

SYMPOSIUM ON CHARACTERIZATION AND CHEMISTRY OF OIL SHALES
PRESENTED BEFORE THE DIVISIONS OF FUEL CHEMISTRY AND
PETROLEUM CHEMISTRY, INC.
AMERICAN CHEMICAL SOCIETY
ST. LOUIS MEETING, APRIL 8 - 13, 1984

NITROGEN-CONTAINING COMPONENTS FROM SHALE OIL AS MODIFIERS
IN PAVING APPLICATIONS

By

H. Plancher and J. C. Petersen
Western Research Institute, University of Wyoming Research Corporation, P. O. Box 3395
Laramie, Wyoming 82071

INTRODUCTION

One of the major causes of asphalt pavement failure is moisture-induced damage. The detrimental effects of moisture and/or repeated freeze-thaw cycles in asphalt concrete pavements have long been recognized by state and federal agencies and the motoring public. Moisture-induced damage has been studied in our laboratory from a chemical and mechanistic viewpoint related to the bonding and debonding of asphalt components from the aggregate surfaces (1-3). Results from these studies indicated that certain nitrogen-containing molecules naturally present in the asphalt might be involved in reducing the sensitivity of the asphalt-aggregate mixtures to moisture-induced damage. Infrared spectrometric (1, 3-6) and elemental nitrogen analyses (3) of asphalt components removed by hot pyridine extraction from previously benzene-extracted aggregates showed that nonpyrrolic nitrogen might, in part, be responsible for an increased resistance of the asphaltic pavements to moisture-induced damage.

During the development of a water susceptibility test (WST) to indicate the susceptibility of asphalt-aggregate mixtures to repeated freeze-thaw cycles, we found that WST briquets prepared from pyridine-pretreated aggregates were highly resistant to damage during the test (2). Evidence that pyridine-type compounds in shale oil retarded the detrimental effects of moisture resulted from the analysis of a 30-year-old pavement constructed from a shale oil residue (rich in pyridine-type compounds) and uncrushed river run gravel (7). Additional studies conducted at Texas A&M University (8) and in our laboratory (9-10) further indicated that pyridine-type nitrogen in asphalts reduced the effects of moisture damage in asphaltic pavements. Nitrogen of the pyridine type is naturally present in asphalts in varying small amounts; however, shale oil contains significant amounts (1.3 wt %) of pyridine-type homologs.

As part of our continuing research on moisture damage in asphaltic pavements, we began investigating the strength of nitrogen compound-aggregate interactions before and after subjecting the nitrogen compound-treated aggregates to a warm water-benzene soak. Temperature-programmed thermal desorption of the nitrogen compounds from the treated aggregate surfaces through three different temperature ranges was used to determine the relative strength or stability of the nitrogen-aggregate bond. Upon thermal desorption, nitrogen in the evolved gases was determined by a chemiluminescent detector (3, 9, 10).

Another area investigated was the ability of nitrogen-rich shale oil fractions to disperse asphaltenes in oxidatively-aged asphalts in anticipation of their use as potential recycle agents for aged petroleum asphalts. Pavement rehabilitation projects frequently add recycle or rejuvenating agents to aged asphaltic pavements to restore desired viscoelastic properties to the embrittled asphalt binder.

EXPERIMENTAL

Materials

Petroleum Asphalts - Four extensively studied (1, 6, 11-15) asphalts of widely varying composition and identified by code numbers B-2959, B-3036, B-3051 and B-3602 were supplied by the Federal Highway Administration (FHWA), Materials Division.

Aggregates - The aggregates, obtained from various asphalt paving projects, were crushed in a disk grinder equipped with ceramic plates, wet screened to 20 to 35 mesh size, rinsed with distilled water and dried at 150°C for 24 hours. Aggregates were heated again at 150°C prior to use. Identification of the aggregates appears in the text.

Solvents - Reagent-grade benzene and pyridine were dried by refluxing them for 8 hours over CaH_2 before final distillation through a Vigreux column.

