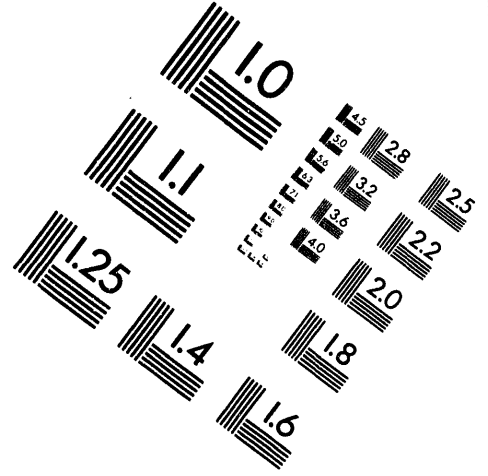
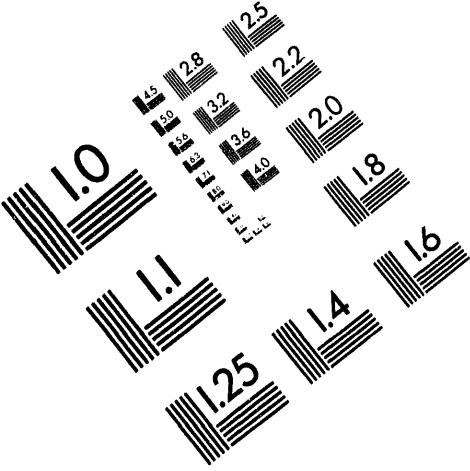




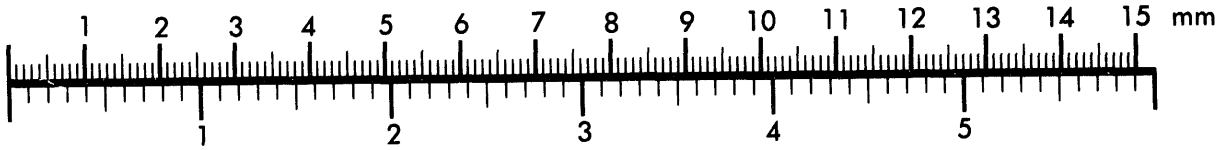
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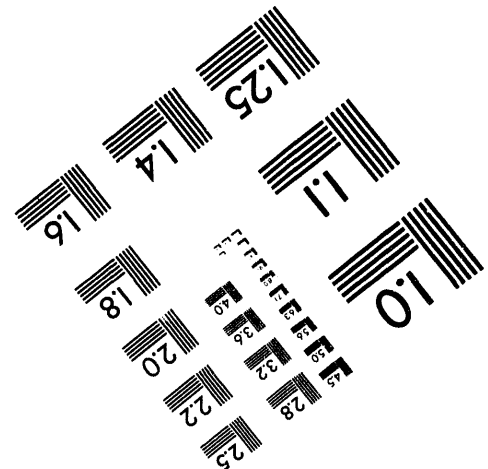
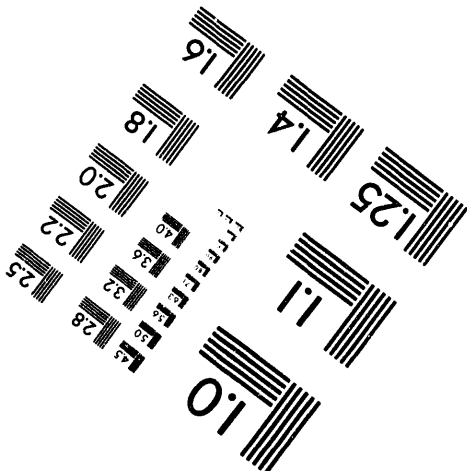
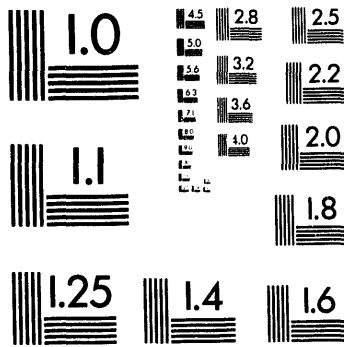
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READINESS THROUGH RESEARCH

**CHARACTERIZATION OF ASPHALT ADDITIVE
PRODUCED FROM HYDRORETORTED ALABAMA SHALE**

by

**David M. Rue
Michael J. Roberts**

**Paper Presented at the
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INSTITUTE OF GAS TECHNOLOGY

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CHARACTERIZATION OF ASPHALT ADDITIVE PRODUCED FROM HYDRORETORTED ALABAMA SHALE

