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DEVELOPMENT OF SUPERIOR ASPHALT RECYCLING AGENTS

Phase I: Technical Feasibility

Technical Progress Report

By

Jerry A. Bullin

Charles J. Glover

Richard R. Davison

Jay Chaffin

Moon-Sun Lin

July 1995

Work Performed Under Contract No. DE-FC04-93AL94460

For

U.S. Department of Energy

Office of Industrial Technologies

Washington, D.C.

By

Texas Transportation Institute

College Station, Texas

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In Cooperation with
Texas A&M University
Research Foundation
Texas Transportation Institute
Department of Chemical Engineering

PREFACE

This report documents the technical progress made on the DOE funded project "Development of Superior Asphalt Recycling Agents" for the time period covering August 1993 through July 1994. Cost sharing for this study is being supplied by the Texas Department of Transportation and the Texas Advanced Technology Program. Bruce Cranford and Diana Sinclair are the Program Managers for the DOE Office of Industrial Technologies. Porter Grace is the Technical Manager for the DOE Albuquerque Operations Office. Frank Childs, the Project Technical Monitor, is on the staff of Scienteck, Inc., Idaho Falls, Idaho. Professors Jerry A. Bullin, Charles J. Glover and Richard R. Davison are the Co-Principal Investigators and are co-authors of this report along with current PhD candidates Jay M. Chaffin and Moon-Sun Lin.

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CHAPTER 1

INTRODUCTION AND SUMMARY

About 27 million tons of asphalt and nearly twenty times this much aggregate are consumed each year to build and maintain over two million miles of roads in this country. Over a cycle of about 12 years on the average, these roads must be reworked and much of these millions of tons of rock and asphalt cannot be reused with present recycling technology. Instead, much of the maintenance is accomplished by placing thick layers (hot-mix overlays) of new material on top of the failed material. This results in considerable waste of material, both in terms of quality aggregate (which is diminishing in supply) and in terms of asphalt binder. In addition, the new asphalt binder represents a significant source of potential energy (greater than that of a similar amount of coal).

The main impediment to recycling asphalt binder is the poorly developed science of recycling agent composition and, as a result, optimum recycling agents are not available. An excellent recycling agent should not only be able to reduce the viscosity of the aged material, but it must also be able to restore compatibility. The properties of the old material and recycling agent must be compatible to give both good initial properties and aging characteristics, and this must be understood. Many currently available commercial recycling agents address only the need to reduce viscosity and may in fact exacerbate problems with material compatibility.

The agent must also be inexpensive and easily manufactured. A large quantity of potential feedstock for the production of recycling agents is available and much of it is now fed to cokers. This material could be recovered by supercritical extraction which is an existing refinery technology. A supercritical pilot plant is available at Texas A&M and has been used to produce fractions for study.

The objective of this research is to establish the technical feasibility (Phase I) of determining the specifications and operating parameters necessary to produce high quality recycling agents which will allow most, if not all, of old asphalt-based road material to be recycled. The initial and aged properties of the recycled road material should be

comparable to that of new material. It is expected that supercritical fractionation of asphalt can be utilized to fractionate material available at refineries, establish operating parameters, and to reblend these fractions, if necessary, to produce superior recycling agents and to systematically study the effect of varying composition on properties. The advanced road aging simulation procedure, developed at Texas A&M, will be used to determine the aging characteristics of blends of old asphalt and recycling agents so as to relate aging to blend composition.

To accomplish this objective, this study has been broken down into several tasks. The proposed timeline for completion of all tasks is listed in Table 1.1.

Chapter 2 details work accomplished during the first year of this project on Supercritical (SC) Fractionation (Task 1). Task 1 was completed on schedule through the fractionation of three asphalts (AAA-1, AAF-1 and ABM-1) which were acquired from the Strategic Highway Research Program/Long Term Pavement Performance Materials Reference Library (SHRP/LTPP MRL). A fourth asphalt (YBF) was fractionated shortly before the start of this project and several of the fractions from this fourth asphalt were utilized for various experiments in conjunction with this DOE effort. As such, the fractionation of this asphalt is discussed in Chapter 2. A fifth asphalt (Shell AC-20) was also fractionated using the supercritical fractionation unit; however, these fractions were not fully characterized and they are not discussed in Chapter 2. One of the Shell fractions was used for the mixing rules development discussed in Chapter 5.

Chapter 2 also details work accomplished during the first year on Aged Asphalt Production (Task 2). The Pressure Oxygen Vessel (see Appendix A), POV, was utilized, but limited sample size necessitated the development of a new procedure for producing large quantities of asphalt. A laboratory oven was tried, but also proved inadequate. Finally, a new apparatus was constructed that is capable of producing kilogram quantities of quality aged asphalt. The development of this new procedure led to important discoveries as to the importance of oxygen pressure on aging kinetics (Davison et. al, 1994). The diversion into developing a new procedure for producing large quantities of aged material delayed completion of Task 2.

Chapter 3 details work accomplished during the first year on Preliminary Recycling

Table 1-1. Work Plan

Task	Year 1	Year 2	Year 3	% Time
1. Supercritical Fractionation				10
2. Aged Asphalt Production				5
3. Preliminary Recycle Agent Formulation and Recycle Blend Testing				15
4. Expanded Recycle Blend Testing				20
5. Rejuvenated Material Aging and Testing				20
6. Mixing Rules Development				5
7. Lime Additive Testing				5
8. Other Additives Testing				5
9. Processing Schemes Development				5
10. Projection Update and Commercialization Plan				5
11. Reports				5

Agent Formulation (Task 3). Specifically, the asphaltenes from different sources were cross blended with maltenes (non-asphaltenes) from different sources. This cross blending simulates the actual recycling where an asphaltene-free recycling agent from one source is blended with an aged asphalt, with its asphaltenes, from another source. Work on this task continues as planned.

Chapter 4 describes some preliminary work done on Rejuvenated Material Aging (Task 5) and Expanded Recycle Blend Testing (Task 4). A section of interstate I-45 near Madisonville, Texas was recycled nearly at this DOE projects inception. This industrial recycling project was studied in depth. Some unrecycled material was obtained and blended with 5 potential softening agents in the laboratory and compared to the contractor's recycled pavement in terms of aging. On the basis of the aging results, two agents were chosen to blend with the recycled material for testing of pavement core specimens. These tasks were started nearly one year ahead of schedule due to the availability of the I-45 test section.

Chapter 5 discusses work accomplished on Mixing Rules Development (Task 6). Forty-seven aged asphalt/recycling agent pairs were blended at multiple aged asphalt contents and a new, one parameter mixing rule was developed. The work described in Chapter 5 essentially completes work on Task 6 more than 1 year ahead of schedule.

CHAPTER 2

MATERIALS PRODUCTION FOR RECYCLING

To conduct a systematic study of asphalt recycling it is necessary to have recycling agents with a variety of properties and compositions as well as aged asphalts from different sources and hardened to varying degrees. The agents have been obtained from several sources including low viscosity asphalt, commercial agents and agents obtained from the supercritical fractionation of asphalt. Rather than obtain aged asphalt from cores which is very labor intensive and complicated by the extraction process, a method was developed for laboratory aging.

SUPERCRITICAL FRACTIONATION

Davison, et al. (1991, 1992) described the SC fractionation apparatus design and operation in detail, which was developed under TxDOT Studies 1155 and 1249. Modifications were made to the apparatus for TxDOT Study 1314 (Davison et al., 1994) and this DOE effort because they were both necessary and convenient. However, the basic process and operating conditions remained unchanged. A brief description of the process, operating conditions, and apparatus modifications follow.

Process Description

The following description is taken primarily from the TxDOT Study 1249 (Davison et al, 1992) report with appropriate modifications. The unit operates at a constant pressure above the critical pressure of the solvent. The SC fractionation unit separates heavy petroleum products into up to four fractions according to solubility in SC solvents. The temperatures of the separators determine the density of the solvent and, consequently, the solvent power in each vessel. Components of the feed precipitate when no longer soluble in the solvent. The lightest, most-soluble materials are removed by decompression during solvent recovery.

Figures 2-1 and 2-2 illustrate schematically the SC unit. The solvent is pumped to the operating pressure in S1-S3 by MP1. Several hours are required to bring the temperatures to the desired steady-state values. The steady-state operating temperature in S4 determines the steady state pressure for S4. Once steady-state conditions are achieved, MP2 is activated, introducing feed material into the circulating solvent stream. The temperature in each separator determines the solubility in the SC solvent. The insoluble material is transferred from the separator to its corresponding collector periodically to avoid potential plugging problems while the soluble material travels to the next separator. Finally, the overhead mixture from S3 passes through the control valve, where the pressure is reduced to significantly subcritical value. At these gaseous conditions, none of the asphaltic material is soluble and complete separation of the solvent is achieved. The solvent then passes overhead, is condensed in WC1 and flows back into the solvent reservoir.

Operating Conditions

The fractionation in TxDOT Study 1155 (Davison et al., 1991) employed n-pentane as the supercritical solvent. The major problem encountered with the use of n-pentane is that a large portion of the feed material remains insoluble even at the supercritical conditions. The unit tended to become plugged and required much maintenance. To rectify this situation, cyclohexane was used to perform an initial fractionation of the asphalt (and reduced crudes) in TxDOT Study 1249 (Davison et al., 1992). However, the use of cyclohexane resulted in other problems including reduced selectivity and higher operating pressures and temperatures. For TxDOT Study 1314, (Davison et al., to be published) and this DOE effort, n-pentane was chosen as the sole SC solvent. The operating pressures and temperatures were chosen based on the results obtained in TxDOT Studies 1155 and 1249 (Davison et al., 1991 and 1992) and are given in Table 2-1. Note that F8 through F5 were obtained from a first pass through the four stage unit and F4 through F1 were produced by refractionation of F5 (and sometimes F6). The use of n-pentane necessitated several modifications to the apparatus to eliminate potential problems.

Figure 2-1. Supercritical Unit Process Diagram

S0	Solvent Tank	S1-S4	Separators
C1-C4	Collectors	A1	Asphalt Tank
In-line Filter/mixer		Valve
Control Valve		Thermocouple
Tubing Wall Temperature Thermocouple		Temperature Monitor and Controller
Pressure Controller		Pressure Gauge
Heating Tape Heater		Metering Pump
Dual Purpose Heater/Cooler		Water Cooled Condenser

Figure 2-2. Legend for Supercritical Fractionation Unit Diagram

Table 2-1. Supercritical Operating Conditions and Fraction Yields

Fraction	T (°C)	P (bar)	Fraction Percentage			
			YBF	ABM	AAF	AAA
F8	191	49.3	24.1±3.9	16.4±1.5	28.5±6.9	35.2±4.2
F7	204	49.3	9.8±2.3	8.3±1.2	6.4±0.5	4.0±0.2
F6	213	49.3	14.7±6.3	8.8±2.2	9.0±0.9	6.8±1.5
F5	149	3.3	53.7±4.0	67.0±3.2	56.7±5.4	54.1±2.5
F4	213	49.3	10.7	3.1±1.8	2.0	0.9±0.0
F3	221	49.3	18.8	25.2±2.6	30.4	17.1±3.7
F2	230	49.3	18.2	22.8±0.5	16.5	20.1±9.2
F1	149	3.3	6.4	16.3±1.2	7.8	19.2±12.5

Apparatus Modifications

The plugging problems encountered with the use of n-pentane are due mainly to settling effects resulting from mixing the solvent and the asphalt at a low point in the apparatus and then pumping the mixture upward. This problem was eliminated by moving the mixing point to the top of the SC unit. Thus, insoluble material will settle into the separator and not the pump.

Moving the mixing point required redesigning the heaters between the pumps and the first separator. The previous heaters were removed and discarded after it was determined that a large amount of insoluble coke had built up in the tubing. This coke deposition was a direct result of the high operating temperatures necessary for cyclohexane separation. This coke build up also indicated that the modifications to the SC unit for TxDOT Study 1249 (Davison et al., 1992) to reduce the heat load on the initial heaters were not wholly successful. To further reduce the heat load, a steam condensation preheater (H0) was installed between the solvent pump and the mixing point. Steam condensation is a safe, efficient, and uniform method for heat transfer. Ideally, all of the heat input would be delivered by steam heaters. Electrical resistance heating tape heaters were installed

between the asphalt pump and the mixing point to preheat the asphalt. New straight tubing heaters equipped with electrical resistance heating tapes and heat transfer cement were installed between the mixing point and the first separator. The number of heaters was not changed; however, the length for heat transfer was greatly increased. The net effect of installing the preheaters and redesigning the other heaters is more evenly distributed heat input. This, in combination with the use of n-pentane, should prevent coking from occurring again.