Products Derived from Shale Oil and Petroleum Liquids - A shale oil basic nitrogen concentrate, a petrolene fraction from an AC-5 shale oil asphalt, a shale oil distillate fraction and several commercially available recycle agents (identified in the text) were used in the study. The shale oil basic nitrogen concentrate was obtained as a byproduct by Suntech, Inc., Marcus Hook, PA, during the experimental refining of shale oil produced by the Occidental vertical-modified in situ process. The oil sample was obtained from the U. S. Department of Energy's Anvil Points facility. The crude shale oil was first hydrotreated by Suntech (16) to reduce the nitrogen content from 1.5 to 0.5 wt % and then topped to 281°C by distillation. A portion of the distillation residue (4,826 L) was treated with 2.25 wt % anhydrous hydrochloric acid (HCl) in a glass-lined reactor at 43°C and 55.2 kPa to precipitate the hydrochloride salts of the nitrogen compounds. The salts were thermally decomposed at 300°C to liberate the HCl and yield the shale oil nitrogen concentrate. Total yield based on feed material was 13.3 wt %. The petrolene fraction (83.2 wt %) was prepared by digesting 100 g of an AC-5 shale oil asphalt (8) in 4 L n-pentane, removing the asphaltenes by filtration and evaporating the solvent. The shale oil distillate fraction produced from the Union gas combustion process had a corrected boiling range of 342-382°C at 1.013×10^5 Pa.

Solutions for Nitrogen Adsorption-Desorption Studies - 10% (weight/volume) Solutions of the various nitrogen-containing components used in the adsorption-desorption studies were prepared in benzene and used to treat the various aggregates.

Procedures

Nitrogen Compound-Treated Aggregates - One-gram lots of the 60-80 mesh sized aggregate particles were placed in vials containing 2 cc of the nitrogen compound-benzene solution. One hour later, the treated aggregates were recovered by vacuum filtration, washed with benzene and air dried for 48 hours prior to obtaining nitrogen analyses. One-half gram of the treated aggregate was further treated in a vial containing 25 cc of distilled water and 2 cc benzene for 6 hours at 60°C followed by vacuum filtration and water-benzene washings to remove water-displaced nitrogen compounds from the aggregate surfaces. The treated aggregates were air dried and analyzed for nitrogen, as described later.

Asphalt-Aggregate Briquets - Asphalt-coated aggregates used to prepare briquets for the water susceptibility test (WST) were prepared using previously reported procedures (2). Briefly, briquets mounted on a beveled stress pedestal and submerged in water were repeatedly subjected to freeze-thaw cycles until the briquet failed from crack propagation or fracture.

Nitrogen Analyses - Treated aggregates (0.2500 g) were placed in an Antek Model 772 microcomputer-controlled pyroreactor and the temperature was increased from 100 to 600°C at 50°C/minute with a 5-minute isothermal period at 100°C and 7-minute isothermal periods at 150, 300 and 600°C.

Asphaltene Settling Test - To conduct the test, 2 g of asphalt, or 2 g of aged asphalt plus 0.02 g of the recycle agent were digested in 50 cc n-hexane for 24 hours at 20°C. The resultant mixture was transferred into a 50-cc graduated cylinder and the rate at which the asphaltenes settled in the hexane solution was determined (2). The test result was reported as the time in minutes required for the asphaltene meniscus to reach the 25-cc mark on the graduated cylinder. Final volume of precipitated asphaltenes was recorded 24 hours later.

RESULTS AND DISCUSSION

As outlined in the Introduction, considerable evidence from previous studies indicated that pyridine-type compounds in bituminous mixtures reduce the sensitivity of the mixtures to moisture-induced damage. Because shale oil is rich in pyridine-type nitrogen compounds, the use of shale oil nitrogen components as modifiers in petroleum asphalt might be highly desirable. As part of a continuing study of the chemistry of asphalt-aggregate interactions, we examined the adsorption of a shale oil basic nitrogen concentrate on the surface of mineral aggregate and determined the relative sensitivity to displacement of the adsorbed compounds from the surface of the aggregate by water. Results were compared with the adsorption-desorption characteristics of the model nitrogen base, pyridine, on several aggregates of widely differing composition.

