

Shale Oil Products as Replacements  
for Petroleum Counterparts in Pavement Applications

by

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ABSTRACT

Recent laboratory results showed that certain fractions from shale oil exhibit some physical properties that are superior to their petroleum counterparts when utilized in asphalt pavements. Fractions studied were a shale oil asphalt obtained by vacuum distillation of a heavy oil, a basic nitrogen concentrate obtained as a byproduct from the experimental refining of shale oil, and a 342-382°C (648-720°F) shale oil distillate.

Shale oil asphalt-aggregate adsorption studies showed that higher concentrations of asphalt components were adsorbed by the aggregate and that lesser amounts of the strongly adsorbed components were displaced from the aggregate by water than in similar studies involving petroleum asphalts. Shale oil asphalt-aggregate mixtures were more resistant to moisture damage than petroleum-derived mixtures. Addition of 0.5 percent of a basic nitrogen concentrate to a petroleum asphalt-aggregate mixture greatly reduced its susceptibility to moisture damage. In a previous study, a shale oil distillate fraction used as a recycling agent for aged petroleum asphalt produced results comparable to those with a petroleum-derived commercial recycling agent.

These results, together with the actual field performance of a 27-year-old pavement constructed with shale oil residues, clearly show that certain of shale oil's least desirable products from an energy viewpoint have promising potential in extending the useful life of our nation's highways and streets. The use of shale oil products in this vital application would enhance the economics of a shale oil industry and would free equivalent amounts of more energy-desirable petroleum counterparts for use as fuels.

INTRODUCTION

Our increasing dependence on foreign crude oil has created an urgency to develop replacements for petroleum products from other sources of fossil fuels such as shale oil, coal and tar sands. One of the petroleum products now facing shortages, partly

because of increasing diversion of petroleum residues to transportation fuels, is paving asphalts.

In 1978, the paving industry spent between \$8 and \$10 billion for construction and maintenance of roadways and used almost 27 million metric tons of petroleum-derived asphalt. Twenty-seven million metric tons of asphalt represent the energy equivalent of about 3 percent of the U.S. crude oil consumption, over 79000 m<sup>3</sup> (500,000 barrels per day), that is being diverted to nonenergy use.

Recent studies at Texas A&M University sponsored by the Laramie Energy Technology Center showed that asphalt prepared from shale oil had unusual properties when used to replace petroleum-derived asphalts as pavement binders (Button 1978, 1980). The present study supplements and extends the Texas study by providing insight into the reasons for some of the unusual performance properties imparted to bituminous concrete mixtures by using products derived from shale oil. Successful future application of shale-oil-derived materials in pavements should reduce our dependence on petroleum products, find uses for byproducts of shale oil upgrading, and improve the performance characteristics of bituminous concrete pavements. To answer performance-related questions regarding the use of shale oil products in pavement applications, we 1) studied the bonding characteristics of a shale oil asphalt coated aggregate surface by analyzing the chemical components adsorbed on the mineral aggregate surface and their subsequent displacement from the surface by water; 2) analyzed a 27-year-old pavement that was constructed using shale oil residues; and 3) confirmed the test results from the bonding studies using a model experiment. In a previous study, a shale oil distillate fraction used as a recycling agent for aged petroleum asphalt produced results comparable to those with a petroleum-derived commercial recycling agent (Wilson 1979). Results from these studies have shown that certain products and byproducts from shale oil that are least desirable for use as fuel have promising potential as materi-

als for building and in extending the useful life of our nation's highways and streets.

## EXPERIMENTAL

### Materials

Aggregates. - Hol limestone, native to the Washington, D. C., area, was supplied by the Federal Highway Administration (FHWA) Materials Division. This aggregate, used in previous studies (Ensley 1972, Petersen 1974, Plancher 1977-A, 1977-B), was crushed in a Bico-Braun disk grinder equipped with ceramic plates. The crushed aggregate was wet screened without surfactants to 0.417 to 0.833 mm (20-35 mesh size), rinsed with distilled water, and dried at 150°C (302°F) for 24 hours. Precrushed quartzite aggregate was obtained from the University of Wyoming. This aggregate was from the same source as had been used to construct a portion of I-80 near Walcott Junction, east of Rawlins, Wyoming.