Once these initial modifications were made, the unit was tested. The test run ended when a fire occurred due to operator error. The pump had been shut off and no fluid was passing by the heaters. Without any mechanism for dissipation of heat, the temperature rose until the stainless steel tubing melted and ignited the solvent. The Halon fire suppression system described in Appendix A of TxDOT Study 1155 (Davison et al., 1991) performed properly and the operator was not injured. As a direct result of this incident, extensive modifications were made to the apparatus to ensure that this could not happen again.

As an upgrade in the safety systems, relays were installed to prevent operation of the electrical resistance heaters if the solvent pump is not activated. In addition, thermocouples were installed between the heating tapes and the tubing wall in six locations. These thermocouples are connected to a high temperature alarm that will shut off the pump, and thus, interrupt the power to the heaters. The ultraviolet flame detectors were moved inside the apparatus hood, also. These modifications make the SC unit nearly fool proof.

As a precaution, every bank of electrical resistance heaters was replaced in case they had been stressed but had not failed. An additional heater was installed between separators 1 and 2 to reduce individual heater load. In addition, the unit was streamlined by removing all tubing allowing individual separator bypass. A binary or ternary cut may still be made by adjusting the operating temperatures accordingly. Tubing allowing periodic sampling of the overhead products and the unused second asphalt feed tank were also removed.

Additionally, a much larger removable collection vessel was installed to assist in collection of the solid fraction collected in C1. In addition, the collection vessel C2 was replaced with a removable collection vessel. Ball valves were installed between S1 and C1

to eliminate plugging problems collecting the hardest fraction. Finally, rupture disks were installed upstream of each relief valve to protect them from corrosion.

Even with these extensive modifications and tightened safety requirements, less than six months were lost. In the eighteen months of operation, the unit performed relatively problem free as only one heating tape burned out, requiring replacement.

ASPHALT FRACTIONATION

Four different asphalts were fractionated and analyzed in detail for this study. One asphalt was acquired from a local hot-mix contractor and three asphalts were obtained from the SHRP Materials Reference Library. A representative for the hot mix contractor indicated that the asphalt we acquired is an AC-20 manufactured by the Fina Petrochemical Corporation in Fina's Baytown, Texas refinery. This asphalt is identified as YBF. We were unable to confirm the producer of YBF and we were also unable to determine the crude source or processing scheme. Furthermore, this asphalt was completely uncharacterized. We determined that the other asphalts for fractionation must be better documented and have been characterized to some extent.

The asphalts previously studied by our research group had been acquired in only small quantities for routine lab testing or had been exhausted in previous supercritical fractionation studies (TxDOT Studies 1155 and 1249). Therefore, we would either have to obtain additional quantities of these asphalts or completely characterize new asphalts. We decided that it would be preferable to acquire large quantities of asphalts that we had already characterized. Because refineries adjust operating conditions frequently, not to mention that they switch crude sources, we decided that asphalts acquired in the past would not be suitable for study in this work. We chose to study asphalts whose crude source and processing could not change, the SHRP asphalts. The asphalts acquired in conjunction with the SHRP program were sampled at one instant in time and can be considered the only 'standard' asphalts in the world. Furthermore, many of these asphalts have been studied extensively not only by our research group, but throughout the world as well. As such, a large data base exists for these asphalts. Fifteen gallons each of SHRP asphalts AAA-1,

AAF-1, and ABM-1 were acquired, however, not all of this material was used for fractionation studies. Some of these asphalts were used for other experiments.

Asphalt Properties

Our analyses on the asphalts are tabulated in Table 2-2 and the results obtained during the SHRP program on the SHRP asphalts are given in Table 2-3.

Table 2-2. Tank Asphalt Data

Asphalt	Grade	60°C Viscosity (Poise)	Saturate	n-Hexane Asphaltene	Aromatic
YBF	AC-20	3100	7.5	17.6	74.9
ABM-1	AR-4000	2200	6.8	6.7	86.5
AAF-1	AC-20	1950	11.1	14.8	74.1
AAA-1	150/200 Pen	915	9.8	16.9	73.3

Table 2-3. SHRP Data

Asphalt	60°C Viscosity (Poise)	Saturate	n-Heptane Asphaltene	Napthene Aromatic	Polar Aromatic
ABM-1	2230	9.0	7.1	29.6	52.4
AAF-1	1872	9.6	13.3	37.7	38.3
AAA-1	864	10.6	16.2	31.8	37.3

The properties of interest are the 60°C "viscosity" and composition. The compositional information generated during this study is given for saturate, n-hexane asphaltene, and total aromatic content. No determination was made regarding the napthene/polar or aromatic/resin content. It is immediately apparent from Tables 2-2 and 2-3 that our data are different from the SHRP data in all aspects. This is due to using a controlled stress rheometer (see Appendix A) instead of a capillary viscometer to determine viscosity,

precipitation of asphaltenes with n-hexane (C_6) instead of n-heptane (C_7), and saturate determination from high performance liquid chromatography (HPLC) analyses (see Appendix A) instead of traditional Corbett fractionation.

The asphalts chosen for this study were picked to represent the widest variation in hardening susceptibility (HS), a reasonable indication of physico-chemical properties. The hardening susceptibility (HS) is the slope of $\ln \eta$ versus carbonyl area, where the carbonyl area is defined to be the area under the Fourier transform infrared (FTIR) absorbance curve between 1820 and 1650 cm^{-1} . The HS has been determined (*prior* to the bulk of Study 1314) for more than 20 asphalts with values ranging from 1.0 to 5.3. AAA-1 has a 20.7 bar (300 psia) O_2 HS of 5.2, one of the highest ever determined. To represent an average HS, SHRP AAF-1 was selected. This asphalt has a 20.7 bar O_2 HS of 3.8. Finally, AAG-1 was selected to be fractionated because it possesses an anomalously low HS of 1.0. This HS is more than 1 point below the HS of any other asphalt ever studied. However, only a limited amount of this asphalt was available and we had to substitute with SHRP ABM-1. The HS for ABM-1 had not been determined but this asphalt was obtained from the same refinery using the same processing method and crude source as AAG-1, only at a different point in time. It would be necessary to invest at least some time to characterize this asphalt. However, the variations between AAG-1 and ABM-1 were hoped to be small. Indeed, the 20.7 bar pure O_2 HS for ABM-1 was determined to be no different than the HS of AAG-1.

Fractionation

YBF was the first asphalt fractionated. This asphalt was fractionated in four batches (runs) with the standard operating conditions shown in Table 2-1. The data in this table also include the fraction yields for each of the asphalts fractionated. One trial run was made with slightly adjusted operating conditions, but the difference between cuts was not significant, so no further experimentation was performed. F5 and F6 from the 4 runs with the same operating conditions were combined and fed through the unit for a second pass. The operating conditions were controlled such that the temperature for separation of F4 was the same as the temperature for separation of F6. This way, F4 should contain all of the material from F6. In fact, second cut fractionation of the combined F5 and F6 material

produced a much larger F4 than the sum of the F6 material.

The next asphalt fractionated was SHRP ABM-1. This asphalt also was fractionated in four batches using the same operating conditions as those used for the initial fractionation of YBF. A large overhead fraction (F5) containing approximately 65% of the asphalt, was recovered from each run. A small amount of ABM-1 F5 was refractionated in a preliminary run using the same operating conditions as those used for refractionation of YBF combined fractions F5 and F6. The yields in separators 2 and 3 (F3 and F2, respectively) were sufficient to warrant using these operating conditions. Nearly all of the remaining ABM-1 F5 was then fed through the unit for fractionation into fractions F4-F1. A small clean-up fraction was obtained in the first separator. Two approximately equal sized fractions F3 and F2 were collected.

Several problems were encountered with the fractionation of SHRP AAA-1. The transfer lines between S1 and C1 tended to plug with solid material. This is undoubtedly due to the large amount of asphaltenes (16.9% n-hexane asphaltenes and surely much more than this in n-pentane asphaltenes) present in this asphalt. This asphalt prompted the switch from needle valves to ball valves in this transfer line. Asphalt AAA-1 was fractionated in four batches using the standard operating conditions. However, two of these runs were aborted at various stages due to plugging problems. No mass balance was possible on these runs; however, some light fraction F5 was obtained. The F5 materials from three of the runs were combined and refractionated separately from the F5 material from the fourth run. As such, the properties of the fractions from these second cuts vary quite drastically.

The final asphalt fractionated was SHRP AAF-1. By the time this asphalt was fractionated, most of the operating problems had been worked out so only 2 runs were needed to produce a sufficient quantity of F5 for further fractionation. The F5 materials from these two runs were combined and refractionated in a single run.

Fraction Properties

The trends reported in TxDOT Studies 1155 and 1249 (Davison et al., 1991 and 1992) were observed once again. The fraction viscosities, molecular weights (M_w) determined by gel permeation chromatography (GPC, see Appendix A), and composition

data are tabulated in Table 2-4. The viscosities and M_w values for the most part increase monotonically for fractions F1-F4 and for F5-F8, while the saturate contents decrease monotonically, for the most part, for fractions F1-F4 and F5-F8. Also, the asphaltene content decreases for F5-F8 and the aromatic content increases for fractions F1-F4 and for fractions F5-F7. Deviations from a strictly monotonic trend are attributed to possible contamination in the recovery process and random errors in sample preparation. The apparent discontinuity of properties between F4 and F5 is due to refractionation of F5 to produce F4-F1. This refractionation redistributes the material, concentrating the aromatics in F4 and the saturates in F1.

Figure 2-3 shows the trends in viscosity for all the asphalts and Figures 2-4 to 2-6 show the composition trends for all asphalts and Figure 2-7 shows fraction molecular weights. It is clear from these figures that there are significant differences between asphalts. Of particular importance are the differences in viscosities of fractions F3 and F2 between the asphalts. For some reason, possibly the high aromatic and low saturate contents in the whole asphalt, the fractions obtained from ABM-1 are much more viscous than the fractions from the other asphalts.

The data are reported in Table 2-4 with statistical accuracy. Those data points with only a mean were measured only once. The data points with standard deviation values may have been measured as many as 12 times (the viscosity of ABM-1 F3). Those values that have large deviations typically fall into one of two categories. The first category includes fractions where the residual pentane is difficult to remove. This will have a large effect on the viscosity and compositional analysis. Fractions 7 and 8 are highly subject to this problem. The second category is fractions with multiple samples such as YBF F5-F8. The data for these fractions represent at least four data points from the four different fractionation runs. These errors result from minor differences in operating conditions (all asphalts) and from performing the different refractionation runs with potentially widely different materials (AAA-1). Many of these problems can be eliminated by operating a supercritical fractionation unit continuously, as occurs in industry.

Table 2-4. Representative Supercritical Fraction Properties

Fraction	Viscosity (poise)	M _w	Saturates (wt %)	Asphaltenes (wt %)	Aromatics (wt %)
YBF F1	6	649	33.1	1.5	65.4
YBF F2	29.2 ± 7.3	895	22.7 ± 0.9	2.6 ± 0.4	74.8 ± 0.6
YBF F3	137.4 ± 9.0	1152	11.0	0.1	84.1 ± 0.8
YBF F4	1040	1388	7.6	2.4	90
YBF F5	43.2 ± 5.2	986 ± 19	16.2 ± 3.0	2.4 ± 0.5	81.4 ± 3.2
YBF F6	1813 ± 835	1460 ± 51	6.2 ± 1.3	2.5 ± 1.1	91.3 ± 1.5
YBF F7	5.95 × 10 ⁵ ± 3.91 × 10 ⁵	1912 ± 182	1.3 ± 0.8	7.5 ± 1.8	91.2 ± 1.8
YBF F8	--	2668 ± 96	0.3 ± 0.3	63.4 ± 5.1	36.3 ± 5.2
ABM F1	11.1 ± 1.5	495 ± 9	17.5 ± 0.6	0.0 ± 0.0	82.6 ± 0.6
ABM F2	91.1 ± 8.0	748 ± 28	12.9 ± 0.6	0.0 ± 0.0	87.1 ± 0.6
ABM F3	627.3 ± 18.7	918	7.7 ± 0.7	0.0 ± 0.1	92.3 ± 0.7
ABM F4	1610	1085	9.5 ± 2.2	0.0 ± 0.0	90.6 ± 2.2
ABM F5	115.8 ± 17.1	758 ± 4	11.5 ± 0.5	0.0 ± 0.0	88.5 ± 0.7
ABM F6	8.21 × 10 ⁴ ± 1.32 × 10 ⁴	1266 ± 36	3.4 ± 0.2	0.3 ± 0.5	96.4 ± 0.5
ABM F7	1.44 × 10 ⁷ ± 1.10 × 10 ⁷	1531 ± 44	1.7 ± 0.1	6.7 ± 2.0	91.6 ± 2.0
ABM F8	--	2232 ± 63	1.0 ± 0.4	47.7 ± 1.7	51.4 ± 1.9
AAA F1	2.0 ± 0.1	572 ± 27	31.3 ± 3.4	0.5 ± 0.6	68.3 ± 2.8
AAA F2	14.5 ± 3.2	875 ± 6	20.0 ± 1.5	0.2 ± 0.3	79.8 ± 1.4
AAA F3	99.2 ± 28.5	1237 ± 5	11.0 ± 1.3	0.4 ± 0.5	88.6 ± 0.8
AAA F4	76.1 ± 81.8	1178 ± 285	16.2 ± 6.5	0.6 ± 0.6	83.2 ± 5.9
AAA F5	10.7 ± 0.5	902 ± 5	22.7 ± 0.3	0.2 ± 0.0	77.2 ± 0.2
AAA F6	250	1701 ± 304	7.6 ± 4.6	0.6 ± 0.2	92.0 ± 4.3
AAA F7	30,000	2257 ± 233	6.2 ± 0.6	6.5 ± 1.6	87.4 ± 1.0
AAA F8	--	4867 ± 83	1.8 ± 0.8	62.0	36.8
AAF F1	2.1	661	32.6	0.8	66.6
AAF F2	11.7 ± 1.6	928	23.5 ± 0.4	0.4 ± 0.1	76.2 ± 0.4
AAF F3	67.1 ± 8.0	1111	14.3 ± 0.1	0.4 ± 0.3	85.4 ± 0.4
AAF F4	315.6	1334	10.0	1.0	89.0
AAF F5	15.9 ± 0.2	966 ± 15	24.6 ± 0.4	0.1 ± 0.1	75.4 ± 0.4
AAF F6	3,000	1417 ± 27	8.1 ± 0.1	1.1 ± 0.1	90.9 ± 0.1
AAF F7	50,000	1696 ± 17	6.2 ± 1.7	7.4 ± 0.4	86.5 ± 1.3
AAF F8	--	2495 ± 1	1.2 ± 0.6	51.5 ± 2.1	47.3 ± 2.7