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ABSTRACT

Shale oil, produced from beneficiated Alabama shale by pressurized fluidized-bed hydroretorting, was fractionated to produce shale oil asphalt additives (SOA). Three shale oil fractions boiling above 305°C were added to standard AC-20 asphalt to improve pavement properties. The physical properties and aging characteristics of AC-20 asphalt binder (cement) containing SOA are similar to those of unmodified AC-20 asphalt binder. Asphalt pavement briquettes made with AC-20 asphalt binder containing 5 to 10 percent SOA have superior resistance to freeze-thaw cracking and a greater retention of tensile strength when wet compared to pavement briquettes containing AC-20 binder alone.

Introduction

Asphalt cements used in U.S. highway pavements are made from high boiling petroleum fractions. An asphalt pavement must have the proper combination of chemical and structural properties, and these properties must remain relatively unchanged through exposure to a wide range of conditions over many years. The presence of water and freeze-thaw cycling are particularly harmful to highways in the northern states.

Nitrogen compound additives have been found to reduce water damage by strengthening the asphalt cement-aggregate bond,^{1,2} and amidoamine and imidazole anti-strip agents are commercially available.³ Another method of increasing the asphalt nitrogen content is to use a high nitrogen content shale oil^{4,5} or tar sand oil⁶ fraction as the asphalt additive.

The replacement of petroleum asphalt with Western shale oil and tar sand asphalts has produced pavements with higher nitrogen contents and superior resistance to moisture induced damage.^{7,8,9,10} Improvement has been seen in both the tensile strength after a water soak and the resistance to cracking from freeze-thaw cycling.

Eastern oil shale has been examined recently as a source of asphalt additives. Oil from Eastern shales has a high nitrogen content, and the shale resource is located close to large asphalt markets with readily available water

supplies. Conventional retorting, however, produces asphalt additives that are unstable and exhibit poor aging properties.^{11,12} Hydroretorting using a pressurized, fluidized bed (PFH), produces an oil yielding stable additives that appear to age better. The additives from PFH oil increase pavement resistance to water-induced damage.

Experimental

A series of laboratory-scale, batch PFH tests was conducted to determine the optimum conditions for producing high boiling oil fractions usable as asphalt modifiers. In each test, a 125 gram shale sample was charged to a fluidized sand bed maintained at the desired hydroretorting conditions.¹³ Temperature and hydrogen pressure were varied over wide ranges, and a 20 minute shale residence time was used to achieve high oil production. Gas chromatography simulated distillation using modified ASTM method D2887¹⁴ was used to fractionate the oil.

Three high-boiling point oil fractions were selected as potential shale oil asphalt additives (SOA). Shale oil boiling above 305°, 350°, and 395°C (582°, 662°, and 743°F) was selected for SOA-1, SOA-2, and SOA-3. Because batch PFH tests produce less than 50 grams of oil, oil from a bench-scale PFH test was fractionated to produce sufficient quantities of SOA for asphalt binder and pavement characterization tests.

A total of seven asphalt binders were prepared for characterization tests. The SOA were blended with a standard AC-20 petroleum asphalt used in Illinois pavement construction. Characterization tests were conducted on the seven asphalt binders and on pavements containing the binders. Pavement samples were produced with the asphalt binders using limestone aggregate, limestone fines, and a commercial mix design formula. Standard ASTM tests¹⁵ were used for characterization along with a water susceptibility test (WST).¹⁶ The WST is a non-standard test designed to quantify the resistance of a pavement to water induced freeze-thaw cracking. Pavement briquettes weighing 50 g are placed in water, frozen (at -10°C) for 24 hours, and thawed (at 60°C) for 24 hours. Cycling is repeated until the briquette cracks.

Results and Discussion

Laboratory-scale batch PFH tests were conducted to determine the optimum conditions for producing shale oil asphalt additives. Shale oil feedstock for SOA characterization tests was generated from the same beneficiated Alabama Chattanooga shale by PFH processing in a continuous bench-scale retort. An analysis of the shale concentrate is presented in Table 1. The beneficiated shale contains 32 percent organic carbon, essentially no mineral carbonate, and a significantly lower sulfur to carbon ratio than the raw shale. Oil yield is 94 l/t (22.5 GPT) by Fischer Assay and greater than 240 l/t (57.5 GPT) by PFH processing at 7.0 MPa (1000 psig) in hydrogen.

