 22	18
Benzo(e) pyrene	14 - 40	26	Not found	
Perylene	5 - 16	12		6

TABLE VII - TYPICAL BENZO(A)PYRENE EMISSIONS FROM VARIOUS SOURCES (3)

<u>SOURCE</u>	<u>$\mu\text{g}/1000 \text{ m}^3$ of gas</u>
ASPHALT HOT-MIXING (at immediate source) 13 *	
POWER STATION, GAS	100
POWER STATION, COAL	300
AUTOMOTIVE DIESEL	5,000
REFUSE BURNING	11,000
COKE OVEN VOLATILES	35,000
HOME FURNACE, COAL	100,000

* Average of samplings in this program

3. Air Programs; Standards of Performance for New Stationary Sources promulgated By EPA (6).

4. Standards or Codes by different states and municipalities such as those issued by the Los Angeles Air Pollution Control District (7).

Furthermore, Threshold Limit Values (TLV's) for Chemical Substances in Workroom Air by American Conference of Governmental Industrial Hygienists (ACGIH) (8) was also considered. Threshold Limit Values as promulgated by ACGIH are not a regulatory standard. However, these values are considered by other agencies who issue standards. Additionally, in the ACGIH publication a limiting value for asphalt fumes is included which, in light of findings of this study, merits further consideration, as discussed briefly later.

Table VIII compares OSHA standards for air contaminants and EPA primary ambient air quality standard with the maximum values of various substances determined for eight samples of asphalt emissions collected at the Edison and Greensboro plant. The secondary ambient air quality standards promulgated by EPA are only marginally different from the primary standards and, therefore, are not included in this table.

Data in Table VIII clearly indicate that all values are well within appropriate OSHA standards for workroom air contaminants. It may be safely concluded that there is no significant air pollution or employee health problem associated with emissions from hot asphalt paving mixtures. This is further supported by the facts that (1) sampling was accomplished in an enclosed space where emissions were highly concentrated and (2) the sampling location was selected as the area where most concentrated emissions might occur. It is also an area in which plant workers are seldom exposed.

Asphalt is sometimes erroneously associated with coal-tar bitumen which is known to contain substantially more polynuclear aromatic hydrocarbons. The OSHA regulations, which originated with ACGIH Threshold Limit Values, are a case in point. They list a value of 0.2 mg/m^3 for polycyclic aromatic hydrocarbons in coal-tar pitch volatiles (benzene soluble fraction) and the ACGIH applied this regulation also for other organic materials, including petroleum asphalt. The distinctive difference between two materials, however, was dramatically demonstrated by the University of Nebraska report (9) which compared eight different asphalts with two coal-tar pitches. The highest benzo(a)pyrene content found in asphalt was 0.0027 wt. percent compared with 1.25 wt. percent in one of the tars. The highest benzo(e)pyrene in the asphalt samples was 0.0052 wt. percent compared with 0.70 percent in one of the tars. Other studies report similar differences in these two distinctly different materials namely, petroleum asphalt and coal-tar pitch.

Threshold Limit Values recommended by ACGIH (8) include a limiting value of 5 mg/m^3 for asphalt (petroleum) fumes. The closest measure related to this listing would be the benzene soluble portion of the particulates which varied from 0.2 to 5.4 mg/m^3 and averaged 1.8 mg/m^3 for eight samplings (see Table V). The ACGIH explained their recommended value of 5 mg/m^3 on basis of good housekeeping while reducing the risk of carcinogeneity (10). However, ACGIH also stated that animal inhalation studies have not yielded evidence of

**TABLE VIII - COMPARISON OF OSHA AIR CONTAMINANT AND EPA
PRIMARY AIR QUALITY STANDARD EMISSIONS AT HOT-MIX ASPHALT PLANT**

Substance	Time Weighted Averages		Measured Emissions
	OSHA Standards	EPA Primary Air Standards	Max. Concentrations (8 Samplings)
Carbon monoxide, ppm	50	9	6
Nitrogen dioxide, ppm	5	0.05	<0.1
Sulfur dioxide, ppm	5	0.14	<2
Hydrogen sulfide, ppm	20 (1)		1.5
Phenol, ppm	5		<1
Ozone, ppm	0.1	0.08	<0.1
Hydrocarbons (stoddard solv.), ppm	500		1.5 (3)
Hydrocarbons (benzene), ppm	10	0.24	< 1 (4)
Particulate Matter, mg/m ³		0.365	7.2 (5)
Polynuclear aromatics (total), mg/m ³	0.2 (2)		0.00036 (5)
Vanadium, V ₂ O ₅ fume, mg/m ³	0.1 (1)		0.0001
Nickel, metal and soluble compounds as Ni, mg/m ³	1		0.00004
Cadmium fume, mg/m ³	0.1		<0.00005
Lead and inorganic compounds, mg/m ³	0.2		<0.00005

- (1) Ceiling value or acceptable ceiling concentration
(2) Listed as coal-tar pitch volatiles (benzene soluble fraction)
(3) C₇ - C₁₄ Hydrocarbons
(4) C₂ - C₆ Hydrocarbons
(5) Trapped by high volume sampler