Figure 2-3. Fraction Viscosity Versus Fraction Number

Figure 2-4. Asphaltene Content Versus Fraction Number

Figure 2-5. Aromatic Content Versus Fraction Number

Figure 2-6. Saturate Content Versus Fraction Number

Figure 2-7. Refractive Index Molecular Weight Versus Fraction Number

Fraction Uses

Fractions YBF F3 and F2 were used for recycling experiments with two different asphalts. These fractions and YBF F5 were also used for the extensive mixing rules study. In addition to these fractions, ABM-1 fractions F5, F3, and F2, AAA-1 fractions F3 and F2, and AAF-1 fractions F3 and F2 were utilized in the mixing rules study. Asphaltenes from ABM-1 F7 were used in the study to determine the effect of molecular size (weight) on the physico-chemical properties of asphaltic materials.

AGED ASPHALT PRODUCTION

For the project to avoid unreasonable delays, it was necessary to determine a suitable method of rapidly producing, in the laboratory, large amounts of asphalts comparable to asphalt aged over many years in pavement service. Four different methods were used to age material for this study. Initially, aged material was produced in the POV (see Appendix A). Some tests were run aging material on cookie sheets in a laboratory oven. Finally, a new

apparatus was developed for aging a large quantity of asphalt by bubbling air through a well mixed asphalt sample at moderate temperature.

Initially, aged materials were produced by aging in the POV. At the start of this project, the POV was the accepted method of artificially aging asphalts. The material was weighed into trays (maximum of 5g per tray). These trays were then placed in the POV at 20.7 bar (300 psia) O₂ at temperatures between 87.8°C and 98.9°C (190°F and 210°F) for a predetermined amount of time. The pressure effect on aging had not been determined at this point in the project. Up to 350g (70 trays of a maximum of 5g) can be produced per POV. The material also has to be frozen with liquid nitrogen and then chipped into a new container. As such, the POV method for aging large quantities of asphalt is very labor intensive.

One interim aging method consisted of weighing asphalt onto cookie sheets and placing them in a laboratory oven to age at approximately 148.9°C (300°F). Other materials are placed into and removed from this oven periodically, so the temperature control is not optimum. The asphalt in the trays was stirred twice per day and the trays were rotated to ensure uniform aging. However, the quantity produced did not justify the labor required, so this method for producing large quantities of material was discarded.

The final method used to produce aged material was aging in a well mixed, air bubbled (AB) reaction vessel. An apparatus was built to age large quantities of asphalt in a uniform manner. The apparatus consisted of a variable speed 1/15th horsepower motor which drove a 2" diameter mixing shaft placed in a half full gallon can of asphalt. Later, a second apparatus was constructed using a variable speed 1/4 horsepower motor. The can was wrapped with a heating tape connected to a variable transformer and a thermocouple actuated on/off controller.

Building air passes through a surge tank, filter, and a copper coil placed in a mineral oil temperature bath before being fed to the asphalt. The air is introduced to the asphalt through a 5" diameter sparging ring made from 1/4" stainless steel tubing with 14 nearly uniformly spaced 1/16" holes. The inlet air temperature is controlled by adjusting both the temperature of the oil bath and the air flow rate. The operating temperature of the air-bubbled reaction vessel must be high enough for the oxidation to proceed at an appreciable

rate, but not so high as to drastically alter the reaction mechanism or reaction products. Additionally, the temperature must be high enough to soften the asphalt so that the asphalt can be well mixed by the mixing paddle.

SHRP AAA-1 asphalt was aged in the AB vessel at 149.8°C, 121.1°C, and 93.3°C (300°F, 250°F and 200°F) to study the effect of aging temperature on the reaction products. Samples were taken periodically to monitor the progress of oxidation. The viscosity and carbonyl areas were measured and plotted in Figure 2-8. This vessel is primarily responsible for determining that the hardening susceptibility is a function of pressure. The hardening susceptibilities (HS) (slope of $\ln$ viscosity versus carbonyl area) were determined and compared to the HS generated from samples aged in the POV. Lau et al. (1992) showed that the POV HS is independent of aging temperature for temperatures up to 93.3°C (200°F). In addition, Martin et al. (1990) and Lunsford (1994) have shown that the POV HS is approximately representative of the relationship between viscosity and carbonyl area in asphalt binder extracted from pavement samples. However, the HS used by these researchers was the 20.7 bar (300 psia) O₂ HS. Comparison with the 0.2 bar (2.9 psia) O₂ HS may result in a different conclusion.

Figure 2-8 clearly shows that the AB HS is a function of temperature, with increasing deviation from the POV HS for increasing temperature. The POV HS shown in Figure 2-8 is the 0.2 bar (2.9 psia) O₂ HS. Initially, the AB HS was compared to the 20.7 bar (300 psia) O₂ POV HS. There was significant deviation, so it was thought that the AB apparatus was aging the material improperly. In fact, the AB aged HS is what led us to the pressure dependence on the HS. The 93.3°C (200°F) HS measured for two different samples is equal to the POV HS. As a result of these data, it was determined that the products of oxidation at 149.8°C (300°F) are not the same as those formed through oxidation at 93.3°C (200°F) with respect to the relationship between viscosity and carbonyl area.

Large quantities of SHRP AAA-1 and SHRP AAF-1 were produced in the air-bubbling (AB) apparatus. Both asphalts were aged to two different viscosity levels. The aged AAA-1 samples are designated as AAA-AB7 (SHRP AAA-1 air-bubbled sample 7) and AAA-AB8, and the aged AAF-1 samples are designated as AAF-AB1 and AAF-AB2. To produce pavement-like materials, the reaction temperature was targeted at 93.3°C

(200°F) initially. This temperature was not maintained precisely, however, the temperature was never allowed to exceed 110°C (230°F). These materials were used extensively in the mixing rules study discussed in Chapter 5.

Figure 2-8. Effect of Air Bubbler Temperature on HS

CHAPTER 3

EXPERIMENTS WITH MIXTURES OF ASPHALTENES AND MALTENES FROM DIVERSE SOURCES

Previously, Lin et al. (1993) developed a model for the effect of asphaltenes on viscosity. In addition, the hardening susceptibility (HS) was related to this function and the rate of asphaltene formation with oxidation as measured by the growth of the carbonyl peak (AFS), as shown in equation 3-1.

$$HS = \frac{\partial \ln \eta}{\partial CA} = \frac{\partial \ln \eta}{\partial \%AS} \times \frac{\partial \%AS}{\partial CA} \quad (3-1)$$

It was concluded that AFS (the last term of equation 3-1) was the same whether whole asphalts or maltenes were oxidized. In other words the existing asphaltenes have little, if any, effect in the formation of new asphaltenes. However, this function is quite different for specific asphalts and maltenes.

The present study was undertaken to explain the interaction of asphaltenes and maltenes from different sources, as would occur in recycling, and to better understand the difference, if any, between the original asphaltenes and those produced by oxidation.

EXPERIMENTS AND METHODOLOGY

Asphaltenes fractionated from SHRP AAD-1, AAG-1, AAK-2 and a supercritical fraction of SHRP ABM-1 were blended with the maltenes fractionated from SHRP AAD-1 in 10/90, 20/80 and 40/60 asphaltene/maltene ratios by weight. In addition, three asphaltenes (from SHRP AAD-1, AAG-1 and AAK-2) were also blended with the maltenes from SHRP AAG-1 in the same ratios as those described above. A total of 21 blends were produced by this blending scheme. Blends of 10%, 20% and 40% asphaltenes from SHRP AAG-1 into the

maltene from SHRP AAD-1 were designated GD1, GD2, and GD4 respectively. Similarly blends of AAK-2 asphaltene in AAD-1 maltene were designated KD1, KD2, and KD4. Also formed were blends DD1, DD2 and DD4 by blending D asphaltenes with D maltenes. Other blends were (BMD1, BMD2, BMD4), (DG1, DG2, DG4), (KG1, KG2, KG4) and (GG1, GG2, GG4).

All blends except the three blends made by adding asphaltene from SHRP AAD-1 into its own maltene (DD1, DD2, and DD4) were laboratory aged in a POV at 20.7 bar pure oxygen, at temperatures of 71.1, 82.2, and 93.3°C (100, 180 and 200°F) for aging times from 1 to 24 days depending on the aging temperature. 1.5 gram samples were weighed into the aluminum trays giving an effective film thickness of 0.6 mm. These thin films minimized oxygen diffusion effects on the samples.

The changes in compositional, chemical, and rheological properties of the aged blends were measured by HPLC, FTIR, and Dynamic Mechanical Analysis (DMA), respectively (see Appendix A). GPC (see Appendix A) was used to characterize the difference between the molecular weight distribution of aging-produced asphaltenes and original asphaltenes from unaged asphalts. For maltenes, original asphaltenes, whole asphalts, and blends, approximately 0.07 gram of sample was first dissolved in 10 mL Tetrahydrofuran (THF). For produced asphaltenes, the filter-washed solution was injected directly into the column. Molecular weight and molecular weight distribution were calculated based on a calibration using polystyrene standards.

RESULTS AND DISCUSSION

For the unaged whole asphalts, maltenes, and blends, Table 3-1 shows the percent asphaltenes (measured by the procedure described in Appendix A), the low frequency limiting viscosity (η_0^*), and the relative viscosity (η_r) (defined as the η_0^* for a blend divided by the η_0^* for the maltene from which the blend is made). The carbonyl areas of the unaged blends are not shown because these are defined to be zero in this study. For a given unaged asphaltene/maltene blend, the absolute viscosities increase with the amount of asphaltene

Table 3-1. The Weight Percentage of n-Hexane Asphaltenes (%A), Low Frequency Limiting Viscosities (η_0), and Relative Viscosity of Maltenes, Whole Asphalts, and Blends

	10%			20%			40%			MALTENE OR ASPHALT		
	%A ^a	η_0^b	η_r^c	%A ^a	η_0^b	η_r^c	%A ^a	η_0^b	η_r^c	%A ^a	η_0^b	η_r^c
AAD-1 MALTENE										0.7	2.3	1.0
AAD-1 ASPHALT										23.2	133.2	57.9
GD	10.7	9.88	4.3	20.9	62.1	27.0	39.2	17400	75652.2			
KD	10.9	10.0	4.3	20.8	65.0	28.3	39.7	18700	8130.4			
DD	10.6	10.7	4.7	20.8	85.2	37.0	41.7	39300	17087.0			
BMD	10.0	7.0	3.0	20.0	36.3	15.8	40.0	6260	2721.7			
AAG-1 MALTENE										0.3	73.0	1.0
AAG-1 ASPHALT										6.2	192.5	2.6
GG	12.5	503.7	6.9	22.9	5610	76.8	42.3	4.0×10^6	54794.5			
KG	12.2	478.7	6.6	20.6	3190	43.7	37.2	5.58×10^5	6643.8			
DG	13.4	496.0	6.8	23.6	5160	70.7	40.1	1.13×10^6	15479.5			

^a %A weight percentage.

^b η_0 in Pa · s at 60°C.

