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ASPHALT HOT-MIX
EMISSION STUDY

Asphalt Institute Research Report
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PREFACE

When hot asphalt paving mixtures are discharged from the mixing chamber, a blue haze (often referred to as "blue smoke") sometimes arises from the mixture. Because of increasing interest in all matters affecting the environment, The Asphalt Institute undertook an investigation to determine the composition of emissions, both visible and invisible, arising from hot asphalt mixes; this report presents results of the investigation.

An Ad Hoc Technical Committee on Environmental Studies, composed of well-qualified specialists, was organized to develop plans for and evaluate results of the study. Members of the committee were:

L. W. Corbett, Chairman, Exxon Research and Engineering Company
E. R. Averill, Mobil Oil Corporation
D. K. Chapman, Ashland Oil, Incorporated
W. J. Kari, Chevron Asphalt Company
Soma Kurtis, Marathon Oil Company
E. W. Starke, Shell Oil Company
V. P. Puzinauskas, The Asphalt Institute.

The Asphalt Institute gratefully acknowledges the many contributions of these committee members and expresses sincere appreciation to their respective companies for providing their services.

The sampling and testing of these emissions require considerable expertise and special equipment. Exxon Research and Engineering Company, well recognized for its capabilities in this area, was retained by the Institute to sample and test the emissions. This work was most ably handled by T. D. Searl, R. A. Brown and G. T. DeFreese.

The first phase of the investigation was carried out at an Edison Asphalt Corporation plant in Edison, N. J. The Institute is most appreciative of the assistance and cooperation of Dan Christy and other plant personnel; Bill Abbott of the New Jersey Asphalt Pavement Association; and R. Bruce Noel, then of the Institute staff.

A Thompson-Arthur plant in Greensboro, N. C. was the site of the second phase of the investigation. The Institute acknowledges with sincere appreciation the assistance and cooperation of Tom Pickett and other plant personnel; Ben Ross, Jr., of the North Carolina Asphalt Pavement Association; and G. S. Triplett of the Institute staff.

The Asphalt Institute was responsible for the sampling and testing of asphalt and aggregates used in the asphalt paving mixes and for collecting a variety of pertinent information and data. This part of the investigation was under the supervision of V. P. Puzinauskas of the Institute's headquarters staff.

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ABSTRACT

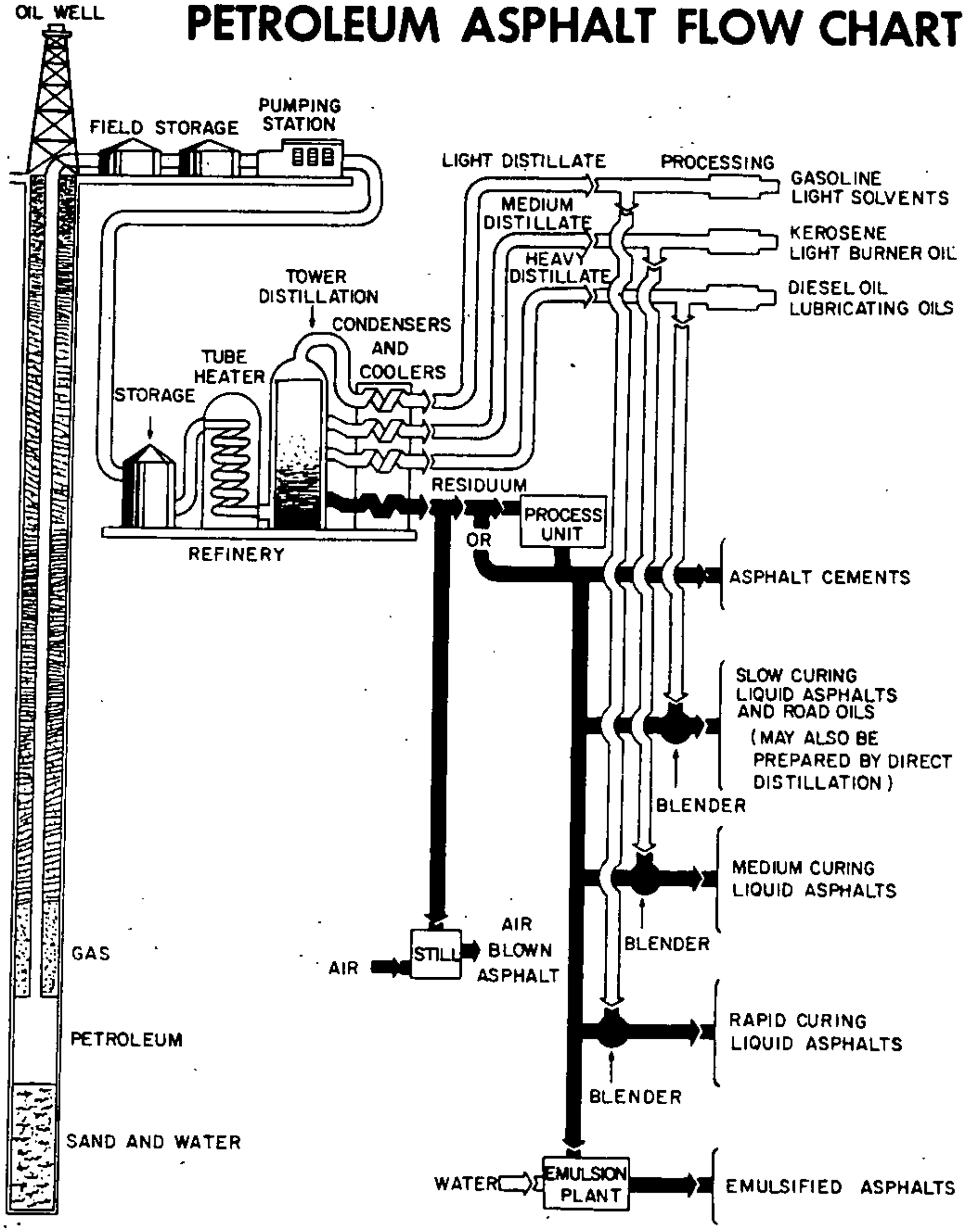
The findings of this study may be summarized by the statement that THERE IS NO SERIOUS AIR POLLUTION OR EMPLOYEE HEALTH PROBLEM RESULTING FROM THE USE OF PETROLEUM-DERIVED ASPHALT IN HOT-MIXES.

The findings are based on eight complete sets of emission samples taken at two hot-mix plants involving four asphalts from three refineries. The emission samples were taken following the discharge of the mix from the mixing chamber. In most of the samplings the immediate area was shrouded to concentrate the emissions, to exclude extraneous matter and to provide more uniform sampling conditions.

Most of the air contaminants found in the emissions were at extremely low concentrations and all fell well within currently applicable limits established by the Occupational Safety and Health Administration (OSHA). Analysis of gaseous substances included carbon monoxide, nitrogen dioxide, sulfur dioxide, hydrogen sulfide, carbonyl sulfide, mercaptans, ozone, aldehydes, phenols and C_2 to C_{14} hydrocarbons. Solid particulates were also collected and found to contain only trace amounts of polynuclear aromatic hydrocarbons and metal compounds, much lower than are typically found in emissions from other industrial and commercial sources. The Threshold Limit Value (TLV) for asphalt (petroleum) fumes of 5.0 mg/m^3, recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) was also considered and found to be slightly exceeded in one sampling. However, each sampling was found to be well within this limit on a time weighted basis (and sampling was made under exaggerated conditions not typical of a workman's exposure). Furthermore, this TLV limit is intended primarily to apply to substances high in polynuclear aromatics, whereas it has been shown that asphalt fumes contain extremely low concentrations of these compounds and are largely made up of innocuous saturated type hydrocarbons.

Under the shrouded, concentrated sampling conditions, the amount of volatile organic hydrocarbons occasionally exceeded the 0.24 ppm limit set forth in the Ambient Air Quality Standards promulgated by the Environmental Protection Agency (EPA). However, it is inconceivable that this limit would ever be reached at the "fence line" of a hot-mix asphalt plant. The same applies to other compounds considered to be air contaminants.

PETROLEUM ASPHALT FLOW CHART



REPORT ON
ASPHALT HOT-MIX EMISSION STUDY

GENERAL

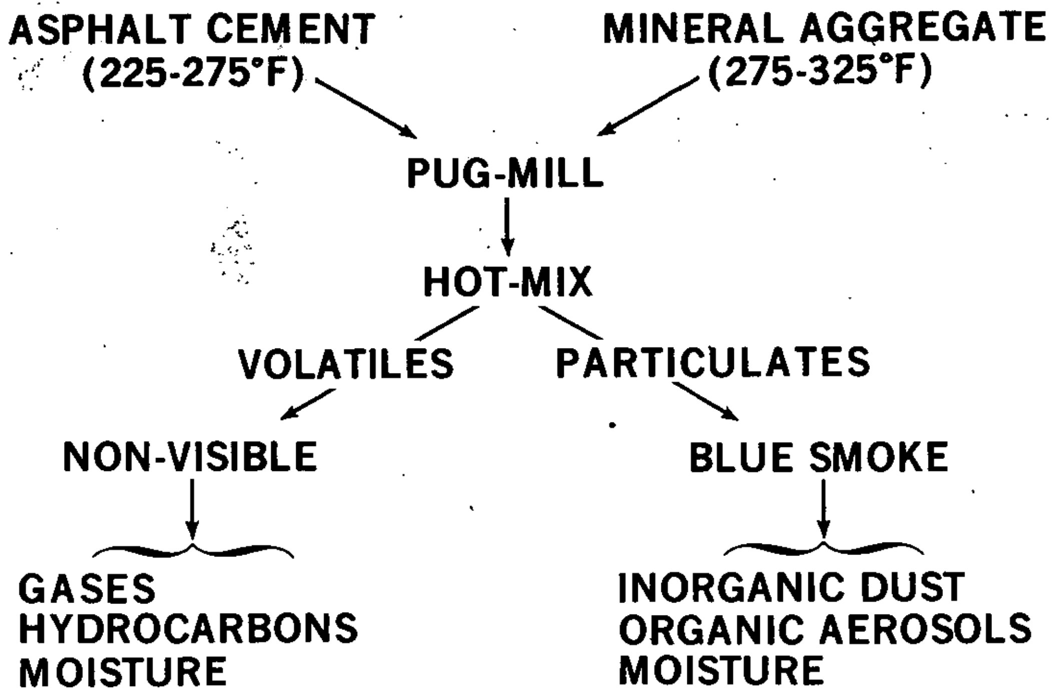
1. Asphalt is a black, cementitious, thermoplastic material derived from the refining of crude petroleum. Asphalt is not to be confused with or compared to tar, which is produced by the pyrolysis or destructive distillation of organic substances, mostly coal. There are substantial differences in the chemical composition of the two materials, and in most of their physical properties.

2. There are several types of asphalt and a number of grades in each type (References 1 and 2). The type primarily used for paving highways, airfields, streets, parking lots and similar areas is asphalt cement. This material is thermoplastic, semisolid and highly viscous at normal temperatures. It must be heated to fluid consistency and thoroughly mixed with heated aggregates, such as crushed stone or gravel, and sand, to provide a paving mix. These mixes are normally prepared at temperatures in the range of 275-325 F. The asphalt cement is usually about 5 to 6 percent by weight of the total mix. Practically all such mixes are prepared in asphalt hot-mix plants in which the mixing of asphalt and aggregate is accomplished in a twin-shaft, counter-rotating pugmill. In most instances the hot asphalt paving mix is discharged from the mixing chamber directly into a truck for transport to the paving site. A rapidly increasing trend, however, is to discharge the mix into a skip hoist or bucket elevator for conveyance to a nearby hot-mix storage or surge bin. Haul trucks are then loaded from the storage bin.

3. When a hot asphalt paving mix is discharged from the mixing chamber, a blue haze frequently arises from the mix. It is often referred to as "blue smoke" and usually appears for only a few seconds, if at all, immediately after discharge of the mix from the pugmill. With the increasing concern about matters affecting the environment, and the health and safety of workers, the Board of Directors of The Asphalt Institute authorized the Institute to undertake an investigation to determine the composition of emissions both visible and invisible, arising from hot asphalt paving mixes.

4. The Institute organized an Ad Hoc Technical Committee on Environmental Studies to plan the emission studies and evaluate the results. This committee was composed of specialists in the environmental field, industrial hygiene, analytical chemistry and asphalt technology. The specific objective of the study, as stated by the committee, was to "Identify the level and composition of organic vapors and particulate matter in the immediate vicinity of hot asphalt pugmill mixing, with composition to include identification of all possible organic components that could be derived from the asphalt binder."

HOT-MIX EMISSIONS



5. Recognizing that highly specialized personnel and equipment would be required to carry out the objective of the study, the Institute made contractual arrangements with Exxon Research and Engineering Company to accomplish the sampling and analyses of the emissions. Institute personnel were responsible for making arrangements for access to the hot-mix asphalt plants at which the study was to be made, for sampling and testing materials used in preparing the mixes and for other matters pertinent to the proper conduct of the investigation.

REGULATORY STANDARDS

6. Regulatory standards considered in establishing the scope of this investigation were as follows:

(a) Occupational Safety and Health Administration (OSHA) Standards (3, 5)

(b) Ambient Air Quality Standards promulgated by the Environmental Protection Agency (EPA) (4, 6)

(c) EPA Standards of Performance for New Stationary Sources (7, 8, 9)

(d) Standards of several states and municipalities (16, 17, 18).

These are believed to include all currently applicable requirements for emission-producing sources of this type.

SAMPLING AND TESTING PROGRAMS

Edison, N. J. Study

7. The emission sampling program was initiated at an Edison Asphalt Corporation hot-mix plant in Edison, N. J. The plant had a 3-ton capacity pugmill mixing chamber for mixing the hot aggregates and asphalt cement. The hot asphalt mix was discharged from the mixing chamber into a rail-mounted skip hoist and transported to the hot storage bins. The plant facilities are more fully described and illustrated in Exhibit A.

8. Three asphalt cements were used in preparing the asphalt mixes. Two were from one refining source and the third from another refinery. Although crude stocks for the two refineries were from different origins, the asphalt cements from the two refineries were generally similar in their test properties, as indicated in Exhibits A and B. All complied with requirements for the AC-20 grade of asphalt cement as prescribed in Tables I and II, Specification M-226 of the American Association of State Highway and Transportation Officials (AASHTO) (2).

9. During the course of the emission sampling program two types of asphalt hot mixes were prepared, one a base-course mix and the other a surface-course mix. Granite-gneiss screenings and siliceous sand were used as the fine aggregate in both mixes. The coarse aggregate portion of the surface-course mix was a basaltic traprock and the base-course mix contained a granite-gneiss coarse aggregate. The gradation, specific gravity and water absorption characteristics of the individual aggregates blended together to prepare the base and surface course mixes are given in Exhibit A.

10. Samples of the prepared asphalt hot mixes were taken at the plant. Later, the asphalt cement and aggregates were separated in the laboratory. Various test properties of these two components were measured, and the detailed results are reported in Exhibit A.

11. Six sets of asphalt hot-mix emission samples were obtained, two on each of three days. A variety of sampling equipment was used for each set of samples to provide materials suitable for the various analytical procedures to be used. Standard sampling methods were used where available and, in all cases, sampling techniques were those considered to be reliable and consistent with those published in the Federal Register. Details of the emission sampling methods are given in Exhibit B.

12. Normally, the area beneath the pugmill discharge gate is unenclosed to provide free access for trucks, skip hoists or bucket elevators used to transport the asphalt hot-mix. The first two sets of

emission samples were taken from a platform immediately adjacent to the unenclosed area between the pugmill discharge gates and the skip hoist. It became apparent, however, that extraneous dust and gases from the surrounding area were entering the sampling area and could materially affect the test results. Also, varying wind velocities affected emission concentrations and were considered not to be conducive to uniform or optimum sampling conditions. The sampling area, including the sampling platform, was therefore enclosed by a plastic shroud while the remaining four sets of emission samples were obtained. This is discussed further and illustrated in Exhibits A and B.

13. 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 petroleums. It was known, however, that other widely and successfully used asphalt cements had appreciably different physical characteristics. The Committee 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.

Greensboro, N. C. Study

14. 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 Exhibit C.

15. Asphalt cement with the desired characteristics from a single source was used in preparing the asphalt hot-mix. Details of the properties of the asphalt cement used in the Greensboro study are given in Exhibits C and D. It met all requirements for the AC-20 grade of asphalt cement as prescribed in Tables I and II, Specification M-226 of the American Association of State Highway and Transportation Officials (AASHTO). A comparison of the front end distillations of asphalts used in the Edison and Greensboro studies also is given in Exhibit D.

16. The mineral aggregate used in the paving mixture produced at the Greensboro plant was a blend of crushed granite coarse aggregate, siliceous sand and granitic screenings. The gradation, specific gravity and water absorption characteristics of the individual aggregate fractions are listed in Exhibit C.

17. Samples of the prepared asphalt hot-mix were taken at the plant. Later, the asphalt cement and aggregates were separated in the laboratory. Various test properties of these two components were measured; and the detailed results are reported in Exhibit C.

18. Two sets of asphalt hot-mix emission samples were taken on a single day at the Greensboro plant. Sampling devices were similar to those used in the Edison study. Details of the sampling methods used are given in Exhibit B.

19. The emission sampling area was located at the end of the screw conveyor, where the mix was fed on to the bucket elevator. The area and sampling devices were enclosed in a plastic shroud, as in the Edison study. This is illustrated and more fully described in Exhibits C and D.

20. Analytical methods used in the Greensboro study were the same as those used in the Edison study; references to these methods appear in Exhibit B. Detailed analytical test results obtained from the Greensboro emission samples are compared with results from the Edison samples in Exhibit D.

DISCUSSION OF EMISSION TEST RESULTS

General

21. Table I summarizes the test results on six sets of asphalt hot-mix emission samples from the Edison, N. J. plant and two from the Greensboro, N. C. plant. Complete details are given in Exhibits B and D.

22. As previously noted, the Edison, N. J. asphalt paving mixes contained asphalt cements from two refining sources, produced from different crude petroleum origins. The Greensboro site was selected to provide an asphalt cement from a third refinery source and another crude petroleum origin. The two asphalts used at the Edison plant had relatively high flash points and low volatility while the asphalt used at Greensboro was selected because it had a relatively lower flash point and higher volatility. Asphalts having the lower flash points frequently display more volatility, as indicated by the percent weight loss in the Thin Film Oven Test (1).

23. Table I indicates that the range of non-visible components (ppm by volume) was quite similar for samples taken at both plants. With regard to particulates, the total quantity did not differ greatly between the two plants, but the percentage of benzene solubles in the particulates was somewhat higher at Greensboro than at Edison. This may have been due to more fugitive dust in and around the shrouded space at the Edison plant. The higher percentage and higher quantity of benzene solubles (mg/m^3) found at Greensboro is typical of the lower flash point and higher volatility asphalts. This is further indicated by the comparative front end distillation characteristics of the three asphalt cements shown in Figure D.4, Exhibit D of this report. The amounts of polynuclear aromatics found at Greensboro varied somewhat from those at Edison. However, extremely low concentrations were found at both test sites. The same can be said for metals, which were at extremely low concentrations, if present at all.

OSHA Regulations

24. Table II lists OSHA air contaminant standards along with the maximum of each substance found for the eight samplings. The data clearly indicate that all values are well within OSHA standards and that there

should be no significant air pollution or employee health problems associated with emissions from hot asphalt paving mixes.

25. Non-visible gaseous or volatile components of the asphalt hot-mix emissions, from carbon monoxide through C_{14} hydrocarbons, are all at very low levels and well within limits set forth in OSHA standards. Some of the non-visible components were sampled at the peak of the emission, whereas others were sampled continuously over a 1 or 2 hour sampling period. Since all sampling was done under a shroud, the sampling conditions were highly concentrated and would never be encountered under normal working conditions.

26. Analysis for metals showed that vanadium and nickel, which are typically found in most petroleums, were at extremely low levels in the particulate fractions (benzene solubles) in all samplings. Cadmium and lead, if present, were well below the suggested OSHA limits.

Threshold Limit Values (TLV)

27. Table III lists TLV recommended by the ACGIH (10) and includes a limiting value of 5 mg/m^3 for asphalt (petroleum) fumes, average 8-hour exposure. 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 for the eight samplings, averaging 1.6 mg/m^3. The highest value of 5.4 comes from one of the Greensboro samplings and may be explained partly on the basis that an asphalt of relatively high volatility was involved. The ACGIH explained the recommended TLV of 5 mg/m^3 as based on maintaining good housekeeping while reducing the risk of possible carcinogenicity (11). The ACGIH further reported that inhalation studies indicate that fumes from heated petroleum roofing asphalt did not produce cancers in the lungs of rats and guinea pigs inhaling such fumes for 2 years. Also the Baylor and Weaver (12) study reported no significant differences between the health of asphalt workers and a group of controls. The ACGIH report concludes with the statement "It was the opinion of the industrial hygienists making these surveys that working conditions were satisfactory when asphalt fume levels were kept below 10 mg/m^3."

28. Findings from the samples in this asphalt hot-mix emissions study indicate that total polynuclear aromatics were at an extremely low level compared with even the proposed ACGIH value (see footnote, Table III). Mass spectrometric analyses of both the benzene soluble particulates as well as the dry ice trap condensate from distillation showed that these fractions contained 65 percent or more of saturated hydrocarbons. This distinguishes them further from the carcinogenicity concept of tars and pitches versus asphalt (petroleum) fumes as indicated in the ACGIH report. Contiguous fractions from asphalt indentified as volatile organic compounds (VOC) (Table I) also were found by GC/MS analysis to contain more than 60 percent of saturated type compounds.

29. It is emphasized that the slight amount by which even the total benzene soluble portion of the particulates exceeded the maximum value recommended by ACGIH was determined on the basis of concentrated samples taken in a shrouded area. Such a condition relative to a workman's exposure

certainly is not to be expected under normal field operating conditions. It may therefore be concluded that the occasional excess of asphalt (petroleum) fumes measured under shrouded conditions in this asphalt hot-mix emission study, as compared with the TLV recommended by the ACGIH, will have no detrimental effects on the safety and health of workers in the vicinity.

EPA National Ambient Air Quality Standards and Other Prevailing Emission Standards

30. The national primary and secondary ambient air quality standards promulgated by EPA for six contaminants are shown in Table IV. These standards apply to air contaminant concentrations at or beyond the "fence line." Meteorological conditions and distances of the emission source from the "fence line" are the chief factors in relating source emission concentrations with "fence line" concentrations. The findings based on samples taken under shrouded conditions, at the source, indicate that there should be no problems with respect to meeting these EPA standards.

31. Emission concentrations of 3 to 6 ppm were found for carbon monoxide, less than 0.1 ppm for ozone, less than 0.1 for nitrogen dioxide, 0.4 ppm or less for aldehydes and less than 1 ppm for C_2 to C_6 hydrocarbons. These values are so low (reflecting levels associated with natural background concentrations) that it can be concluded that the hot-mix operation represents no air pollution problem with respect to these contaminants.

32. Sulfur dioxide of less than 2 ppm taken at the peak of visible emission is significantly under the 5ppm average limit for 8 hours as set forth in the OSHA regulation (i. e., hypothetically working in front of a furnace or in a working enclosure). The values found are also significantly low with respect to the most common and most stringent regulation of 500 ppm as suggested for refinery tail gas units or 2000 ppm for other refinery process sources (7).

33. Non-methane hydrocarbons (NMH) in the C_2 to C_6 range were found to be present at a level of less than 1 ppm, based on grab samples taken directly in the emission and during the short period in which the visible emission prevailed. By analysis it was also found that these are predominantly saturated hydrocarbons which are considered to be non-harmful and not responsive to photochemical activity. It should be pointed out again that all grab samples were taken directly in the shrouded emission area which, by all expectations, must be considered to be at a much higher level than conceivably could be found in the surrounding work area or at the fence line or beyond.

34. The Volatile Organic Compounds (VOC) measured here as C_7 to C_{14} at the emission source ranged from 0.5 to 1.5 ppm (3 to 9 mg/m^3), which might be considered in light of EPA ambient quality standards in Table IV listing a limit of 160 μ/m^3 (or 0.24 ppm). Considering an essential one point source emitting VOC at a maximum of 1.5 ppm, it is extremely unlikely that the 0.24 limit would ever be exceeded at a fence line. Furthermore, the standards listed in Table IV for non-methane hydrocarbons are now being considered as guidelines and not as a mandatory standard.