Shale Oil Pavement Samples. - Several chunks from a pavement constructed 27 years ago, using shale oil residue as a pavement binder, were obtained from the Anvil Points road near Rifle, Colorado.

Shale Oil Asphalt. - An AC-5 viscosity-graded shale oil asphalt was prepared by vacuum distillation of a shale oil residue produced from Colorado oil shale by the gas combustion process (Button 1978).

Shale Oil Basic Nitrogen Concentrate. - A sample of a shale oil basic nitrogen concentrate produced as a byproduct from the experimental refining of a partially hydrogenated Paraho shale oil was obtained from Suntech, Inc.

Petroleum Asphalts. - Four extensively studied asphalts (Welborn 1966, Schmidt 1966, Halstead 1966, Ensley 1972, Petersen 1974, Plancher 1977-A, 1977-B) of widely varying composition and identified by code numbers B-2959, B-3036, B-3051, and B-3602 were supplied by FHWA, Materials Division.

Solvents. - Reagent-grade solvents were used throughout this study. Benzene and pyridine were

dried by refluxing for 8 hours over calcium hydride before final distillation through a Vigreux column.

### Procedures.

Preparation of Asphalt-Coated Aggregates. - Aggregates were coated with shale oil or petroleum asphalts using various weight percentages of asphalt as indicated in the tables. Samples of the asphalt and aggregate were individually preheated at 150°C (302°F) for 1 and 3 hours, respectively, before mixing them in an evaporating dish. The coated aggregate was held at 150°C (302°F) in an oven for 4.5 hours with occasional stirring; the oven was shut off, and the samples in the oven were slowly cooled to ambient temperature. Coated aggregates were stored in the dark at ambient temperature for 62 hours before further treatment.

A slight modification of the above procedure was used if small quantities of organic-type additives were used. The desired quantity of additive was accurately weighed into an evaporation dish containing the asphalt, and the resulting mixture was dissolved in benzene or toluene to provide a homogenous solution. The solvent was removed by evaporation under a stream of nitrogen. [Final traces of solvent are removed during the 1-hour pre-mix heat treatment at 150°C (302°F).]

Isolation of the Nonadsorbed Shale Oil Fraction (NA). - Asphalt-coated aggregate was transferred as a benzene slurry into a separatory funnel that contained a glass wool plug between the coated aggregate and the stopcock. The coated aggregate was washed by slowly percolating cold benzene through the aggregate bed without agitation until the benzene extract became colorless. The benzene-soluble fraction (NA) was centrifuged to remove aggregate fines, and the fraction was recovered by solvent removal in a rotary film evaporator at 92°C (198°F) and 0.3 kPa (2 torr). Similar procedures were used to recover the benzene solubles from the 27-year-old pavement after it had been predried at 60°C (140°F) overnight.

Isolation of Materials Strongly Adsorbed on the Aggregate Surface but Displaceable by Water (SA/WD). - The benzene-washed aggregate particles from the above extraction were dried overnight at 30°C (86°F) at 8 to 13 kPa (60 to 100 torr) and

transferred to a glass vessel containing distilled water. Pressure within the vessel was slowly reduced to 0.3 kPa (2 torr), and this pressure was maintained until gas bubbles ceased to appear in the 5-cm (2-inch) water layer above the aggregate surface (about 45 minutes). The reduced pressure was maintained for an additional half-hour before returning the vessel and its contents to atmospheric pressure. After this vacuum water-saturation procedure, the submerged aggregate was frozen for 21 hours at -11°C (12°F) and then heated for 24 hours at 60°C (140°F).

Following the freeze-thaw, heat-treat conditioning, the contents in the glass vessel were transferred to a separatory funnel and the water was drained from the aggregate. Two separate 500-ml volumes of benzene were slowly percolated through the wet aggregate to remove the SA/WD components that were not water soluble but that were displaced from the aggregate surface by the water treatment; the benzene washes were combined with the water initially drained from the aggregate. The water was then removed from the combined water-benzene mixture using the benzene-water azeotrope. The resulting benzene solution contained the strongly adsorbed asphaltic material displaced from the aggregate surface by water (SA/WD).