^c η_r dimensionless at 60°C.

blended. When comparing blends comprised of various maltenes, the absolute viscosity shows no correlation with asphaltene content because different maltenes have very different viscosities. However, despite some scatter, as shown in Figure 3-1, the relative viscosity of all blends regardless of the sources of asphaltenes and maltenes behave similarly with respect to the total asphaltene content. In addition to the maltene viscosity, the maltene solvent power or ability to disperse the asphaltenes affects the resulting rise in viscosity with asphaltene content. Therefore, Figure 3-1 suggests that the SHRP AAD-1 and AAG-1 maltenes may have similar solvation power, although they are very different in chemical nature, and that the asphaltene-maltene interactions do not vary widely for all materials

Figure 3-1. Viscosity of Unaged Blends as a Function of Asphaltene Content

studied in this work.

Figure 3-2 shows a plot of HS for SHRP AAD-1 and AAG-1 whole asphalts aged at 20.7 bar (300 psia) pure oxygen and various temperatures from 60 to 104.4°C (140 to 220°F).

Figure 3-2. Hardening Susceptibilities of SHRP AAD-1 and AAG-1

The HS (slope of the regression line) is independent of aging temperature, which indicates that the aging mechanism stays the same within the temperature range studied. However, the HS of asphalt AAD-1 is significantly higher than that of asphalt AAG-1. That is, for the same amount of carbonyl increase, AAD-1 will harden much more than AAG-1. This indicates that the carbonyl groups formed during oxidative aging do not directly cause an increase in the viscosity of asphalt. Many investigators including Traxler (1961), Anderson et al. (1976), Plancher et al. (1976) and Lee and Huang (1973) have shown that the viscosity

increase as an asphalt ages results from the formation of asphaltenes produced by oxidation. Figure 3-1 also suggests that the increase in asphaltene content results directly in an increase in the viscosity of blends with only relatively slight dependence on asphaltene sources. As shown by Lin et al. (1993), the HS of an asphalt material can be further studied by considering separately the increase in viscosity due to the increase in asphaltene content and the increase in asphaltene content due to the increase in carbonyl area (AFS).

First, consider the increase in asphaltene content due to the carbonyl formation. Girdler (1965) showed that asphaltenes produced by oxidation have a higher oxygen content than those originally present. This is shown in Figure 3-3 where the carbonyl areas of asphaltene produced by aging SHRP AAD-1 maltenes are noticeably larger than the carbonyl

Figure 3-3. FTIR Spectra of Produced Asphaltenes for SHRP AAD-1

area of the asphaltenes originally present. Figure 3-3 shows a direct evidence that the carbonyl formation results directly in the formation of asphaltenes by oxidative aging of maltene. Figure 3-4 shows a plot of produced asphaltene versus carbonyl area for AAD-1 maltene, AAD-1 whole asphalt, and blends made by adding various asphaltenes into AAD-1

Figure 3-4. Asphaltene Content Increase Versus Carbonyl Area Growth for SHRP AAD-1

maltene. The slopes of the data, AFS, for each blend are quite different from one another. It was pointed out in a previous work (Lin et al., 1993) that, for a given maltene or asphalt, the asphaltene production for a given amount of carbonyl formation approaches zero as the total asphaltene content increases. Figure 3-4 illustrates the AFS decrease encountered as the starting asphaltene content of the blends studied increases. For example, the AFS of KD4 (solid squares) is smaller than that of KD2 (solid triangles), the AFS of KD2 is smaller than

that of KD1 (solid circles), and the AFS of KD1 is smaller than that of AAD-1 maltene. This result suggests that the AFS is a function of total asphaltene content including both produced and original asphaltenes. This is not surprising as asphaltenes should continue to react with oxygen to produce carbonyl groups without producing more asphaltenes, but this probably is also due to the depletion of the reactive polar aromatics.

To compare the difference in the AFS of blends having varied original asphaltene sources blended with the same maltene, the carbonyl area for a given blend is adjusted to that of the maltene with the same asphaltene content by adding a constant to the carbonyl area of the blend. For example, the carbonyl area of unaged GD2 is adjusted to be the same as the carbonyl area of AAD-1 maltenes aged to an asphaltene content of 20%. However, the constant is different for each blend depending on the original asphaltene content of the blend. The results of this shifting are shown in Figures 3-5 and 3-6. For all of the blends, asphalts, and maltenes studied, the data form a single curve for materials from the same maltene. This indicates that the AFS is not affected by the type of asphaltenes which is produced by aging or originally present in different sources.

However, the AFS of SHRP AAG-1 maltene is much lower than that of SHRP AAD-1 maltene. Figure 3-7 compares the AFS of the blends made from SHRP AAG-1 maltene with that of the blends made from SHRP AAD-1 maltene. Evidently, AFS is a strong function of the maltene in the blend and is a function of the total asphaltene content but not a strong function of the type of asphaltene.

Next, consider the increase in viscosity resulting from asphaltene formation. Lin (1993) showed that the asphaltenes naturally present and those produced by oxidation have similar effects on the increase in the viscosity of the asphalt. However, the effects of asphaltenes from different asphalts in a given maltene before and after aging the blends were not addressed. In this work, the effects of asphaltenes from several sources on the increase in the viscosity of asphalt blends were studied and compared to the effects of those naturally occurring and those produced by maltenes from AAG-1 and AAD-1. Figure 3-8 compares the

Figure 3-5. AFS for SHRP AAD-1 Asphalt and Asphaltene/Maltene Blends

Figure 3-6. AFS for SHRP AAG-1 Asphalt and Asphaltene/Maltene Blends

Figure 3-7. Comparison of AFS for SHRP AAD-1 and AAG-1

Figure 3-8. Viscosity/Asphaltene Relationship for Unaged DD Blends and Aged AAD-1 Maltene

difference in the viscosity/asphaltene behavior of blends made by adding ADD-1 original asphaltene into AAD-1 maltene and that of aged AAD-1 maltene. The symbols DD1, DD2, and DD4 represent the blends made by adding approximate 10%, 20%, and 40% of AAD-1 original asphaltene into AAD-1 maltene while the symbol M represents the aged AAD-1 maltene. It should be noted that, as shown in Table 3-1, the asphaltene contents for the DD blends shown in Figure 3-8 are slightly different from 10%, 20%, or 40% which is the percent of asphaltenes mixed. This discrepancy arises because the asphaltene contents used in this work were always determined by precipitation. The differences between the asphaltene contents determined by precipitation and those actually mixed are due to the interaction between the asphaltenes and the maltene, even in dilute solution. However, the differences are not significant and are usually within the error of asphaltene measurement.

For the same asphaltene content, the viscosity of the aged maltene is consistently lower than that of the DD blends. To further understand the cause for this difference, GPC was utilized to measure the molecular size distribution of the original asphaltenes and the maltene-produced asphaltenes. Figure 3-9 shows that the asphaltenes produced by aging the AAD-1 maltene have a much smaller molecular size (longer retention time) than the original AAD-1 asphaltenes. Yen et al. (1961) showed that asphaltenes form aggregates through aromatic stacking. Upon oxidative aging, as shown in Figure 3-3, the asphaltenes produced contain large numbers of carbonyl groups that can produce polar-polar interactions. Storm et al. (1990) indicated that the asphaltene molecular weight measured mass spectroscopy was usually significantly lower than that measured either by Vapor Pressure Osmometry (VPO) or GPC. Therefore, the GPC determined molecular size of the asphaltenes can be a measure of the severity of the asphaltene aggregation. Pal and Rhodes (1989) and Graham et al. (1984) showed that the effects of particle concentration on the viscosity of suspensions when the particles aggregate increase as the average number of particles per aggregate increases. This explains why the viscosity of aged maltene is somewhat lower than that of the DD blends. The lower viscosities for the aged maltenes are due to the lower molecular weight of the produced asphaltenes.

Figure 3-9. GPC of Original and Produced Asphaltene for SHRP AAD-1

Figures 3-10, 3-11, and 3-12 show the viscosity/asphaltene relationship for aged and unaged blends made by adding the original asphaltenes of SHRP AAG-1, SHRP AAK-2, and the supercritical fraction of SHRP ABM-1 to SHRP AAD-1 maltene. Again, Figures 3-10, 3-11, and 3-12 show that the viscosities of the unaged blends are higher than those of the aged maltenes. Furthermore, the differences in the viscosities of unaged blends and aged maltene are most severe for the DD blends and in order of DD>KD>GD>BMD. This is consistent within the ranking of the GPC molecular weight of original asphaltenes, SHRP AAD-1>AAK-2>AAG-1>ABM-1 S2, as shown in Figure 3-13. However, for aged blends, the viscosities lie between the unaged blends and aged maltene because the asphaltene of the aged blends contain both original asphaltenes and produced asphaltenes. Figure 3-14 shows all the viscosity/asphaltene data for the blends made by adding the original asphaltenes

Figure 3-10. Viscosity/Asphaltene Relationship for Aged GD Blends and AAD-1 Maltene

Figure 3-11. Viscosity/Asphaltene Relationship for Aged KD Blends and AAD-1 Maltene

Figure 3-12. Viscosity/Asphaltene Relationship for Aged BMD Blends and AAD-1 Maltene

Figure 3-13. GPC of Original Asphaltenes for Four SHRP Asphalts

Figure 3-14. Viscosity/Asphaltene Relationship for Aged DD, GD, KD and BMD Blends and AAD-1 Maltene

studied into SHRP AAD-1 maltene.

Although there are differences in the viscosity/asphaltene relationship for different blends, all data in the practical viscosity range of 100 to 50,000 Pa·s lie in a narrow band. For asphaltenes in AAG-1 maltene, Figures 3-15 to 3-18 show similar behavior. However, for blend GG, the viscosity of the aged blend is essentially identical to that of the unaged blend. This can be explained by the fact, as shown in Figure 3-19, that the molecular weight distribution of the asphaltenes produced by AAG-1 maltene is very similar to that of the original asphaltenes as determined by GPC. Figure 3-20 shows all the reduced viscosity/asphaltene data for all the blends studied in this work. For aged blends, the maltene source alters the behavior of the increase in relative viscosity with asphaltene content. However, for a given maltene, all aged blends do not show significant differences with respect

Figure 3-15. Viscosity/Asphaltene Relationship for Aged GG Blends and AAG-1 Maltene

Figure 3-16. Viscosity/Asphaltene Relationship for Aged KG Blends and AAG-1 Maltene

Figure 3-17. Viscosity/Asphaltene Relationship for Aged DG Blends and AAG-1 Maltene

Figure 3-18. Viscosity/Asphaltene Relationship for Aged GG, KG and DG Blends and AAG-1 Maltene

Figure 3-19. GPC Chromatogram of Original and Produced Asphaltene for SHRP AAG-1

Figure 3-20. Reduced Viscosity Versus Asphaltene for Blends Studied

to asphaltene sources.

As stated previously the HS can be considered as the product of two functions. Based on the results presented in this study, the first term on the right hand side of equation 3-1,

($\frac{\partial \ln \eta}{\partial \%AS}$), does not vary greatly with asphaltene sources for the two maltenes studied. On

the other hand, the second term on the right hand side of equation 3-1, the AFS, is very different for AAD-1 maltene compared to AAG-1 maltene. This indicates that the main difference in HS for different asphalts can be attributed to a different AFS. Therefore, for recycling, the recycling agent should be designed or selected to have low AFS, which is primarily a function of maltene composition. A low AFS rejuvenator can significantly suppress the formation of asphaltenes during oxidation, and therefore further improve the service life of a recycled pavement. For blends of a given asphaltene with different maltenes, the difference in the increase in relative viscosity with asphaltene content is also a less significant factor than the difference in AFS. In other words, asphaltenes, if produced, will ultimately cause hardening that does not vary greatly with maltene sources. Furthermore, dilution of asphaltenes by the agent will reduce the eventual increase in viscosity as the rejuvenated pavement ages because the increase in viscosity is much less for low asphaltene content than for high asphaltene content.

CHAPTER 4

INTERSTATE 45 RECYCLING

A section of Interstate 45 (I-45) near Madisonville, Texas that was recycled in September and October, 1993 was chosen as a recycling test section. The section of I-45 that was recycled starts at 1993 mile marker 137 and extends to mile marker 141. A two mile stretch between mile marker 141 and mile marker 143 was not recycled and then recycling continued for four miles between mile marker 143 and mile marker 147 using Hot-In-Place-Recycling (HIPR). Hot-In-Place-Recycling is a process where the existing material is heated in place, a set depth of the pavement is roto-milled, fresh hot mix and/or rejuvenator is added, and the mixture is replaced on the road through the screed. All of this takes place in a continuous train of equipment. Addition of fresh hot mix allows the aggregate gradation of the pavement to be altered and slightly softens the pavement. Addition of rejuvenator reduces the viscosity and increases the penetration value. The final mixture should result in a pavement with the desired gradation and a viscosity similar to that of a fresh hot mix pavement.

SAMPLING

TxDOT personnel from the Bryan, Texas office assisted in obtaining 42 core samples I-45 in the vicinity of Madisonville, Texas. Specifically, the cores were taken from the northbound outside lane in the sections of pavement that were recycled. These cores were taken at four locations, each location having different characteristics.