Adsorption-Desorption from Mineral Surfaces of Nitrogen Compounds in Shale Oil Basic Nitrogen Concentrate

Figure 1 illustrates the scheme used to evaluate the adsorption-desorption and water-displacement characteristics of the nitrogen compounds in the shale oil basic nitrogen concentrate that are strongly adsorbed on mineral aggregate surfaces. Briefly, nitrogen components adsorbed on mineral aggregate particles from a dilute benzene solution of the concentrate are thermally desorbed both before and after subjecting the treated aggregates to a warm water-benzene soak to displace water-sensitive components. Thermal desorption is accomplished in a temperature-programmed furnace and the displaced nitrogen is detected as a function of temperature by a nitrogen

detector.

A shale oil basic nitrogen concentrate produced as a byproduct during stream cleanup in the experimental refining of shale oil by Suntech, Inc. (16) was used to evaluate the interactions of shale oil nitrogen compounds with mineral aggregate surfaces. Properties of the concentrate are summarized in Table I. The material was a semiviscous liquid at ambient temperature. Infrared analysis of the byproduct in tetrahydrofuran showed strong doublet bands at about 1600 and 1560 cm^{-1} , which on treatment with HCl were replaced by a new band at about 1230 cm^{-1} . This behavior is typical of pyridines and indicates a high concentration of pyridine types in the concentrate. This, of course, is not surprising because its isolation from the experimental refining stream was by HCl extraction followed by springing of the HCl from the basic adduct by thermal treatment.

TABLE I

PROPERTIES OF SHALE OIL BASIC NITROGEN CONCENTRATE FROM STREAM CLEANUP DURING EXPERIMENTAL REFINING OF SHALE OIL

Gravity, °API	16.0
5% boiling point, °C	297
95% boiling point, °C	524
Carbon, wt %	84.03
Hydrogen, wt %	11.06
Nitrogen, wt %	3.97
Chlorine, wt %	0.045
Aromatics, ^{13}C NMR, %	27

Figure 2 shows the desorption thermograms of the nitrogen components from the shale oil basic nitrogen concentrate that had been adsorbed on two paving aggregates—one from Colorado and one from FHWA Region 10 (Oregon) (3, 17). Note that most of the nitrogen was desorbed in the 300 to 600°C range, indicating a strong bond with the aggregate surface. Subjecting the treated aggregates to a warm water soak in the presence of benzene to solubilize water-displaced components reduced the amount of strongly adsorbed nitrogen components on the aggregate surfaces; however, significant amounts were resistant to water displacement, as indicated by the thermograms. A considerable amount of the nitrogen desorbed from the FHWA Region 10 aggregate in the 300 to 600°C range was particularly resistant to displacement by water. Because pyridine-type compounds are suspect as the dominant type in the shale oil basic nitrogen concentrate contributing to the nitrogen thermogram, model compound studies using the parent compound pyridine were conducted to further elucidate the role of pyridine compounds in reducing moisture damage in asphalt pavements.

Adsorption-Desorption from Mineral Surfaces of Model Compound Pyridine

The Colorado and FHWA Region 10 aggregates were treated with a dilute solution of pyridine in benzene in a manner similar to their treatment with the shale oil basic nitrogen concentrate and thermograms of the nitrogen desorption obtained. Figure 3 shows the thermograms obtained both before and after subjecting the pyridine-treated aggregates to the warm water-benzene soak. Note the similarities between these thermograms for pyridine and those for the shale oil basic nitrogen concentrate shown in Figure 2. The Colorado aggregate had a greater affinity for nitrogen found to desorb in the 150 to 300°C range than did the FHWA Region 10 aggregate and the nitrogen in this desorption region was quite resistant to water displacement. The Colorado aggregate showed a reduced amount of adsorption in the 300 to 600°C range compared with the FHWA Region 10 aggregate.