Seven laboratory-scale batch tests were conducted with beneficiated Alabama shale. Product oil weight fractions as a function of boiling point were determined by GC simulated distillation. Table 2 summarizes the carbon conversions to oil and to high boiling oil fractions. Total oil yield increases with increasing hydrogen pressure, and the product oil from hydrotreating at 7.0 MPa contains 2.5 times the fraction of feed carbon converted to oil by Fischer Assay. The maximum oil yield is obtained at 500°C, declines as temperature is increased to 575°C, and declines significantly at higher temperatures.

The optimum PFH conditions for converting shale carbon to high boiling oil for asphalt additive are similar to the optimum total oil yield conditions. The greatest total and high-end yields are both obtained at 500°C. Hydrogen pressure increases up to 4.2 MPa increase the production of total and high boiling oil. However, further increases up to 7.0 MPa produce higher oil yields mostly through production of lower boiling oil. The PFH production of high boiling shale oil for SOA appears to be highest at a temperature of 500°C and a pressure of approximately 4 to 5 MPa.

Before shale oil asphalt additives were prepared, a 2 liter sample of raw shale oil from a test conducted in a continuous bench-scale unit was separated into five boiling point fractions. Elemental analyses of the fractions are presented in Table 3. Distillation results show much of the oil boils at high temperatures. Three-fourths of the oil boils above 343°C and almost 45 percent boils above 454°C.

Figure 1 shows nitrogen is concentrated in the high boiling oil fractions. Ninety-five percent of the oil nitrogen is concentrated in the 75 percent of shale oil boiling above 343°C. The heaviest 45 percent of the oil contains 68 percent of the nitrogen and has a nitrogen content of 2.0 percent. High boiling oil fractions with high nitrogen contents were selected for evaluation as potential asphalt additives. The analyses also showed sulfur is fairly evenly distributed as a function of boiling point, and the carbon to hydrogen ratio increases with increasing boiling point.

Seven asphalt binder samples were characterized using a series of standard ASTM procedures. The samples included two lots of standard AC-20 binder (from the same supplier) and five blends of AC-20 binder with 2 to 10 weight percent SOA. Additives were obtained by vacuum distillation of a bench-scale PFH product oil. SOA-1, -2, and -3 correspond to 71, 65, and 50 percent of the total oil, respectively. A minimum SOA boiling point of 300°C was selected to minimize changes in physical properties when combined with a standard binder. Binder and pavement sample compositions are presented in Table 4.

Characterization tests included penetration at 4° and 25°C (ASTM D5), kinematic viscosity at 135°C (ASTM D2170), absolute viscosity at 60°C (ASTM D2171), ductility at 25°C (ASTM D113), solubility in trichloroethylene (ASTM D2042), vanadium content (by ICP), and the thin film oven loss (TFOL) test (ASTM D1754). The TFOL was followed by tests for penetration at 25°C, ductility at 25°C, and absolute viscosity at 60°C. The binder characterization test results are presented in Table 5.

The two lots of unmodified AC-20 binder (SA-1 and -6) are similar with absolute viscosities of 2259 and 2232 P. This is within the defined 1600 to 2400 P range for AC-20 binder (ASTM D3381). Penetration is also acceptable, ductility is high at greater than 150 cm, and solubility in TCE is greater than 99 percent. The addition of 5 weight percent SOA-1 softens the asphalt and produces viscosity and penetration values in the AC-10 range instead of the AC-20 range. This lowest boiling point additive causes the binder to have an unacceptably high TFOL weight loss and to harden significantly more than the AC-20 binder during the TFOL test.

Table 1. BENEFICIATED ALABAMA SHALE ANALYSIS

Moisture, wt %	1.51
Ultimate, wt % dry	
Ash	53.85
Total Carbon	32.08
Organic Carbon	32.06
Hydrogen	3.02
Sulfur	9.12
Nitrogen	0.84
Oxygen (HTW)	5.40
Fischer Assay, l/t	94
GPT	22.5