The first coring location starts exactly at 1993 mile marker 138 (MM138) and extends 4.6 m (15 ft) north. Ten cores were taken at this location. This section of pavement between MM137 and MM139 showed no obvious signs of distress. The pavement material from this location consisted solely of hot mix asphalt overlay placed in 1987. The section between MM137 and MM139 appears to be a TxDOT control section.

The second location that was cored starts 412 m (1352 ft) past 1993 mile marker 139

and extends 5.2 m (17 ft). The pavement in the vicinity of this location was suffering from severe rutting. To eliminate the ruts, maintenance crews had placed rubberized crack seal in large patches in the wheel ruts. This had resulted in some traction problems over the previous winter, so the maintenance crews had also placed some cold mix asphalt on top of the crack seal patches to improve traction. Eleven cores were taken from one patch of this crack seal from the right wheel path.

The third location that was cored was in the neighborhood of mile marker 140. The pavement in this location also was suffering from rutting and had been treated only with the rubberized crack seal in the wheel ruts. Again, the crack seal had only been used in patches. Eleven cores were taken from one crack seal patch located 19.7 m (64.5 ft) past MM140. The cores were taken over a distance of 5.5 m (18 ft).

The last location studied (between MM143 and MM147) had been treated at some time with the crack seal to eliminate rutting. However, the entire section of road was later treated with a 0.64 cm (¼ in) rubberized chip seal. Ten cores were taken starting 6.1 m (20 ft) past MM145 extending 5.8 m (19 ft).

The cores can be considered as the untreated material from their relative locations. In addition to these cores, samples were taken periodically throughout the recycling process to follow the physical property (viscosity) changes that occur in the pavement at different stages of the recycling process. By taking samples of the heated and milled material, or post-heater (PH) material, it is possible to determine the change in viscosity that takes place as a result of the heating conditions used in the HIPR process. In fact, this material, and not the untreated material, should be considered as the base starting material for recycling. Samples of the add-hot-mix or add-mix and emulsified rejuvenating agent were also obtained, but as yet have not been used for any analyses. Finally, samples of the rejuvenated asphalt were obtained from regions similar to those locations that were cored. The rejuvenated material was obtained prior to passing through the screed and is referred to as pre-screed (PS) material.

At least 0.0076 m³ (2 gal) of PH material, at least 0.0038 m³ (1 gal) of add hot mix, and at least 0.0038 m³ (1 gal) of PS material was obtained from locations near the locations that were cored. PH material was obtained 19.5 m (64 ft) South of MM138 and the PS

material was obtained 25.3 m (83 ft) South of MM138. There were no major problems with the recycling of this untreated, undistressed pavement.

PH material was taken from 431 m (1414 ft) north of MM139 and PS material was taken 425 m (1394 ft) north of MM139. These MM139+ locations do not correspond exactly with the MM139+ cores, but were taken from locations having material similar to that in the cores. Some problems were encountered with recycling the material in the vicinity of this location. First, the location lies in a slight depression, so there was some trapped moisture which did not allow proper heating. This problem was compounded by the presence of the rubberized crack seal, which not only helped to trap the moisture, but also prevented good heat transfer from the heaters to the pavement. In addition, the crack seal patches tended to burn, rather than soften and be mixed in with the other bituminous material.

PS samples were taken from 95.4 m (313 ft) South of MM140 and PH samples were taken from 88.1 m (289 ft) south of MM140. These MM140— sampling locations do not correspond to the MM140 core locations, but were taken from pavement with similar crack sealed areas. The recycling in this area suffered mainly from the burning rubber problem. This section of pavement is located on the crest of a slight incline and had little of the moisture problems associated with the MM139+ location.

The final location where samples were acquired is located near 1993 MM145. Severe problems were encountered with recycling the material that had been treated with the chip seal coat. The moisture content was a serious problem in this section because the chip seal had trapped a large amount of water in the pavement. In addition, the presence of continuous polymer modified chip seal caused the entire area of the pavement to burn and resulted in oily rejuvenated asphalt. For both safety reasons and to ensure high quality recycling, the top 1.9 cm ($\frac{3}{4}$ in) were milled off of the pavement between MM143 and MM147 before the recycling was completed. PS samples were taken from 3.66 m (12 ft) North of MM145 and PH samples were obtained from 6.10 m (20 ft) North of MM145. As a result of the milling, the recycled material mix was adjusted to include more add-mix to accommodate for this lost material and keep a level driving surface.

ANALYSES AND SAMPLING

One 7.5 cm (3 in) core from each location was tested to determine the void content. Some difficulty was encountered trying to determine the void content of the cores with the crack or chip seal, but values were obtained. These values are tabulated in Table 4-1 and they indicate that the rutting problems were not as a direct result of the void content.

Cores from each location were extracted and recovered using the process described by Burr et al. (1993). The extracted binders were subjected to FTIR and GPC analyses to determine if the extraction process had altered the binder and to confirm that complete solvent removal had been achieved. Once it was determined that the binder was solvent free and unchanged by the solvent, the 60°C limiting dynamic viscosity was measured. The viscosities of the extracted cores are listed in Table 4-1.

Some of the cores were cut into two 3.75 cm (1.5 in) sections to determine if there were significant variations in viscosity with depth. If variations do occur with depth, it is necessary for TxDOT and other highway departments across the nation to consider only the depth of material to be recycled when determining the initial pavement properties. This study shows that there is significant variation with depth. MM 138 Core # 1, #2 and #6 have viscosities of 12,200, 21,300, and 21,800 poise, respectively. These values were obtained from full 7.5 cm (3 in) core samples. MM138 Core #9 top and #10 top have viscosities of 58,000 and 43,500 poise, respectively. MM138 Core #9 bottom has a viscosity of 10,100 poise. Although these data are limited, it is clear that there are significant differences in pavement properties with depth. The post-heater (PH) material was extracted and analyzed similar to the core binder. The viscosities of the PH materials are also given in Table 4-1. From a limited amount of data on only MM138 samples, it is clear that the PH material has a viscosity similar to that of the top part of the cores that were extracted. MM138 Core #9 top and #10 top have viscosities of 58,000 and 43,500 poise while MM138 PH Extraction #1 has a viscosity of 44,200 poise and the combined binder from MM138 PH Extractions #1 and #2 has a viscosity of 53,000 poise. From the core extractions and the post-heater extractions, it is clear that TxDOT probably under estimated the viscosity (over estimated the pen) of the binder to be recycled. This would undoubtedly result in recycled

Table 4-1. I-45 Extraction Data

Sample	Viscosity	Void Content
MM 138 Core #3	21,300	3.8
MM 138 Core #1	12,200	-
MM 138 Core #6	21,800	-
MM 138 Core #9 Bottom	10,100	-
MM 138 Core #9 Top	58,000	-
MM 138 Core #10 Top	43,500	-
MM 138 PH Ext. #1	44,200	-
MM 138 PH Ext. #2	52,000	-
MM 138 PS Ext. #1	9,600	-
MM 138 PH	53,000	-
MM 139 Core #3	37,800	5.6
MM 139 PH Ext. #1	80,600	-
MM 139 PH Ext. #2	73,000	-
MM 139 PS Ext. #1	16,800	-
MM 139 PH	90,000	-
MM 140 Core #7	29,500	7.0
MM 140 PH Ext. #1	30,700	-
MM 140 PH Ext. #2	32,500	-
MM 140 PS Ext. #1	17,600	-
MM 140 PH	38,000	-
MM 145 Core #1	31,000	6.1
MM 145 PH Ext. #1	49,000	-
MM 145 PH Ext. #2	42,000	-
MM 145 PS Ext. #1	7,320	-
MM 145 PH	54,000	-

asphalt that is hard and brittle.

To examine this possibility, pre-screed (PS) materials were also extracted and recovered. The viscosity of the recycled material from MM138 PS Extraction #1 is around 10,000 poise compared to the TxDOT target viscosity of 3,800 poise. This confirms that either TxDOT underestimated the viscosity of the binder to be recycled or the contractor did not add enough of the add-mix or rejuvenating agent. The data for MM138 should be considered as solid, reliable data; however, the data from the other locations may be unreliable due to the presence of the rubberized crack seal. This rubber complicates the extraction and recovery process and may influence the properties of the recovered binder. As a result, no specific conclusions have been made concerning material from the MM139+, MM140-, and MM145 locations, even though the chip seal was removed from the MM145 location.

RECYCLING STUDIES

The extracted PH materials were blended with 6 softening agents. Two of the recycling agents are supercritical fractions, YBF F3 and YBF F2. The other four softening agents are two commercial recycling agents and two AC-3 asphalts from different refineries. Each PH/softening agent pair was mixed using a procedure similar to that specified in ASTM D4887. The amount of softening agent required was not determined from the suggested mixing rule in ASTM D4887. Instead, the necessary amount of softening agent was determined from early mixing rules, not the mixing rules described in Chapter 5. The criteria for an acceptable blend was that the blend viscosity should be within 10% of the viscosity for the PS material at the same location. Tremendous difficulty was encountered in achieving this target viscosity with one of the AC-3 asphalts so the recycled blends using this softening agent were not studied further.

Five samples of the five laboratory blends and the contractor's blend for each of the four I-45 locations (24 total blends, 120 total samples) were aged in the POV at 82.2°C (180°F) and 20.7 bar O₂ (300 psia). These aged materials were characterized by FTIR and their viscosities were determined. From these data, the hardening susceptibility (HS) for

each recycled blend was determined. The 20.7 bar O₂ HS was chosen as the property for comparison between laboratory blends and the contractor's blend because the HS is a good representation of the physico-chemical properties of the asphalt. Poor temperature control in the POV, the elevated oxygen pressure, and the small amount of sample prevented comparison on the basis of oxidation or hardening rate. However, some conclusions can be drawn from the viscosity of similarly aged materials.

The HS for each recycled mixture is given in Table 4-2. The 'Abilene' AC-3 softening agent blends have the worst HS for 3 of the 4 locations. The rest of the agents yield blends that have low HS for some locations and yield blends with high HS at others. These comparisons are based strictly on a relative scale. It is clear that there is little difference between the laboratory blends and the contractor's mix. Additionally, there is little difference between the commercial agents and the supercritical fractions in terms of HS.

The viscosity of the most highly aged samples for each blend are also given in Table 4-2. All of the most highly aged samples were aged for the same amount of time at the same temperature so comparisons are valid. These data show that the AC-3 softening agent blends age far more than any of the other blends for each location and that the aged contractor's blends have the second highest viscosity for 3 of the 4 locations. The common link between the AC-3 blends and the contractor's blends is that these blends were made by blending an asphalt, with its own asphaltenes with an aged asphalt. This results in blends with higher asphaltene levels than the blends made with the supercritical fractions and the commercial agents alone. These conclusions further confirm that asphaltene content is a critical variable to consider in recycling.

The blends made using commercial agents and those produced using supercritical fractions follow no systematic pattern. Although the HS for the contractor's blends are similar to those of the other recycling agents, the single point viscosity comparison shows that using only recycling agents is superior to using an asphalt in combination with a rejuvenating agent. However, no clear distinction between the supercritical fractions and the commercial agents exists using these limited analyses. Clearly some additional criterion for comparison is needed in the future.

Table 4-2. Blend HS and Most Highly Aged Sample Viscosity

PH Location	Rejuvenating Agent	HS	Highest Viscosity 10 ⁵ Poise
MM 138	Contractor	2.37	5.32
	YBF F3	2.66	4.55
	YBF F2	2.21	4.72
	Sun 125	2.02	3.61
	Exxon NUSO 95	2.25	4.44
	'Abilene' AC-3	2.54	13.3
MM 139+	Contractor	2.80	8.98
	YBF F3	2.20	8.91
	YBF F2	2.51	7.50
	Sun 125	2.28	5.95
	Exxon NUSO 95	2.56	8.61
	'Abilene' AC-3	2.95	24.4
MM 140-	Contractor	2.63	10.6
	YBF F3	2.49	14.7
	YBF F2	2.41	15.9
	Sun 125	2.44	17.0
	Exxon NUSO 95	2.61	19.1
	'Abilene' AC-3	2.99	25.2
MM 145	Contractor	2.63	4.36
	YBF F3	2.44	2.76
	YBF F2	2.60	3.51
	Sun 125	3.1	3.20
	Exxon NUSO 95	2.83	3.02
	'Abilene' AC-3	3.24	10.6

CORE TESTING

Based on the HS obtained from the aging of the laboratory recycled blends and the single point viscosity comparison, two recycling agents were chosen for further study. Supercritical fraction YBF F2 and Sun Hydrolene 125 (Sun 125) were chosen to be blended with the remaining unextracted PH material from all four I-45 locations. The blending and all subsequent core tests were performed by Texas Transportation Institute (TTI) personnel. The blending was performed according to standard procedures using recycling agent content determined from the blending experiments above. The blends made with the commercial agent and the supercritical fraction and the contractor's pre-screed material were compacted into laboratory cores using the Texas gyratory method (TEX 206F). Three cores were made for each recycled material. The cores were tested to determine air voids by ASTM methods D2041 and D2726. Finally, the cores were subjected to mechanical property testing. The cores were subjected to indirect tension (ASTM D4123), resilient modulus (ASTM D4123), and Hveem stability testing (ASTM D1560).