Of potential significance to moisture-induced damage is the relative amounts of nitrogen desorbed within each temperature range and the resistance of that nitrogen to displacement to water. This can best be described by quantification of the data from Figure 3 as displayed in Table II. Even though the Colorado aggregate showed a higher total relative surface density (RSD) of adsorbed pyridine molecules than the FHWA aggregate before water displacement (40.6 vs 33.3, respectively), the adsorbed pyridine was more easily displaced from the Colorado aggregate surface by water as indicated by comparing the total RSD's of the same two aggregates after water treatment (7.4 vs 17.7, respectively). Also, the RSD of nitrogen in the 300 to 600°C range after water treatment was 13.6 for the FHWA Region 10 aggregate compared with 4.9 for the Colorado aggregate. Related studies using these aggregates in laboratory-prepared asphalt-aggregate mixtures have shown a relationship between the relative amount of nitrogen desorbed in the 300 to 600°C range and its resistance to water displacement to the resistance of the asphalt-aggregate mixtures to moisture damage. This is illustrated for the two aggregates in question by the data in Table III. Note the greatest tensile strength retention ratio of pavement mixtures and increased cycles to failure in the WST for the FHWA Region 10 asphalt-aggregate mixture when subjected to the

accelerated laboratory moisture damage conditioning. These data, together with data on additional asphalt-aggregate systems published elsewhere, support the proposition that adsorption of those pyridine-type nitrogen compounds in petroleum asphalts, although in much lower concentrations than in shale oil products, are important to the resistance of asphalt-aggregate mixtures to moisture damage. Thus, pyridine-type nitrogen components from shale oil should have potential value as asphalt modifiers in improving the moisture resistance of pavement mixtures.

TABLE II

THERMAL DESORPTION OF PYRIDINE FROM AGGREGATE SURFACES BEFORE AND AFTER WATER TREATMENT

Aggregate Source	Surface Area m ² /g	Water- Benzene Soak	Nitrogen Detector Readout	Relative Surface Densities ^a in Temperature Range, °C			
				<150	150-300	300-600	Total
FHWA							
Region 10	1.92	no	64,019	2.6	19.2	21.5	33.3
		yes	43,021	0	4.1	13.6	17.7
Colorado	1.95	no	79,340	9.6	19.5	11.5	40.6
		yes	14,463	0	2.5	4.9	7.4

a. Nitrogen detector readout counts divided by aggregate surface area.

TABLE III

RESISTANCE OF ASPHALT-AGGREGATE MIXTURES TO MOISTURE-INDUCED DAMAGE^a

Aggregate-Asphalt System	Tensile Strength Ratio from Accelerated Moisture Conditioning	Cycles-to-Failure in Water Susceptibility Test
FHWA Region 10	0.6	5
Colorado	0.2	3

a. Data from (3).

Laboratory Evaluation of Shale Oil Products in Asphalt Paving Applications

Three different shale oil-derived products were evaluated in our laboratory for their potential application in asphalt paving. These included a shale oil AC-5 asphalt prepared by a vacuum distillation of a gas combustion shale oil, the shale oil basic nitrogen concentrate discussed earlier and a 342 to 382°C distillate fraction from a partially hydrotreated shale oil. The nitrogen concentrate was evaluated both as an antistripping agent and for potential use as a recycle agent and the distillate fraction was analyzed only as a recycle agent. Pavement rehabilitation projects frequently add recycle agents to the aged asphaltic pavements being recycled to restore desired viscoelastic properties to the embrittled asphalt binder.