HTW - high temperature water

Table 2. THE EFFECTS OF PFH CONDITIONS ON OIL YIELD FRACTIONS

Test	Temperature, °C	H ₂ Pressure, MPa	Total C Conversion to Oil, %	C Conversion to Oil Boiling Above	
				343°C	468°C
35-B-1	503	1.7	49.7	32.6	18.5
35-B-2	664	1.6	30.7	17.7	9.6
35-B-3	504	4.3	61.4	41.5	22.4
35-B-4	578	4.3	56.1	36.7	22.0
35-B-5	666	3.9	43.1	25.9	14.2
35-B-6	508	7.2	71.2	44.2	22.8
35-B-7	656	6.9	39.3	25.0	13.3
FA	500	0	22.9	NA	NA

Table 3. ELEMENTAL ANALYSES OF OIL FRACTIONS FROM A BENCH-SCALE TEST AT 496°C AND 7.0 MPa

Oil Boiling Range, °C	Whole Oil	Fraction of			
		Carbon	Hydrogen	Sulfur	Nitrogen
----- wt % -----					
-82	1.4	83.45	13.39	1.61	0.18
+82 - 182	7.6	84.49	12.72	1.56	0.20
+182 - 343	16.1	85.95	11.59	1.57	0.32
+343 - 454	30.4	86.56	10.03	2.00	1.13
+454	44.5	86.89	8.61	1.77	1.98
Whole Oil	100.0	86.52	10.00	1.92	1.29