Isolation of Materials Strongly Adsorbed on the Aggregate Surface not Displaceable by Water (SA/NWD). - The strongly adsorbed material that remained on the aggregate surface after the water treatment was removed by an 8-hour pyridine extraction of the aggregate in a modified Soxhlet extractor (Plancher 1977-A, 1977-B). Both the SA/WD and the SA/NWD fractions were concentrated by solvent removal in a rotary film evaporator and were filtered through a 0.9- to 1.4-micron fritted glass funnel before final solvent removal in the evaporator as stated earlier. Trace amounts of pyridine remaining in the SA/NWD extract were removed by adding benzene and repeating the solvent-removal procedure until the pyridine odor was undetectable. The total removal of benzene and pyridine in the recovered fractions was established by the absence of infrared absorption bands at 670 and 698  $\text{cm}^{-1}$ , respectively, in carbon disulfide solution.

Analytical Methods. - Ketones, carboxylic acids, dicarboxylic anhydrides, and 2-quinolone

types were quantitatively determined by a differential infrared spectrometric technique previously described (Petersen 1975). Sulfoxide concentrations were determined from the area of the 1030  $\text{cm}^{-1}$  infrared absorption band (Plancher 1977-A). Phenolic -OH and pyrrolic -NH concentrations were determined by selective chemical reaction and differential infrared spectroscopy using procedures similar to those previously developed. Both -NH and -OH groups form a hydrogen bonding band at 3300  $\text{cm}^{-1}$  in tetrahydrofuran. The area under the band attributed to the NH functional group was obtained by reacting the sample with sodium hydroxide and obtaining a differential spectrum with the untreated sample. The area attributed to the -OH group was obtained by difference. Molar absorptivities used in the calculations of the concentrations of the phenolic -OH and the pyrrolic -NH were  $1.45 \times 10^4$  liters/mole. $\text{cm}^2$  and  $1.54 \times 10^4$  liters/mole. $\text{cm}^2$ , respectively.

Nitrogen content in the respective samples was determined on an Antek\* Model 720 chemiluminescent nitrogen analyzer.

Preparation of Asphalt-Aggregate Briquets. - Briquets used in the water susceptibility test (WST) (Plancher 1980) were 19.05 mm (0.750 inches) thick, 41.33 mm (1.627 inches) in diameter and weighed approximately 50 grams. To prepare a briquet 19.05 mm (0.750 inches) thick, a trial test briquet is first fabricated and its thickness measured. The required amount of mixture can then be calculated using proportion relationships. Briquets were prepared by the following procedure. Place an evaporating dish containing about 60-g of asphalt-aggregate mixture in a 150°C (302°F) oven and heat the mixture exactly 20 minutes. Quickly weigh the calculated amount of mixture into the briquet mold, insert the ram into the cylinder, and compact the mixture at 2812 kg (6200 pounds).

After compaction, the briquet is carefully extruded from the mold and separated from the ram-briquet-base plate interface by applying a gentle snapping action at the briquet interfaces.

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\*Mention of specific brand names or models of equipment is made for information only and does not imply endorsement by the Department of Energy.

Water Susceptibility Test. - After the briquet was cured for 3 days at ambient temperature, it was placed on a plastic stress pedestal inside a jar. Enough distilled water was added to totally submerge the briquet, and the sealed jar was placed in a refrigerator at -11°C (12°F) for 24 hours. The jars were removed from the refrigerator, thawed in warm water, and placed in an oven at 60°C (140°F) for 24 hours. The jars were then removed from the oven, and the briquets examined for the appearance of cracks. If no cracks were visible, freeze-thaw cycles were repeated until cracks were evident. The final test result was the number of freeze-thaw cycles required to induce cracking in the briquet.

#### RESULTS AND DISCUSSION

Data from the Texas A&M study showed that Marshall specimens of typical road mixtures prepared from shale oil asphalts had superior resistance to physical property loss during the water immersion-compression test and exhibited greater flexibility at subambient temperatures than a petroleum asphalt control (Button 1978, 1980). Other studies in our laboratory involving petroleum asphalts strongly suggest that petroleum asphalts containing basic nitrogen type compounds such as pyridines and quinolines also produced asphalt-aggregate mixtures that were resistant to moisture damage. These observations coupled with the knowledge that pyridine and quinoline type compounds occur in shale oil prompted the following laboratory study.