Evaluation of Petroleum- and Shale Oil-Derived Asphalts by WST Procedure - Data in

Table IV summarize the results obtained during the WST evaluation of several asphalt-aggregate mixtures prepared from petroleum and shale oil-derived asphalts using the same limestone aggregate. This particular aggregate was selected because previous studies showed that it produced moisture-sensitive mixtures (1). Comparisons between the number of freeze-thaw cycles in the WST required to induce failure in petroleum vs shale oil asphalt briquets using this aggregate clearly showed that the shale oil asphalt significantly improved the briquet water resistance compared to its petroleum counterparts. The shale oil asphalt briquet showed no signs of failure after 100-plus cycles, after which the test was finally terminated. The petroleum asphalt briquets failed in seven or fewer cycles. Related studies conducted at Texas A&M University using the same shale oil asphalt showed superior moisture-damage resistance for laboratory paving mixtures (8). These WST and Texas results lend support to the previous proposition that pyridine-type compounds in shale oil produce asphalt-aggregate bonds that resist the detrimental action of water.

Evaluation of Shale Oil Basic Nitrogen Concentrate as an Additive to Petroleum Asphalts to Improve Moisture Resistance of Asphalt-Aggregate Mixtures -

WST briquets were prepared using a Venezuelan asphalt and a quartzite aggregate that produced water-sensitive mixtures in a section of I-80 in eastern Wyoming. This section of interstate highway began to show signs of moisture-induced damage shortly after it was constructed. Addition of 5 wt % (based on asphalt content) of

the shale oil basic nitrogen concentrate to the asphalt-aggregate mixture in the laboratory resulted in an increase in briquet cycles-to-failure from less than one complete freeze-thaw cycle for the untreated briquet to five cycles before the shale oil-modified briquet developed cracks. This is a significant increase and demonstrated the value of using a shale oil basic nitrogen concentrate as an antistripping agent in petroleum asphalts.

TABLE IV
EVALUATION OF BRIQUETS PREPARED FROM PETROLEUM AND
SHALE OIL-DERIVED ASPHALTS

Petroleum Asphalts ^a	Briquet ^b Wt, g	Cycles-to-Failure,
		WST
B-2959	50	1
B-3036	50	2
B-3051	50	7
B-3602	50	2
Shale oil asphalt	50	>100

a. Asphalts obtained from FHWA.

b. All briquets prepared using 5% asphalt and 95% Hol limestone (7).

In another experiment, two different silicate aggregates from Texas that had produced moderate to severe stripping problems in pavements were evaluated using the nitrogen thermal desorption analysis technique previously described and the WST procedure. Although both aggregates showed relatively low interactions of the aggregate with model nitrogen compounds, the moderate stripping aggregate showed more interaction than the severely stripping aggregate. The shale oil basic nitrogen concentrate was compared with two commercial antistripping agents for its ability to reduce moisture damage using these two aggregates. Briquets containing 6 wt % AC-20 asphalt modified with 1 wt % (based on asphalt content) of the antistripping agents and 5 wt % shale oil basic nitrogen concentrate were prepared. The shale oil basic nitrogen concentrate was added at 5 wt % because its nitrogen content was correspondingly lower than that of the antistripping agents. Test results are shown in Table V. The commercial antistripping agents showed erratic response and sometimes increased rather than decreased the sensitivity of the briquet to moisture damage. The shale oil basic nitrogen concentrate was the only additive that was beneficial in the test on both aggregates when compared with the control.

TABLE V
EFFECT OF ADDITIVES ON SILICATE AGGREGATES

Additive	% Added	WST, Cycles to Failure	
		Severe Stripping	Moderate Stripping
		Aggregate	Aggregate
-0-	-	5	17
Amidoamine	1	4	7
Imidazole	1	10	6
Shale oil basic nitrogen concentrate	5	23	25

Evaluation of Shale Oil Fractions as Potential Recycling Agents for Aged Asphalts

Important criteria for the recycling of asphaltic pavements are the restoration of pavement flexibility and durability. Restoration of these properties depends upon the ability of recycle agents to improve compatibility by softening the aged asphalts and dispersing the highly associated asphaltene-like components in the aged asphalt. The asphaltene settling test (AST) was developed as a potential indicator of asphalt compatibility (18). In the test, the asphalt is dispersed in hexane and the settling time of the resultant asphaltenes is measured. In theory, an observed increase in the asphaltene settling time from the addition of a recycle agent to an aged asphalt is indicative of the ability of the recycle agent to disperse polar components of the asphalt and improve its compatibility.