The void content for all the cores was extremely low. Typical laboratory cores have voids near 3.0%. Only 4 cores out of 36 had voids above 3.0%, with several having voids of 2.0% or less. The average void content for each recycled mixture are shown in Figure 4-1. The low voids data indicate that it is likely that the mixes were over-asphalted. This was to be expected from the laboratory mixes, which were blended using pure, which included fresh add-mix, recycling agent and unaltered post-heater material; however, the contractor's mix should have had the proper asphalt content.

All of the cores had non-passing initial Hveem stabilities. It was decided that the cores might require time to cure, or let the recycling agent fully disperse into the aged asphalt. The cores were allowed to cure for several weeks before they were retested. The retesting results show that curing had little or no effect on the Hveem stabilities as shown in Figure 4-2. These generally poor Hveem stabilities indicate that the aggregate used is of poor quality, or of the wrong gradation. Too many fines

Figure 4-1. Laboratory Core Air Voids

Figure 4-2. Laboratory Core Hveem Stabilities

would result in the poor stabilities and the low voids observed. The aggregate gradation was not determined in this study and this conclusion is purely speculation.

Once the Hveem Stabilities were measured, the cores were subjected to resilient modulus testing. Resilient moduli for some of the laboratory cores are shown in Figure 4-3. These data are within the normal values for typical core specimens. Finally, the cores were subjected to destructive indirect tension testing. The average tensile strength at failure is plotted in Figure 4-4. These IDT results are also within the usual range.

The results of the core tests indicate that mixes made with the supercritical fraction recycling agent YBF F2 and Sun 125, although over-asphalted, are no worse than those made from the contractor's mix in terms of physical properties and may be better in terms of the limited aging data collected.

Figure 4-3. Laboratory Core Resilient Moduli

Figure 4-4. Laboratory Core Indirect Tensile Strength

CHAPTER 5

MIXING RULES

Irving (1977a) conducted a survey of equations proposed to effectively describe the viscosity of binary liquid mixtures. This survey identified more than fifty equations proposed to predict either the dynamic or kinematic viscosity of binary liquid mixtures. Irving (1977b) also determined the effectiveness of the various mixture equations. Irving concluded that Equation 5-1, the equation proposed by Grunberg and Nissan (1949), was the best overall mixing rule in terms of accuracy and simplicity for predicting the viscosity of non-aqueous binary systems.

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \quad (5-1)$$

The Grunberg interaction parameter, G_{12} , is usually considered to be a constant, however, G_{12} may be a function of x_i where x_i may be mole, mass, or volume fraction. Irving determined that the viscosity of a mixture can be predicted to within 30% of the actual viscosity when an average, constant value of G_{12} was used for classes of mixtures (i.e. polar/polar). In addition, Irving's calculations (1977b) indicate that the choice of units for x_i (mole, mass, or volume fraction) make little difference in the accuracy of the model. Mehrotra (1992, 1990) has used the Grunberg equation to model bitumen/gas and bitumen/solvent systems. However, very little effort has been focused on using this equation to predict the viscosity of asphalt/softening agent mixtures. Instead, the majority of predictions are based on two other models.

The method proposed by Epps et al. (1980) is based loosely on the mixing rule of Roelands (1966). The nomograph presented by Epps suggests that $\log \log \eta$ for the mixture is a linear combination of $\log \log \eta$ for the pure components in terms of mass fraction or volume fraction and the Roelands model uses $\log \log 10\eta$. Other variations of the Roelands model have been proposed for recycled asphalts including that proposed by Dunning and Mendenhall (1978). Although Epps' rule has received much attention, the rule most commonly used to estimate a recycled asphalt binder's viscosity is the procedure specified in ASTM D4887. This procedure,

also suggested by The Asphalt Institute (1981), is the graphical representation of the equation proposed by Arrhenius (1887). The Arrhenius equation is a special case of the Grunberg equation with G_{12} equal to zero. Irving (1977b) concluded that using the Grunberg model with G_{12} equal to zero resulted in errors larger than those obtained using an optimized or average value of G_{12} , if they were available. Large errors may require actual blending to determine a mixture's viscosity. Epps and ASTM indicate that some degree of trial and error blending may be necessary to achieve an accurate viscosity for a recycled binder.

The results of Irving indicate that it is possible to use an average interaction parameter for the Grunberg model to describe certain classes of mixtures. The present study was undertaken to determine if the Grunberg equation can be used for describing aged asphalt/softening agent mixtures and if an average interaction parameter can be used for asphalt/softening agent pairs.

EXPERIMENTAL METHODS

To produce viscosity mixing rules, tank asphalts were artificially aged and then blended with softening agents at multiple aged asphalt contents. Once the aged material had been produced, it was reheated in a laboratory oven and homogenized with a mixing paddle driven by a hand-held drill. Ideally, all of the aged material for a single asphalt was weighed at the same time so that all of the blends would have the same base material. For one asphalt, the sample was reheated, causing the viscosity to change. This viscosity change was taken into account and had no effect on the results of this study.

After the aged material was weighed into tins, the softening agent was added. Each blend contained no less than 30 g. It was determined that 30 g would be sufficient for viscosity testing and also minimize blend homogeneity problems. Each blend was mixed using a procedure similar to that specified in ASTM D4887.

The primary property of interest was the 60°C low frequency limiting dynamic viscosity. Representative viscosities for all materials examined in this study are listed in Table 5-1.

Compositional analyses of the softening agents were performed via HPLC analysis as described in Appendix A.

Table 5-1. Representative Viscosities for Aged Asphalts and Softening Agents Studied

MATERIAL	Type ^a	η (poise)
POV AAA-1	AA	22,500
AAA-AB7	AA	22,900 ^b
AAA-AB8	AA	36,600
AAF-AB1	AA	52,500
AAF-AB2	AA	20,900
Oven Coastal	AA	100,000
POV ABM-1	AA	47,200
NUSO 95	CRA	1.3
Mobil 120	CRA	1.8
Sun 125	CRA	3.0
Cyclogen	CRA	8.9
AAF F2	SCF	12
AAA F2	SCF	13
YBF F2	SCF	38
YBF F5	SCF	47
AAF F3	SCF	70
AAA F3	SCF	79
ABM F2	SCF	98
ABM F5	SCF	100
YBF F3	SCF	138
Shell F3	SCF	165
ABM F3	SCF	650
DS AC-3	LVA	310
DS AC-5	LVA	500
Shell AC-5	LVA	575
SHRP AAV	LVA	630
SHRP ABH	LVA	900

^a AA - Aged Asphalt, CRA - Commercial Recycling Agent,
SCF - Supercritical Fraction, LVA - Low Viscosity Asphalt

^b Initial Value

AGED ASPHALT PRODUCTION

Four asphalts were used in this study. Two of these asphalts were aged to multiple viscosities giving a total of seven aged materials. Three tank asphalts were obtained from the SHRP/LTPP MRL and one tank asphalt was obtained from the Coastal refinery in Corpus Christi, Texas. Two samples were aged in a Pressure Oxygen Vessel (POV) at 82.2°C (180°F) and 20.7 bar (300 psia) pure oxygen. One sample was produced by aging in a laboratory oven. The majority of the aged material was produced in the Air-Bubbled (AB) reaction apparatus.

Small amounts of SHRP AAA-1 and SHRP ABM-1 were POV aged. The quantity of POV AAA-1 produced was sufficient to blend with only one softening agent and the amount of POV ABM-1 was sufficient for blending with two softening agents. The Coastal asphalt was aged in 6 mm (1/4") films on cookie sheets placed in a laboratory oven at approximately 110°C (230°F). The trays were rotated and the asphalt was stirred twice per day to encourage uniform aging. This oven-aged Coastal was blended with four softening agents. To produce the large amounts of material that were necessary for this study, a different aging procedure had to be developed.

Large quantities of SHRP AAA-1 and SHRP AAF-1 were produced in the air-bubbling (AB) apparatus. Both asphalts were aged to two different viscosity levels. The aged AAA-1 samples are designated as AAA-AB7 (SHRP AAA-1 air-bubbled sample 7) and AAA-AB8, and the aged AAF-1 samples are designated as AAF-AB1 and AAF-AB2. To produce pavement-like materials, the reaction temperature was controlled at 93.3°C (200°F) initially. Extreme effort was not expended to maintain this temperature precisely, however, the temperature was never allowed to exceed 110°C (230°F).

SOFTENING AGENTS

Twenty-one different softening agents were utilized in this study. These twenty-one softening agents can be separated into two main classifications, low viscosity asphalts (LVA) and recycling agents. The recycling agents can be further separated into commercial (CRA) agents and supercritical fractions (SCF). Additionally, the n-hexane maltene of one of the asphalts was

used for one experiment.

Two low viscosity asphalts (LVA), AAV and ABH were obtained from the SHRP/LTPP MRL. Additionally, two LVA (an AC-3 and an AC-5) were obtained from the Diamond Shamrock (DS) refinery in Dumas, Texas and are LVA (an AC-5) was acquired from the Shell refinery in Deerpark, Texas. Four non-emulsified commercial agents (CRA), Sun Hydrolene 125, Witco Cyclogen, Exxon NUSO 95 and Mobil Mobilsol 120, were obtained. The supercritical fractions (SCF) were produced in the four stage asphalt supercritical extraction pilot plant at Texas A&M University.

The supercritical fractions were produced from five source asphalts. These source asphalts for the supercritical fractionation were obtained from a local pavement contractor, Shell, and the SHRP/LTPP MRL. The asphalt acquired from the local contractor is an AC-20 asphalt and is identified as YBF. The YBF, SHRP AAA-1, ABM-1, and AAF-1 asphalts were fractionated in two runs. The first run removed the asphaltenes and heavy polar aromatic materials and produced a large low molecular weight fraction rich in naphthene aromatics and saturates. The majority of this fraction was further fractionated into four additional fractions. The lightest of the fractions is designated as fraction 1 (F1) and the heaviest is designated as fraction 8 (F8). The majority of the supercritical fractions used in this study are either F2 or F3 from these two run fractionations, however, some of the lightest fraction from the primary fractionation (F5) was used as a recycling agent. The Shell asphalt, an AC-20, was fractionated in only one run. As a result, the fraction used in this study, F3, contains a small amount of asphaltenes.

EXPERIMENTAL DESIGN AND RESULTS

The first two experiments were performed to determine the validity of the approach and to test the air-bubbling aging technique. The first, preliminary experiment consisted of blending Sun Hydrolene 125, or simply Sun 125, with the POV AAA-1 in 10% increments of aged asphalt by mass. Figure 5-1. shows that 10% increments are not necessary to determine the relationship between viscosity and asphalt mass fraction. Furthermore, this experiment shows that the blends exhibit significant deviation from the viscosity predicted by the ASTM

Figure 5-1. Viscosity for POV AAA-1 and AAA-AB7 Blends with Sun 125

nomograph, the straight line connecting the pure materials (lines not shown on Figure 5-1).

The second experiment was performed using Sun 125 as the recycling agent and AAA-AB7 as the aged asphalt. AAA-AB7 has approximately the same viscosity as the POV AAA-1 used in the first experiment. Aged material content varied from 0% to 100% in 20% increments. The value of the Grunberg interaction parameter was determined by fitting the data from these two experiments in terms of $\ln$ viscosity. Figure 5-1 shows that the Grunberg equation is capable of modeling the data for these first two experiments. The data for the AB-aged material show only minor differences from the data from the POV-aged material blends. The result of this experiment further supports the ability of the air-bubbling apparatus to produce quality aged material.

The first aged asphalt studied systematically was AAF-AB2. This material was blended with three asphalts and eight recycling agents. Each AAF-AB2/softening agent pair was blended at levels from 0% to 100% in 20% increments. The data for all AAF-AB2/softening agent pairs

are adequately described by the Grunberg model. Although Figure 5-2 shows that there is some deviation between the data and the fit through the data, a single parameter for each asphalt/softening agent pair is able to model the data. In addition, this parameter is constant, independent of aged asphalt mass fraction. It is immediately obvious from these data that there is a negative deviation from the straight line that would connect the pure-component endpoints for the supercritical and commercial recycling agents.

Figure 5-3 shows that the data for the low viscosity asphalt softening agents, however, are near or above the straight lines representing the ASTM nomograph (lines not shown on Figure 5-3). This suggests that the supercritical and commercial recycling agent blends should be treated separately from the low viscosity asphalt softening agent blends.