#### Laboratory Study of the Adsorption of Shale Oil Asphalt Components on Mineral Aggregate and Their Subsequent Displacement by Water

This laboratory study was designed to establish what types of shale oil components were strongly adsorbed on a mineral aggregate surface and how resistant they were to displacement by water. A mixture of 5 percent by weight of the shale oil asphalt on 0.417-0.833 mm (20-35) mesh aggregate was desorbed to obtain the NA, SA/WD, and SA/NWD fractions as detailed in the procedures section.

Data in Table 1 show that 0.248 percent of the total asphalt was found in the SA fraction (calculated values from the SA/WD and SA/NWD fractions). This compares with an average of 0.160 percent for four different petroleum asphalts on the same aggregate (Plancher 1977-B). Further, only 0.014 percent of the total shale oil (5.7 percent of the SA fraction) was displaced by water, compared to 0.022 percent for the petroleum asphalts (13.8 percent of the SA fraction) (Plancher 1977-B). Thus, more material was found in the SA fraction using the shale oil asphalt than when using petroleum asphalts, and correspondingly less of the SA shale oil fraction was displaced from the aggregate by water. This indicates that the shale oil asphalt formed a stronger bond with Hol limestone that was more resistant to water than did the petroleum asphalts.

Although the data in Table 1 show that the total nitrogen was not significantly concentrated in any one of the SA fractions; treatment of the

TABLE 1. - Chemical analysis of shale oil asphalt components adsorbed on Hol limestone and their displacement by water

Asphalt or fraction	Wt % of total asphalt	Total N, wt %	Concentration, mol/liter						
			Pyrrolic NH	Phenolic OH	Ketones	Carboxylic acids	Dicarboxylic anhydrides	Sulf-oxides	2-Quinolones
Original shale oil asphalt	100	4.01	0.5	--	0.44	trace	0.015	0.025	0.045
NA <sup>1</sup> fraction	99.75	4.01	0.5	0.75	1.1	0.026	0.07	0.025	0.045
SA/WD <sup>2</sup> fraction	0.014	3.91	N.D. <sup>3</sup>	N.D.	trace	0.08	0.38	N.D.	0.62
SA/NWD <sup>4</sup> fraction	0.234	4.37	0.10	1.0	0.78	0.22	0.20	N.D.	0.12
SA <sup>5</sup> fraction	0.248	4.35	0.094	0.94	0.74	0.212	0.210	--	0.148

<sup>1</sup>Nonadsorbed

<sup>2</sup>Strongly adsorbed, water displaced

<sup>3</sup>Not detectable

<sup>4</sup>Strongly adsorbed, not water displaced

<sup>5</sup>Total strongly adsorbed (calculated values from SA/WD and SA/NWD fractions)

SA/NWD fraction with hydrochloric acid (HCl) indicated that basic nitrogen compounds reactive to HCl were concentrated in this fraction. This conclusion is based on an almost complete shift of the 1600  $\text{cm}^{-1}$  infrared band to almost 1625  $\text{cm}^{-1}$  following the acid treatment. The C=N band for basic nitrogen occurs in the 1600  $\text{cm}^{-1}$  region. Treatment of the NA fraction with HCl produced a much smaller change in the 1600  $\text{cm}^{-1}$  band than for the SA/NWD fraction. Because the SA/NWD fraction accounts for most of the nitrogen in the SA fraction, we conclude that the major portion of the nitrogen compounds involved in the asphalt-aggregate bond are of the basic nitrogen compound types.

Additional insight into the role of nitrogen compounds in the shale oil asphalt-Hol limestone bond is gained by examining the SA/WD fraction. Although the percent nitrogen in this fraction is nearly the same as in all other fractions, this fraction is high in 2-quinolones (0.62 moles/liter) which account for 22 percent of the nitrogen in the fraction. Although the 2-quinolones are a major type displaced by water, they account for only 1.1 percent of the total nitrogen in the SA/WD fraction.

Carboxylic acids are concentrated eightfold in the SA fraction compared to the NA fraction, and the concentration of acids in the SA/WD fraction is only about one-third that in the SA/NWD fraction. These results are in opposition to data obtained using petroleum asphalts (Plancher 1977-B) in which carboxylic acids were highly concentrated on the aggregate surface but were readily displaced from the aggregate surface by water. Also, the concentration of pyrrolic NH in SA/NWD fraction was one-fifth that of the the original shale oil asphalt. These pyrrolic NH materials were not expected to be found in the SA/NWD fraction because of their weak-bonding characteristics. This implies that the weakly

bonding pyrrolic NH and the carboxylic acids found in the SA/NWD fraction are not actively involved in the bonding process with the Hol limestone but are associated with polyfunctional molecules bonded to the aggregate by basic nitrogen functionality. Thus, the much higher ratio of basic nitrogen to carboxylic acids involved in the bonding process with shale oil asphalts compared to typical petroleum asphalts is believed to be the major factor contributing to the superior moisture damage resistance of pavement mixtures prepared from shale oil asphalts.