Data in Table VI show AST results using 6 different potential recycle agents on an 85- to 100- pen Midcontinent (Hawkins) asphalt that was previously laboratory-aged from a viscosity value

of 6.7×10^4 Pa. s (at 25°C) to 4.3×10^6 Pa. s to simulate pavement aging. Cyclopave and the shale oil distillate fraction caused about a 42 and a 25% decrease in asphaltene settling time, respectively. The three remaining commercial additives (Paxole, Dutrex and Ashland) showed similar settling times to the control, suggesting minimum interactions of those additives with the polar components of the asphalt. Only the shale oil basic nitrogen concentrate significantly increased the asphaltene settling time. Although asphaltene settling time reflected the dispersion characteristics of asphaltenes in a dilute hexane mixture, the solvent power of the additive on the neat mixture, although important to flow properties, may not be reflected in the settling time results.

TABLE VI

LIST OF PROPERTIES MEASURED FOR AGED ASPHALT TREATED WITH SIX RECYCLE AGENTS

<u>Recycle Agent^a</u>	<u>AST^b</u> <u>min.</u>	<u>Final</u> <u>vol, cc</u>
None (control)	76.1	10.0
Cyclopave	43.9	9.0
Shale oil distillate	56.8	9.3
Paxole 1009	72.6	10.1
Ashland 100	73.0	9.8
Dutrex 739	77.6	10.3
Shale oil basic nitrogen concentrate	93.5	11.0

a. 1 wt % additive, based on asphalt content.

b. Asphaltene settling time in minutes.

A correlation between the increase in asphaltene settling time and the final volume of precipitated asphaltenes was observed while conducting the AST. Data from Table VI are plotted in Figure 4. The increase in volume with increased settling time is attributed to a better dispersion of the asphaltenes, which become more flocculent in the hexane solution.

Based on measurements using asphalts from varying sources, mildly aged asphalts usually showed an increase in asphaltene settling time on addition of most commercial and shale oil-derived liquid additives. The shale oil distillate fraction usually produced longer settling times than the other additives. When the level of aging was increased, greater variations in the asphaltene settling times were obtained with the different recycle agents. On moderately or highly aged asphalts, the shale oil basic nitrogen concentrate and the shale oil petroleum fraction were more effective in dispersing asphaltenes than the commercial agents.

SUMMARY

Previous evidence that pyridine-type compounds may be responsible for increased resistance of asphalt-aggregate mixtures to moisture damage were reinforced by several recently completed studies. Experiments utilizing selected shale oil fractions known to contain pyridine compound types showed that these fractions were effective as petroleum-asphalt modifiers in reducing the sensitivity of the asphalt-aggregate mixtures to moisture damage and also showed potential as recycling agents for restoring desired viscoelastic properties to aged asphaltic pavements. The use of shale oil products in this vital application would likely be of economic importance in a synthetic fuels industry by utilizing these less fuel-desirable components in nonfuel uses and make available equivalent amounts of more energy-desirable petroleum counterparts for use as fuels.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support provided this project by the Department of Energy and the Federal Highway Administration in a cooperative program designed to make effective use of our natural resources and conserve the energy value of our fossil fuels. The authors are indebted to Dr. Abe Schneider, Suntech, Inc. and to Mr. Edgar B. Smith, Western Research Institute, who were instrumental in the procurement of the shale oil basic nitrogen concentrate sample.