35. A similar situation pertains to particulate emissions. It was found that the total particulates from this source ranged from 0.5 to 7.2 mg/m^3 (500 to 7200 μ/m^3) which is well below the 90 mg/m^3 (90,000 μ/m^3) limit set forth by EPA for new hot-mix asphalt concrete plants (9).

Petroleum Asphalt versus Other Sources of Bitumen

36. Asphalt is sometimes erroneously associated with coal-tar bitumens which are known to contain substantially more polynuclear aromatics. The OSHA regulation is a case in point where petroleum asphalt and coal-tar pitch are classified together. The distinction, however, was dramatically illustrated by the University of Nebraska report (13) which compared asphalts from eight different sources with coal-tar pitches from two sources. The highest benzo(a)pyrene found in any of the asphalts was 0.0027 wt. percent compared with 1.25 wt. percent found in one of the coal-tar pitches. The highest benzo(e)pyrene found in any of the asphalts was 0.0052 wt. percent compared with 0.70 wt. percent in one of the tars. Smith (14) also reported benzo(a)pyrene in a typical coke oven emission benzene solubles at 0.41 wt. percent, whereas Exhibit D indicates a maximum of 0.0005 wt. percent of the same compound in the benzene solubles extracted from particulates gathered during these studies.

37. Another comparison may be made when considering the benzo(a)pyrene content found in the emissions from asphalt hot-mixing, which ranged from 3 to 20 μg/1000 m^3 at the source, and averaged 11 μg/1000m^3. This is significantly lower than that typically found in other sources shown below (15).

Source	μg/1000 m^3 of emitted gas
Refuse burning	11,000
Power station, coal	300
Power station, gas	100
Automotive Diesel	5,000
Coke Oven volatiles	35,000
Home furnace, coal	100,000

CONCLUSIONS

38. Based on the comprehensive analysis of eight sets of asphalt hot-mix emission samples taken under concentrated conditions in shrouded areas, on 4 days at two locations and including four asphalt cements of varying characteristics from three refineries, conclusions are as follows:

(a) There are no significant air pollution or employee health problems associated with emissions from hot asphalt paving mixes.

(b) All gaseous substances and particulates have been identified in emissions from asphalt hot mixes including carbon monoxide, nitrogen dioxide, sulfur compounds, ozone, aldehydes, hydrocarbons and others. They are all at extremely low levels and well within the current OSHA standards and that allowed under National Ambient Air Standards.

(c) The range of Volatile Organic Compounds (VOC) found was 0.5 to 1.5 ppm. The maximum concentration allowed by EPA as a National Ambient Air Standard is 0.24 ppm. Considering that the 1.5 ppm was the maximum found at the source under the concentrated sampling conditions, it is inconceivable that the 0.24 ppm limit would ever be exceeded at the "fence line" under ambient conditions.

(d) The TLV tables of the ACGIH limit asphalt (petroleum) fumes to 5.0 mg/m^3 whereas they were found to range from 0.2 to 5.4 mg/m^3 (averaging 1.6 mg/m^3). It was also shown that the proportion of polynuclear aromatics was extremely low in this fraction and well below 0.2 mg/m^3 required by OSHA and ACGIH for benzene-soluble coal-tar pitch volatiles. Thus there are no employee health hazards in these fumes, especially in view of the concentrated sampling conditions and the highly improbable chance that employees would ever be exposed to such conditions for any meaningful period of time.

(e) The Polynuclear Aromatics (PNA) in emissions from asphalt hot mixes are much lower than those from other common emission sources.

TABLE I

COMPOSITION OF ASPHALT HOT-MIX EMISSIONS

Sample Location	Edison, N. J.	Greensboro, N. C.
Number of Samples	6	2
Non-Visible Components (ppm)		
Carbon monoxide (CO)	4-6	3-4
Nitrogen dioxide (NO_2)	<0.1	.05-.08
Sulfur dioxide (SO_2)	<2	<0.5
Hydrogen sulfide (H_2S)	<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 (ØOH)	<1	<1
Ozone (O_3)	<0.1	---
Methane (CH_4)	2-3	2-3
Non-methane Hydrocarbons (C_2-C_6) (NMH)	<1	<1
Volatile organic compounds (C_7-C_{14}) (VOC)	0.5-1.5	0.5-1.0
Particulates (mg/m^3)		
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.

TABLE II

COMPARISON OF OSHA AIR CONTAMINANT STANDARDS WITH EMISSIONS AT HOT-MIX ASPHALT PLANT

Substance	OSHA STANDARD (Time Weighted Average)	Emissions, Maximum (8 Samplings)
Carbon monoxide, ppm	50	6
Nitrogen dioxide, ppm	5	<0.1
Sulfur dioxide, ppm	5	<2
Hydrogen sulfide, ppm	20 (1)	1.5
Phenol, ppm	5	<1
Ozone, ppm	0.1	<0.1
Hydrocarbons (stoddard solvent), ppm	500	1.5 (3)
Hydrocarbons (benzene), ppm	10	<1 (4)
Polynuclear aromatics (2) (total), mg/m^3	0.2	0.00036
Vanadium V_2O_5 fumes, 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) C_7 - C_{14} Hydrocarbons
(4) C_2 - C_6 Hydrocarbons

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.

TABLE III

COMPARISON OF ACGIH THRESHOLD LIMIT VALUES WITH EMISSIONS AT HOT-MIX ASPHALT PLANT

Substance	Threshold Limit Value (Time Weighted Average)	Emissions, Maximum (8 Samplings)
Carbon monoxide, ppm	50	6
Nitrogen dioxide, ppm	5 (1)	<0.1
Sulfur dioxide, ppm	5	<2
Hydrogen sulfide, ppm	10	1.5
Phenol, ppm	5	<1
Ozone, ppm	0.1	<0.1
Hydrocarbons (stoddard solvent), ppm	100	1.5 (3)
Hydrocarbons (benzene), ppm	10	<1 (4)
Asphalt (petroleum) fumes, mg/m^3	5	5.4 (5)
Polynuclear aromatics (2), (total), mg/m^3	0.2	0.00036
Vanadium (V_2 O_5) as V fumes, mg/m^3	0.05 (1)	<0.0001
Nickel, metal and insoluble compounds (as Ni), mg/m^3	1	0.00004
Cadmium oxide fume (as Cd), mg/m^3	0.05 (1)	<0.00005
Lead, inorganic fumes and dust, mg/m^3	0.15	<0.00005

(1) Ceiling value or acceptable ceiling concentration
(2) Listed as coal-tar pitch volatiles (benzene-soluble fraction)
(3) C_7 - C_{14} Hydrocarbons
(4) C_2 - C_6 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.

TABLE IV

NATIONAL PRIMARY AND SECONDARY AMBIENT AIR QUALITY STANDARDS (EPA) (4)

Air Contaminant	Time Basis	Primary		Secondary	
		μg/m^3	ppm	μg/m^3	ppm
Particulate matter	Annual geometric mean	75		60	
	Max. 24 hr. concentration	260		150	
Sulfur oxides	Annual arithmetic mean	80	0.03		
	Max. 24 hr. concentration	365	0.14		
	Max. 3 hr. concentration			1,300	0.50
Carbon monoxide	Max. 8 hr. concentration	10,000	9.0	10,000	9.0
	Max. 1 hr. concentration	40,000	35.0	40,000	35.0
Photochemical oxidants	Max. 1 hr. concentration	160	0.08	160	0.08
Hydrocarbons, non-methane	Max. 3 hr. concentration	160	0.24	160	0.24
Nitrogen oxides	Annual arithmetic mean	100	0.05	100	0.05

NOTES: Except for particulate matter, annual mean values shall not be exceeded more than once a year

Hydrocarbons, non-methane (gaseous or vaporized) are not considered to be mandatory standards but as guides only

Photochemical oxidants considered to be met if ozone is less than cited value

REFERENCES AND BIBLIOGRAPHY

1. Asphalt As A Material, Information Series No. 93 (IS-93), The Asphalt Institute.

2. Specifications for Paving and Industrial Asphalts, Specification Series No. 2, (SS-2), The Asphalt Institute.

3. Federal Register, Vol. 39, No. 125, Part II, 23502-23828, (June 27,1974).

4. Federal Register, Vol. 36, No. 84, 8186-8201 (April 30, 1971).

5. Federal Register, Vol. 36, No. 105 (May 29, 1971).

6. Federal Register, Vol. 36, No. 158, Appendix B (August 14, 1971).

7. Background Information for Proposed New Source Performance Standards: EPA Vol. 1 & 2, NTIS (June 1973).

8. Federal Register, Vol. 38, No. 111, 15406-15415 (June 11, 1973).

9. Federal Register, Vol. 39, No. 47, Part II 9308-9323 (March 8, 1974).

10. "Threshold Limit Values for Chemical Substances and Physical Agents in Work Room Environments." American Conference of Governmental and Industrial Hygienists (1974).

11. Documentation of Threshold Limit Values, 3rd Edition, ACGIH, (1971).

12. Baylor, C. H. and Weaver, N. K., Archives of Environmental Health, 17, (August 1968).

13. Wellcave, L., Garcia, H., Feldman, R., Lijinsky, W., and Shubik, P., Toxicol, Appl. Pharmacol, 18, 41 (January 1971).

14. Smith, W. M., Yearbook, Am. Iron and Steel Institute, 163-80 (1970).

15. Hangebranck, R. P., von Lehmden, D. J., Meaker, J. E., Sources of Polynuclear Hydrocarbons in the Atmosphere, U. S. Public Health Service Publication No. 999-AP-33 (1967).

16. Los Angeles Air Pollution Control District Rule 66, Promulgated in 1966 and amended in 1973.

17. New Jersey Air Pollution Control Code, Chapter VIII (March 1, 1967).

18. New Jersey Air Pollution Control Code, Chapter 13 (March 5, 1973).

19. Air Pollution Engineering Manual, Chapter 7, 2nd Ed., EPA Office of Air Quality Planning and Standard Research, Research Triangle Park, N. C. (May 1973).

20. Asphalt Plant Manual, Manual Series No. 3 (MS-3), The Asphalt Institute

21. Federal Register, Vol. 38, No. 218, 31388-31400 (November 13, 1973).

22. Particulate Polycyclic Organic Matter, Nat. Academy of Sciences, Washington, D. C. (1972).

23. Petroleum Asphalt and Health, API Med. Res. Report EA 7103 (Dec. 1, 1971).

24. "Tentative Methods of Analysis for Polynuclear Aromatic Hydrocarbons in Coke Oven Effluents," Health Lab. Science, 11, 218-227 (July 1974).

25. Ackerson, D. H. and Southerland, J. H., Compilation of Air Pollutant Emission Factors, (April 1973).

26. Colucci, J. M. and Begeman, C. R., Environmental Science and Technology 5, 145-150 (February 1971).

27. Green, "Particulate Clouds: Dusts, Smokes and Mists," (1974).

28. Golz, H. H., Am. Petroleum Institute Letter, October 1973 to John Stender, OSHA.

29. Magee, E. M., Hall, H. J. and Varga, G. M., "Potential Pollutants in Fossil Fuels," EPA-R2-73-249 (June 1973).

30. Mole, P. J., Total Environmental Control of a Modern Asphalt Batching Plant, 66th Annual Meeting of the Air Pollution Control Association (June 1973).

31. Sanderson, H. P., "Analysis of Pollutants Emitted from Asphalt Plants," u. g. Minn. Thesis (1969).

32. Von Lehmden, D. J, Hangebranck, R. P. and Meaker, J. E., Jr. Polynuclear Hydrocarbon Emissions From Selected Industrial Processes, Air Pollution Control Association, 15 306 (July 1965).

EXHIBIT A

ASPHALT HOT-MIX
EMISSION STUDY

PLANT, SAMPLING PROGRAM AND MATERIALS

EDISON, N.J. PLANT

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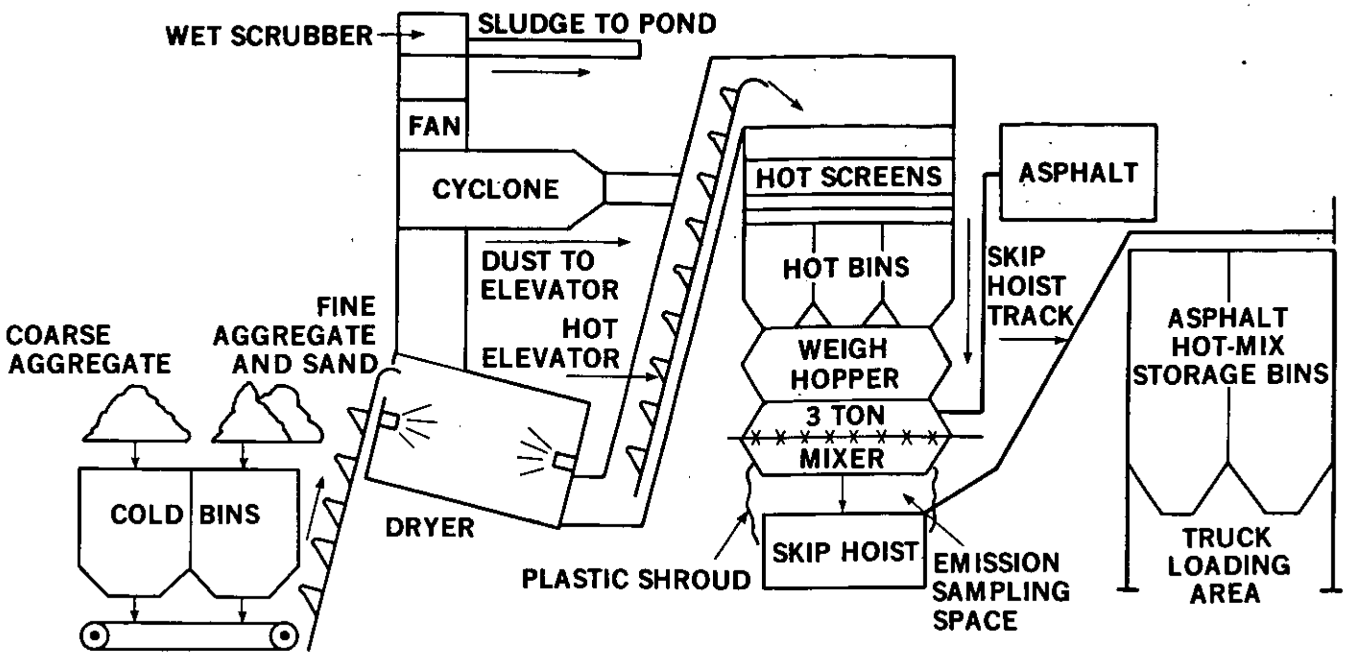

Figure A1. Schematic Diagram-- Asphalt Hot-Mix Plant Flow Chart

EXHIBIT A

ASPHALT HOT-MIX PLANT

A1. The Asphalt Hot-Mix Emission Study was initiated at an asphalt hot-mix plant of the Edison Asphalt Corporation (Halecrest Company) located on Talmage Road in Edison, New Jersey. The plant site included three hot-mix plants: (1) Pioneer continuous mix plant of 220 to 260 tons per hour capacity; (2) Barber-Greene batch plant of 3-ton pugmill capacity, and (3) McCarter batch plant of 3-ton pugmill capacity. During most of the sampling time at least two plants were in operation. Only occasionally were all three plants active.

A2. The McCarter plant, equipped with a burner on each end of the dryer, was selected for this first phase of the study. In this plant, the paving mixture could be discharged either directly into a transport truck or into a skip-hoist. The skip-hoist transported and deposited the mixture into hot storage or surge bins. Figure A1 is a schematic diagram of the plant indicating the flow of materials through the plant and into the asphalt hot-mix storage bins. It also indicates the sampling area which was enclosed with a plastic shroud during most of the sampling periods. Purpose of the shroud was to concentrate the emission samples, prevent the inclusion of extraneous materials in the samples and eliminate effects of cross-wind variables on emission sampling. Figures A2 through A7 are photographs of the plant, various plant components and sampling equipment in various operational stages.

A3. The skip-hoist afforded several advantages in sampling the asphalt 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 the vapors originating from oil used to coat truck beds was avoided. The skip-hoist structure permitted construction of a platform for placement of the equipment used for sampling the asphalt emissions. With continual truck traffic it would have been more difficult to maintain and operate these sampling devices. The arrangement facilitated shrouding of the sampling area, providing the benefits noted above.

A4. The nominal mixing cycle for each 3-ton batch was one minute. Approximately 15 seconds were scheduled for the weighing and dry mixing of mineral aggregates and the remaining 45 seconds for the introduction of asphalt cement, wet mixing and mixture discharge from the pugmill. However, because of interruptions in the flow of materials or plant operation, 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 from the pugmill the asphalt emissions were visible immediately after the mixture hit the bottom of the skip-hoist and they lingered for only a couple of seconds after the discharge was completed.

A5. The plant operation and mixture preparation procedures described above are considered typical of many asphalt hot-mix plants throughout the U. S.

EMISSION SAMPLING PROGRAM

A6. Six complete sets of emission samples were obtained, two on each of 3 days. During the first sampling day (Samplings 1 and 2 on September 25, 1973) the sampling space below the pugmill and above the skip-hoist was unenclosed, as is normal in such 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 sheet on all four sides (see Figures A6 and A7). The partially enclosed sampling space measured about 10 feet by 10 feet by 5 feet high. Thus, a total of approximately 500 cubic feet was enclosed by the shroud.

A7. During emission sampling, wind velocity, humidity, temperature of the mixture and various other factors were measured. This information is summarized in Table A.I. Measurement of mixture temperature was accomplished by an infra-red electronic thermometer aimed at the mixture being discharged into the skip-hoist. Generally, temperatures measured by this method agreed rather well with occasional measurements made with bimetallic dial thermometers.

A8. It should be noted that there were appreciable variations in the duration of the individual samplings, the amount of mixture produced during each sampling, the mixture temperature and other factors. While these variations probably influenced emission test results to some extent, an accurate assessment of the effects of such variations was neither possible nor intended.

MATERIALS

Asphalt Cements

A9. The Exxon Company supplied the asphalt cement used in mixes for the first two samplings. For the remaining four samplings, asphalt cement from Chevron Asphalt Company was used. The Exxon asphalt was refined from mixed pipeline crudes and the Chevron asphalt from Middle-East and Venezuelan crude blends. However, there are differences in a few of the physical properties of Chevron asphalts sampled on the two dates. Samples of the asphalt cements for detailed laboratory analyses were taken at the time of the emission samplings. Table A.II includes comprehensive test properties of the three asphalt cements used in this project. Inspection of the data indicates only marginal differences between these materials. All three asphalts complied with the requirements for the AC-20 grade for asphalt cement in Tables 1 and 2 of Specification M 226, American Association of State Highway and Transportation Officials (AASHTO). Temperature susceptibilities, heat stabilities, and sensitivity to shear at low temperatures (77°F) are considered about average for AC-20 asphalt cements.

Mineral Aggregates

A11. Four types of mineral aggregate were used to prepare base and surface course mixtures complying either with Pennsylvania Turnpike Authority or New Jersey Highway Department requirements. The coarse aggregate for the base course mixture was granite-gneiss from a Glen Gardner, N. J., quarry. The coarse aggregate for the surface course was a basaltic traprock from a Bound Brook, N. J. quarry. Stone screenings from the Glen Gardner quarry and silicious sand from South Amboy constituted the fine aggregates for both base and surface course mixtures. No mineral filler (passing U.S. Std. Sieve No. 200) was added to either mix, because the stone screenings contained an amount of fines sufficient to comply with filler requirements of the job-mix formula.

A12. Table A.III lists pertinent properties for mineral aggregates sampled during the 3 sampling days. These data indicate variations in test properties for any given aggregate. These variations, however, are normal for mineral aggregates used to prepare hot-mix asphalt paving mixtures.

Paving Mixes

A13. Samples of paving mixtures were taken immediately after discharge from the pugmill during all 3 sampling days. During the first sampling period (Samplings 1 and 2) base and surface mixtures were prepared and single samples of both mixtures were obtained. The asphalt cement and aggregates were later separated in the laboratory by a standard extraction process. Asphalt contents and properties of asphalts and mineral aggregates derived from these mixtures are summarized in Table A.IV. During the second and third sampling periods only base course mixtures were prepared. Multiple samples were obtained during these periods to determine variability in the mixtures. During the second sampling period seven samples were obtained, and during the third period eleven samples were secured. Data for these samples are presented in Tables A.V and A.VI.

A14. Appreciable variation in asphalt content and in the properties of recovered asphalts and mineral aggregates are shown in Tables A.IV, A.V. and A.VI. This variation is evident not only for samples taken during different sampling periods but also for samples within a given sampling period. For example, average asphalt contents for a base mix varied between 5.0 and 5.4 percent. On the other hand, asphalt content for mix samples obtained during the third sampling period (Table A.VI) varied between 4.24 and 5.54 percent. Viscosities at 140°F for asphalts recovered from samples obtained during the third sampling period varied between approximately 2200 and 3400 poises. Extraction error, asphalt content and mixture temperature are among the factors causing variations in the properties of the recovered asphalts.

A15. Variations in test properties shown in Table A.IV, A.V and A.VI are typical of those found in asphalt hot-mix plant operations. Thus, the results of these emission studies should be considered as representative and indicative of results to be expected at other asphalt hot-mix plants using similar asphalt cement.