#### Analysis of Binder Recovered from Anvil Points Road

The shale-oil-derived asphalt binder from a still-serviceable 27-year-old pavement sample from Anvil Points, Colo., was selectively desorbed using procedures previously described for the laboratory study. The pavement sample prior to extraction showed no visual evidence of water stripping of the binder, even though the pavement core came from an area where a natural bog occurred. Before extraction, the pavement chunks were broken into smaller fragments and dried overnight at 60°C (140°F) to ensure that no residual moisture remained in the fragments. Considerable difficulty was encountered during the recovery of the benzene-soluble (NA) fraction because the shale oil constituents had limited solubility in cold benzene. Other fractions were obtained as described earlier.

Chemical analyses of the three fractions are shown in Table 2. The SA/WD fraction was high in nitrogen, a result not expected because basic-type nitrogen compounds were suspected of being associated with moisture-resistant mixtures and should be found in the SA/NWD fraction. This anomaly is partially explained by the high concentration of

TABLE 2. - Chemical analysis of Anvil Points shale oil road core binder extracts

Binder, fraction	Wt. % of		Concentration, mol/liter							
	total pave- ment	Total N, wt %	Pyrrolic NH	Phenolic OH	Ke- tones	Carboxylic acids			Dicar- boxylic anhy- drides	2-Quino- lones
						Free	Salts	Total		
NA <sup>1</sup>	4.35	2.70	0.6	0.15	1.4	0.045	0.029	0.074	0.124	0.036
SA/WD <sup>2</sup>	0.13	5.84	0.4	0.46	1.3	0.16	0.03	0.19	0.276	0.14
SA/NWD <sup>3</sup>	0.49	3.40	0.7	0.39	1.7	0.044	0.087	0.13	0.18	0.085

<sup>1</sup>Nonadsorbed

<sup>2</sup>Strongly adsorbed, water displaced

<sup>3</sup>Strongly adsorbed, not water displaced

2-quinolones and carboxylic acids in the SA/WD fraction. Previous studies showed that both types are readily displaced from an aggregate surface by water (Plancher 1977-B). Because pyrrolic NH is known to form weak hydrogen bonds, the pyrrolic NH groups in the fraction may have been molecularly associated with molecules containing functional groups not affected by water. Surprisingly, the SA/WD fraction was an oily liquid, and this indicates that the components displaced by the water treatment are relatively low molecular weight materials. The presence of low-molecular-weight materials was not apparent in the SA/NWD fraction.

The SA/NWD fraction was a brittle solid and showed a high percentage of carboxylic acids present as carboxylic acid salts. Carboxylate salts often occur in the SA/WD fraction of petroleum asphalts. Whether their presence in the shale oil SA/NWD fraction is a function of their insolubility in benzene or of a strong bond formation with the aggregate surface is not known. Appreciable amounts of phenolic OH and pyrrolic NH were found in the SA/NWD fraction, but only small amounts of pyrrolic NH have been found in the corresponding fraction from petroleum asphalts. Finally, the SA/NWD fraction was higher in nitrogen than the NA fraction, which is consistent with previous observations that basic nitrogen compounds are strongly adsorbed on aggregate surfaces.

Evaluation of Briquets Prepared from Petroleum- and Shale Oil-Derived Asphalts

Data in Table 3 show how a water-susceptibility test (WST) was used to evaluate the resistance of

TABLE 3. - Evaluation of briquets prepared from petroleum and shale oil-derived asphalts

Petroleum asphalts <sup>1</sup>	Briquet <sup>2</sup> weight, g	Cycles to failure
B-2959	50	1
B-3036	50	2
B-3051	50	7
B-3602	50	2 <sup>3</sup>
Shale oil asphalt		
Shale oil	50	>18

<sup>1</sup>Asphalts obtained from FHWA

<sup>2</sup>All briquets prepared using 5 percent asphalts and 95 percent Ho1 limestone