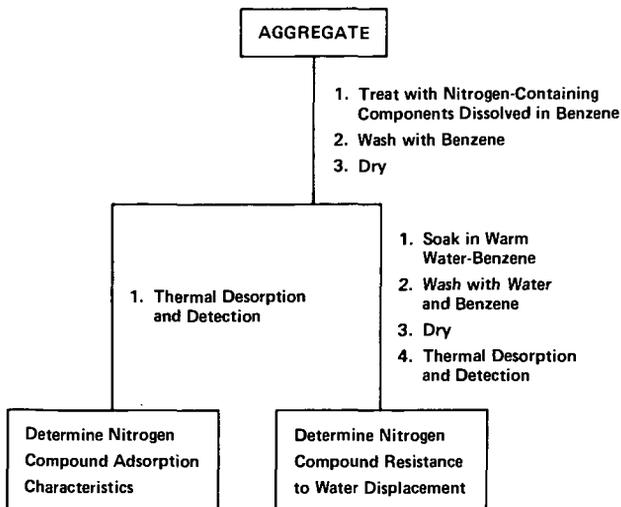


Figure 1. Scheme for studying adsorption-desorption and water displacement characteristics of nitrogen compounds on aggregate surfaces.

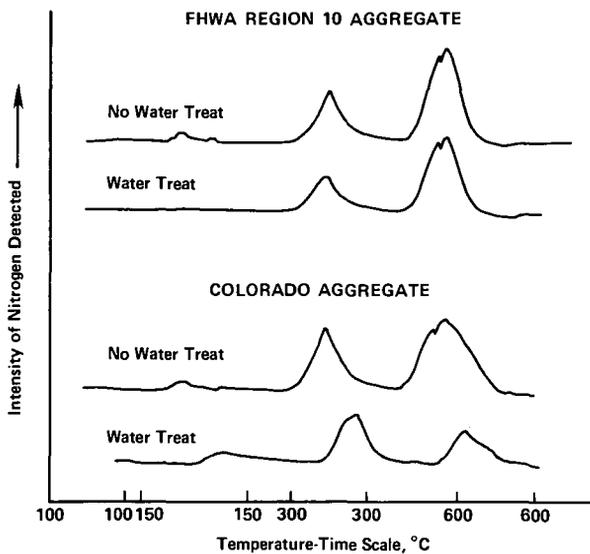


Figure 2. Adsorption-desorption of shale oil nitrogen compounds from FHWA Region 10 and Colorado aggregates.

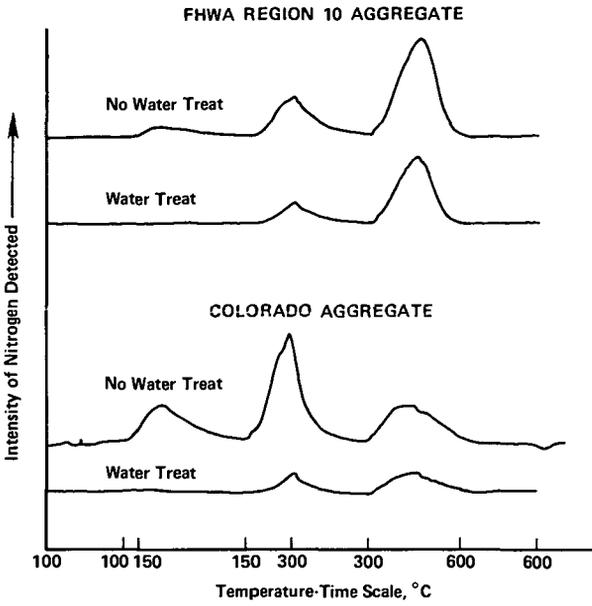


Figure 3. Nitrogen desorption thermograms of pyridine adsorbed on paving aggregates.