TABLE A.I

EMISSION SAMPLING CONDITIONS

SAMPLE NO.	1	2	3	4	5	6
DATE	9-25-73	9-25-73	10-2-73	10-2-73	11-20-73	11-20-73
TIME	7:53 AM to 10:00 AM	10:10 AM to 12:28 PM	7:30 AM to 8:40 AM	8:47 AM to 9:44 AM	12:01 PM to 1:07 PM	1:24 PM to 2:44 PM
DURATION OF SAMPLING, MIN	127	138	70	57	66	80
NUMBER OF BATCHES	96	90	60	50	60	60
TONNAGE OF MIX	279	270	180	150	180	180
ASPHALT CEMENT (AC-20)	Exxon	Exxon	Chevron	Chevron	Chevron	Chevron
MIXTURE TEMP. RANGE, °F	280-336	250-312	295-312	297-305	300-326	301-342
AMBIENT TEMP., °F	60	62	66	65	50	51
WEATHER CONDITIONS	Partly Cloudy	Partly Cloudy	Overcast	Overcast-Misty	Sunny	Sunny
WIND VELOCITY, mph	3 to 8.5	Approx. 3.0	Approx. 3.0	Calm	Gusty	Gusty
SAMPLING AREA	Open	Open	Partially Enclosed	Partially Enclosed	Partially Enclosed	Partially Enclosed

TABLE A.II

PROPERTIES OF ASPHALT CEMENTS

SAMPLING NUMBER	1 & 2	3 & 4	5 & 6
ASPHALT SOURCE	**Exxon**	**Chevron**	**Chevron**
ORIGINAL ASPHALT			
VISCOSITY			
140°F, poises	2000	1678	1849
275°F, cS	394	387	409
77°F, mP at 0.05 s^{-1}	1.60	1.65	1.60
TEMPERATURE SUSCEPTIBILITY			
275°F - 140°F	3.558	3.500	3.490
SHEAR SUSCEPTIBILITY			
0.1 s^{-1} - 0.01 s^{-1}	0.014	0.065	0.074
DUCTILITY, cm			
77°F, 5 cm/min	150+	150+	150+
39.2°F, 1 cm/min	12.75	7.75	11.10
PENETRATION, 0.1 mm			
77°F, 5 s, 100 g	72	70	69
FLASH POINT, COC, °F	610	605	605
SOLUBILITY			
Trichloroethylene, percent	99.99	99.94	99.95
SPECIFIC GRAVITY, 77°F	1.019	1.022	1.026
ASH, PERCENT	0.12	0.15	0.12
THIN FILM OVEN TEST (TFOT) RESIDUE			
WEIGHT LOSS, PERCENT	-0.104	-0.056	-0.053
VISCOSITY			
140°F, poises	4454	3660	4253
275°F, cS	565	531	607
$\frac{\text{VISC. AT 140}^{\circ}\text{F AFTER TFOT}}{\text{VISC. AT 140}^{\circ}\text{F BEFORE TFOT}}$	2.23	2.18	2.30
DUCTILITY, cm			
77°F, 5 cm/min	150+	150+	150+
PENETRATION, 0.1 mm			
77°F, 5 s, 100 g	45	46	43
Pen. retained, percent	62.5	65.7	62.4

TABLE A.III

PROPERTIES OF MINERAL AGGREGATES

AGGREGATE TYPE	COARSE AGGREGATE				SCREENINGS			SAND		
COURSE	Base	Base	Base	Surf.	Surf. & Base	Base	Base	Surf. & Base	Base	Base
SAMPLING NUMBER	1 & 2	3 & 4	5 & 6	1 & 2	1 & 2	3 & 4	5 & 6	1 & 2	3 & 4	5 & 6
AGGREGATE GRADATION										
SIEVE SIZE					Percent Passing					
1"	100.0	100.0	100.0							
3/4"	80.0	69.4	87.4							
1/2"	33.0	22.7	45.6	100.0						
3/8"	9.5	6.4	21.9	95.6	100.0	100.0	100.0			
No. 4	2.5	3.0	7.3	40.8	94.7	91.3	94.2	100.0	100.0	100.0
No. 8	2.1	2.5	4.4	13.5	73.1	68.0	69.8	99.9	96.7	99.1
No. 16	2.0	2.2	3.7	7.3	53.4	47.5	49.8	99.5	91.2	97.1
No. 30	1.9	1.9	3.2	5.6	38.3	33.1	33.5	96.3	78.4	89.6
No. 50	1.8	1.7	2.4	5.0	26.6	23.3	22.2	57.9	42.7	55.3
No. 100	1.4	1.3	1.7	4.2	16.0	14.5	13.2	13.6	11.1	9.0
No. 200	1.1	1.0	1.3	3.5	10.3	9.8	8.4	5.7	6.5	2.6
SPECIFIC GRAVITY										
APPARENT										
Ret. Sieve No. 4	2.716	2.771	2.925	3.016						
Pass Sieve No. 4	---	---	---	3.014	2.887	2.792	2.839	2.664	2.657	2.659
BULK										
Ret. Sieve No. 4	2.678	2.733	2.811	2.912						
Pass Sieve No. 4	---	---	---	2.838	2.859	2.745	2.812	2.624	2.612	2.645
WATER ABSORPTION, PERCENT										
Ret. Sieve No. 4	0.6	0.5	1.4	1.2	---	---	---	---	---	---
Pass Sieve No. 4	---	---	---	2.1	0.4	0.6	0.4	0.6	0.7	0.2

TABLE A.IV

PROPERTIES OF RECOVERED ASPHALTS AND AGGREGATES*

COURSE	Base	Surface
DATE RECOVERED	10-5-73	10-4-73
GRADATION OF RECOVERED AGGREGATE		
SIEVE SIZE	PERCENT PASSING	
1"	100.0	---
3/4"	86.5	---
1/2"	77.6	100.0
3/8"	67.0	98.9
No. 4	49.6	73.6
No. 8	41.1	50.9
No. 16	35.0	42.6
No. 30	30.0	36.2
No. 50	19.4	23.7
No. 100	8.3	10.2
No. 200	5.7	7.0
ASPHALT CONTENT, WT. PERCENT	5.23	5.52
PROPERTIES OF RECOVERED ASPHALT		
VISCOSITY		
140°F, poises	2732	3232
275°F, cS	476	484
PENETRATION		
77°F, 5 s, 100 g	66	59
ASH, WT. PERCENT	1.02	1.01

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*Recovered from asphalt paving mixes prepared on September 25, 1973 during emission samplings Nos. 1 and 2.

TABLE A.V

PROPERTIES OF RECOVERED ASPHALTS AND AGGREGATES*

COURSE	Base	Base	Base	Base	Base	Base	Base
DATE RECOVERED	10-24-73	10-25-73	10-26-73	10-29-73	10-30-73	11-1-73	11-2-73
GRADATION OF RECOVERED AGGREGATE							
SIEVE SIZE				PERCENT PASSING			
1"	100.0	100.0	100.0	100.0	100.0	100.0	100.0
3/4"	91.4	94.9	92.7	97.2	90.8	88.0	94.5
1/2"	76.9	88.4	80.5	85.8	82.0	74.9	78.9
3/8"	69.5	84.0	73.1	76.4	72.3	68.4	72.7
No. 4	56.9	74.9	61.1	64.1	59.8	58.2	59.7
No. 8	47.1	61.8	49.5	52.6	48.6	44.8	50.5
No. 16	37.5	53.5	41.9	43.3	37.2	36.2	44.0
No. 30	30.2	45.3	32.9	33.7	26.2	29.2	37.1
No. 50	19.3	26.5	19.3	19.4	15.4	19.1	22.0
No. 100	9.2	9.3	7.7	7.6	7.3	10.4	7.9
No. 200	6.9	5.9	4.4	4.6	4.6	8.5	4.5
ASPHALT CONTENT, WT. PERCENT	5.12	5.95	5.62	5.75	5.65	5.15	5.41
PROPERTIES OF RECOVERED ASPHALT							
VISCOSITY							
140°F, poises	2724	2265	2232	2104	2123	2191	2411
275°F, cS	484	440	445	431	432	426	460
PENETRATION							
77°F, 5 s, 100 g	56	62	62	65	63	63	62
ASH, WT PERCENT	1.21	1.19	0.81	0.83	0.48	0.99	0.94

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*Recovered from asphalt paving mixes prepared on October 2, 1973, during emission samplings Nos. 3 and 4.

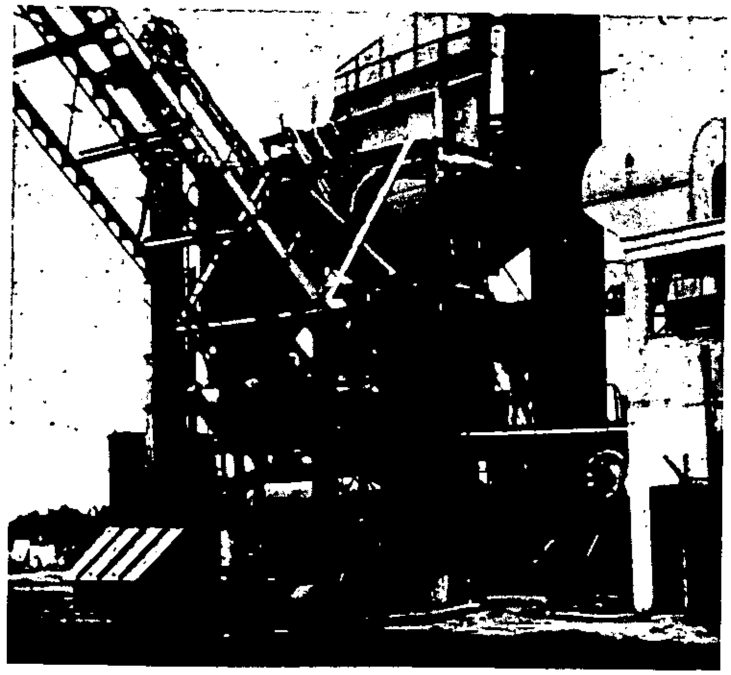

Figure A2. Edison Asphalt Plant

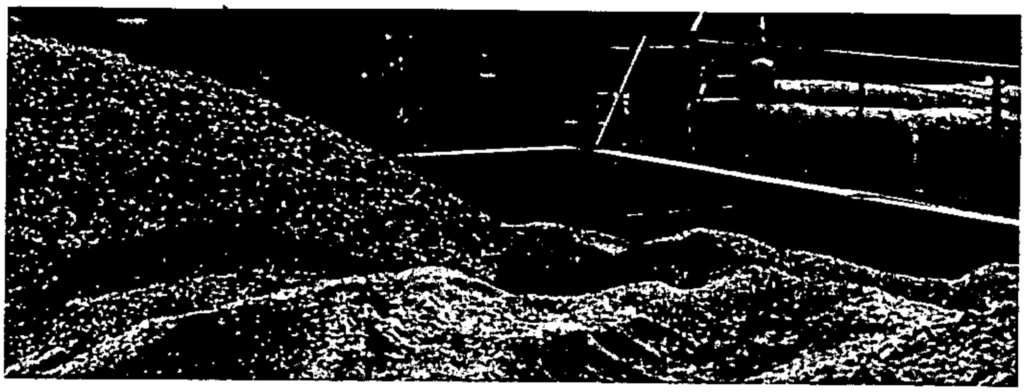

Figure A3. Mineral Aggregate Stock Piles

Figure A4. Discharge of Paving Mixture to Skip Hoist

TABLE A.VI

PROPERTIES OF RECOVERED ASPHALTS AND AGGREGATES*

COURSE	Base	Base	Base	Base	Base	Base
DATE RECOVERED	1-15-74	11-27-73	11-28-73	11-29-73	11-30-73	12-3-73
GRADATION OF RECOVERED AGGREGATE						
SIEVE SIZE			PERCENT PASSING			
1"	100.0	100.0	100.0	100.0	100.0	100.0
3/4"	91.1	93.6	80.5	97.4	93.9	88.5
1/2"	68.8	84.7	69.0	82.4	84.6	82.1
3/8"	59.6	76.0	62.6	74.9	74.7	71.5
No. 4	45.8	57.6	48.0	59.4	57.0	53.5
No. 8	35.9	43.9	39.1	45.8	43.5	42.2
No. 16	31.2	38.8	34.2	38.5	36.7	35.4
No. 30	26.9	33.5	29.4	32.6	31.1	29.8
No. 50	17.9	20.4	18.7	21.6	20.8	20.3
No. 100	6.7	6.4	6.2	7.4	7.1	8.0
No. 200	3.8	3.5	3.4	4.0	4.2	5.0
ASPHALT CONTENT, WT. PERCENT	4.24	5.39	4.57	5.31	5.04	5.25
PROPERTIES OF RECOVERED ASPHALT						
VISCOSITY						
140°F, poises	3381	2603	2164	3078	2851	2737
275°F, cS	603	468	441	535	588	522
PENETRATION						
77°F, 5 s, 100 g	50	61	62	57	60	64
ASH, WT. PERCENT	1.11	0.5	0.5	0.6	0.7	0.6

(continued)

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*Recovered from asphalt paving mixes prepared on November 20, 1973, during emission samplings Nos. 5 and 6.

TABLE A.VI (continued)

PROPERTIES OF RECOVERED ASPHALTS AND AGGREGATES*

COURSE	Base	Base	Base	Base	Base
DATE RECOVERED	12-6-73	12-7-73	12-10-73	12-12-73	12-13-73
GRADATION OF RECOVERED AGGREGATE					
SIEVE SIZE			PERCENT PASSING		
1"	100.0	100.0	100.0	100.0	100.0
3/4"	89.6	96.1	97.1	95.3	91.7
1/2"	76.9	81.6	84.6	81.5	73.7
3/8"	69.5	74.9	80.8	73.3	64.5
No. 4	54.2	54.3	66.2	57.1	49.7
No. 8	45.1	43.7	60.3	49.2	39.2
No. 16	38.9	38.0	53.3	44.4	34.0
No. 30	33.2	33.2	45.5	38.8	29.3
No. 50	21.5	22.6	30.3	25.5	20.4
No. 100	6.6	7.6	9.7	7.5	7.3
No. 200	3.6	4.6	6.3	3.9	4.4
ASPHALT CONTENT, WT. PERCENT	5.04	5.52	4.92	5.44	4.54
PROPERTIES OF RECOVERED ASPHALT					
VISCOSITY					
140^{o}F, poises	3403	2420	2540	3278	3085
275^{o}F, cS	517	497	498	543	511
PENETRATION					
77^{o}F, 5 s, 100 g	55	67	65	55	57
ASH, WT. PERCENT	0.6	0.7	1.4	0.9	0.9

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*Recovered from asphalt paving mixes prepared on November 20, 1973, during emission samplings Nos. 5 and 6.

Figure A5. Transport of Mixture to Surge Bins

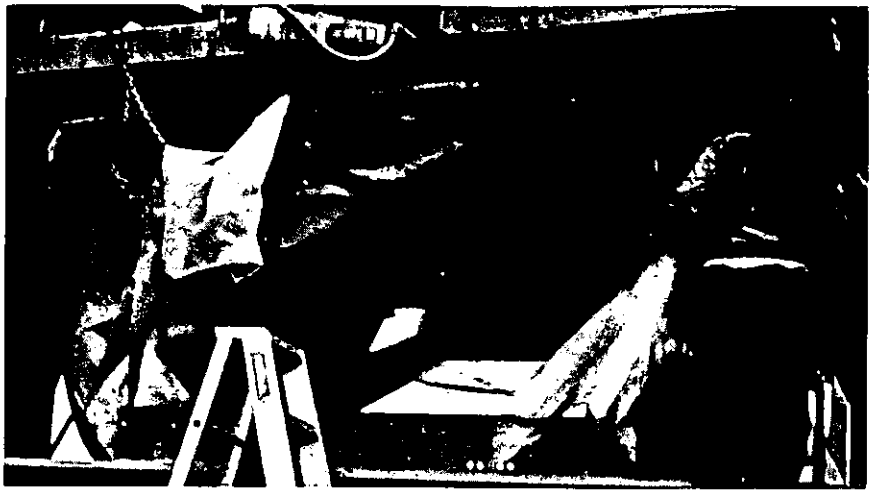

Figure A6. Placing Plastic Shroud

Figure A7. Enclosed Sampling Space

EXHIBIT B

ASPHALT HOT-MIX EMISSION STUDY

SAMPLING AND ANALYSIS OF EMISSIONS

EDISON, N.J. PLANT

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For submission to The Asphalt Institute

Report No. AID.1DJX.74
March 1, 1974

EXHIBIT B

SUMMARY

The "Blue Smoke" emissions coming from an asphalt hot pugmill were sampled, analyzed and the principal components identified. Samples were collected on four different days between the end of August and the middle of November, 1973. Standard methods were used to measure most of the components but extensive instrumentation and "Inhouse" technique was needed for others and for characterization purposes.

The principal constituents are hydrocarbons ranging from C_7 through C_{32}. These hydrocarbons are similar to those normally present in crude petroleum up to and through the light gas oil range. They appear to come from a very small distillable fraction of asphalt. The hydrocarbons measured in the various testing periods appeared similar even though the asphalts were manufactured from two different crude sources. The polynuclear aromatic hydrocarbons are low compared to those reported for other similar industrial processes. More significant, perhaps, is that for the two asphalt sources involved, the average concentration of benzo(a)pyrene (11 μg/1000 m^3 air) was just slightly more than a range of 1.18-7.49 μg/1000 m^3 reported for urban air(1).

The gas and particulate phase were sampled as they occurred in the immediate vicinity of asphalt hot pug mill mixing. During sampling, the skip ran between the sampling location and the top of the storage silo. For many of the more volatile components, grab samples were taken only when the Blue Smoke was at maximum intensity. The remainder were sampled continuously for one hour or more covering both maximum and minimum intensities. The concentration ranges found, and a composite analysis of the benzene soluble portion of the particulates are presented in the summary tables.

A special method, developed during the program, employed carbon tetrachloride and infrared spectroscopy to absorb and measure the C_7 to C_{14} hydrocarbons might prove of value in other areas as well as in further studies of this nature. There is, at present, no standard method for quantitatively measuring materials in this boiling range.

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(1) "Biological Effects of Atmospheric Pollutants, Particulate Polycyclic Organic Matter" p. 47 by Committee on Biological Effects of Atmospheric Pollutants, National Academy of Science, Washington, D.C., 1972.

TABLE B.I

CONCENTRATION RANGE FOR COMPONENTS

Compound	Formula	Range ppm, vol.	Comments
Methane	CH_4	2-3	Grab Sample
C_2-C_6 Hydrocarbons	CxHy	<1	Grab Sample
Hydrogen Sulfide	H_2S	<0.2 - 1.5*	Grab Sample
Carbonyl Sulfide	CO_S	<0.2	Grab Sample
Mercaptans	RSH	<0.2*	Grab Sample
Sulfur Dioxide	SO_2	<2.●	Grab Sample
Carbon Monoxide	CO	4-6	Grab Sample
Aldehydes	RCO	<0.1	Continuous Sample
Phenols	ϕOH	<1.	Continuous Sample
Ozone	O_3	<0.1	Continuous Sample
Nitrogen Dioxide	NO_2	<0.1	Continuous Sample
		mgs/m^3	
C_7-C_{14} Hydrocarbons		3-9	Continuous Sample
High Volume Sample			Continuous Sample
Total Particulates			
Test 1, 2		2.6 - 6.4	Open Platform
Test 3, 4		2.6 - 3.3	Shrouded Platform
Test 5, 6		6.0 - 7.2	Shrouded Platform Hi Vol. Position Changed
Benzene Soluble			
Test 1, 2		0.3 - 0.5	
Test 3, 4		0.7 - 0.9	
Test 5, 6		1.8 - 2.8	
		$micrograms/1000m^3$	
Pyrene	$C_{16}H_{10}$	44 - 240, 107 avg.	
Benz(a) anthracene	$C_{18}H_{12}$	5 - 24, 11 avg.	
Benzo(a)pyrene	$C_{20}H_{12}$	3 - 20, 11 avg.	
Benzo(e)pyrene	$C_{20}H_{12}$	14 - 40, 26 avg.	
Perylene	$C_{20}H_{12}$	5 - 16, 12 avg.	
		$micrograms/m^3$	
Nickel	Ni	0.005	
Vanadium	V	0.02 -0.08	

● Not detected by odor.

TABLE B.II

COMPOSITE ANALYSIS OF THE BENZENE SOLUBLE PORTION OF THE PARTICULATES

Physical Appearance	Brown, low viscosity oil
Infrared Spectroscopy	Aromatic oil, somewhat oxidized
Gas Chromatograpny	
Boiling Range, °F	530 - 980
n-paraffin distribution	C_{16} - C_{32}
Mass Spectrometry	
Paraffins, %	28
Cycloparaffins	
1-ring, %	11
2-ring, %	11
3-ring, %	18
Aromatics	
1-ring, %	10
2-ring, %	10
3-ring, %	6
Sulfur Aromatics, %	6
Elemental Analysis	
Carbon, % C	85.3
Hydrogen, % H	12.0
Sulfur, % S	1.8
Nitrogen, % N	0.07
C/H Ratio	7.1

INTRODUCTION

In July, 1973, The Asphalt Institute contracted with the Analytical and Information Division of Esso Research and Engineering Company to sample and analyze for common organic and particulate pollutants in the immediate vicinity of asphalt hot pug mill mixing. The emission aroung a pug mill is commonly called Blue Smoke. Sampling was done at the Halecrest Asphalt plant in Edison, N. J.

In the study, six sets of samples were collected on three different days: September 25, October 2, and November 20, 1973. A shroud was used in sampling on the latter two days. Commonly used methods of our laboratory (including ASTM standard methods) were applied to these samples to measure pollutants, such as: volatile hydrocarbons, carbon monoxide, volatile sulfur compounds, nitrogen dioxide, aldehydes, phenols, ozone, metals, total particulates, benzene solubles and polynuclear aromatic (PNA) hydrocarbons.

The organic nature of the particulates was also studied based on examination by gas chromatograph, mass spectrometer, infrared and an ultraviolet absorption spectrophotometer.

SAMPLING AND ANALYSIS

In order to achieve the objective of this study, a variety of sampling and analytical procedures were required. Some of the volatile compounds had to be collected in evacuated metal bombs, whereas, to successfully analyze for sulfur compounds, glass bombs were utilized to avoid decomposition on metal side walls. Many of the organics were collected in chemical bubblers. Particulates were collected on glass fiber filters in High Volume Samplers as described in the Federal Register. In order to provide a comprehensive guide as to the methods employed in this study, Table B.III lists the chemical components that were measured, the method of sampling, and a reference to the method of analysis. Some additional detail on the procedure is presented further on in this section. Ambient air in the vicinity of the plant was not examined because the plant was considered a source and background values would be insignificant.

In operation, the pug mill gives off Blue Smoke on an intermittent basis. Continuous sampling over a period of one or two hours, therefore, provides a composite sample of Blue Smoke and no Blue Smoke. Samples collected in evacuated bombs, on the other hand, were generally taken during the height of a plume.

The sampling equipment was placed on a 3 by 8 foot steel platform that was constructed immediately beneath the pug mill. The edge of the platform just touched the skip as it was being loaded with the hot asphalt. Photographs of the sampling platform and equipment are presented in Figures B1 - B3.

In order to assess the sampling and analytical methods, a trial run was carried out in which all samples were analyzed by the intended methods. This trial run indicated that the methods were generally satisfactory. Some minor changes in procedure were suggested, however, and these were put into practice. Table B.IV summarizes the pertinent sample collection information. It will be noted that a shroud was used for tests 3 - 6 to shroud the sampling area around the pug mill. The volume enclosed by the shroud was 500 cu ft.

TABLE B.III

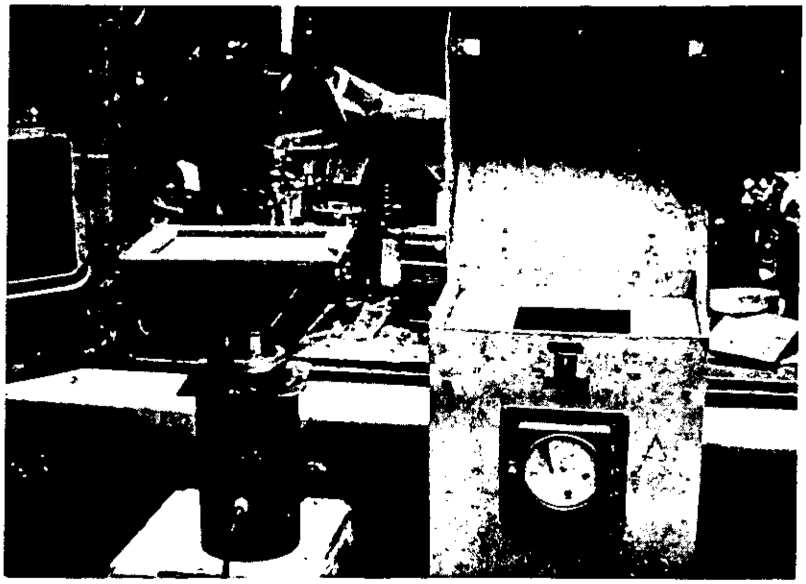
SUMMARY OF SAMPLING AND ANALYTICAL METHODS

Component	Sample Collection	Method of Analysis
Air	300 ml bomb	ASTM D 2650-68T., "Method of Test for Chemical Composition of Gases by Mass Spectrometry."
Volatile Hydrocarbons	10 liter bomb	E. E. Wigg, R. J. Campion, and William L. Petersen, "The Effect of Fuel Hydrocarbon Composition on Exhaust Hydrocarbons and Oxygenates Emissions", SAE Paper #720251. Presented at Auto Eng. Congress, Detroit, Mich. (Jan. 1972).
C_7-C_{14} Hydrocarbons	CCl_4 trap	R. G. Simard, I. Hasegawa, W. Bandaruk, and C. E. Headington, Anal. Chem. 23, 1384 (1951).
Carbon Monoxide	10 liter bomb	Federal Register, Vol. 36 #84 Part 2, April 30, 1971.
Volatile Sulfur Compounds	250 ml glass sample tubes	D. F. Adams and R. K. Koppe, Tappi, 42, 601 (1959) S. S. Brody and J. E. Chaney, J. of Gas Chromatography, 4, 42,(1966). F. V. Wilby, Am. Gas Assoc. Oper. Sect. Proc., Year 1965 Pages 65-136.
Nitrogen Dioxide	Chemical bubbler	ASTM D 1607-69, "Standard Method of Test for Nitrogen Dioxide Content of Atmosphere (Griess-Saltzman Reaction)."
Aldehydes	Chemical bubbler	L. A. Jones, J. C. Holmes and R. B. Seligman, Anal. Chem. 28, 199 (1956).
Phenols	Chemical bubbler	A. S. Wexler, Anal. Chem. 35, 1936 (1963).
Ozone	Chemical bubbler	ASTM D 1609-60, "Standard Method of Test for Oxidant (Ozone) Content of the Atmosphere."
Particulates	High Volume Sampler	Code of Federal Regulations, Title 40, Appendix B, Environmental Protection Agency, U. S. Federal Register Office, "Reference Method for the Determination of Suspended Particles in the Atmosphere (High Volume Method)."
Benzene Solubles	--	E. C. Tabor and D. H. Fair, J. Air Pollution Control Assoc., 11, 403 (1961)

TABLE B.III (continued)

Component	Sample Collection	Method of Analysis
Particulates (Continued)		
Polynuclear Aromatic Hydrocarbons	--	R. A. Brown, T. D. Searl, W. H. King, Jr., W. A. Dietz, and J. M. Kelliher, "Rapid Methods of Analysis for Trace Quantities of Polynuclear Aromatic Hydrocarbons and Phenols in Automobile Exhaust, Gasoline and Crankcase Oil". U. S. Nat'l Tech. Inform. Serv. PB Rep. Issue No. 219025/4 Year 1971, Page 56 pp. (Method will be published in Manual of Intersociety Methods, vol. 2 (1974).
Hydrocarbons	--	ASTM D 2887-72T "Boiling Range Distribution of Petroleum Fractions by Gas Chromatography." W. A. Dietz, P. K. Starnes, and R. A. Brown, "Wax Analysis, Gas Chromatography." Petroleum Waxes: Characterization, Performance and Additives, Special Technical Association Publication No. 2 (ASTM-TAPPI, 1963). A. Hood and M. J. O'Neal, Advances in Mass Spectrometry, Waldron, p. 175 (1959). M. E. Fitzgerald, V. A. Cirillo, and F. J. Galbraith, Anal Chem. 34, 1276 (1962).
Carbon, Hydrogen, Nitrogen	--	R. D. Condon, Microchem. J. 10,408, 1966. R. Culmo, Mikrochim. Acta Year 1969, 175.
Nickel, Vanadium	--	J. Hansen and C. R. Hodgkins, Anal. Chem. 30, 368 (1958).