<sup>3</sup>Water used in the test became highly colored after testing and briquet turned from black to brown

several asphalt-aggregate mixtures prepared from petroleum and shale oil-derived asphalts to moisture damage using the same aggregate (Ho1 limestone) in each test. Comparison between the number of freeze-thaw cycles required to induce failure in petroleum vs shale oil asphalt briquets clearly show that the shale oil briquet was more resistant to moisture damage than its petroleum counterparts. The shale oil briquet showed no signs of failure after 18 freeze-thaw cycles, after which the test was terminated. These results support the previous observations that shale-oil-derived asphalt forms a stronger bond that is more resistant to moisture damage than petroleum asphalts.

Effect of Basic Nitrogen Compounds on Reducing Moisture Damage in Asphalt-Aggregate Mixtures

As mentioned earlier, there was sufficient evidence to suspect that the basic nitrogen-type compounds in shale oil contribute significantly to the increased resistance of bituminous concrete mixtures to moisture damage. Thus, two experiments were designed to further investigate this possibility. The first experiment involved adding trace amounts of a shale oil basic nitrogen concentrate to a petroleum asphalt-aggregate mixture and determining if the resultant mixtures were more resistant to moisture damage. In the second experiment, the aggregate was pretreated with pyridine before coating it with asphalt. Briquets prepared from the various mixtures were evaluated by the WST.

The WST results in Table 4 show that a petroleum asphalt-quartzite aggregate briquet developed cracks after one freeze-thaw cycle. The addition of trace amounts of the shale oil basic nitrogen concentrate to the mixture resulted in an increase from one to five freeze-thaw cycles before the briquets developed cracks. This is a significant increase and demonstrates that the basic-type nitrogen com-

TABLE 4. - Effect of adding shale oil nitrogen concentrate to briquets prepared from petroleum asphalt-aggregate mixtures

Asphalt	Wt., g		Cycles to failure
	Additive	Aggregate	
B-3051	Shale oil	Quartzite	
5.00	0 (Control)	95	1
4.95	0.05	95	2
4.75	0.25	95	5
4.50	0.50	95	6

pounds may be responsible for the increased resistance to moisture damage.

In the second experiment aggregate pretreated with pyridine was obtained by Soxhlet extracting Hol limestone with pyridine for several hours, dried at 220°C (428°F), and coated with asphalt B-3051 using the prescribed coating procedures. Results from the water susceptibility test on briquets made from this mixture showed that the cycles to failure increased from seven for the untreated aggregate to greater than twenty for the treated aggregate. The test was terminated at 20 cycles.

Results from these two experiments support our proposition that basic-type nitrogen compounds, probably of the pyridine or quinoline types, are important constituents in asphalts; syncrudes that contain these types should have a beneficial effect in reducing the sensitivity of bituminous concrete mixtures to moisture damage.

#### Potential Use of a Shale Oil Distillate as a Rejuvenating Agent in Recycling of Aged Petroleum Pavements

The recycling of aged asphalt pavements is a rapidly developing practice that offers significant energy-saving, conservation, and environmental advantages over new construction. Current recycling practices involve adding a rejuvenating agent to an aged bituminous concrete mixture so that the agent restores the viscoelastic properties of the mixture to a predetermined value. These agents are generally obtained as a byproduct from the lube-oil refining process, and their function in the recycling process is to redisperse the asphaltenes in the asphaltic binder. The agents should also restore the compatibility or the molecular balance of the modified binder so that it possesses good aging characteristics.

Wilson and co-workers (Wilson 1980) recently completed an engineering study using various syncrude liquids as rejuvenating agents. A shale oil distillate having a boiling range between 342 and 382°C (648-720°F) was prepared because this distillate had viscoelastic properties similar to those of the commercial additives which were used as controls. Their study showed that in most instances the shale oil distillate performed as well as the commercial agents.

## CONCLUSIONS

Previous hypotheses that basic-type nitrogen compounds may be responsible for increased resistance of bituminous concrete mixtures to moisture damage were strengthened by this study. Various experiments utilizing selected shale oil fractions known to contain the desired types of basic nitrogen compounds showed that (1) these compounds could compete successfully with carboxylic acids for the aggregate surface bonding sites (in previous studies, acids were preferentially adsorbed on the aggregate surfaces) and (2) shale oil-derived asphalts or the addition of basic nitrogen compounds to asphalt-aggregate mixtures significantly reduced the susceptibility of the pavement mixtures to moisture damage.