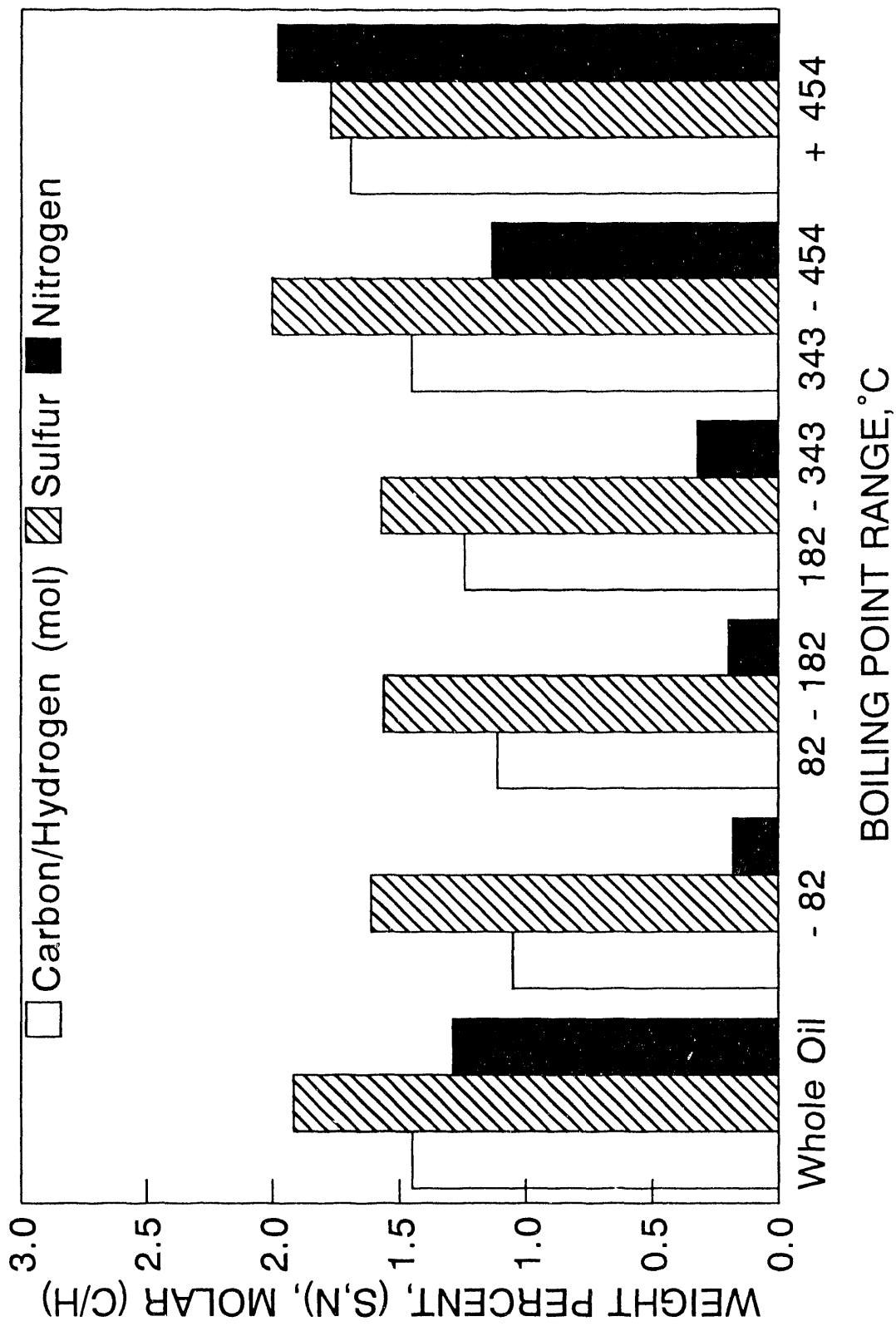


Figure 1. ALABAMA SHALE OIL BOILING POINT FRACTION COMPOSITIONS

Table 4. ASPHALT BINDER AND PAVEMENT SAMPLE COMPOSITIONS

Binder Sample	SA-1	SA-2	SA-3	SA-4	SA-5	SA-6	SA-7
Binder Composition, wt %							
AC-20 Binder	100	98	95	90	95	100	95
SOA-1	0	0	0	0	5	0	0
SOA-2	0	2	5	10	0	0	0
SOA-3	0	0	0	0	0	0	5
Pavement Sample	SAP-1	SAP-2	SAP-3	SAP-4	SAP-5	--	SAP-7

Additive Boiling Point Ranges:
 SOA-1: +305°C
 SOA-2: +350°C
 SOA-3: +395°C

Pavement Mix:
 5.5 wt% binder
 55.8 wt% 1 cm limestone
 38.7 wt % limestone fines

Table 5. ASPHALT BINDER CHARACTERISTICS

Binder Sample	SA-1	SA-6	SA-5	SA-2	SA-3	SA-4	SA-7
Additive	No	No	5% SOA-1	5% SOA-2	5% SOA-2	10% SOA-2	5% SOA-3
Penetration (cm)							
25°C (100 mg, 5s)	55	57	69	60	65	66	66
4°C (200 mg, 1 min)	18	--	26	20	20	18	--
Viscosity							
Kinematic at 135°C (cSt)	407	--	314	366	327	344	--
Absolute at 60°C (P)	2259	2232	1528	1938	1634	1607	1661
Ductility at 25°C, 5/60 (cm)	150+	150+	150+	150+	150+	150+	150+
Solubility in TCE (wt %)	99.9	--	99.9	99.9	99.9	99.9	99.9
Vanadium Content (ppmw)	260	240	230	250	280	250	260
Thin Film Oven Loss, 5 h at 163°C (wt %)	0.18	0.10	0.54	0.30	0.32	0.30	0.14
TFOL Residue Tests							
Penetration at 25°C	34	36	35	35	36	36	40
% of original	61.8	63.2	50.7	58.3	55.4	54.5	60.6
Ductility at 25°C (cm)	150+	--	150+	150+	150+	150+	--
Absolute Viscosity at 60°C (P)	5455	5182	4789	4974	4124	4312	4078
Ratio After/Before	2.41	2.32	3.13	2.57	2.52	2.68	2.46

The higher boiling SOA-2 and -3 additives cause less softening of the total mixture and form binders with penetration and viscosity values within the AC-20 range. Ductilities of binders containing SOA-2 and -3 are still high, and solubilities in TCE are greater than 99 percent. Increasing the binder SOA-2 concentration from 2 to 10 weight percent makes the binder softer but does not significantly affect other properties.

The TFOL test approximates the changes in asphalt binder properties during hot mixing. The test also gives some indication of the age hardening of an asphalt cement. The addition of SOA-1 leads to a high TFOL weight loss and binder hardening. The TFOL weight loss using SOA-2 is lower but still higher than desired for a binder. SOA-2 causes the binder to harden more than AC-20 alone. However, the penetration after the TFOL test is the same for the AC-20 binder with no additive and with SOA-2 added. SOA-2 decreases the absolute viscosity after the TFOL test.

Additive SOA-3 produces no increase in the TFOL weight loss. The modified binder containing this additive has the same percentage change in penetration as the original AC-20 binder, and the ratio of TFOL residue to original binder absolute viscosity is only 5 percent higher for the modified binder than for the AC-20 binder.