NOTE: Where the less than (<) values are indicated, the numbers represent the sensitivity of the sampling or testing procedure used. If the component is present at all, it is below the value shown.

asphalt-induced lung cancer after two years exposure to asphalt fumes. Further, it recognized a statistical study by Baylor and Weaver (11) reporting that no difference in health of asphalt workers and a group of controls was observed. Based on these and other studies the ACGIH expressed the opinion that working conditions were satisfactory, provided asphalt fumes were kept below 10 mg/m³ level. Thus, 5 mg/m³ and even 10 mg/m³ for petroleum asphalt fumes may be unduly restrictive. The findings of The Asphalt Institute study, as reported here, show that major portions of hydrocarbon emissions from asphalt consist of saturated type hydrocarbons generally considered harmless even at concentrations higher than those now suggested.

The EPA primary ambient air quality standards for six contaminants are compared in Table VIII with the maximum values found in all the asphalt emission samplings. Because EPA standards apply to air contaminants at or beyond the "fence line," it is evident that concentrations at the "fence line" will be dependent upon not only the amounts emitted at the source, but also by the distance from the source and by the prevailing meteorological conditions. Table VIII indicates that maximum values for a majority of the components in asphalt emissions "at the source" are close to or only slightly greater than EPA air quality standards for "fence line" conditions. However, because the asphalt emissions were sampled under exaggerated conditions, namely at the peak of the plume and in an enclosed space, it is believed that emissions from asphalt would not present a problem with respect to meeting these EPA standards. Dispersion calculations, taking into account the dilution effects of wind and other weather conditions, are being carried out by Gentry (12) of the University of Maryland. Based on the findings of The Asphalt Institute report, it will also be indicated that concentration levels will be further greatly reduced, thus supporting the statement above. This qualification applies also to particulate emissions found at a maximum level of 7.2 mg/m³, which is higher than 0.365 mg/m³ specified by EPA as a primary quality standard for particulate matter. This value, however, is well below the 90 mg/m³ limit set on particulates by EPA for standards of performance for new stationary sources, such as newly-constructed asphalt plants.

VI. SUMMARY AND CONCLUSIONS

A comprehensive analysis of eight sets of samples of emissions originating from petroleum asphalt during the hot-mix process for preparation of asphalt paving mixes has been accomplished. Samples were collected on four days at two locations involving four asphalt cements of varying characteristics from three refineries. All gaseous substances, vapors and particulates which possibly could be associated with asphalt, including hydrocarbons, carbon monoxide, nitrogen dioxide, volatile sulfur compounds, ozone, aldehydes, phenols, metals and polynuclear aromatics, were identified using well recognized and accepted sampling techniques and analytical procedures. Based on test data of these analyses the following is concluded:

1. No significant air pollution or employee health problems can be expected or associated with the emissions from hot preparation of asphalt paving mixtures.

2. All gaseous substances and particulates identified were at extremely low concentrations, some of them no more than those found in typical urban air.

3. Test data indicate that there is no significant difference in the amount or the composition of emissions involved from asphalts from different sources or used in different hot-mix plants.

4. Concentrations of all air contaminants were found to be well within the current OSHA standards for workroom conditions.

5. Despite the exaggerated sampling conditions, asphalt emissions compare favorably with national air quality standards promulgated by EPA. Some air contaminants at the source in an enclosed space were found to exceed marginally the limits prescribed by EPA. However, because of dispersion of source pollutants, it is inconceivable that the EPA limits at the "fence line" would ever be exceeded by the emissions originating at the pugmill in asphalt hot-mix plants.

6. The TLV tables published by ACGIH limit asphalt (petroleum) fumes to 5 mg/m^3 on a time weighted basis. In The Asphalt Institute study, which involved 8 complete samplings, petroleum fumes were found to range from 0.2 to 5.4 mg/m^3 (averaging 1.6 mg/m^3) under concentrated sampling conditions under a shroud in the immediate vicinity of the emission. It was also shown in this study that asphalt fumes are largely made up of saturated hydrocarbons and that the percentage of polynuclear aromatics is extremely low. Thus it is believed that the TLV limit for asphalt (petroleum) fumes is too limiting and not accurately defined.

7. The polynuclear aromatics (PNA) in asphalt emissions averaged approximately 0.00013 mg/m^3 which is well below 0.2 mg/m^3 required by OSHA, and by ACGIH for benzene-soluble coal-tar pitch volatiles and other organic substances including petroleum asphalt. Thus, we calculate that there are no health hazards resulting from PNA in emissions from hot-asphalt paving mixes.

8. The levels of polynuclear aromatics in emissions from asphalt hot mixes are much lower than those for other common emission sources.

9. Asphalt is derived from crude petroleum by processes not involving thermal degradation, whereas coal tar results from high temperature destructive carbonization of coal. This study, and others cited, verify the substantial difference between petroleum asphalt and coal tar, which suggests that these two materials should not be placed in the same category by regulatory agencies.

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