Table 5-2 shows the value of the interaction parameter for each asphalt/softening agent pair. The interaction parameter varies considerably depending on the softening agent, indicating that using an average value for the interaction parameter would result in substantial error. The only noticeable trend from these data is that the interaction parameter decreases, becomes more negative, as the recycling agent viscosity decreases. From this, it was hypothesized that some of the variation in this parameter is due solely to the viscosity difference between the softening agent and the aged asphalt.

To eliminate this viscosity effect, it is necessary to normalize the data. The Grunberg equation may be rearranged such that the pure component endpoints are zero for the pure softening agent and unity for the pure aged asphalt. The normalized Grunberg model is given as Equation 5-2, with the aged asphalt as component 2 and the recycling agent as component 1.

$$DLV = \frac{\ln (\eta_m / \eta_1)}{\ln (\eta_2 / \eta_1)} = (1 + \frac{G_{12}}{\ln (\eta_2 / \eta_1)}) x_2 + (\frac{-G_{12}}{\ln (\eta_2 / \eta_1)}) x_2^2 \quad (5-2)$$

The Dimensionless Log Viscosity (DLV) can be fit as a second order polynomial with respect to x_2 , aged asphalt mass fraction. The coefficient on the second order term can be viewed as the normalized Grunberg interaction parameter. Figure 5-4 shows the normalized viscosity plotted as a function of mass fraction for the AAF-AB2/softening agent pairs. The data

Figure 5-2. Viscosity for Blends of AAF-AB2 with 8 Recycling Agents

Figure 5-3. Viscosity for Blends of AAF-AB2 with 3 Low Viscosity Asphalts

Table 5-2. Aged Asphalt/Agent Grunberg Interaction Parameter G_{12}

ASPHALT	AGENT	G_{12}	ASPHALT	AGENT	G_{12}
POV AAA-1	Sun 125	-5.80	AAA-AB7	Sun 125	-6.31
AAA-AB7	Cyclogen	-6.28	AAA-AB7	YBF F2	-5.42
AAA-AB7	YBF F5	-4.28	AAA-AB7	ABM F2	-4.63
AAA-AB7	YBF F3	-3.45	AAA-AB7	ABM F3	-4.10
AAA-AB7	SHRP ABH	0.03			
AAA-AB8	Cyclogen	-6.33	AAA-AB8	AAA F2	-5.47
AAA-AB8	YBF F5	-4.03	AAA-AB8	AAA F3	-4.77
AAA-AB8	AAF F3	-4.52	AAA-AB8	DS AC-3	---
AAA-AB8	DS AC-3 Maltene	---	AAA-AB8	Shell AC-5	1.14
AAA-AB8	SHRP AAV	-0.46	AAA-AB8	NUSO 95	-6.23
AAAF-AB1	NUSO 95	-8.42	AAAF-AB1	AAF F2	-5.88
AAAF-AB1	ABM F2	-4.88	AAAF-AB1	AAA F3	-4.56
AAAF-AB1	Shell F3	-3.64	AAAF-AB1	ABM F5	-4.90
AAAF-AB1	DS AC-5	2.57	AAAF-AB1	SHRP ABH	0.08
AAAF-AB1	DS AC-3	2.18	AAAF-AB1	ABM F3	-3.99
AAAF-AB1	Mobil 120	-7.69			
AAAF-AB2	Sun 125	-6.24	AAAF-AB2	Mobil 120	-7.50
AAAF-AB2	AAA F2	-4.83	AAAF-AB2	AAF F2	-5.26
AAAF-AB2	ABM F5	-3.95	AAAF-AB2	YBF F3	-3.39
AAAF-AB2	AAF F3	-3.81	AAAF-AB2	Shell F3	-3.12
AAAF-AB2	Shell AC-5	-0.37	AAAF-AB2	SHRP AAV	-0.88
AAAF-AB2	DS AC-5	1.82			
Oven Coastal	Sun 125	-10.71	Oven Coastal	Cyclogen	-9.28
Oven Coastal	YBF F3	-6.54	Oven Coastal	YBF F5	-6.90
POV ABM-1	ABM F3	-1.48	POV ABM-1	ABM F2	-3.39

Figure 5-4. Dimensionless Log Viscosity for AAF-AB2 Blends

for the asphalt/recycling agent pairs show remarkably little difference when analyzed in this manner. Even though recycling agent saturate content varies from 8% to 23% and the aromatic content varies from 77% to 92% (data not included), all of the recycling agents produce the same DLV for a given aged asphalt mass fraction. This result complicates the correlation of interaction parameter with recycling agent chemical composition.

The low viscosity asphalt (LVA) softening agents do not collapse to a single grouping of data. SHRP AAV and the Shell AC-5 have similar interactions with AAF-AB2 and would be well predicted by the ASTM nomograph, but the DS AC-5 exhibits significant positive deviation. Even though these low viscosity asphalt (LVA) softening agents do not exhibit behavior similar to the recycling agents, blends with all three low viscosity (LVA) asphalt softening agents can be modeled using the Grunberg equation in either the standard or normalized forms. Additionally, the AAF-AB2 data show that it may be possible to use an average value for the normalized interaction parameter for asphalt/recycling agent systems.

The next aged asphalt studied was AAF-AB1. This material was blended with three low viscosity asphalts (LVA) and eight recycling agents. Each asphalt/softening agent pair was blended at levels from 0% to 100% in 20% aged asphalt increments. Of these eleven softening agents, one of the asphalts and four of the recycling agents were the same as those blended with AAF-AB2. One of the recycling agents, ABM-1 F3, has a viscosity in the AC-5 range but with no asphaltenes and a low saturate content.

The data for these asphalt/softening agent pairs are also well described by the Grunberg model. As Table 5-2 shows, the value of the interaction parameter varies considerably from softening agent to softening agent and is different for an agent blended with AAF-AB1 and that same agent blended with AAF-AB2. Without exception, the absolute value of the interaction parameter was larger for an AAF-AB1/agent pair than for an AAF-AB2/agent pair. Once again, this suggests that there is some effect due solely to the viscosity difference between the aged asphalt and the softening agent.

The normalized viscosity data for the AAF-AB1 softening agent blends are plotted in Figure 5-5. There is more variation in the data for the AAF-AB1/recycling agent blends than there is for the AAF-AB2/recycling agent blends, but there is still remarkably little difference.

The AAF-AB1/recycling agent and AAF-AB2/recycling agent data are plotted together in Figure 5-6. It is clear that there is much similarity between the two sets of data. Blends of recycling agents with 20,900 poise AAF-1 and blends with 52,500 poise AAF-1 have essentially the same DLV for a given aged asphalt mass fraction, indicating that an average normalized interaction parameter can be used for AAF-1/recycling agent mixtures.

As was the case in the AAF-AB2 blends, the AAF-AB1/low viscosity asphalt (LVA) softening agent pairs do not collapse to a single grouping of data. Figure 5-5 shows that the DS AC-3 and DS AC-5 exhibit similar positive deviations but SHRP ABH shows no significant deviation from the behavior predicted by the ASTM nomograph. The behavior for the high viscosity supercritical fraction ABM-1 F3 is similar to the behavior of the recycling agents, demonstrating that a high viscosity material can exhibit negative deviations. Once again, the Grunberg model seems adequate to describe all of the data.

Next, AAA-AB7, which was blended with Sun 125 in the second experiment, was blended with seven additional softening agents. The normalized Grunberg equation is able to

Figure 5-5. DLV Versus Aged Asphalt Mass Fraction for Blends Using AAF-AB1

Figure 5-6. DLV for Blends of AAF-AB2 and AAF-AB1 with Recycling Agents

model the AAA-AB7 data, as shown in Figure 5-7. Again, there is significant deviation between the (supercritical fraction (SCF) and commercial (CRA)) recycling agents and the low viscosity asphalt (LVA) softening agent. There are two important features of these experiments. The first is that the ABM-1 F3 agent, a high viscosity supercritical fraction, shows moderate deviation from the rest of the recycling agents. The second noticeable feature is that there is more scatter among the mixture data for AAA-AB7 blends than for AAF-AB2 blends, even though these aged materials have similar viscosities. This implies that AAF-AB2 will exhibit similar recycling behavior independent of the recycling agent used and that the mixture viscosity behavior of AAA-AB7 can be slightly altered by the choice of recycling agent.

Aged material AAA-AB8 was blended with six recycling agents, 3 low viscosity asphalts, and DS AC-3's maltene. Once again, the recycling agents, both supercritical fractions (SCF) and commercial (CRA), form a narrow band with respect to DLV and the low viscosity asphalts (LVA) do not as shown in Figure 5-8. There are two significant results from the AAA-AB8 data. First, the Shell AC-5 shows positive deviation from the ASTM nomograph with this asphalt that it did not with AAF-AB2. Second, the Grunberg model fails miserably for the DS AC-3 and its maltene, Figure 5-9. In fact, the DS AC-3 and maltene data are highly sigmoidal, exhibiting negative deviation at low AAA-AB8 levels and positive deviation at high AAA-AB8 mass fractions. Additionally, Figure 5-9 shows that the DS AC-3 blends have larger DLV's than the maltene blends. Therefore, removing the asphaltenes from DS AC-3 has only a minor effect. This further complicates the correlation between viscous interaction and compositional parameters.

The oven-aged Coastal was blended with four different recycling agents. Aged asphalt content varied from 0% to 100% in 25% increments. The data from these blends also form a narrow band in terms of the DLV; however, this narrow band, shown in Figure 5-10, is significantly lower than the data for the other blends. Although these Coastal blends result in DLVs lower than the majority of the other asphalt blends, they are still not as low as the data for the AAA-AB7/ABM-1 F3 blends, Figure 5-7. The data obtained for the POV ABM-1 blends are somewhat higher than the average for the rest of the data. In fact, the POV ABM-1/ABM-1 F3 blend data shown in Figure 5-11 are closest to the diagonal line representing the ASTM suggested mixing rule. Thus, blends made with ABM-1 F3 as the recycling agent form both the

Figure 5-7. DLV for AAA-AB7 Blends

Figure 5-8. DLV for AAA-AB8 Blends

Figure 5-9. Anomalous Behavior of AAA-AB8/DS AC-3 Blends

Figure 5-10. DLV for Oven Coastal Blends

Figure 5-11. DLV for POV ABM-1 Blends

high and low boundaries of data collected in this study.

DISCUSSION OF RESULTS

All of the recycling agent blend data collected in this study were placed on the same plot of DLV versus asphalt mass fraction. An overall mixing rule was determined by fitting the DLV data to a second order polynomial. The complete data and overall fit are shown in Figure 5-12. This overall DLV mixing rule was used to predict the amount of recycling agent necessary to obtain specification blends for all of the asphalt/softening agent pairs used in this study with the exception of the AAA-AB7/DS AC-3 material blends. The log log η mixing rule suggested by Epps and the ASTM nomograph were used for comparison. Two target viscosities were chosen for comparison. A target viscosity of 2000 poise was chosen because this is the specification for an AC-20 asphalt and the probable target viscosity for Hot Mix Recycling. A

Figure 5-12. DLV Mixing Rule for All Recycling Agent Blends

target viscosity of 5000 poise was also chosen. This is a reasonable value for an AC-20's viscosity after Thin Film Oven Test (TFOT) treatment and a probable target viscosity for Hot-In-Place Recycling. The amount of recycling agent required was calculated for each mixing rule and then the actual mixture viscosity was determined from the Grunberg interaction parameter for the individual asphalt/softening agent pair. If the predicted softening agent content was less than 10%, the data were considered unreliable because unrealistically high actual viscosities resulted (mostly for the Epps rule). The resulting viscosities were calculated and an average value was obtained for the recycling agent blends as a group and for the low viscosity asphalt softening agents as a group.

The average viscosities that would result from prediction using each model are given in Table 5-3. In addition to the average viscosity, the range of viscosities resulting from each model are listed. From these data, it is obvious that the DLV mixing rule using an average normalized interaction parameter is superior to the other two mixing rules. This is to be

Table 5-3. Comparison of Viscosities Resulting from Various Mixing Rules**Supercritical and Commercial Recycling Agents****Target Viscosity 2000 dPa•s (poise)**

Model	Avg. Viscosity	Low	High
DLV	2040±390	1100	3000
Epps	1920±1200	780	6730
ASTM	700±370	160	2340

Supercritical and Commercial Recycling Agents**Target Viscosity 5000 dPa•s (poise)**

Model	Avg. Viscosity	Low	High
DLV	5010±840	3120	7350
Epps	4380±1490	2140	9190
ASTM	1880±570	540	3460

Low Viscosity Asphalt Softening Agents**Target Viscosity 2000 dPa•s (poise)**

Model	Avg. Viscosity	Low	High
DLV	5320±2200	2960	8800
Epps	3310±1190	1910	5090
ASTM	2430±680	1660	3410

Low Viscosity Asphalt Softening Agents**Target Viscosity 5000 dPa•s (poise)**

Model	Avg. Viscosity	Low	High
DLV	11500±4300	6900	19200
Epps	8380±3000	4800	13000
ASTM	6180±2000	4030	9500

expected because the DLV mixing rule is based on the very data that it is predicting. However, the ability of the DLV mixing rule to produce AC-20 blends nearly 95% of the time is an extraordinary result given the extreme variation, both in terms of standard deviation and range, for the other two models. This shows that the current methods are inadequate at predicting proper recycling agent content. In fact, the ASTM nomograph results in completely unacceptable viscosities for better than 95% of the hypothetical mixtures. This substantiates the findings of Irving (1977b) as to the accuracy using G_{12} equal to zero. Use of the ASTM nomograph would certainly result in much trial and error to obtain the correct viscosity for these asphalt/recycling agent blends.