Figure Bl



COMPONENTS OF HIGH VOLUME SAMPLER

HIGH VOLUME SAMPLERS IN PLACE

Figure B2

SAMPLING PLATFORM ENCLOSED WITH SHROUD

WORKING UNDER THE SHROUD

Figure B3

DISCHARGE OF MIX INTO SKIP HOIST

SKIP HOIST IN RECEIVING POSITION UNDER SHROUD

TABLE B.IV

SAMPLE COLLECTION AT HOT PUGMILL IN 1973

Date	Test No.	Air Temp. (°F)	Shroud	Asphalt Being Processed
Aug. 31	Trial	95	No	A
Sept. 25	1, 2	68	No	A
Oct. 2	3, 4	60	Yes	B
Nov. 20	5, 6	58	Yes	B

Air

To sample; small stainless steel bombs were evacuated at the time of the test and then thrust into the plume and opened. The concentration of air was measured on a Dupont Model #21-103 mass spectrometer.

Volatile Hydrocarbons (C_1-C_6)

Samples were collected in 10-liter stainless steel pressure vessels. To accomplish this, the vessels were evacuated to 0.02 millimeters of mercury in the laboratory. In tests 1 to 4 the vessels were opened wide as the asphalt dropped from the pug mill to the skip. In tests 5 and 6, however, the valves were opened slightly to allow sample to enter over a 15 minute period.

Samples of this type were analyzed for C_2-C_6 hydrocarbons using a combination of two GC measurements, as shown in Table B.V.

TABLE B.V

MEASUREMENT OF VOLATILE HYDROCARBONS

	$C_1 - C_2$	$C_2 - C_6$
Sample Size	2 ml	5 - 25 ml
Column	Packed - Porapak Q & T	DC-200 Coated Open Tubular
	Length - 15 cm	Length - 97 meters
	O.D. - 0.32 cm	I.D. - .025 cm
Temp. Program	0° to $130^{\circ}C$	-70° to $130^{\circ}C$

C_7-C_{14} Hydrocarbons

Another measurement of hydrocarbons was obtained in which a carbon number range of C_7-C_{14} was observed. These hydrocarbons were removed by passing the air from the sample area at 15 liters per minute through two chilled carbon tetrachloride impingers (300 ml size). The trapped hydrocarbons in each impinger were measured by infrared. The impingers appeared to be quite efficient in as much as, in each test the first impinger contained eighty percent of the total hydrocarbons that were trapped.

After the IR measurement the solution was evaporated in a small glass still to about 0.5 ml. A portion of this solution was analyzed by gas chromatograph. The gas chromatographic procedure was the same one used to examine hydrocarbons in the organic particulates as listed in Table B.III. Contents of a different impinger were analyzed for total saturate hydrocarbons by a GC/MS measurement.

Carbon Monoxide

For the carbon monoxide measurement, samples were taken from the same 10 liter bombs used for volatile hydrocarbons. A Hilger-Watts Model SC/LC nondispersive infrared (NDIR) analyzer measured CO with a sensitivity of 1 ppm (gas vol.).

Volatile Sulfur Compounds

The sulfur compounds were sampled with 250-ml glass, gas sampling tubes. These were cleaned and thoroughly dried in the laboratory. At the plant each one was evacuated and immediately carried to the testing area. When the vapors arose from the skip, the tube was put in the midst of the smoke and the stopcock opened. The evacuation and filling was then repeated. To prevent any possible condensation of water, the sampling tube was kept above 70°F at all times. This precaution was followed because, in the presence of water droplets, SO_2 and H_2S may react to form elemental sulfur.

A GC method of analysis is employed in which hydrogen sulfide, carbonyl sulfide, sulfur dioxide and mercaptans are separately resolved on a 15 cm column of a 0.32 cm O.D. packed with Triton X-305. A flame photometric sulfur detector was employed for tests 1-4 and a microcoulometric detector for tests 5 and 6.

A chemist who has worked on the detection and measurement of odors for over 20 years made odor observations during all of the tests noticing particularly the presence or absence of the sulfur compounds noted above. With the exception of carbonyl sulfide, the odor thresholds of these compounds are less than 1 ppm.

Nitrogen Dioxide, Aldehydes, Phenols, Ozone

These compounds are sampled by absorption in prescribed chemicals. To facilitate this portion of the sampling, a portable apparatus was fabricated that would hold two absorption trains at the same time. A single vacuum pump drew gas through both trains. Each train had a trap to protect the pump, a rotameter and either one or two absorbers. Wherever necessary, the absorber was chilled in an ice bath. As the trains were set up on the platform at the edge of the skip where they were enveloped by the emissions, it was not necessary to employ a probe. Filters or glass wool were not used to keep out particulates; the entrance to the first bubbler was simply turned 90° down from the horizontal. The trains were run for at lease a half hour for each test. The flow rates varied from 0.5 liters per minute for the nitrogen dioxide to 15 liters per minute for the carbon tetrachloride bubblers.

Nitrogen Dioxide - In the ASTM Method employed, NO_2 is absorbed in an azo dye forming reagent. A stable pink color is formed that can be evaluated by visual comparison with standards or by its absorption at 550 mm.

Aldehydes - The aldehydes were collected by passing the gas through an iced bubbler containing 2,4 dinitrophenylhydrazine. This solution was prepared by saturating 250 ml of 2N HCl with DNPH reagent at room temperature. The solution was cooled at 0°C overnight and then filtered. The filtrate was extracted with three 100 ml portions of cyclohexane to remove any traces of aldehyde-DNPH derivatives.

At the conclusion of sampling, the solution was allowed to come to room temperature. The aldehyde-DNPH derivatives were separated from the unreacted DNPH reagent by extraction with cyclohexane (3 separate 2-minute extractions of 25, 15 and 10 ml.). Extraction efficiency measurements with solutions of known aldehyde content showed about 95 percent recovery. The UV absorption method of Jones et. al. (Table B.III) was used to obtain quantitative data on the aldehydes. One advantage of the DNPH method is that, if desired, the cyclohexane solution can be evaporated to a low volume, and a gas chromatographic analysis performed to obtain the individual aldehydes present in the sample.

Phenols - For the determination of phenols, air was passed through 10 per cent sodium hydroxide in a bubbler at one liter per minute. After sampling, the solution was acidified to pH 4 and the phenols separated from interfering materials by the usual steam distillation. To measure the phenols on the distillate, the differential UV spectrophotometric method of Wexler was employed. The difference spectrum of the alkaline form of the phenolic substance was recorded against an identical concentration in slightly acid solution. Almost all phenols react and possible interferences due to nonionizing, nonphenolic species are cancelled out. If large amounts of phenols were present, they could be extracted and characterized by gas chromatography.

Ozone - The ASTM Standard Method of Test D-1609 was used to measure the ozone concentration. Micro amounts of oxidant (ozone) are collected by absorption in a solution of alkaline potassium iodide. The iodine equivalent to the concentration of oxidant present in the air is released by acidification and determined spectrophotometrically by measuring the absorption of the triiodide ion at 352 nm. The test for ozone was only carried out in the last sampling period.

Particulates

The particulates were determined by the EPA specified method, "Reference Method for the Determination of Suspended Particles in the Atmosphere, High Volume Method, (High Vol.)." In this method, air is drawn into a covered housing and through a filter by means of a high-flow-rate blower at a flow rate (1.13 to 1.70 m^3/min.; 40 to 60 $ft.^3$/min.) that allows suspended particles having diameters of less than 100 µm. (Stokes equivalent diameter) to pass to the filter surface. Particles within the size range of 100 to 0.1 µm. diameter are ordinarily collected on glass fiber filters). The mass concentration of suspended particulates in the ambient air ($mg./m.^3$) is computed by measuring the mass of collected particulates and the volume of air sampled.

Two High Volumes with covered housings were placed on the sampling platform in the sampling area. Although the vibrations were considerable, it was not necessary to fasten them. There was insufficient space between the top of the High Volumes and the steelwork above to conveniently open the High Vols. to change the filters. Therefore, about six inches were cut off the legs of one; designated A. The second was left untouched, but in order to change the filter the High Vol. had to be tipped down to a 45° angle.

A modified High Vol. which had been adapted to fit on a tripod was also used. This instrument, designated MOD C, was more portable than the regular High Vols. The High Vols. were run for one or two hour periods.

Limited use was made of a Monitaire sampler(2) in which a silver membrane filter is employed to sample at a low gas rate. This sampler is effective in coke oven effluent sampling where a small gas sample of ∿6 ft.^{3} provides sufficient sample for analysis. In the testing of this program, however, the silver membrane filter provided insufficient sample for analyses other than for examination by an optical microscope.

Total Particulate - Total particulate is determined gravimetrically by conditioning the filter, before and after use, in a constant humidity room and weighing. This value includes both the inorganic and organic portions of the sample.

Benzene Solubles - The organic compounds of the particulates are dissolved in benzene. This was accomplished by cutting a filter into small pieces and placing them in a 43 x 123 mm Soxhlet thimble which in turn was placed in a Soxhlet extractor. Benzene was added and the extraction carried out for four hours. Some of the benzene was then transferred to a 100-ml beaker and placed on a steam bath under nitrogen. The remaining benzene was added and the volume reduced to about 4-7 ml. The remaining solution was then transferred to a weighed, one dram vial. The benzene was evaporated and the vial reweighed to get the weight of the benzene solubles. No correction for a blank filter was needed based on an actual measurement which proved to be neglible.

Characterization of Benzene Solubles - A principal objective of the study was to measure the concentration of individual PNA hydrocarbons, such as, behz(a)anthracene (BaA), benzo(a)pyrene (BaP) and others. In addition, it was desired to obtain some overall compositional information. The methods employed are briefly described.

Polynuclear Aromatic Hydrocarbons - After the Soxhlet extraction, a sample to be analyzed is spiked with known quatities of carbon-14 labeled BaA and BaP. The sample is then transferred to a 100-ml beaker and evaporated on a steam bath under nitrogen to dryness as described earlier for the measurement of benzene solubles. This residue is dissolved in cyclohexane and caustic treated to remove some acidic compounds. Then a PNA hydrocarbon concentrate is obtained by solvent elution off a column of partially deactivated alumina. The solvents are cyclohexane, cyclohexane-benzene, benzene, and benzene-methanol. The fraction containing the PNA's is reduced to a small volume by evaporation on a steam bath. An aliquot of this sample is injected into a gas chromatograph and fractions are collected for measurement by UV and, in the case of BaA and BaP peaks, also for carbon-14 activity. These activities, compared with known concentrations originally added, give factors by which to relate the concentrations of each PNA to its total weight in the sample.

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(2) R. T. Richards, D. T. Donovan and J. R. Hall, Amer. Ind. Hyg. Assoc. J., 28, 590 (1967).

Composition - Gas chromatography and mass spectrometry were the principal tools used to obtain compositional information. UV and infrared spectra also provided insight as to the nature of the benzene solubles. Analyses were conducted directly on the sample itself as well as on fractions as collected from solvent elution of sample through the column of partially deactivated alumina.

A new GC technique, ASTM Test Method D-2887, provided boiling range distribution of the benzene solubles. This method is applicable to petroleum products and fractions with a final boiling point of 1000°F or lower at atmospheric pressure. The method is limited to samples having a boiling range greater than 100°F and having a vapor pressure sufficiently low to permit sampling at ambient temperature.

Analytical instrumentation for the compositional study briefly described in the preceding section included: Perkin-Elmer Model 900 gas chromatographs, a Dupont Model 21-103 mass spectrometer on line with an IBM 1800 computer, a Beckman Model 12 infrared and a Cary 11 ultraviolet spectrophotometers and a Hewlett Packard Model 7620 gas chromatograph for the distillation.

RESULTS AND DISCUSSION

The results of the measurement of all the pollutants are discussed separately in the following sections. Some of the significant findings are worthwhile to mention at this point. All of the compounds that occur in the gas phase, such as, volatile hydrocarbons, sulfur and oxygenated compounds were either found in relatively small concentrations or not detected at all. For these latter, only an upper limit of concentration was reported.

Use of the CCl_4 impinger was a sampling procedure devised during the course of the work. It is important to note that the principal material collected in this trap was found to be a hydrocarbon fraction, which is comparable to the light to middle distillate fractions found in virtually all crude petroleum. This material is generally identified as a C_7-C_{14} fraction. As will be described more thoroughly, these hydrocarbons are very similar to the lowest boiling fractions collected from the asphalts that were being processed during the plant tests. The CCl_4 impinger appears to trap a different boiling point range of organics than are being monitored by workers in the air environmental field.

In characterizing the particulates, it became evident that the benzene solubles portion were similar to the next higher boiling fraction of the asphalts, containing about 70 per cent saturate hydrocarbons from C_{14}-C_{32}. This composition is similar to that of a gas oil.

Some individual polynuclear aromatic hydrocarbons were measured. two of these, BaA and BaP, have been previously studied in plant emissions and the concentrations found in this study are low for an industrial process.

Air

Samples from tests 1-4, inclusive, were found to be 99.9 percent air (O_2,N_2,H_2O) with 0.1% CO_2. Since this mass spectrometric measurement is sensitive to 0.1% of individual hydrocarbons and other organics, the measurement provides qualitative confirmation that the gaseous emissions do not contain a major amount of contaminant.

Volatile Hydrocarbons

The complete results for methane and other volatile hydrocarbons (C_2-C_7) are summarized in Table B.VI. Methane occurs at a level normally found in ambient air. Other volatile hydrocarbons are low.

TABLE B.VI

VOLATILE HYDROCARBONS, ppm

Component	Method of Sampling	Test No. 1[a]	2[a]	3	4	5	6
Methane	10 liter Bomb	1.8	1.9	2.3	2.9	2.8	3.0
C_2-C_7	10 liter Bomb	<1	-	<1	<1	<1	<1

a - No shroud.

C_7-C_{14} Hydrocarbon

The results obtained by infrared analysis of the carbon tetrachloride traps through which the emissions were drawn are given in Table B.VII.

TABLE B.VII

ORGANIC MATERIAL REMOVED BY CARBON TETRACHLORIDE

	Oil mg/m^3				
	Test				
Trap	1	3	4	5	6
1st	2.3	6.4	8.7	4.3	2.2
2nd	0.5	0.6	0.7	0.7	0.3
Total	2.8	7.0	9.4	5.0	2.5

The data indicate that 80 percent of this material is trapped in the first bubbler. To identify the organics most of the carbon tetrachloride from test 4 was removed, and the residue was injected into a gas chromatograph, giving the chromatogram shown in Figure B4. For comparison purposes, the chromatogram of the dry ice trapped portions

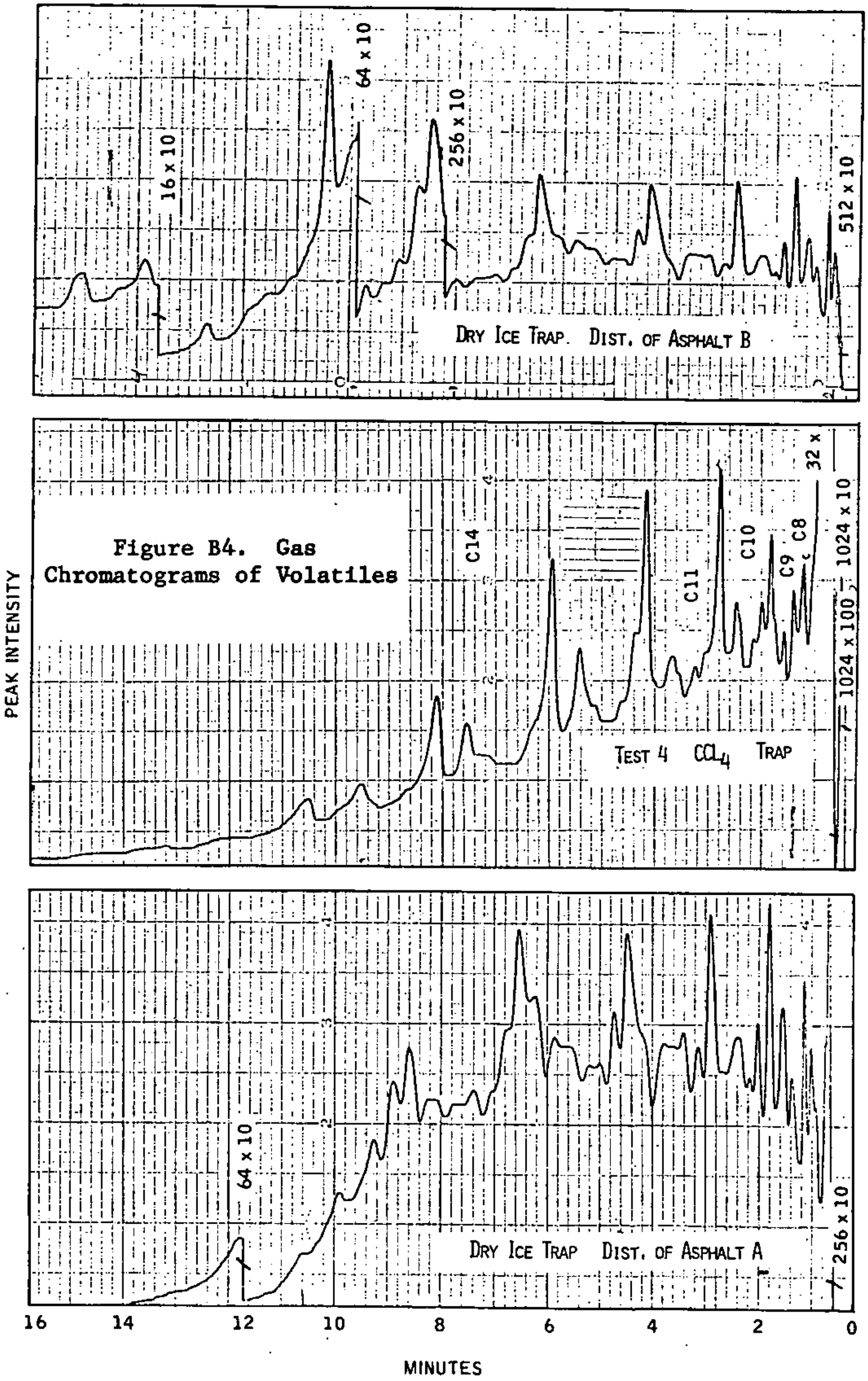

Figure B4. Gas Chromatograms of Volatiles

from the vacuum distillation of the asphalts used in the plant are also presented. The boiling range and the peak configuration of the trapped material and the volatiles from the bulk asphalt are quite similar ranging in hydrocarbon distribution from C_7 to C_{14}.

The mass spectrometric analyses of the same dry ice cuts, presented in Table B.VIII, suggests the same boiling range as measured by GC and also show that the material is light to middle distillate in nature. The average elemental analysis of carbon 86.6, hydrogen 12.0, sulfur 0.3, nitrogen 0.01, and oxygen 0.16 percent confirm that the material is primarily hydrocarbon in nature.

TABLE B.VIII

MASS SPECTROMETRIC ANALYSIS OF MATERIAL FROM ASPHALT DISTILLATION RETAINED IN DRY ICE TRAP

Component	Asphalt A	Asphalt B
	Wt. %	
Paraffins	27.	31.
1-Ring Napthenes	24.	24.
2-Ring Napthenes	13.	13.
3-Ring Napthenes	0.9	1.
Benzene	0.2	0.2
Toluene	8.	6.
C_8 Aromatics	2.	2.
C_9 Aromatics	5.	4.
C_{10} Aromatics	5.	4.
C_{11} Aromatics	3.	3.
C_{12} Aromatics	2.	2.
C_{13} Aromatics	0.8	0.8
Indane & Tetralin	4.	4.
Dicyclics	5.	5.
Tricyclics	0.4	0.3

Additional evidence was found to show the similarity between volatiles from asphalt and C_7-C_{14} organics in a CCl_4 trap. In test 3, for example, a GC/MS analysis clearly showed that saturate hydrocarbons were >60 percent of the total hydrocarbons present. This agrees with the composition of dry ice trap fractions as reported in Table B.VIII. Some oxygenates were also observed as might be expected from mild oxidation of saturate hydrocarbons.

Sulfur, Oxygenated Compounds

Table B.IX summarizes the measurements for sulfur and oxygenated compounds. Except for one isolated instance when a small quantity of hydrogen sulfide was found (Test 4, 1.5 ppm), no evidence was found for carbonyl sulfide, hydrogen sulfide or mercaptans. Within the sensitivity of the test and sampling time, these compounds were reported as being at <0.2 ppm. Their absence or extremely low concentration at the sample site was also indicated by the absence of sulfide or mercaptan odors. No sulfur dioxide was found and the maximum possible concentration of 2 ppm in the plume is even below the Threshold Limit Value of 5 ppm for workroom air as defined by industrial hygienists(3).

Carbon monoxide was observed to be present at levels normally found for ambient air. The 4-6 ppm found for these samples is extremely low compared with 1450 ppm as found for 1975 Federal Auto Emission Standards.

Aldehydes, phenols and oxides of nitrogen were absent within the sensitivity of the tests and sampling times.

TABLE B.IX

SULFUR AND OXYGENATED COMPOUNDS

		Test No.					
Component	Trial	1	2	3	4	5	6
	- - - - - - - - ppm (gas vol.) - - - - - - - -						
Carbonyl Sulfide	<0.2	<0.2	<0.2	<0.2	<0.2	<0.5	<0.5
Hydrogen Sulfide	<0.2	<0.2	<0.2	1.5	<0.2	<0.5	<0.5
Mercaptans	<0.2	<0.2	<0.2	<0.2	<0.2	<0.5	<0.5
Sulfur Dioxide	<2.	<2.	<2.	<2.	<2.	<2	<2
Carbon Monoxide	6	4	4	6	4	--	--
Aldehydes	<0.1	<0.1	<0.1	<0.1	<0.1	<.1	
Phenols	<1	<1	<1			<1	
Nitrogen Dioxide	<0.1	<0.1	<0.1			<.1	<.1

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(3) TLV's Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1972. Obtainable from Chairman, TLV Committee, American Conference of Governmental Industrial Hygienists.