A series of tests was conducted on pavement briquettes containing the five binders containing SOA and one of the standard AC-20 binders. Pavement characterization test results are shown in Table 6. No differences were found in the specific gravity, voidage, and stability properties of the various briquettes. The only differences were found in the pavement flow properties and the moisture damage properties measured by the ratio of wet to dry tensile strengths (ASTM D4867) and the water susceptibility test. Pavement briquettes containing 2 to 10 percent SOA-2 in the binder show a reduction in flow of 5 to 10 percent. The change is only significant for the binders with 5 and 10 percent SOA-2.

The addition of SOA-2 to the asphalt binder increases the tensile strength retention of a pavement when wet. Tensile strength tests were not conducted with pavement samples containing SOA-1 or SOA-3. The high retention of tensile strength demonstrates an improvement in binder-aggregate bonding with the inclusion of shale oil additives. SOA-2 addition leads to a 10 percent decrease in pavement dry tensile strength but to an increase in pavement wet tensile strength.

The water susceptibility test was conducted on six identical pavement briquettes containing six of the seven binders studied. Only one of the two unmodified AC-20 samples was tested. All six briquettes containing

unmodified AC-20 binder and all six briquettes containing 2 percent SOA-1 binder additive failed on the first freeze-thaw cycle. Failure is defined as severe cracking of the sample. Cracking can sometimes be severe enough to break the briquette into several pieces.

The use of 5 percent SOA improves pavement resistance to freeze-thaw cracking with SOA-3 producing the highest pavement integrity. An average of 1.5, 2.0 and 2.2 WST cycles were completed before failure when 5 percent SOA-1, -2, and -3 were used, respectively. In the six WST tests with SOA-3 in the asphalt binder, one briquette failed in the first cycle, three in the second cycle, and two in the third cycle. Inspection of briquettes after WST failure confirmed cracking was not as extensive or severe when the shale oil additives were added to the asphalt.

Conclusions

PFH processing of beneficiated shale produces shale oil yields of more than 200 percent of Fischer Assay at hydrogen pressures of 4.2 and 7.0 MPa. The highest yield of the high boiling point fraction of the shale oil usable as an asphalt additive was achieved at 500°C and 4.2 MPa. Increasing the hydrogen pressure did not increase the yield of the oil fraction boiling above 343°C.

The PFH shale oil fraction boiling above 395°C (SOA-3) can be used as an asphalt additive and could be the major product of a PFH processing plant. Lower boiling point fractions are unacceptable as binder additives because the binder is softened and loses weight when heated. SOA-3 addition to the binder improves the pavement wet to dry tensile strength ratio and significantly increases the resistance of pavement samples to freeze-thaw cracking. Including 5 percent SOA-3 in the binder does not alter the weight loss from the TFOL test, the percent change in penetration is almost unchanged, and the TFOL residue to original viscosity ratio is almost the same as the ratio for the unmodified AC-20 binder.

Approximately half of the product oil from the PFH processing of Eastern oil shales can be used as asphalt additives which reduce pavement susceptibility to moisture induced damage and appear to be stable in a binder mixture. The remaining oil can be upgraded and used for transportation fuel and other products. A slate of products including high value asphalt additives holds promise for improving the economics of the PFH process.

Acknowledgements

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Table 6. ASPHALT CHARACTERISTICS

Pavement Sample	SAP-1	SAP-5	SAP-2	SAP-3	SAP-4	SAP-7
Asphalt Binder	SA-1	SA-5	SA-2	SA-3	SA-4	SA-7
Maximum Specific Gravity	2.522	--	2.523	2.522	2.522	--
Marshall Density	2.338	--	2.330	2.336	2.342	--
Air Voids (%)	7.3	--	7.6	7.4	7.1	--
VMA* (%)	19.9	--	20.2	20.0	19.8	--
Voids Filled (%)	63.3	--	62.4	63.0	64.1	--
Stability at 60°C (N)	10940	--	10320	10720	10450	--
Flow at 60°C (mm)	2.84	--	2.87	2.54	2.72	--
Wet Tensile Strength/Dry Tensile Strength (%)	63.3	--	81.1	77.9	76.5	--
WST Freeze-Thaw Cycles to Failure†	1.0	1.5	1.0	2.0	2.0	2.2

* Voids in mineral aggregate

† Water susceptibility test, average of six samples

Technology Center) for support of this work. Donation of the mix formula and aggregate by Vulcan Materials and the AC-20 binder by Seneca Petroleum is greatly appreciated. The efforts of R. Romero and D.E. Fleming in conducting PFH and asphalt characterization tests at IGT are also noted with appreciation.

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