For prediction of the low viscosity asphalt softening agent data, the DLV mixing rule does not perform very well. The average, deviation, and range are all larger than those obtained by the other mixing rules. The ASTM nomograph procedure is best at predicting the low viscosity asphalt softening agent data. In fact, this method is remarkably good considering that these data include the blends formed by the DS asphalts and the Shell AC-5.

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APPENDIX A

EXPERIMENTAL METHODS

SUPERCRITICAL FRACTIONATION

The supercritical fractionation unit has been described in Study 1155 (Davison, 1991) and Study 1249 (Davison, 1992). Recent modification as well as the operating conditions used in this work are discussed in Chapter 2.

PRESSURE OXYGEN VESSEL (POV) CONFIGURATION II

This unit is described in Lau (1992) and Davison (1992). In order to improve on aging simulation capacity, four additional units were constructed and a central control panel was installed as shown in Figure A-1. Because of temperature gradient problems, an additional heating tape was installed to increase the heat input near the vessel bottom. Operation of the unit in this mode is as follows: Asphalt samples of 2.4 grams are prepared in aluminum trays. The dimensions of the tray are 7.0 cm (2.75 in) by 3.5 cm (1.38 in). When the asphalt is evenly distributed by slightly heating, the effective film thickness is 1 mm (0.039 in). After preparing the asphalt samples, loading the sample rack, and allowing the temperature in the POV to reach equilibrium, the operator places the rack inside the POV and bolts the cover flange to the top. The vent valves, oxygen feed valves, and vacuum valves are closed. A vacuum pump evacuates the air in the vessel to a pressure of 0.03 atm absolute. The vessels are slowly pressurized to the desired level by manipulating the oxygen cylinder regulator and oxygen feed valves. Once the desired oxygen pressure is reached, the cylinder, regulators, and feed valves are closed. The vessel is isolated for the experimental time period.

During the experiment, samples are periodically removed. To obtain samples, the pressure in the vessel is decreased by slowly venting off the oxygen to the atmosphere until the pressure gauge reads zero. The operator removes the top insulation, unbolts the

Figure A-1. Pressure Oxygen Vessel Control Panel

cover flange, and collects the samples. Samples to be aged further are loaded back into the vessel, and the process is repeated. The aged samples are saved for chemical and physical analysis.

POV CONFIGURATION III

Temperature gradient problems were still encountered in Configuration II so it was decided to immerse the vessels in glycol-water baths which eliminated the problem.

Figure A-2 shows a schematic of one of the POVs. The actual vessels are behind a steel wall in an explosion proof hood. Each vessel is contained in a steel barrel which is enclosed in a four-sided shield made of *Lexan*™. The vessel is monitored and controlled from

Figure A-2. Pressure Oxygen Vessel and Control Panel

a panel outside the explosion proof hood. The control panel uses a compound pressure gauge to monitor the pressure, a variable transformer to control the amount of electrical power to the heating elements in the water/triethylene glycol bath, an on/off temperature controller, and a recorder to monitor the temperature within the POV. A stirrer is employed in the bath for even temperature distribution. To the left of the control panel is the vacuum pump that evacuates the vessels before charging with oxygen. Three valves per vessel, as labeled in Figure A-1, are used for venting to atmospheric pressure, evacuating to low pressure to remove the air, and charging with oxygen. The oxygen feed valve isolates the POVs from the oxygen cylinder when closed.

CORBETT ANALYSIS

Corbett analyses (ASTM D 4124) separated the components of the samples according to polarity. Some modifications of the Corbett procedure were implemented to reduce sample size and increase efficiency as suggested by Thenoux et al. (1988).

CORBETT ANALYSIS USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY, HPLC

Bishara et al. (1989) developed an analytical method for analyzing the Corbett-type composition for asphalts using high performance liquid chromatography (HPLC). The HPLC method provides a rapid and high-repeatability analysis for determining the composition of an asphalt.

Asphalt samples were weighed to 0.2 ± 0.01 gram in a scintillation vial and mixed with 20 mL of n-hexane. The asphalt/n-hexane solution was further sonicated for 5 minutes to ensure good mixing and set overnight. The asphaltene was removed by filtering the solution through a $0.45 \mu\text{m}$ PTFE membrane syringe filter. The syringe filter was first pre-dried in an oven at 100°C (212°F) for an hour prior to use and the weight of the filter was noted. After filtering, the filter was further dried in an oven at 100°C (212°F) for an hour and the filtered solution was analyzed using HPLC. The weight difference between the filter before and after filtering is the weight of the asphaltene and the asphaltene content is equal to the weight of asphaltene divided by the weight of the asphalt sample.

After removal of asphaltene, $20 \mu\text{L}$ of filtered solution was directly injected into a WATERS $3.9 \times 300 \text{ mm}$ $125 \text{ \AA}$ $\mu\text{Bondapak}$ aminopropylmethylsilyl bonded amorphous silica HPLC column. A flow rate of 2.0 mL/min and a column temperature of 35°C (95°F) were used. Saturates were eluted at 1.7 minutes and were monitored by a Differential Refractive Index (RI) detector, while polar and naphthene aromatics were detected by a ultraviolet (UV) photometer. Naphthene aromatics were continuously eluted after saturates; however, the polar aromatics will strongly absorb on the column and need to be backflushed out at 15 minutes after injection. The saturate content was determined from a calibration of the

RI response of pure saturates from the traditional Corbett column. The total aromatics content, the sum of polar aromatics and naphthene aromatics, is obtained by the difference.

FOURIER TRANSFORM INFRARED SPECTROSCOPY, FTIR

A Mattson Galaxy series 5020 Spectrometer at 4 cm^{-1} resolution and 64 scans measured the infrared absorbance spectra of the samples. The Attenuated Total Reflectance, ATR, method with a Zinc Selenide prism was used (Jemison et al., 1992). To quantify the changes in the spectra, the carbonyl content is defined as the integrated absorbance from 1820 to 1650 cm^{-1} with respect to the baseline at the absorbance of 1820 cm^{-1} . This area is called the *Carbonyl Area* or *CA*. The range of wave numbers includes the following carbonyl compounds: esters, ketones, aldehydes, and carboxylic acids. The primary absorbance peak for the oxidized asphalt is located at 1700 cm^{-1} and corresponds to ketone formation.

At low aging pressures of 2 and 0.2 atm oxygen, an oxygen diffusion problem may be significant. To partially eliminate this diffusion problem, only the exposed surface, *ES*, of the film was analyzed for kinetic data. The depth of penetration of the IR beam for the ATR prism was 1 micron. For analysis, a quarter of the material in the aluminum tray was removed and the *ES* placed on the prism face. To insure good contact at the sample/prism interface, the sample was compressed. Heating of the sample was avoided if possible.

For oxygen diffusion determinations in the asphalt film it was required to measure FTIR spectra at both the *ES* and the substrate interface, *SI*. This procedure required two ATR prisms. Spectra of POV-aged asphalts and model compounds containing carbonyl groups were analyzed with both prisms. The agreement in the two ATR prisms is within 2% based on *CA* determinations, and it was concluded that the two prisms are equivalent.

The actual procedure for measuring the *ES* and *SI* spectra with the two ATR prisms is explained. First, the *ES* spectrum is measured with one of the ATR prisms. The second prism is placed in the sample compartment and the required backgrounds and purge references are collected. The aluminum is removed, and the *SI* surface is ready for analysis.

The second prism face is placed on the *SI* surface creating a sandwich configuration with the asphalt film. Good surface contact between the second prism and the *SI* surface was sometimes difficult to achieve since heating the samples was avoided and excessive compression would damage the prism. When sufficient contact was achieved, the prism configuration was placed in the sample compartment, and the *SI* spectrum was collected.

For measuring the spectrum of asphaltenes, the material was dissolved in THF and the solution deposited on the ATR prism drop by drop allowing the THF to evaporate. When the film was sufficiently thick it was further dried with a heat gun.

DYNAMIC MECHANICAL ANALYSIS, DMA

The rheological properties of neat and aged asphalt were measured on a Carri-Med 500 Controlled Stress Rheometer. The specific properties used to characterize the asphalts were the low frequency limiting complex viscosity, η_o^* , and the reciprocal of the loss compliance, $(1/J'')$. Both properties were measured at a temperature of 333.3 K (140°F) and values of $(1/J'')$ are reported at a frequency of 10 rad/s. The value of η_o^* is independent of frequency or shear rate (Lau et al., 1992). The geometry consisted of a 2.5 cm (1 in) parallel plate with a 0.5 mm (0.02 in) gap. Torque levels were such that the behavior of the asphalt was linear visco-elastic in the frequency range of 100 to 0.1 rad/s. η_o^* was not measurable at 333.3 K (140°F) and 0.1 rad/s on samples with viscosity higher than 200,000 poise. For these hard samples, rheological measurements were performed at both 333.3 and 363.2 K (140° and 195°F). The moduli curves were superimposed at 333.3 K (140°F) using time-temperature superposition (Ferry, 1985) and η_o^* was calculated.

HEXANE ASPHALTENE DETERMINATION

Asphaltenes, %A, are the insoluble portion of the asphalt in a paraffinic solvent. The hexane %A of neat and aged asphalts were precipitated as described by Pearson et al., (1986). Solutions of 0.2 grams of asphalt in 20 mL of hexane were made, sonicated for 30

minutes, and precipitated for 12 hours. The solutions were filtered through pre-weighed 0.4 micron membranes. After drying for approximately three days, the membranes were post weighed. The difference in the weight of the membrane relative to the sample weight multiplied by 100 is the %A.

GEL PERMEATION CHROMATOGRAPHY, GPC

A WATERS GPC 600E system was used to determine the molecular weight, *MW*, distributions of asphalts and detect for trace amounts of solvent after extraction and recovery (Burr et al., 1991). Three columns in series of decreasing pore size of 1000, 100, and 50 Å separated the sample based on molecular size or hydrodynamic volume. The first two columns were 305 mm (12 in) long and were obtained from WATERS. The final column, from PLGel, was 610 mm (24 in) long. Solvent detection after extraction and recovery required this final column (Burr et al., 1991). The mobile phase was tetrahydrofuran, THF, at a flow rate of 1 mL/min. The injection volume was 100 μ L. A Differential Refractive Index detector, RI, monitored the elution of the sample through system. Isothermal operation of the columns and detectors was at 313.2 K (104°F).

The system was calibrated with a known set of polystyrene, PS, standards at a concentration of 0.025 g/mL. Based on the retention time or elution volume of the PS and the known *MW*, a calibration curve was constructed and a high order polynomial was used to fit the data points providing a smooth function through the data. Furthermore, the retention times for the asphalt samples were in the range of the PS standards. Errors introduced from extrapolation of the polynomial outside of the retention time range were eliminated since this calibration curve was not used for retention times outside the calibration range.

After calibration, samples were prepared at a concentration of 0.020 g/mL. The samples were sonicated for 30 minutes and filtered through 0.4 micron membranes, removing insoluble particles that could damage the GPC columns. Samples are analyzed within 2 days of preparation decreasing the effect of solvent aging (Burr et al., 1991). The weight average molecule weight based on RI *MW* was calculated from the measured

chromatogram and calibration curve.

EXTRACTION AND RECOVERY OF FIELD-AGED ASPHALT

Two different procedures were used. The extracting solvent for both procedures was the same, a mixture of 15% ethanol and 85% TCE by volume. The first procedure is an automated system that continuously feeds and removes solvent (Burr et al., 1993). The second procedure is a manual method, extracting the asphalt with discrete volumes of solvent. The manual or micro method is similar to ASTM D 2172-81 Method A. In both procedures, a rotary evaporator recovered the asphalt from the extraction solution. To minimize the solvent effects on the asphalt during recovery, the asphalt concentrations were kept as high as possible, and the oil bath temperature was maintained at 388.9 K (240°F). For final recovery, the temperature was increased to 444.4 K (340°F). To insure sufficient solvent removal, the final recovery process was extended 30 minutes beyond the detection of the last drop of solvent in the collection flask. To detect for incomplete solvent removal, all of the extracted asphalts were analyzed with GPC (Burr et al., 1991).