Particulates

Total particulates and their benzene solubles as collected in High Volume Sampler filters are presented in Table B.X. The shroud prevents the Blue Smoke from being blown away by the wind and also keeps out extraneous inorganic material from the rest of the plant. This makes the total particulate obtained on Tests 3 and 4 less than that obtained in Tests 1 and 2. It also makes the total amount of benzene soluble higher as well as the percent benzene soluble on the total particulate. In all the sampling through test 4 the front of the High Volume Sampler faced the front of the platform and the back faced the skip. This enabled the sampling rate to be observed during the test period. However, as the opening at the back is smaller than at the front, and the front is quite close to the shroud it was decided to turn the samplers 90 degrees closer to the skip. This change and the lower ambient temperature could account for the higher mass of benzene solubles in Tests 5 and 6. The high volume samples draw about 50 cu ft per minute or about one tenth of the volume enclosed by the shroud. Scaling up the benzene soluble by a factor of ten to account for a 10 per cent sample and the number of tons made during the sampling period to a days output (1000 tons) gives the data shown in Table B.XI.

Polynuclear Aromatic Hydrocarbons - The results obtained by the GC/UV method for the polynuclear aromatic compounds in the particulates are presented in Table B.XII. The average value of 11 micrograms per 1000 cubic meters for both the benzo(a)pyrene and the benz(a)anthracene, respectively, are low for the plume from an industrial process. More significant is that the average concentration of benzo(a)pyrene (11 µg/1000 m^3 was just slightly more than a range of 1.18 to 7.49 µg/1000 m^3 reported for urban air. The following statement from a Public Health Publication$^{(4)}$ also notes the low levels of most polynuclear aromatic compounds in the particulates from a road asphalt plant.

> "Nearly all the emissions reported from this hot-road-mix plant are attributed to combustion gases emitted from the rotary dryer and not to effluent gases from the mixing chamber. This is evidenced by the results for a sample of the suspended particulates collected directly from the mixing chamber. Of the 10 polynuclear hydrocarbons under consideration only anthracene was qualitatively identified."

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(4) R. P. Hangebrauck, D. J. von Lehmden and J. E. Meeker, Sources of Polynuclear Hydrocarbons in the Atmosphere, U.S. Dept. of Health, Education, and Welfare, Public Health Service, Bureau of Disease Prevention and Environmental Control, Cincinnati, Ohio, 1967

TABLE B.X

PARTICULATE MATTER BY HIGH VOLUME SAMPLER

Test	High Volume Sampler[a]	Total Particulate	Benzene Soluble	Benzene Solubles (Rel.%)
		mg/m³	mg/m³	
Trial	A	4.5	.35	8.
	A	11.3	.25	2.
	C	5.4	.22	4.
#1	A	2.6	.37	14.
	B	2.8	.49	18.
#2	A	5.1	.25	5.
	B	6.4	.36	7.
#3	A	3.3		
(Shrouded)	B	3.0	0.67	22
#4	A	3.2		
(Shrouded)	B	2.6	0.67	26
	3A + 4A		.92	28
#5[b]	A	6.7	2.80	39
	B	7.2	2.54	38
#6[b]	A	6.0	2.31	38
(Shrouded)	B	6.7	1.80	27

---

a - Samplers A and B were conventional although the legs of A had been cut off. C was a portable sampler.

b - High Volume turned so that front is only 90 degrees from skip rather than 180 degrees as in other tests.

TABLE B.XI

PARTICULATE MATTER AND BENZENE SOLUBLES (IN MILLIGRAMS) PER 1000 TONS OF ASPHALT CONCRETE PRODUCED IN AN 8 HOUR DAY

Test No.	1	2	3	4	5	6	Avg.
Total Particulates	1900	4700	1900	1900	3700	3800	(3000)
Benzene Solubles	300	300	400	500	1400	1300	(700)

TABLE B.XII

POLYNUCLEAR AROMATIC COMPOUNDS IN HIGH VOLUME PARTICULATE MATTER

PNA	Trial	1	2	3	4	5	6	Avg.
	- - - - - - - - micrograms/1000 m^3 - - - - - - - - - -							
Pyrene	--	90	60	56	44	240	150	107
Benz(a)anthracene	--	10	7	8	5	11	24	11
Benzo(a)pyrene	9	20	14	12	17	3	4	11
Benzo(e)pyrene	15	40	30	14	32	26	22	26
Perylene	12	16	13	11	14	12	5	12

Characterization of Benzene Solubles - In order to compare the benzene solubles and the distillation fractions of the asphalt the various features of both will be discussed together.

Table B.XIII lists the physical properties of the asphalt cements taken from Halecrest Asphalt plant storage immediately following sampling on the three dates shown. These asphalts are all viscosity graded AC-20, passing the New Jersey specifications as well as AASHO M 226 Table II and ASTM D To Be Designated Table II. Exxon supplied asphalt (A) used on 9-25-73 (Test 1 and 2), and Chevron the asphalt (B) used on 10-2-73 (Test 3 and 4 and 11-20-73 (Test 5 and 6). Figure 5 (lower portion) shows the composition(5) of the asphalt cements used on the first two sampling dates. It will be noted that there is considerable similarity between the two sources of asphalt, even though the crude sources are known to be distinctly different.

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(5) L. W. Corbett, Anal. Chem. 41, 576 (1969).

TABLE B.XIII

EXAMINATION OF AC-20 ASPHALT CEMENT USED DURING SAMPLING OF BLUE SMOKE

Sample No.	A	B	B
Sample Date	9-25-73	10-2-73	11-20-73
Asphalt Source	Exxon	Chevron	Chevron
Physical Properties			
Abs. Vis @ 150 F	1990	1753	1953
Pen @ 77 F	74	72	70
Pen @ 39.2 F	18	16	20
K. V. @ 275 F	391	380	393
Flash COC F	615	620	595
Sol. TCE, %	99.8	99.7	
Sp. Gr. @ 60 F	1.026	1.030	
TFO, % loss	.04	.04	
Res. Vis. @ 140 F	4657	4219	
Res. Duct. @ 60 F	40	28	
Distillation, % loss	1.17	1.20	
Res. Vis. @ 140 F	2820	2286	
Res. Pen. @ 60 F	57	56	

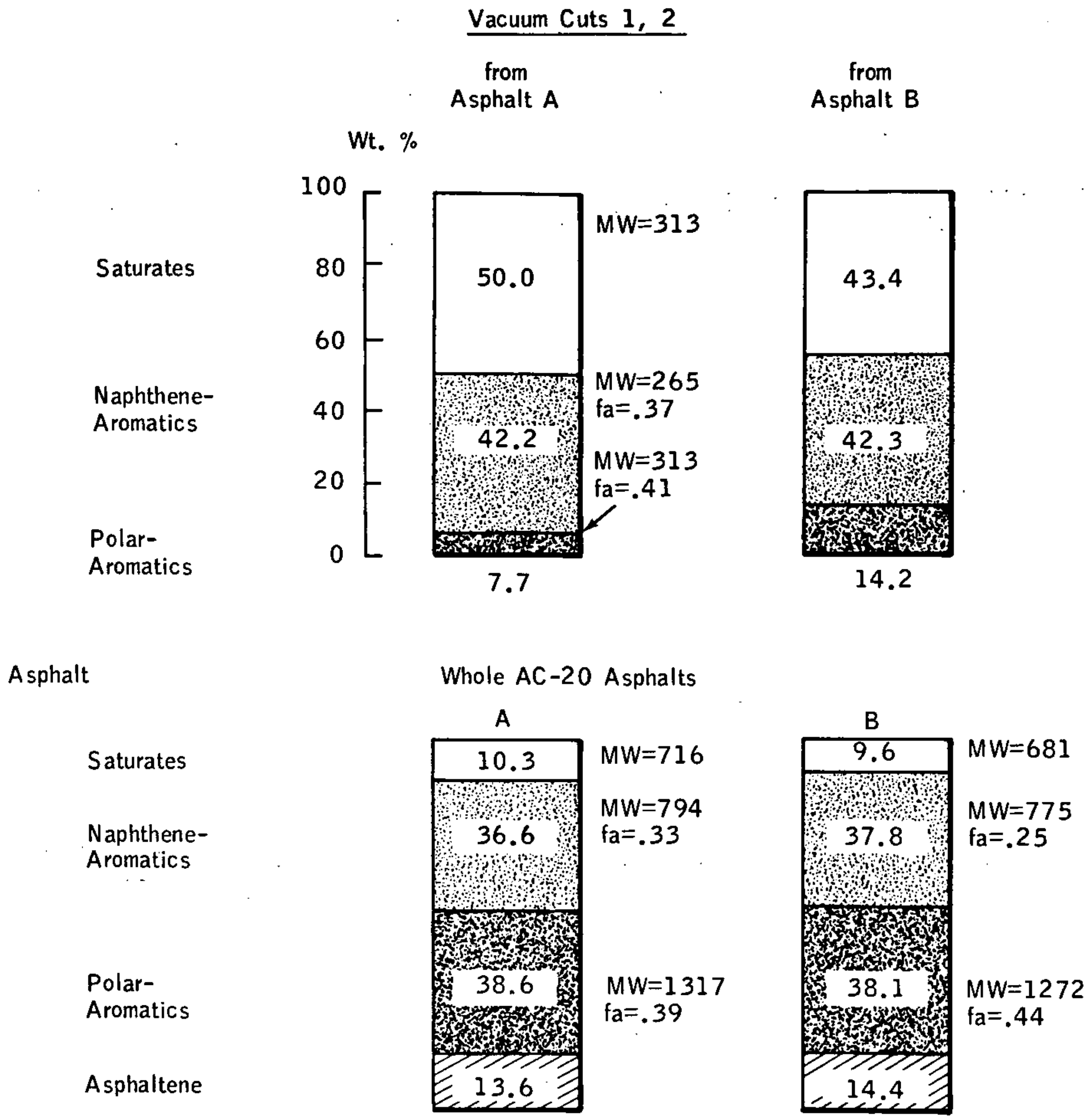
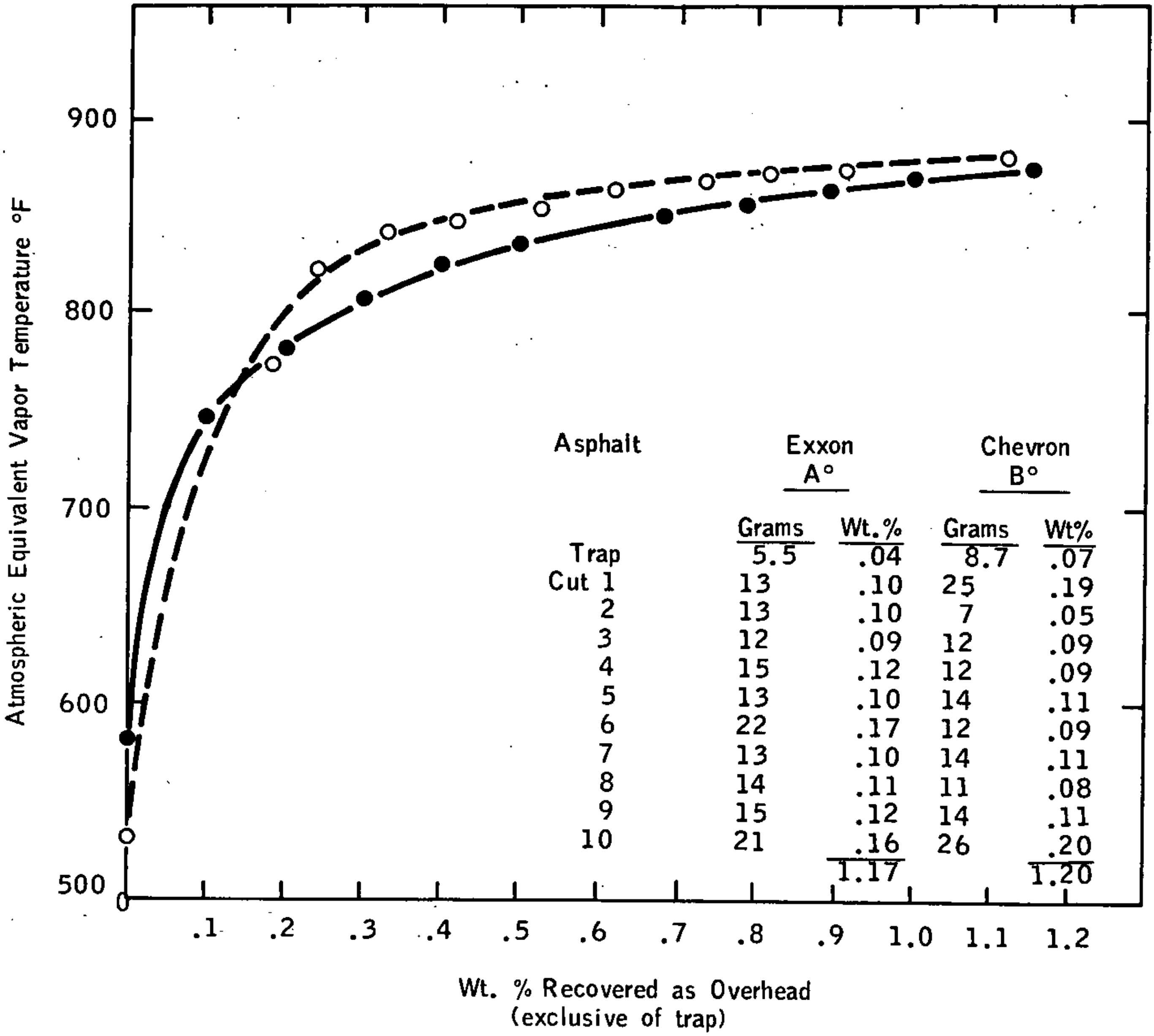


Figure B5. Composition Analyses of AC-20 Asphalt Cements and Front-End Fractions

A high vacuum distillation was performed on the two asphalts as described above. This was done in order to obtain working samples of the most volatile fractions present in the asphalt cement, reasoning that the organic particulates collected from the "Blue Smoke" could bear a resemblance to the front end fractions from the asphalt cement, unless the hot-mixing exposure caused significant chemical changes. Figure B6 shows the distillation characteristics of the front end 1 percent from each of the two asphalts, again showing considerable similarity, especially with respect to volatility. It will be noted that each asphalt has a measured initial boiling point between 500 and 600°F and both have small but measurable fractions collecting in a dry ice trap, thus indicating that their true initial boiling points are lower than 500°F. Table B.XIV lists the molecular weight and elemental analyses of the fractions caught in the trap as well as the succeeding three cuts. The trap fractions are very low in molecular weight and contain less hetero atoms than the next cuts, although there is a gradual increase in molecular weight and content of hetero atoms. Figure B5 also shows the composition analysis of cuts 1 and 2 combined, showing a comparatively higher proportion of saturates and naphthene-aromatics and a minor proportion of polar-aromatics, all in comparison with that found in the original asphalt cement itself. Although it is somewhat surprising that asphalt cements contain these very low molecular weight low boiling fractions, even in a minor percentage, the difference in composition between the overhead fractions and the asphalt cement from which it was derived is consistent with asphalt manufacture by straight vacuum distillation.



Asphalt	Exxon A°		Chevron B°	
	Grams	Wt.%	Grams	Wt%
Trap	5.5	.04	8.7	.07
Cut 1	13	.10	25	.19
2	13	.10	7	.05
3	12	.09	12	.09
4	15	.12	12	.09
5	13	.10	14	.11
6	22	.17	12	.09
7	13	.10	14	.11
8	14	.11	11	.08
9	15	.12	14	.11
10	21	.16	26	.20
		1.17		1.20

Figure B6. Front End Distillation of AC-20 Asphalt Cement Used In Environmental Studies of Emissions Developed at Hot-Mix Plants

TABLE B.XIV

EXAMINATION OF FRONT END FRACTIONS FROM AC-20 ASPHALT CEMENT

Sample No.	Fraction	Mol. Wt.	Elemental Analysis % C	H	N	S	O
A	Trap	189	86.33	12.00	0.009	0.35	0.16
B	Trap	195	85.89	11.93	0.006	0.68	0.16
A	Cut 1	276	86.42	11.84	0.10	1.35	0.28
B	Cut 1	320	85.06	11.47	0.10	2.63	0.20
A	Cut 2	318	--	--	—	—	0.32
B	Cut 2	322	--	—	—	--	0.19
A	Cut 3	345	86.86	11.56	.3	1.87	--
B	Cut 3	374	85.00	10.98	.3	2.81	--

Boiling Point and Carbon No. Range - Aliquots of benzene soluble fractions were combined from Tests 1-2 and 3-4, respectively. A GC distillation of these fractions gave a boiling point range as shown in Table B.XV.

TABLE B.XV

BOILING POINT RANGE OF BENZENE SOLUBLES

Test No.	IBP	50%	FBP
	- - - - - - - -	°F	- - - - - - - -
1 - 2	530	720	980
3 - 4	536	724	--

These boiling points are comparable to those observed for the initial 0.1 to 0.2% of asphalt A (Tests 1-2) and asphalt B (Tests 3-4) as shown in Figure 6.

Gas chromatograms reveal further the similarity between benzene solubles and the front ends of asphalt. Figure B7 compares Test 2 benzene solubles with the front distillation cut of the asphalt being processed at the time, asphalt A. The benzene solubles cover the range, C_{17}-C_{30}, whereas, the distillation cut contains some lower molecular weight hydrocarbons (C_{13}-C_{16}) with an approximately equal upper carbon number. The C_{13}-C_{16} hydrocarbons probably pass through the filter of the High Volume Sampler.

Figure B8 compares a benzene soluble with a front end of asphalt B as used during that particular plant test (No. 4). These two samples behave in approximately the same manner as observed for those materials of Figure B7. The hydrocarbon envelope of asphalt B maximizes at C_{30} in contrast to an C_{23} maximum for the benzene soluble. This may be ascribed to the asphalt B distillation fraction being, relatively, a deeper cut (0.19% vs. 0.1%) as compared with asphalt A. The molecular weight of the fraction from B is also higher, 320 vs. 276.

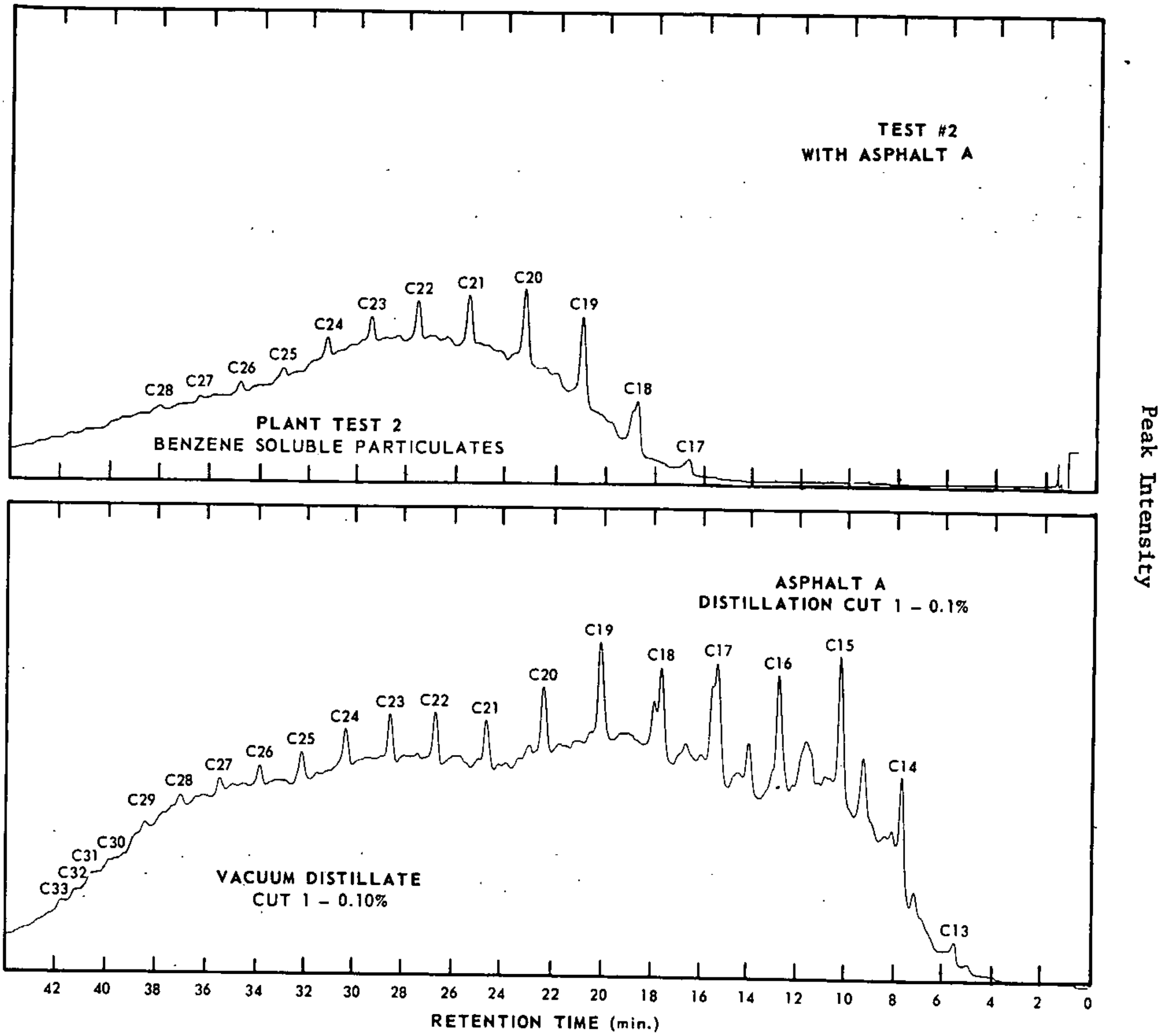


Figure B7. Gas Chromatograms of Asphalt "A" Samples

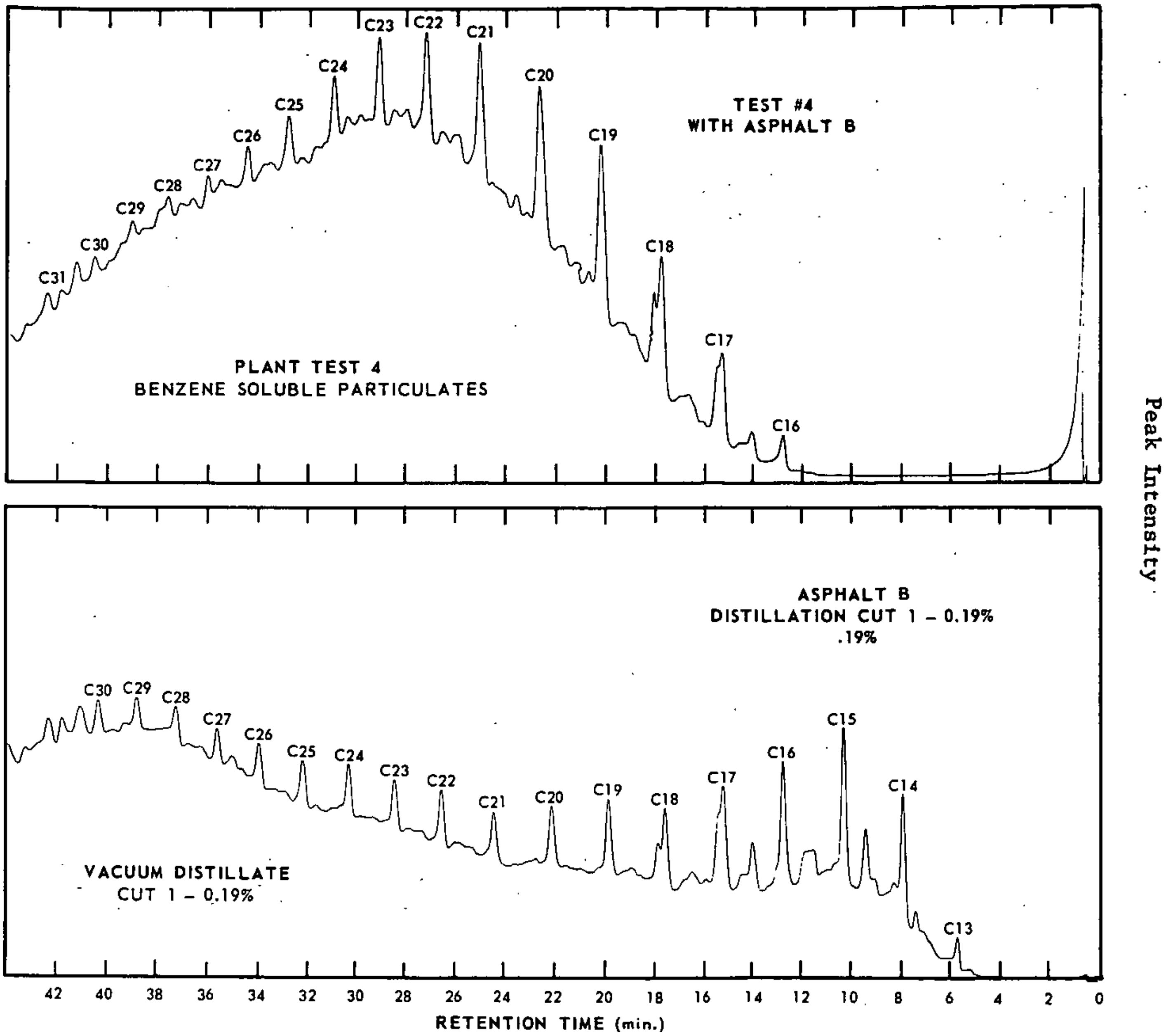


Figure B8. Gas Chromatograms of Asphalt "B" Samples

Composition of Benzene Solubles, Elemental Analysis - The first cuts from the vacuum distillation and the benzene solubles of the particulates were analyzed for elemental composition as shown in Table B.XVI.