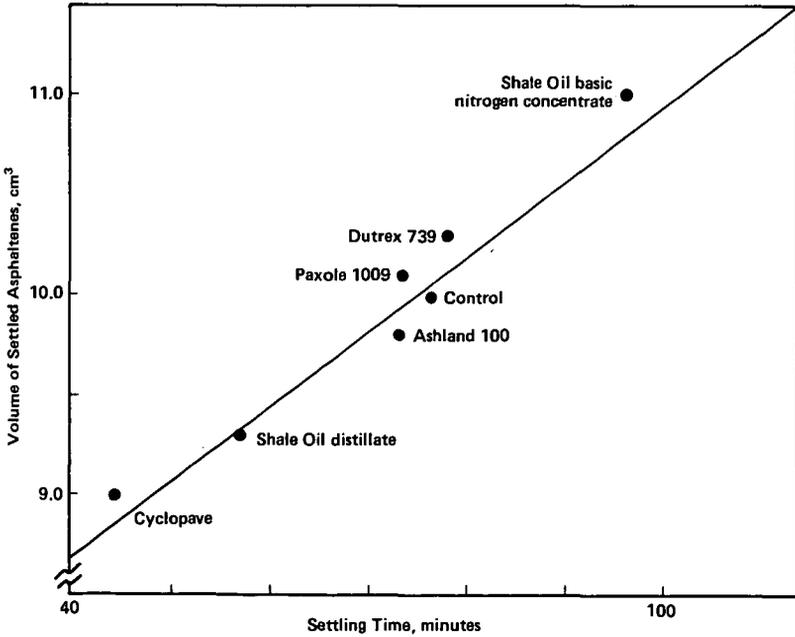


Figure 4. Relationship between asphaltene settling time and final asphaltene volume for aged Hawkins asphalt.

LITERATURE CITED

- (1) Plancher, H., Dorrence, S. M. and Petersen, J. C., Proc. Assoc. Asphalt Paving Technol., 46, 151-175 (1977).
- (2) Plancher, H., Miyake, G., Venable, R. L. and Petersen, J. C., Proc. Can. Tech. Asphalt Assoc., 25, 246-262 (1980).
- (3) Petersen, J. C., Plancher, H., Ensley, E. K., Venable, R. L. and Miyake, G., Trans. Res. Rec. No. 843, 95-104 (1982).
- (4) Petersen, J. C., Anal. Chem., 47, 112-117 (1975).
- (5) Petersen, J. C. and Plancher, H., Ibid., 53, 786-789 (1981).
- (6) Plancher, H. and Petersen, J. C., Proc. Assoc. Asphalt Paving Technol., 45, 1-24 (1976).
- (7) Plancher, H., Miyake, G. and Petersen, J. C., Proc. 13th Oil Shale Symp., Colorado School of Mines, 261-268 (1980).
- (8) Button, J. W., Epps, J. A. and Galloway, B. M., NTIS UC-92b, 121 pp. (1978).
- (9) Plancher, H., Chow, C., Holmes, S. A. and Petersen, J. C., Proc. Internl. Symp., Progressi Nella Technologie Dei Bitumi, Stazione Sperimentale per i Combustibili (Milano, Italy), 263-273 (1981).
- (10) Plancher, H., Smith, E. B., Petersen, J. C. and Anagnos, J. N., Proc. Pan-Pacific Synfuels Conf., Japan Petrol. Inst. (Tokyo, Japan), 2, 684-694 (1982).
- (11) Schmidt, R. J. and Scntucci, L. E., Proc. Assoc. Asphalt Paving Technol., 35, 61-90 (1966).
- (12) Welborn, J. Y., Oglio, E. R. and Zenewitz, J. A., Ibid., 19-60.
- (13) Halstead, W. J., Rostler, F. S. and White, R. M., Ibid., 91-138.
- (14) Petersen, J. C., Barbour, F. A. and Dorrence, S. M., Ibid., 43, 162-177 (1974).
- (15) Ensley, E. K., J. Inst. Petrol., 59, No. 570, 279-289 (1973).
- (16) Lander, H. R., Jr., Tech. Report AFWAL-TR 2135, Wright-Patterson AFB, Ohio (1981).
- (17) Lottman, R. P., NCHRP, Project 4-8(3)/1 Summary Interim Report (1979).
- (18) Plancher, H., Hoiberg, A. J., Subaka, S. C. and Petersen, J. C., Proc. Assoc. Asphalt Paving Technol., 48, 351-374 (1979).