These results, together with actual field performance of a 27-year-old pavement constructed with shale oil residues, show that shale oil products have promising potential in pavement applications. Some of these products are considered to be the the least desirable products for utilization as fuels but may be important products in extending the useful life of our nation's highways and streets. The use of shale oil products in this vital application would enhance the economics of a shale oil 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.

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## REFERENCES

Button, J. W., J. A. Epps, and B. M. Gallaway, "Laboratory Evaluation of Selected Shale Oil Asphalts in Paving Mixtures," Dept. of Energy

- Report No. RF 3403-1, January 1978. Available from National Technical Information Service, Springfield VA 22161.
- Button, J. W., J. A. Epps, and B. M. Gallaway, Presented at Annual Meeting of Transportation Research Board, January 21-25, 1980, Wash., D. C. To be published in a 1980 TRB Record.
- Ensley, E. K., A Study of Asphalt-Aggregate Interactions and Asphalt Molecular Interactions by Microcalorimetric Methods: Postulated Interaction Mechanism." J. Inst. Petrol., v. 59, No. 570, 1973, pp. 279-289.
- Halstead, W. J., F. S. Rostler, and R. M. White, "Properties of Highway Asphalts--Part III, Influence of Chemical Composition." Proc. Assoc. Asphalt Paving Technol., v. 35, 1966, pp. 91-138.
- Petersen, J. C., F. A. Barbour, and S. M. Dorrence, "Catalysis of Asphalt Oxidation by Mineral Aggregate Surfaces and Asphalt Components." Proc. Assoc. Asphalt Paving Technol., v. 43, 1974, pp. 162-177.
- Petersen, J. C., E. K. Ensley, and F. A. Barbour, "Molecular Interactions of Asphalt in the Asphalt-Aggregate Interface Region." Transportation Research Record No. 515, Transportation Research Record, 1974, pp. 67-78.
- Petersen, J. C., "Quantitative Method Using Differential Infrared Spectrometry for the Determination of Compound Types Absorbing in the Carbonyl Region in Asphalts." Anal. Chem., v. 47, 1975, pp. 112-117.
- Petersen, J. C., E. K. Ensley, H. Plancher, and W. E. Haines, "Paving Asphalts: Asphalt-Aggregate Interactions and Asphalt Intermolecular Interactions," Report No. FHWA-RD-77-25, Federal Highway Administration, August 1976.
- Plancher, H., E. L. Green, and J. C. Petersen, "Paving Asphalts: Reduction of Oxidative Hardening of Asphalts by Treatment with Hydrated Lime--A Mechanistic Study." Report No. FHWA-RD-77-147, Federal Highway Administration, April 1977-A.
- Plancher, H., S. M. Dorrence, and J. C. Petersen, "Identification of Chemical Types in Asphalts Strongly Adsorbed at the Asphalt-Aggregate Interface and Their Relative Displacement by Water," Proc. Assoc. Asphalt Paving Technol., v. 46, 1977-B, pp. 151-175.
- Plancher, H., G. Miyake, R. L. Venable, and J. C. Petersen, "Development and Preliminary Application of a Simple Laboratory Test to Indicate the Susceptibility of Asphalt-Aggregate Briquets to Repeated Freeze-Thaw Cycles. To be published as a Federal Highway Administration Report (1980).
- Schmidt, R. J., and L. E. Santucci, "A Practical Method for Determining the Glass Transition Temperature of Asphalts and Calculation of Their Low Temperature Viscosities." Proc. Assoc. Asphalt Paving Technol., v. 35, 1966, pp. 61-90.
- Welborn, J. Y., E. R. Oglio, and J. A. Zenewitz, "A Study of Viscosity-Graded Asphalt Cements." Proc. Assoc. Asphalt Paving Technol., v. 35, 1966, pp. 19-60.
- Wilson, E. M., P. M. Hoyt, D. R. Lamb, D. R. Butzier, H. Plancher, and J. C. Petersen. "Evaluation of Liquids from Shale Oil and Coal Syncrudes for Reclaiming Deteriorated Asphalt Pavements." Final Report to Laramie Energy Technology Center, Contract No. EY-77-C-04-3913, 1979.