TABLE B.XVI

ELEMENTAL ANALYSIS

Sample	Carbon	Hydrogen	Sulfur	Kjeldahl Nitrogen	Oxygen	Carbon/ Hydrogen
Asphalt A, Cut 1	86.42	11.84	1.35	0.10	0.28	7.30
Asphalt B, Cut 1	85.06	11.47	2.63	0.10	0.20	7.42
Benzene Solubles						
Test 1, 2 (A)	85.46	11.96	1.32	-	-	7.14
Test 3, 4 (B)	84.98	11.96	2.21	-	-	7.10
Test 5 (B)	86.20	12.22	-	0.070	-	7.05
Test 6 (B)	84.46	11.62	-	0.069	-	7.25

The elemental analysis of the first vacuum cut of the asphalt and the benzene soluble portion of the particulates are in good agreement. Asphalt B has a higher sulfur content both in the first vacuum cut and in the particulates. The carbon/hydrogen ratios are quite similar and there is little oxygen present in the cuts from the two asphalts. There was insufficient sample to determine oxygen on any of the benzene solubles and to determine nitrogen by the Kjeldahl method on Tests 1-4.

Compound Types - During the course of the study selected samples were analyzed by mass spectrometer to obtain hydrocarbon type analyses. In one instance, a benzene soluble fraction was analyzed. Alumina column fractions prepared for the measurement of individual PNA's were also analyzed. By combining these data on overall composition of a typical benzene soluble was obtained as shown in Table B.XVII. This analysis is quite similar to that of the asphalt distillates as shown in the upper portion of Figure B5.

TABLE B.XVII

HYDROCARBONS IN A TYPICAL BENZENE SOLUBLE FRACTION

Hydrocarbon Type	Wt. %
Paraffins	28
Cycloparaffins	
1-ring	11
2-ring	11
3-ring	18
Aromatics	
1-ring	10
2-ring	10
3-ring	6
Sulfur Aromatics (Benzo, Dibenzothiphenes)	6
	100

Further insight into composition was obtained by infrared inspection. Spectra of the benzene soluble oil from Tests 3-4, and the first cut from the vacuum distillation of asphalt "B" are shown in Figure B9. The carbonyl bands in the 1730 cm $^{-1}$ region are typical of oxidized oils and show that the Blue Smoke material has oxidized more than the vacuum cut. Otherwise, the two spectra are remarkably similar. The peak at 720 cm^{-1} due to long chains of methylene group, and those at 750 - 870 cm^{-1}, which are caused by the aromatic substitution pattern, are frequently used to "fingerprint" the sources of a petroleum sample.

Nickel and Vanadium - Less than one ppm of nickel and vanadium was found in the first vacuum cut of each asphalt. The oil extracted from the deposit on the beam above the skip contained 2 and 24 ppm respectively of nickel and vanadium. Table B.XVIII contains the data on these two elements for the benzene solubles along with the average found for New York City in data collected by Morrow and Brief(6) and the

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(6) N. L. Morrow, R. S. Brief, Environ. Sci. Technol. 5. 786 (1971).

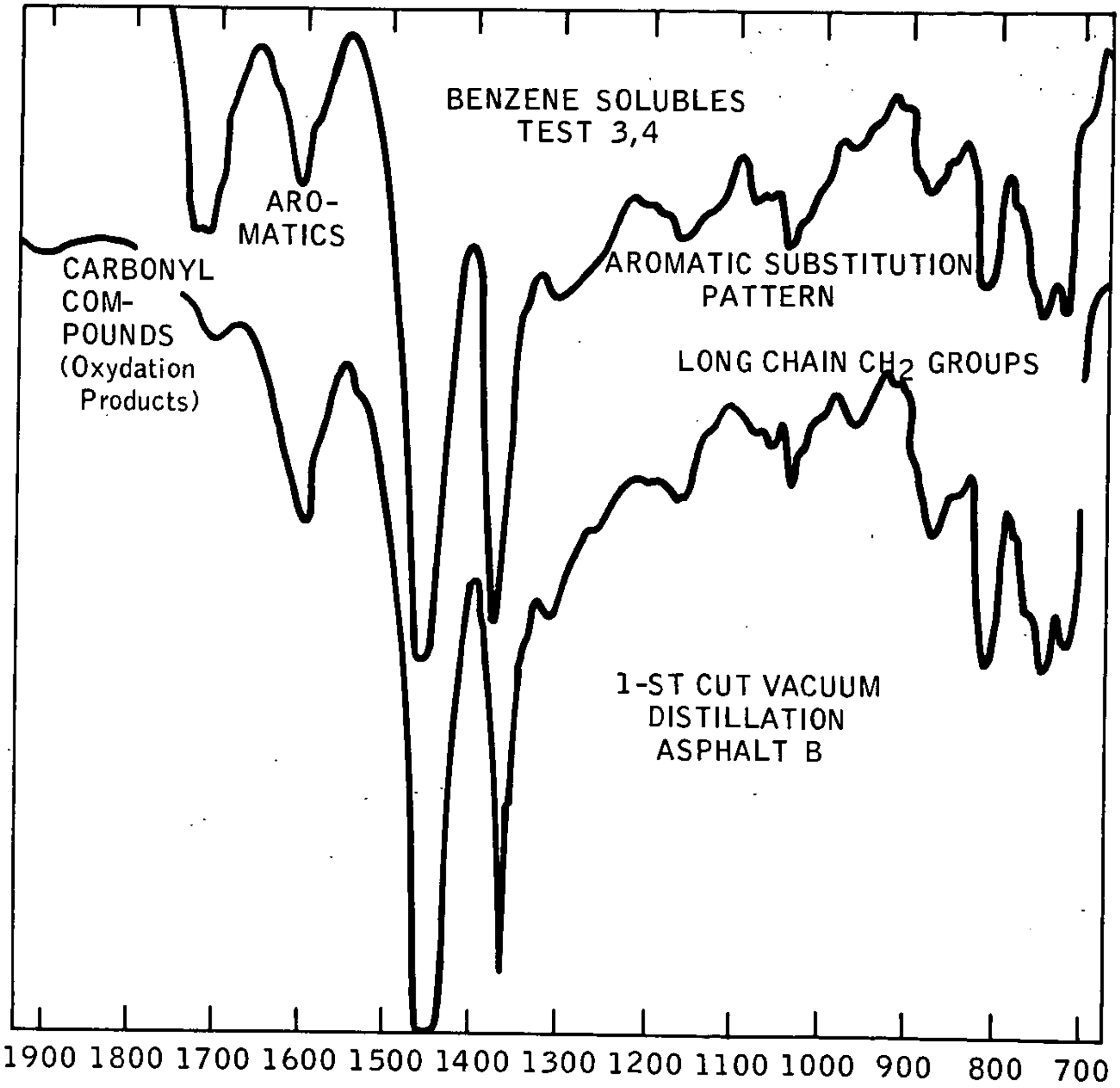

Figure B9. Infrared Spectra

National Air Sampling Network (NASN) (USDEHEW, 1966)(7) for New York City and Newark. These latter studies give the values for total nickel and vanadium and are, therefore, somewhat higher than the values found in the present study.

TABLE B.XVIII

NICKEL AND VANADIUM IN BENZENE SOLUBLES

	Test					
Element	1, 2	3, 4	5, 6	N.Y.C.(6)	N.Y.C.(7)	N.Y.C.(7)
	$\mu g/m^3$					
Nickel	0.005	0.005		0.18	0.14	0.09
Vanadium	0.080	0.020		0.17	0.44	0.19

Total Particulate by Other Methods

An attempt was made to obtain total particulates with a silver membrane filter, but due to the small volume that can be sampled by this method insufficient material was collected to determine gravimetrically.

Particle Size of Particulates

Samples of the particulates collected on a millipore filter was examined under the microscope. The particle size was less than one micron.

ACKNOWLEDGMENTS

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(7) U.S. Department of Health, Education and Welfare, Public Health Service "Air Quality Data from the National Air Sampling Networks and Contributing State and Local Networks, 1966," Washington, D.C., 1968

EXHIBIT C

ASPHALT HOT-MIX EMISSION STUDY

PLANT, SAMPLING PROGRAM AND MATERIALS

GREENSBORO, N.C. PLANT

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EXHIBIT C

ASPHALT HOT-MIX PLANT

C1. Sampling for the second phase of the Asphalt Hot-Mix Emission Study was conducted at Thompson-Arthur Plant No. 1 located on Holden Road in Greensboro, N.C. A general view of the hot-mix asphalt plant is shown in Figure C1. The plant, centrally situated on a 12-acre site, was originally manufactured by the Hetherington and Berner Company; however, a number of the original plant parts, such as hot sieves and pugmill mixer, were later replaced with parts made by the Cedar-Rapids Company. The plant had a 3-ton pugmill capacity.

C2. Four cold bins were available at the plant, and normally all four bins were used for the production of mixes containing coarser aggregates. For finer surface-course mixtures, the normal practice was to use only three cold bins. A drum dryer 30 feet long and about 7 feet in diameter, inclined on a 12:1 slope and rotating at 6 rpm was used for aggregate drying. The dryer was equipped with a Size 12 Maxon burner using No. 2 heating oil as a fuel. Three bins were used for the production of the surface course mixes produced during this study. A 1-minute cycle was used for mixing the individual batches, and this mixing cycle was subdivided as follows: 12 seconds for charging the mixer with aggregates, 2 to 3 seconds for dry mixing and 38 seconds for introducing hot asphalt cement and wet mixing. The remaining 7 to 8 seconds were required for discharge of the finished mixture. During discharge, the asphalt emissions were visible for about 10 seconds as smoke or organic aerosol. A view of the aggregate dryer, hot bins and pugmill mixing chamber is shown in Figure C2.

C3. The paving mixture could be discharged from the pugmill directly into transport trucks. Alternatively, it could be discharged into a hopper attached to a 12-foot long enclosed screw conveyer which then discharged the mixture into a second hopper which, in turn, deposited the mixture on to a bucket elevator for conveyance to the hot-mix storage bins. The hopper beneath the pugmill gates is shown in Figure C3. The enclosed screw conveyer and second hopper are shown in Figure C4. The second hopper was 4 feet high and had an open top measuring about 2.5 by 5 feet. Figure C5 is a schematic diagram indicating the flow of materials through the plant.

EMISSION SAMPLING PROGRAM

C4. The emissions evolving from the mixture when discharged into the second receiving hopper were sampled for analysis. The space surrounding the hopper measuring approximately 8 feet high, 7 feet long and 6 feet wide. This space was enclosed by a polyethylene sheet supported on wooden framing. It formed an enclosure of approximately 340 cubic feet which was sufficient to accommodate two High Volume Samplers and various other sampling devices. Placement of the shroud and a view of the shrouded sampling area are shown in Figures C6 and C7. The High Volume Sampler is visible in these photographs. Two sets of asphalt hot-mix emission samples (Nos. 7 and 8) were obtained on a single day. Table C.I provides miscellaneous data pertinent to both samplings.

C5. Sampling No. 7 was made over a period of 112 minutes during which time 112 batches totaling 336 tons of paving mixture were produced. More than one-half of this amount was the surface (top) course mix; the remainder was a coarser mixture used for the binder or base course. However, samples for only the finer surface-course mixture were obtained for laboratory tests. Sampling No. 8 covered a period of 125 minutes. During this period only the finer surface course mixture was manufactured and a total of 125 batches or 375 tons of mixture were produced.

C6. The temperature of each individaul batch was measured as the mix was discharged from the pugmill with an IR Con Company infra-red thermometer Model CH 346. This device may be seen in Figure C7. As indicated in Table C.I, for sampling No. 7, the temperature for individual batches varied between 297 and 336°F. In sampling No. 8 the temperature ranged between 290 and 335°F.

MATERIALS

Asphalt Cement

C7. Asphalt cement was supplied by the AMOCO Oil Company from a refinery located in the vicinity of Savannah, Georgia. It was produced by straight reduction in a pipe still from a heavy venezuelan crude oil. All pertinent properties of the asphalt cement used to prepare paving mixtures during the Greensboro Test No. 7 and the Test No. 8 are listed in Table C.II. This material complies with requirements for the AC-20 grade of asphalt cement in Tables 1 and 2 of Specification M-226 of the American Association of State Highway and Transportation Officials (AASHTO). The principal differences between properties of the asphalt cements used during the Greensboro samplings and those used in the Edison, N. J. emission samplings (Exhibit A) were in flash point and volatility. The Greensboro asphalt had a Cleveland Open Flash Point about 80°F lower than the three asphalts used in the Edison samplings. Also, weight loss during Thin Film Oven Test heating indicates that the Greensboro asphalt contained more volatile components than the three asphalts used in the Edison, N. J. study.

Mineral Aggregates

C8. Four stockpiles of mineral aggregate were available for the plant cold feed. Some of the stockpiled aggregates are shown in Figure C8. All four aggregate stockpiles were sampled and tested. Gradation, specific gravity, and water absorption characteristics of these aggregates are shown in Table C.III.

Both coarse aggregates, designated by the North Carolina State Highway Department as Standard Size Nos. 4 and 14, were highly angular crushed granite obtained from the Pamona quarry in the vicinity of Greensboro. Siliceous sand of medium angularity was obtained from Candor, N.C., located about 80 miles from Greensboro, and the granitic type screenings originated in a quarry at Jamestown, N.C. Since the screenings and sand contained sufficient amounts of fines passing U.S. Standard Sieve No. 200, no additional mineral filler was needed to prepare paving mixtures. As Table C.III indicates, all aggregates were sound and comparatively dense siliceous materials having rather low water absorption values.

Paving Mixes

C9. In order to verify the uniformity of plant operation, the paving mixes were sampled during both of the Greensboro emission samplings. During sampling No. 7, samples of the mixture were obtained from seven (7) individual batches. Twelve (12) batches were sampled during emission sampling No. 8. One quart samples were obtained from the mixture immediately after discharge into the first hopper.

C10. The asphalt and aggregates were later separated in the laboratory by a standard extraction procedure. Tables C.IV and C.V summarize the results of tests on the separated materials obtained during samplings Nos. 7 and 8. Asphalt contents of mixtures, viscosity at 140°F, 275°F and 77°F, penetration and ductility (both at 77°F) of recovered asphalt, and the gradation of recovered aggregates are shown in the two tables. Temperatures for each sampled batch are also included in these tables.

C11. The asphalt contents of mixture varied only between 5.8 and 6.0 percent during both emission samplings. The percentage of aggregate passing U.S. Standard Sieve No. 8 ranged between 71.5 and 79.1, as the amount of material passing U. S. Standard Sieve No. 200 varied between 6.7 and 9.5 percent of total aggregate. The viscosity of recovered asphalt varied over a relatively wide range. At 140°F, it ranged between 2472 and 3830 poises and at 275°F the viscosity ranged between 415 and 543 centistokes. An examination of data in Tables C.IV and C.V reveals that the reason for viscosity variations cannot be attributed solely to the variation in mixing temperature of the individual batches. The trend of increasing viscosity with increasing batch temperature, although evident, is represented by a rather broad scatter in data points. This in turn indicates that factors other than mixing temperature affect the hardening of asphalt during mixing. The data also indicate that agreement between viscosities at 140°F of recovered asphalts and for the Thin Film Oven Test residue is quite poor. The viscosity of TFOT residue at 140°F averages nearly twice that of asphalts recovered from the batch samples. This suggests that weight loss (i.e., relative volatility) or consistency changes during Thin Film Oven Test heating are not indicative of the amount of emissions to be expected from a given asphalt.

C12. Variations in test properties shown in Tables C.IV and C.V are typical of those from well-controlled plant operations. Thus, the results of emission studies at the Greensboro plant should be considered as representative and indicative of results to be expected at other asphalt hot-mix plants using similar asphalt cements.

TABLE C.I

EMISSION SAMPLING CONDITIONS

SAMPLE NO.	7	8
DATE	June 19, 1974	June 19, 1974
TIME	8:06 AM to 9:58 AM	4:24 PM to 6:28 PM
DURATION OF SAMPLING	112 Minutes	124 Minutes
NUMBER OF BATCHES	112	125
TONNAGE OF MIX	336	375
ASPHALT CEMENT (AC-20)	AMOCO	AMOCO
MIXING TEMP. RANGE, °F	247-336	290-335
AMBIENT TEMP.	69	75
WEATHER CONDITIONS	Clear, calm	Partly Cloudy, Gusty
SAMPLING AREA	Shrouded	Shrouded

TABLE C.II

PROPERTIES OF ASPHALT CEMENT

ORIGINAL ASPHALT	
VISCOSITY	
140°F, poises	2206
275°F, cS	360
77°F, 0.05 s^{-1}, mP	1.45
TEMPERATURE SUSCEPTIBILITY (Range 140-275°F)	3.67
SHEAR SUSCEPTIBILITY AT 77°F (Shear rate range 0.1 - 0.01 s^{-1})	0.00
DUCTILITY, cm	
77°F, 5cm/min	150+
39.2°F, 1cm/min	70.0
PENETRATION, 0.1 mm	
77°F, 5 s, 100 g	70
FLASH POINT, COC, °F	525
SOLUBILITY IN TRICHLOROETHYLENE, Percent	99.94
SPECIFIC GRAVITY AT 77°F	1.027
THIN FILM OVEN TEST (TFOT) RESIDUE	
WEIGHT LOSS, Percent	-0.50
VISCOSITY	
140°F, poises	5733
275°F, cS	574
$\frac{\text{VISC. AT 140°F AFTER TFOT}}{\text{VISC. AT 140°F BEFORE TFOT}}$	2.60
DUCTILITY, cm	
77°F, 5cm/min	150+
PENETRATION, 0.1 mm	
77°F, 5 s, 100 g	41

TABLE C.III

PROPERTIES OF MINERAL AGGREGATES

AGGREGATE TYPE	Coarse (No.4)	Coarse (No.13)	Sand	Screenings
AGGREGATE GRADATION				
SIEVE SIZE		PERCENT PASSING		
1"	100.0			
3/4"	96.2			
1/2"	35.7	100.0		
3/8"	11.6	95.5		100.0
No. 4	2.3	24.9	100.0	97.5
No. 8	1.3	4.9	99.7	84.0
No. 16	0.8	2.4	96.4	64.4
No. 30	0.6	1.5	76.4	47.7
No. 50	0.5	1.1	40.7	33.5
No. 100	0.4	0.9	14.2	22.2
No. 200	0.3	0.7	6.8	15.8
SPECIFIC GRAVITY				
APPARENT				
Retained U.S. Std. Sieve No. 4	2.765	2.776	---	---
Passing U.S. Std. Sieve No. 4	---	---	2.656	2.711
BULK				
Retained U.S. Std. Sieve No. 4	2.733	2.726	---	---
Passing U.S. Std. Sieve No. 4	---	---	2.617	2.700
WATER ABSORPTION, PERCENT				
Retained U.S. Std. Sieve No. 4	0.42	0.67	---	---
Passing U.S. Std. Sieve No. 4	---	---	0.56	0.32

TABLE C.IV

PROPERTIES OF RECOVERED ASPHALTS AND AGGREGATES*

BATCH NUMBER	27	---	42	50	53	61	63
TEMPERATURE OF MIXTURE, °F	315	---	334	324	326	315	315
GRADATION OF RECOVERED AGGREGATE							
SIEVE SIZE				PERCENT PASSING			
1/2"	100.0	100.0	100.0	100.0	100.0	100.0	100.0
3/8"	98.9	98.4	99.0	98.2	98.6	98.2	98.4
No. 4	85.9	88.3	87.5	85.8	84.6	85.9	85.5
No. 8	71.5	75.8	73.5	72.3	72.0	72.8	73.0
No. 16	59.3	63.6	61.7	59.8	60.4	60.8	60.8
No. 30	45.7	49.9	47.4	46.2	47.5	47.1	47.3
No. 50	26.7	30.5	27.0	27.5	29.8	28.7	28.7
No. 100	12.7	15.3	12.1	13.2	15.3	14.9	14.3
No. 200	7.3	9.0	6.7	7.5	9.1	9.2	8.5
ASPHALT CONTENT, WT. PERCENT	5.73	5.86	5.89	5.82	5.90	5.93	5.93
PROPERTIES OF RECOVERED ASPHALT							
VISCOSITY							
140°F, poises	3728	3444	3262	3262	2651	3256	3335
275°F, cS	473	458	476	476	419	494	432
77°F, mP	---	1.78	---	2.12	---	2.11	---
PENETRATION, 0.1 mm 77°F, 5 s, 100 g	53	55	57	57	61	57	55
DUCTILITY 77°F, 5cm/min, cm	150+	150+	150+	150+	150+	150+	150+
ASH, WT. PERCENT	0.01	---	0.01	---	0.01	0.01	0.01

*Recovered from asphalt paving mixes prepared on June 19, 1974, during emission sampling No. 7.

TABLE C.V

PROPERTIES OF RECOVERED ASPHALTS AND AGGREGATES*

BATCH NUMBER	19	22	31	34	51	56
TEMPERATURE OF MIXTURE, °F	303	319	324	300	297	319
GRADATION OF RECOVERED AGGREGATE						
SIEVE SIZE			PERCENT PASSING			
1/2"	100.0	100.0	100.0	100.0	100.0	100.0
3/8"	98.2	98.9	99.5	98.7	99.7	99.5
No. 4	86.5	87.3	88.1	86.8	88.7	91.5
No. 8	75.0	75.4	75.3	75.4	76.2	77.9
No. 16	64.3	64.3	63.9	64.2	64.8	64.8
No. 30	50.1	50.4	49.7	50.4	50.6	49.9
No. 50	29.7	29.5	29.4	30.1	30.9	30.3
No. 100	14.5	14.3	14.4	14.8	15.5	15.1
No. 200	8.8	8.7	8.7	8.9	9.5	9.2
ASPHALT CONTENT, WT. PERCENT	5.84	5.94	5.91	5.80	5.84	5.98
PROPERTIES OF RECOVERED ASPHALT						
VISCOSITY						
140°F, poises	2472	3037	3180	3452	2895	3215
275°F, cS	415	444	449	452	484	473
77°F, mP	---	1.88	---	2.05	---	2.68
PENETRATION, 0.1 mm						
77°F, 5 s, 100 g	---	58	56	52	65	56
DUCTILITY						
77°F, 5cm/min, cm	150+	150+	150+	150+	150+	150+
ASH, WT PERCENT	0.02	0.02	0.02	0.01	0.02	---

*Recovered from asphalt paving mixes prepared on June 19, 1974 during emission sampling No. 8.

(continued)

TABLE C.V (continued)

PROPERTIES OF RECOVERED ASPHALTS AND AGGREGATES*

BATCH NUMBER	76	79	95	103	117	120
TEMPERATURE OF MIXTURE, °F	324	316	312	329	303	313
GRADATION OF RECOVERED AGGREGATE						
SIEVE SIZE			PERCENT PASSING			
1/2"	100.0	100.0	100.0	100.0	100.0	100.0
3/8"	99.2	98.8	99.1	99.0	99.0	99.4
No. 4	91.5	90.9	89.9	89.7	90.0	91.5
No. 8	78.9	79.1	76.8	76.4	76.0	78.0
No. 16	66.2	66.0	64.4	64.2	63.6	65.3
No. 30	51.4	51.3	50.0	49.7	48.8	50.8
No. 50	31.0	31.0	30.8	29.1	29.4	30.5
No. 100	15.3	15.4	15.8	13.7	15.1	15.2
No. 200	9.3	9.3	9.8	8.0	9.3	9.3
ASPHALT CONTENT, WT PERCENT	6.01	6.00	5.96	5.85	5.79	5.95
PROPERTIES OF RECOVERED ASPHALT						
VISCOSITY						
140°F, poises	3434	3626	3331	3830	2856	3307
275°F, cS	455	473	445	543	421	449
77°F, mP	---	2.73	---	2.67	---	1.25
PENETRATION, 0.1 mm 77°F, 5 s, 100 g	48	51	53	52	54	57
DUCTILITY 77°F, 5cm/min, cm	150+	150+	150+	150+	150+	150+
ASH, WT. PERCENT	0.01	0.02	0.02	0.02	0.02	---

*Recovered from asphalt paving mixes prepared on June 19, 1974 during emission sampling No. 8.

Figure C1. Thompson-Arthur Company Asphalt Plant

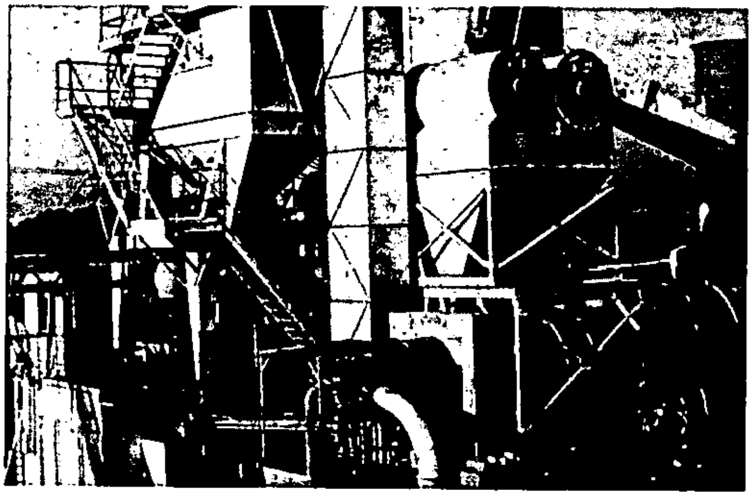

Figure C2. Aggregate Dryer, Hot Bins and Pugmill Mixing Chamber

Figure C3. Hopper Beneath Pugmill

Figure C4. Screw Conveyor Trough

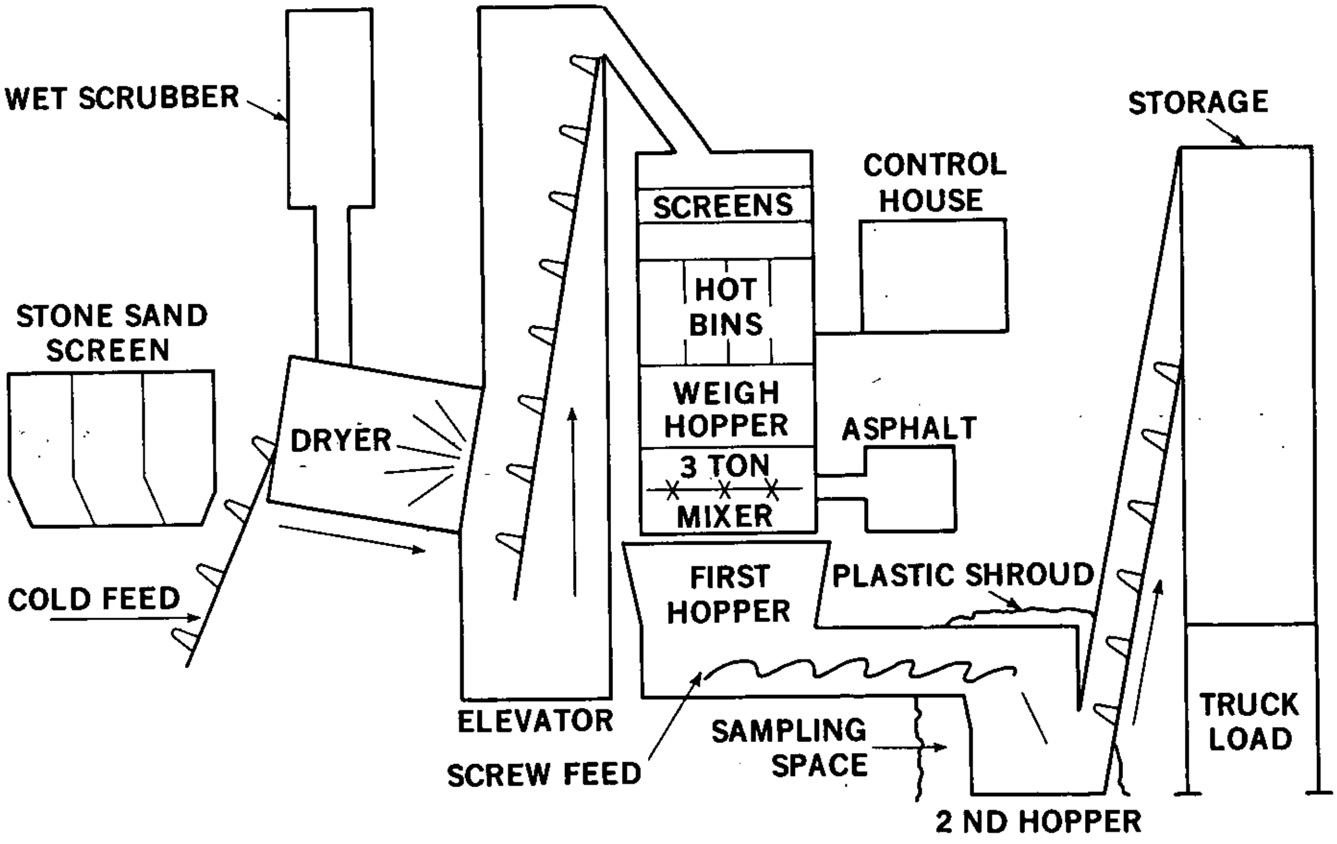

Figure C5. Schematic Diagram Asphalt Hot-Mix Plant Flow Chart

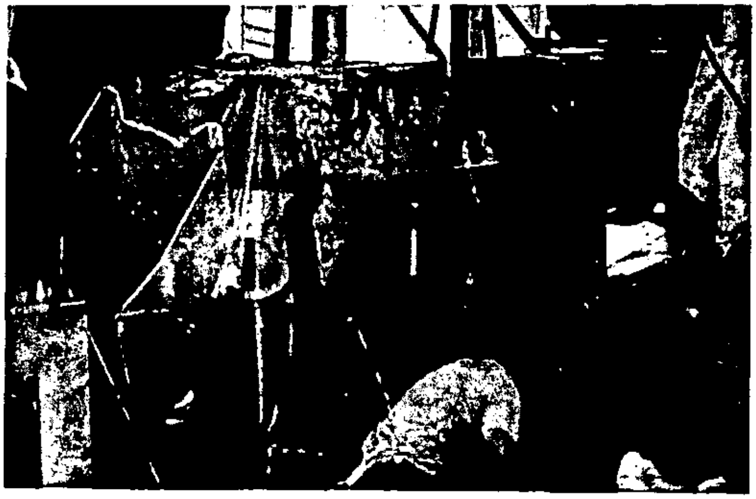

Figure C6. Placing Shroud Around Sampling Area

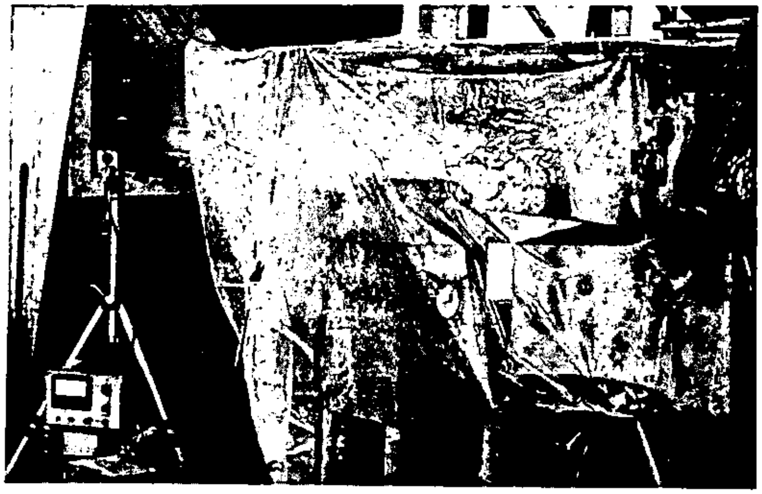

Figure C7. Shrouded Sampling Area

Figure C8. Aggregate Stock Piles

EXHIBIT D

ASPHALT HOT-MIX
EMISSION STUDY

SAMPLING AND ANALYSIS OF EMISSIONS

GREENSBORO, N.C. PLANT

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For submission to The Asphalt Institute

Report No. AID.2DJ.74
September 3, 1974

EXHIBIT D

SUMMARY

The "Blue Smoke" emissions from an asphalt paving plant were sampled, analyzed, and the principal components identified. The results obtained in this study, conducted at the Thompson-Arthur Plant in Greensboro N.C., are compared to the previous results obtained in the New Jersey study as reported by Searl and Brown (1). The tests carried out to date now include the emissions from asphalts from three different sources, representative of material available nationwide.

The principal constituents of the hot-mix emission are hydrocarbons in the C_7 through C_{30} range in both studies. These hydrocarbons with a minor percentage of hetero atom derivatives are very similar to those normally present in the average crude petroleum boiling up to and through the light gas oil range. They appear to be derived from the asphalt used and are very similar to the lowest boiling front-end components removed by vacuum distillation. From elemental, mass spectrometric, and gas chromatographic analyses, it appears that the benzene soluble portion of the particulate emission is very similar to that found by distillation; and we, therefore, believe that this is its source.

The hydrocarbons measured appear similar even though the asphalts were manufactured from three different crude sources.

The polynuclear aromatic hydrocarbons are low compared to those reported for other similar industrial processes. More significant, perhaps, is that for eight tests with the three asphalt sources involved, the average concentration of benzo(a)pyrene (14 $\mu g/1000\ m^3$ air) was just somewhat higher than a range of 1.18-7.49 $\mu g/1000\ m^3$ reported for typical urban air (2).

The gas and particulate phase were sampled as they occurred in the immediate vicinity of asphalt hot pugmill mixing. For many of the more volatile components, grab samples were taken only when the Blue Smoke was at maximum visible intensity. The remainder were sampled continuously for one hour or more covering both maximum and minimum intensities. The concentration ranges found, and a composite analysis of the benzene soluble portion of the particulates are presented in the summary tables.

The sulfur compounds and oxygenated pollutants were either not detected or present at low levels. All of the results are summarized in Tables D.I and D.II showing the range of that found in the North Carolina samples, alongside that found during the New Jersey tests. Study of the particle size by optical and electron microscopy showed that organic particles are less than one micron.

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(1) T. D. Searl and R. A. Brown, Asphalt Hot-Mix Emission Study, AID.1DJ.74 submitted to The Asphalt Institute. (Note by Asphalt Institute: This is Exhibit B of this Asphalt Institute Research Report)

(2) "Biological Effects of Atmospheric Pollutants, Particulate Polycyclic Organic Matter" p. 47 by Committee on Biological Effects of Atmospheric Pollutants, National Academy of Sciences, Washington, D.C., 1972.

TABLE D.I

CONCENTRATION RANGE FOR ASPHALT HOT-MIX EMISSIONS

Compound	Formula	New Jersey Range ppm/vol	North Carolina Range ppm/vol
Methane	CH_4	2 - 3	2 - 3
C_2-C_6 Hydrocarbons	CxHy	<1**	<1**
Hydrogen Sulfide	H_2S	<0.2*- 1.5	<0.2*
Carbonyl Sulfide	COS	<0.2*	<0.2*
Mercaptans	RSH	<0.2*	<0.2*
Sulfur Dioxide	SO_2	<2.*	<0.5*
Carbon Monoxide	CO	4 - 6	3 - 4
Aldehydes	RCHO	<0.1**	0.3 - 0.4
Phenols	ϕOH	<1.	<1.**
Ozone	O_3	<0.1	—
Nitrogen Dioxide	NO_2	<0.1	.05 - .08
		mg/m^3	
C_7-C_{14} Hydrocarbons		3 - 9	3 - 5
High Volume Sample			
Total Particulates			
Test 1, 2		2.6 - 6.4	
Test 3, 4		2.6 - 3.3	
Test 5, 6		6.0 - 7.2	
Test 7, 8			0.5 - 5.7
Benzene Soluble			
Test 1, 2		0.3 - 0.5	
Test 3, 4		0.7 - 0.9	
Test 5, 6		1.8 - 2.8	
Test 7, 8			0.2 - 5.4
		micrograms/1000m^3	
Pyrene	$C_{16}H_{10}$	44 - 240, 107 avg.	96
Benz(a)anthracene	$C_{18}H_{12}$	5 - 24, 11 avg.	32 - 38
Benzo(a)pyrene	$C_{20}H_{12}$	3 - 20, 11 avg.	14 - 22
Benzo(e)pyrene	$C_{20}H_{12}$	14 - 40, 26 avg.	Not Found
Perylene	$C_{20}H_{12}$	5 - 16, 12 avg.	6, 6
		micrograms/m^3	
Nickel	Ni	0.005	0.04
Vanadium	V	0.02 - 0.08*	<0.1*
Cadmium			<.05*
Lead			<.05*

---

* Not detected. If present at all, the compound is at a concentration below that as shown. The less than value represents the sensitivity of the sampling and analysis procedure.

** Small amount detected; less than value shown.

TABLE D.II

COMPOSITE ANALYSIS OF THE BENZENE SOLUBLE PORTION OF THE PARTICULATES

	New Jersey	North Carolina
Physical Appearance	Brown, low viscosity oil	Brown, low viscosity oil
Infrared Spectroscopy	Aromatic oil, somewhat oxidized	
Gas Chromatography		
Boiling Range, °F	530 - 980	550 - 920
n- paraffin distribution	C_{16} - C_{32}	C_{16} - C_{30}
Mass Spectrometry		
Paraffins, %	28	2
Cycloparaffins		
1-ring, %	11	26
2-ring, %	11	19
3-ring, %	18	8
Aromatics		
1-ring, %	10	23
2-ring, %	10	12
3-ring, %	6	4
Sulfur Aromatics, %	6	6
Elemental Analysis		
Carbon, % C	85.3	84.5
Hydrogen, % H	12.0	11.3
Sulfur, % S	1.8	2.5
Nitrogen, % N	0.07	0.01
C/H Ratio	7.1	7.5

INTRODUCTION

In July, 1973, The Asphalt Institute contracted with the Analytical and Information Division of Exxon Research and Engineering Company to sample and analyze for common organic and particulate pollutants in the immediate vicinity of asphalt hot pugmill mixing. Sampling was done at the Halecrest Asphalt plant in Edison, N.J. The results of that study are contained in the first report which was submitted to The Asphalt Institute on March 1, 1974(1).

In the study, six sets of samples were collected on three different days: September 25, October 2, and November 20, 1973. A shroud was used in sampling on the latter two days. Commonly used methods of our laboratory (including ASTM and EPA standard methods) were applied to these samples to measure pollutants, such as: volatile hydrocarbons, carbon monoxide, volatile sulfur compounds, nitrogen dioxide, aldehydes, phenols, ozone, metals, total particulates, benzene solubles and polynuclear aromatic (PNA) hydrocarbons. The organic nature of the particulates was also determined by gas chromatograph, mass spectrometer, infrared and ultraviolet absorption spectrophotometer.

A list of the test methods used is given in Table B.III in the Searl and Brown report (1).

On June 19, 1974 sampling was conducted at a second plant located at the Thompson-Arthur facilities in Greensboro, N. C. Using the same techniques as in the first study, duplicate samples were obtained and tested. This report gives the complete data for the North Carolina tests and summarizes the data obtained in the New Jersey study.

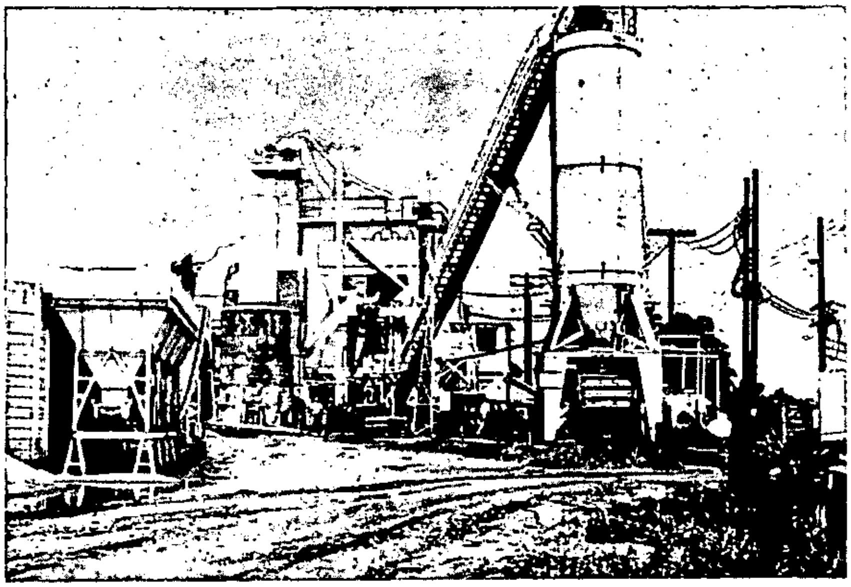
SAMPLING AND ANALYSIS

In order to achieve the objective of this study, a variety of sampling and analytical procedures were required. Some of the volatile compounds had to be collected in evacuated metal bombs, whereas, to successfully analyze for sulfur compounds, glass bombs were utilized to avoid decomposition on metal side walls. Many of the organics were collected in chemical bubblers. Particulates were collected on glass fiber filters in High Volume Samplers as described by EPA in the Federal Register. Table B.III of the first report (1) provides a comprehensive guide to the methods employed in this study, the chemical components that were measured, the method of sampling, and a reference to the method of analysis.

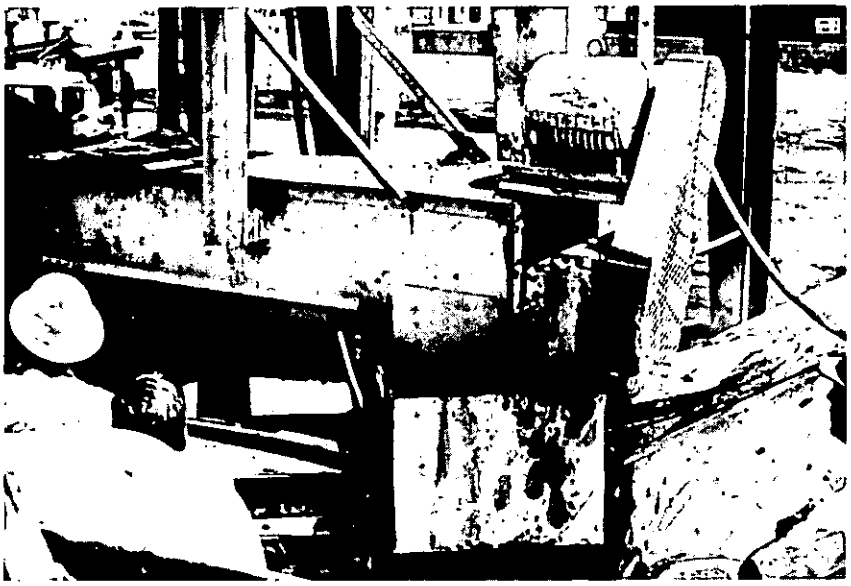
The design of the Thompson-Arthur plant in Greensboro, N. C. is somewhat different than the New Jersey operation. Figures D1-D3 show the Greensboro plant layout. The hot mix is discharged from the pugmill into a hopper, thence through a screw conveyor to an elevator to a storage silo. The area in which most of the emission sampling was done is shown in the lower portion of Figure D1 and the top and bottom portions of Figure D2. This is where the screw conveyor dumps the hot mix onto the elevator carrying the mix to the silo. All sampling done here was underneath a shroud. A portable modified High Volume, not shrouded, was located directly under the pugmill as the mix was dropped onto the screw conveyor, see Figure D3. The sampling parameters for the tests at both locations are given in Table D.III.

Because of the low levels found for some of the pollutants in the New Jersey study, portable MSA sampling apparatus was used in the North Carolina study. This sampled four pollutants simultaneously, i.e., hydrogen sulfide, sulfur dioxide, nitrogen dioxide, and carbon monoxide. The gas chromatographic method for the sulfur compounds was also used.

Figure D1

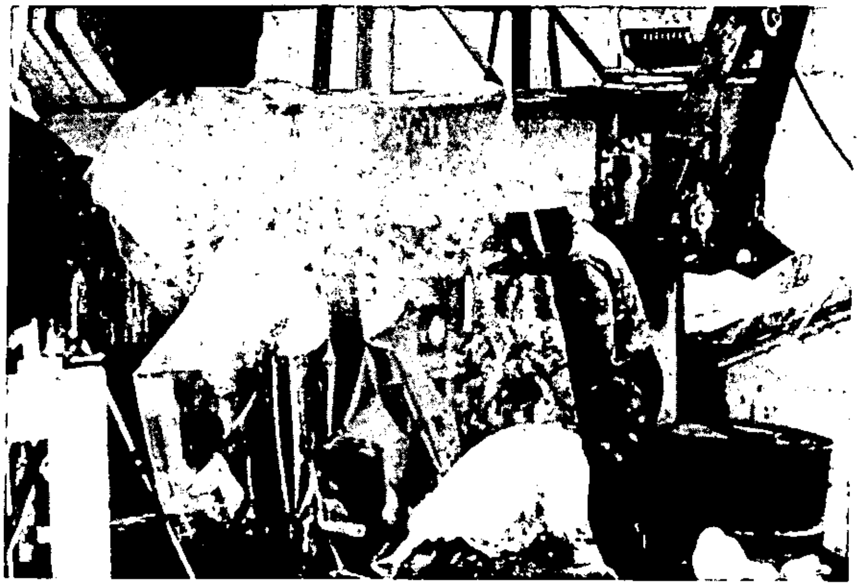


GENERAL VIEW, THOMPSON-ARTHUR PLANT
GREENSBORO, NORTH CAROLINA



SAMPLING AREA WHERE MIX IS DISCHARGED ONTO ELEVATOR

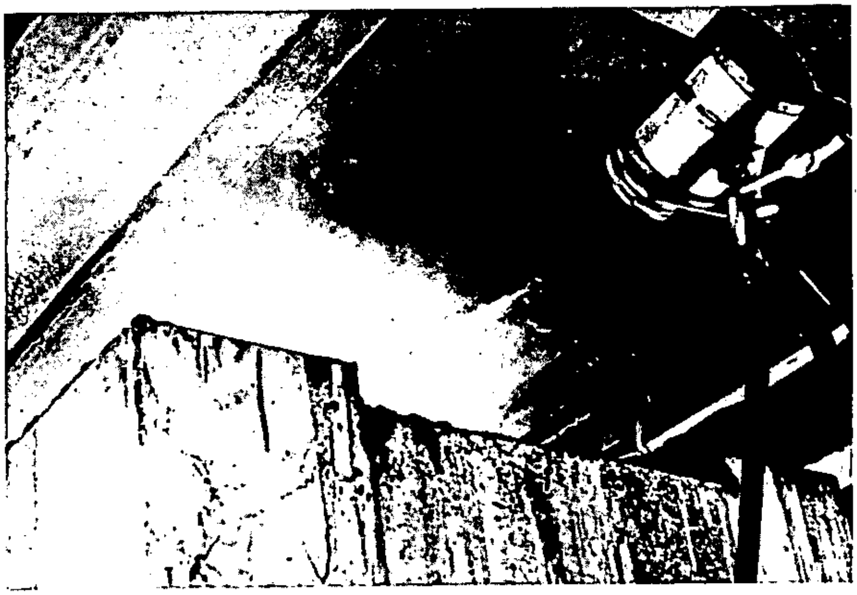
Figure D2



PLACING SAMPLER AND SHROUD

SHROUDED AREA AND TESTING EQUIPMENT

Figure D3



MODIFIED HI-VOL SAMPLER JUST UNDER PUGMILL

TABLE D.III

SAMPLE COLLECTION AT HOT PUGMILLS

Date	Test No.	Air Temp. (°F)	Shroud	Asphalt Being Processed
Aug. 31, 1973	Trial Run Only	95	No	A
Sept. 25, 1973	1, 2	68	No	A
Oct. 2, 1973	3, 4	60	Yes	B
Nov. 20, 1973	5, 6	58	Yes	B
June 19, 1974	7, 8	90	Yes	C

RESULTS AND DISCUSSION

The results of the measurement of all the pollutants at the North Carolina location are discussed in the following section and, where helpful, New Jersey data also are given. In general, the new results are similar to those found in the New Jersey sampling. All of the compounds that occur in the gas phase, such as $C_2 - C_8$ hydrocarbons, sulfur and oxygenated compounds were either found in relatively small concentrations or not detected at all. For these latter, only an upper limit of concentration was reported. Table D.IV contains the results from all tests except the High Volume samplers. Summary, Table D.I, shows test data on samples taken at both the New Jersey and North Carolina locations.

TABLE D.IV

CONCENTRATIONS FOUND FOR ASPHALT HOT-MIX EMISSIONS NORTH CAROLINA TESTS

Compound	Formula	ppm/vol
Methane	CH_4	2 - 3
C_2 - C_6 Hydrocarbons	CxHy	<1**
Hydrogen Sulfide	H_2S	<0.2*
Carbonyl Sulfide	COS	<0.2*
Mercaptans	RSH	<0.2*
Sulfur Dioxide	SO_2	<0.5*
Carbon Monoxide	CO	3 - 4
Aldehydes	RCHO	0.3 - 0.4
Phenols	ϕOH	<1. **
Ozone	O_3	--
Nitrogen Dioxide	NO_2	.05 - .08
		mg/m^3
C_7 - C_{14} Hydrocarbons		3 - 5

* Not detected, if present at all, compound is at a concentration below that as shown. The less than value represents the sensitivity of the sampling and analysis procedure.

** Small amount detected; less than value shown.

Volatile Hydrocarbons

The C_7 - C_{14} hydrocarbons were determined by the carbon tetrachloride absorption-infrared method as in the first report. At that time, gas chromatographic and mass spectrometric analyses showed that the volatile hydrocarbons trapped in carbon tetrachloride and the volatiles from the bulk asphalt were quite similar, showing a range in hydrocarbon distribution from C_7 to C_{14}. Table D.V contains the mass spectrometric analyses of the dry ice cuts from the vacuum distillation of the three asphalts used in all the tests. The asphalt used at Greensboro was designated "C" and its dry ice trap cut is seen to be similar to the comparable fractions of asphalts "A" and "B".

TABLE D.V

MASS SPECTROMETRIC ANALYSIS OF MATERIAL FROM ASPHALT DISTILLATION RETAINED IN DRY ICE TRAP

	Asphalt		
	Wt. %		
Component	A	B	C
Paraffin	27.	31.	31.
1-Ring Naphthenes	24.	24.	26.
2-Ring Naphthenes	13.	13.	19.
3-Ring Naphthenes	0.9	1.	
Benzene	0.2	0.2	0.2
Toluene	8.	6.	13.
C_8 Aromatics	2.	2.	1.
C_9 Aromatics	5.	4.	3.
C_{10} Aromatics	5.	4.	3.
C_{11} Aromatics	3.	3.	0.7
C_{12} Aromatics	2.	2.	0.3
C_{13} Aromatics	0.8	0.8	0.
Indane & Tetralin	4.	4.	2.
Dicyclic Aromatics	5.	5.	0.1
Tricyclic Aromatics	0.4	0.3	--

Particulates

Total particulates and the benzene soluble components thereof, as collected in High Volume sampler filters, are presented in Table D.VI. Compared with the New Jersey tests where the benzene solubles amounted to about 30 per cent of the particulates, the ground level samplers at the left of the screw conveyors had an average of over 90 per cent benzene solubles. At the hot-mix hopper, which duplicates the position of the High-Volumes in the New Jersey test, the benzene solubles are a considerably smaller percentage of the particulates but still are a somewhat higher percentage of the total than in New Jersey. Considerably less particulates are measured at the right hand side of the screw conveyor at the ground level than at the left side.

Polynuclear Aromatic Hydrocarbons - The results obtained by the GC/UV method for the polynuclear aromatic compounds in the particulates are presented in Table D.VII. The higher percentage of benzene solubles are reflected in the somewhat higher concentration of the benz(a)anthracene and benzo(a)pyrene than reported previously(1).

TABLE D.VI

PARTICULATE MATTER BY HIGH VOLUME SAMPLER GREENSBORO, N. C.

Position [a]	Test	Total Particulate	Benzene Soluble	Benzene Soluble
		------ mg/m^3	------	(Rel. %)
Ground Level, Left	7	5.71	5.40	94
Ground Level, Left	8	2.60	2.34	90
Ground Level, Right	7	0.63	0.47	75
Ground Level, Right	8	0.49	0.19	39
Near Hot Mix Hopper	7	21.1	9.8	45
Modified High Volume		22.2		
Near Hot Mix Hopper	8	11.8	4.1	34
Modified High Volume		11.3		

[a] Positions - Ground level samplers shrouded at end of screw conveyor into mix elevator.

Hot mix hopper sampler was close to bottom of pugmill--was not shrouded.

TABLE D.VII

POLYNUCLEAR AROMATICS IN HIGH VOLUME PARTICULATE MATTER GREENSBORO, N. C.

Compound	Micrograms/1000 m^3
Pyrene	96
Benz(a)anthracene	38, 32
Benzo(a)pyrene	22, 14
Benzo(e)pyrene	Not Found
Perylene	6, 6

NOTE: For Test 7 and also Test 8, the left and right sides were composited. The PNA concentration, therefore, are about half what they would be if only the left side sample were used.

Characterization of Benzene Solubles - In order to compare the benzene solubles and the distillation fractions of the asphalt, the various features of both will be discussed together. To assist in understanding the mechanism, information from the first report (1) will be repeated.

Table D.VIII lists the physical properties of the asphalt cements taken from plant storage immediately following sampling on the dates shown. These asphalts are all viscosity graded AC-20, passing AASHTO M 226 Table II, and ASTM D To Be Designated Table II. Exxon supplied asphalt (A) used on 9-25-73 (Test 1 and 2), Chevron the asphalt (B) used on 10-2-73 (Test 3 and 4) and 11-20-73 (Test 5 and 6), and Amoco asphalt (C) was used on 6-19-74. Figure D4 (lower portion) shows the composition (3) of the asphalt cements used during the three emission samplings. It will be noted that these are typical asphalt compositions even though the crude sources are known to be distinctly different.

A high vacuum distillation was performed on the three asphalts as described above. This was done in order to obtain working samples of the most volatile fractions present in the asphalt cement, reasoning that the organic particulates collected could bear a resemblance to the front end fractions from the asphalt cement, unless the hot-mixing exposure caused significant chemical changes. Figure D4 shows the distillation characteristics of the front end 1 percent from each of the asphalts, again showing considerable similarity; but as expected, asphalt "C" is somewhat more volatile. It will be noted that each asphalt has measured initial boiling points between 500 and 600°F plus small but measurable fractions collecting in a dry ice trap, thus indicating that their true initial boiling points might be lower than 500°F. Table D.IX lists the molecular weight and elemental analyses of the fractions caught in the trap as well as some of the continuous cuts. The trap fractions are very low in molecular weight and contain less hetero atoms than the next cuts, although there is a gradual increase in molecular weight and content of hetero atoms. Figure D5 also shows the composition of cuts #1 and #2 combined, revealing a comparatively higher proportion of saturates and naphthene-aromatics and a minor proportion of polar-aromatics, as in comparison with that found in the original asphalt cement itself. Although it is somewhat surprising that asphalt cements contain these very low molecular weight low boiling fractions, even in a minor percentage, the difference in composition between the overhead fractions and the asphalt cement from which it was derived is consistent with asphalt manufacture by vacuum distillation.

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(3) L. W. Corbett, Anal. Chem. 41, 573 (1969).

TABLE D.VIII

EXAMINATION OF AC-20 ASPHALT CEMENT USED DURING SAMPLING OF HOT-MIX EMISSIONS

Sample No.	A	B	B'	C
Sample Date	9-25-73	10-2-73	11-20-73	6-19-74
Asphalt Source	Exxon	Chevron	Chevron	Amoco
Physical Properties				
Ab. Vis @ 140 F	1990	1753	1953	2322
Pen @ 77 F	74	72	70	71
Pen @ 39.2 F	18	16	20	20
K. V. @ 275 F	391	380	393	372
Flash COC F	615	620	595	540
Flash PM F	-	-	-	455
Sol. TCE, %	99.8	99.7	-	-
Sp. Gr. @ 60 F	1.026	1.030	-	-
TFO, % loss	.04	.04	-	.42
Res. Vis. @ 140 F	4657	4219	-	5250
Res. Duct. @ 60 F	40	28	-	26
Distillation, % loss	1.17	1.20	-	0.93
Res. Vis. @ 140 F	2820	2286	-	2905
Res. Pen. @ 60 F	57	56	-	56
Elemental Analysis				
Sulfur, %	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 (if present)	<0.6	<0.1	-	<0.1

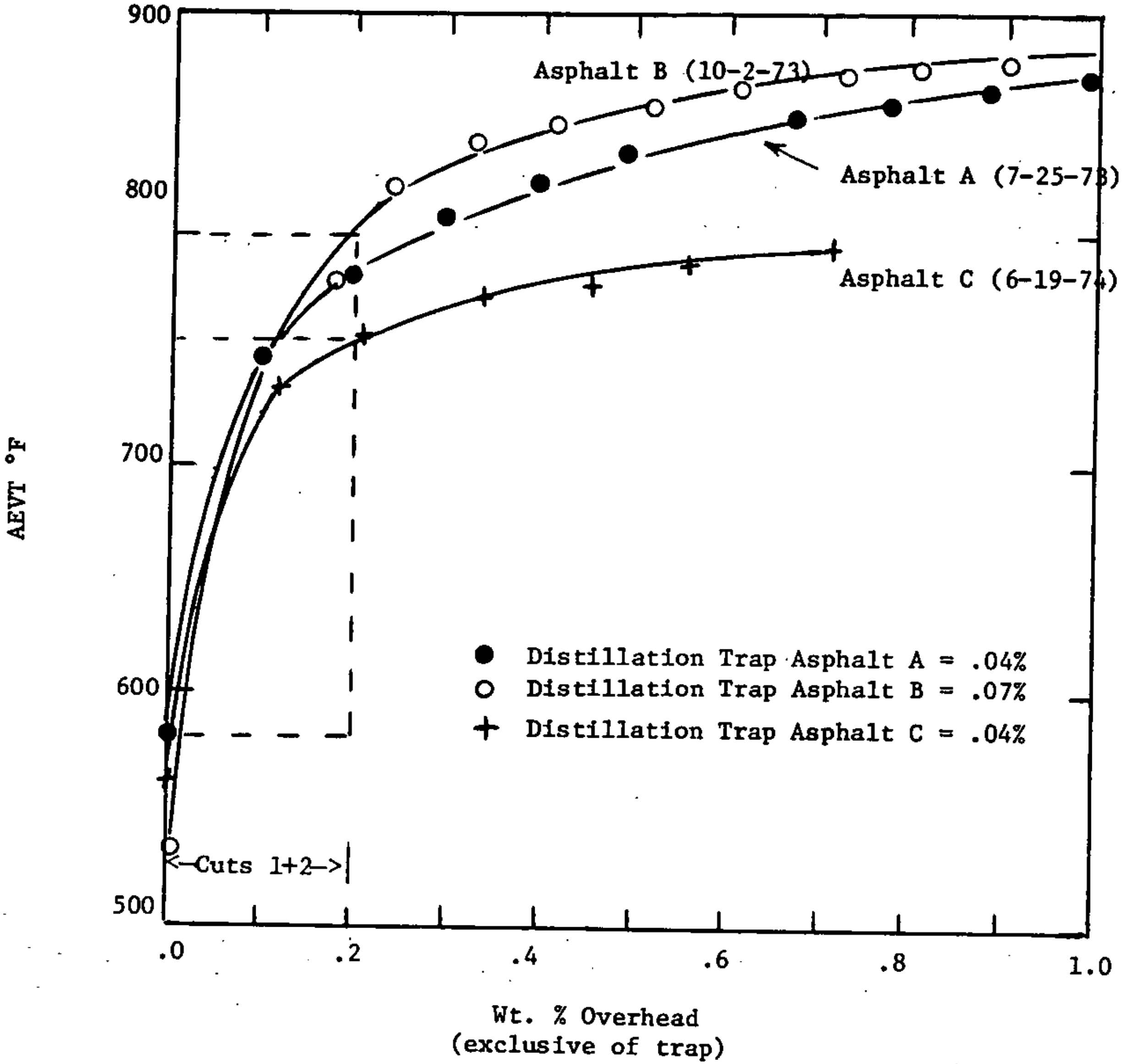
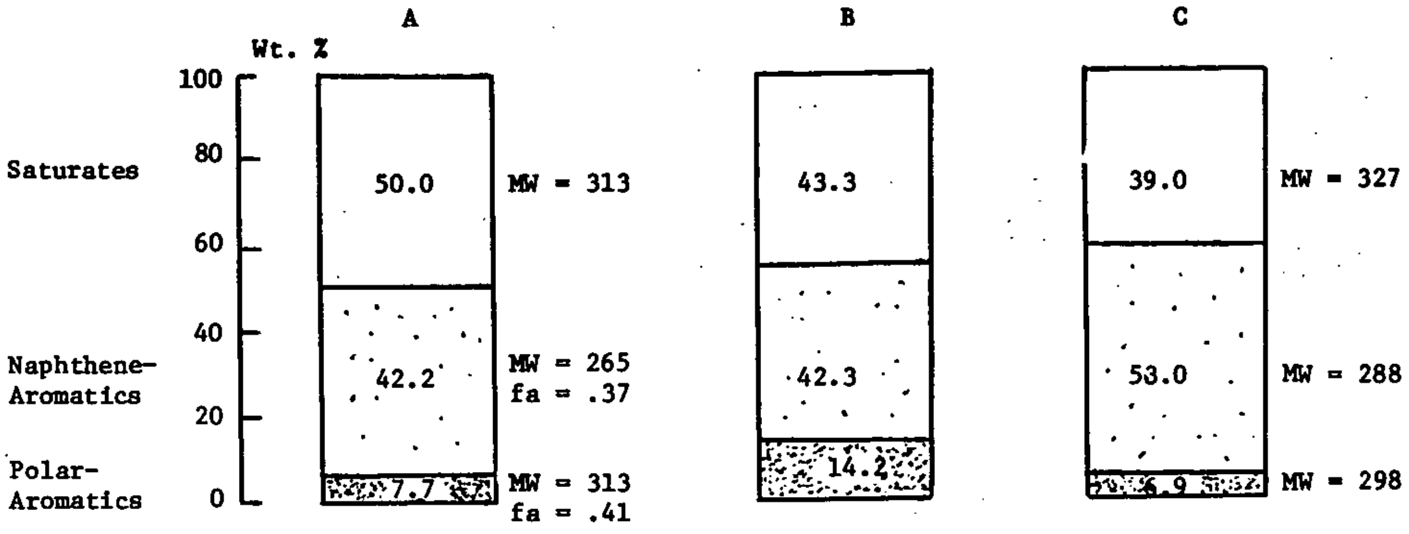


Figure D4. Front End Distillation of AC-20 Used During Hot-Mix Emission Sampling On September 25, 1973, October 2, 1973 and June 19, 1974

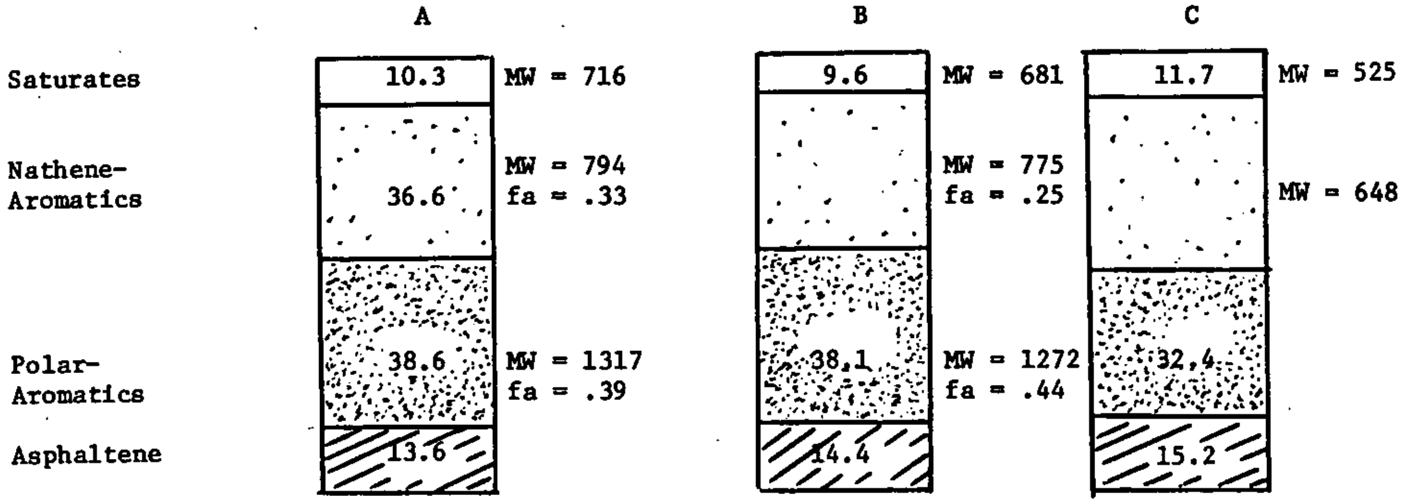
TABLE D.IX

EXAMINATION OF FRONT END FRACTIONS FROM AC-20 ASPHALT CEMENT USED DURING SAMPLING OF HOT-MIX EMISSIONS

Sample No.	Fraction	Mol. Wt.	Elemental Analysis %				
			C	H	N	S	O
A	Trap	189	86.33	12.00	0.009	0.35	0.16
B	Trap	195	85.89	11.93	0.006	0.68	0.16
A	Cut 1	276	86.42	11.84	0.10	1.35	0.28
B	Cut 1	320	85.06	11.47	0.10	2.63	0.20
A	Cut 2	318	--	--	--	--	0.32
B	Cut 2	322	--	--	--	--	0.19
A	Cut 3	345	86.86	11.56	.3	1.87	--
B	Cut 3	374	85.00	10.98	.3	2.81	--
C	Trap	235	84.41	12.58	.7	2.50	0.48
C	Cut 1	285	85.48	10.76	.3	2.72	0.25



Vacuum Cuts 1 + 2 From Asphalt



Whole Asphalt

Figure D5. Composition Analyses of AC-20 Asphalt Cements and Front-End Fractions

<u>Distillation Data on Benzene Solubles</u> - GC distillation(4) of a composite of the benzene solubles from the Greensboro tests gave the calculated temperatures for specified per cents off, shown in Table D.X. The initial, mid, and final boiling points of the benzene solubles from the New Jersey tests are also shown.

TABLE D.X

GC DISTILLATION OF BENZENE SOLUBLES

Per Cent Off.	North Carolina Deg. F	New Jersey Deg. F
0.5	562	530, 536
1.0	575	
2.0	590	
3.0	601	
5.0	615	
7.0	625	
10.0	637	
15.0	652	
20.0	663	
25.0	675	
30.0	685	
35.0	695	
40.0	703	
45.0	712	
50.0	720	720, 724
55.0	728	
60.0	737	
65.0	746	
70.0	757	
75.0	768	
80.0	781	
85.0	796	
90.0	814	
95.0	841	
96.0	848	
97.0	858	
98.0	872	
99.5	916	980

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(4) Performed by W. W. Schulz, AID.

Composition of Benzene Solubles, Elemental Analysis - The first cuts from the vacuum distillation and the benzene solubles of the particulates from all the tests were analyzed for elemental composition as shown in Table D.XI.

TABLE D.XI

ELEMENTAL ANALYSIS

Sample	Carbon	Hydrogen	Sulfur	Kjeldahl Nitrogen	Oxygen	Carbon/ Hydrogen
Asphalt A, Cut #1	86.42	11.84	1.35	0.10	0.28	7.3
Asphalt B, Cut #1	85.06	11.47	2.63	0.10	0.20	7.4
Asphalt C, Cut #1	85.48	10.76	2.72	<.3	0.25	8.0
Benzene Solubles						
Test 1, 2 (A)	85.46	11.96	1.32	--	--	7.1
Test 3, 4 (B)	84.98	11.96	2.21	--	--	7.1
Test 5 (B)	86.20	12.22	--	0.070	--	7.1
Test 6 (B)	84.46	11.62	--	0.069	--	7.2
Test 7, 8 (C)	84.45	11.27	2.49	0.01	--	7.5

The elemental analysis of the first vacuum cut from the asphalt cement and the benzene soluble portion of the particulates are in good agreement. Asphalts "B" and "C" have a high sulfur content both in the first vacuum cut and in the particulates. The carbon/hydrogen ratios are quite similar and there is little oxygen or nitrogen present in the cuts from the three asphalts. There was insufficient sample to determine oxygen on the benzene solubles or nitrogen on Tests 1-4.

Compound Types - During the course of the earlier study, selected samples were analyzed by mass spectrometer to obtain hydrocarbon type analyses. In one instance, a benzene soluble fraction was analyzed. Alumina column fractions prepared for the measurement of individual PNA's were also analyzed. By combining these data, an overall composition of a typical benzene soluble was obtained as shown in Table D.XII. The mass spectrometric analysis(5) of the benzene solubles from Test 7 and 8 are shown also in Table D.XII. Asphalt "C" is low in paraffins;

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(5) Performed by R. J. Pancirov, AID.

this is consistent with the gas chromatographic analysis which showed little n-paraffins to be present. The benzene solubles contain more one-ring aromatic compounds and a greater amount of cycloparaffins than those of the earlier test.

TABLE D.XII

HYDROCARBONS IN A BENZENE SOLUBLE FRACTION

Hydrocarbon Type	Tests 1 - 6	 7, 8
Paraffins	28	2
Cycloparaffins		
1-ring	11	26
2-ring	11	19
3-ring	18	8
Aromatics		
1-ring	10	23
2-ring	10	12
3-ring	6	4
Sulfur Aromatics (Benzo, Dibenzothiophenes)	6	6

Particle Size of Particulates by Microscopy - Samples were collected by impact onto double-faced "Scotch Tape" adhering to glass slides, "Millipore" filters, 1/8 inch circular carbon coated electron microscope specimen grids, and high-volume glass fiber filters. Two locations, the hopper area and the end of the screw conveyor to the silo feed, were sampled at the plant.

The samples were "clean", i.e., not very high in visible particle count or concentration. A few dust-like particles 2 to 5 microns in size were observed. Particles, if present, were less than one micron in size. An oil mist having droplets less than 0.5 microns size would not be observed with the various microscopes employed. The observation obtained with each microscope is present in Table D.XIII(6).

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(6) Performed by P. Skiba, AID.

TABLE D.XIII

RESULTS OF MICROSCOPIC EXAMINATION OF AIRBORNE PARTICLES FROM ASPHALT PLANT

Instrument	Results
Light Microscope	Only a few particles visible. These were in the 2-5 micron range.
Electron Microscope	•An occasional liquid particle .2 to .5 microns. Evaporates in electron beam.
Scanning Electron Microscope	Occasional quartz-like dust particles 2-5 microns. Liquid droplets would be evaporated.

Metals

An emission spectrographic analysis of the benzene solubles for metals showed that cadmium and lead were less than 0.05 μg/m^3. Atomic absorption gave a value of 0.04 μg/m^3 for nickel and <0.1 μg/m^3 for vanadium.

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