Laboratory Study of the Effects of Recycling Modifiers on Aged Asphalt Cement

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ABSTRACT

An on-going research program to study the effects of recycling modifiers on aged asphalt cement is described. So far nine modifiers and one aged asphalt have been investigated. Blends of the modifiers and asphalt were tested chemically and physically in both an unaged condition and after aging in a rolling thin-film oven. Chemical characterization included clay-gel compositional analysis, solubility testing, and high pressure gel permeation chromatography. Physical testing included penetration, viscosity, and ductility testing. The results indicate that the influence of the polar to saturate ratio (P/S) on consistency may diminish with higher levels of aromatic fractions in the modifiers. Higher levels of P/S in the modifiers were also responsible for better properties on aging of the blends. Clay-gel results revealed that the compositional effects of modifiers are not additive in the blends. On aging, the blends increased in asphaltene content and decreased in polar content. Solubility test results revealed that the effects of different modifiers on aged asphalt can be detected. Solubility trends were also observed after aging of the blends. Blends with low aging indices were also found to have an increase in state of peptization after aging.

Since the mid-1970s recycling of asphalt pavements has been a popular concept in the paving industry. As described by Epps et al. (1), recycling can be accomplished either in-place or in a central plant and can be either a hot or cold process. In any case, it almost always involves the use of some type of petroleum product to restore the asphalt binder to some acceptable level of consistency. These petroleum products may be soft asphalts, high polar content oils, or highly aromatic oils. Modifiers are added to the aged binders to

1. Restore the recycled asphalt to a suitable consistency for construction,
2. Restore optimal chemical characteristics to the aged asphalt,
3. Provide sufficient additional binder to coat any new aggregate, and
4. Provide sufficient binder content to satisfy mixture design requirements.

The engineer must have a means of specifying the type and amount of modifier to be used for a particular recycling project. The study presented in this paper was undertaken with this goal in mind for hot, central plant operations.

Organizations such as ASTM and the West Coast User-Producer Group have recognized the need for recycling agent specifications and are currently taking action to develop these specifications. It is widely acknowledged that modifiers should change the consistency of the recycled binder to an acceptable level and increase the life expectancy of recycled mixtures (2-4). Kari et al. (4) have also stated that modifiers should disperse readily in recycled mixtures and produce uniform mixture properties from batch to batch. With respect to chemistry, Davidson et al. (2) have concluded that modifiers should be compatible with the aged asphalts so that syneresis does not occur. Dunning and Mendenhall (3) suggest that the modifiers should also serve to redisperse asphaltenes in the aged binders.

Some of the more commonly used tests to chemically characterize modifiers include the Rostler-Sternberg analysis (2,5-8), clay-gel adsorption chromatography (3), and refractive index (5). Recommended procedures for physical characterization include viscosity measurements at different temperatures (2-5), flash point (2-6), and rolling thin-film oven (RTFO) parameters (3).

The purpose of this research project was to identify useful chemical and physical parameters by which to evaluate modifiers and blends of modifiers and aged asphalt binders. Further research will be conducted on laboratory recycled mixtures.

The experiments in this study were based on clay-gel compositional analysis of the modifiers. The parameters used were the ratios of polar to saturate fractions (P/S) and the percent aromatics in the modifiers. Figure 1 shows the test matrix. The levels of high, medium, and low for both parameters were selected arbitrarily according to the materials on hand.

PHYSICAL CHARACTERIZATION

Modifier Tests

The modifiers were initially tested for flash point

% Aromatics
Polar-Saturate

	LOW	MED	HIGH
LOW	MBD-1 *	MBD-2 +	MBD-3
MED	MBD-4 *	MBD-5	MBD-6A +
HIGH	MBD-7A	MBD-8A	MBD-9

* High Paraffinic Oils

\+ Soft Asphalts

FIGURE 1 Test matrix.

and consistency at different temperatures. The flash point test was performed as a safety precaution for the laboratory. Viscosities were run at 100°, 140°, and 212°F to investigate the temperature susceptibility of these products. The viscosity at 140°F was also used to calculate the percentage of modifiers to be incorporated into the blends.

Tests on Blends

Different percentages of each modifier were blended with the aged asphalt and tested for viscosity at 140°F to determine the final blend percentages for viscosities between 3,000 and 4,000 poises. Consistencies of the final blends were tested over a wide range of temperatures. Penetration values were obtained at 39.2° and 77°F in accordance with ASTM D 5 (9). A temperature-penetration index (TPI) was established according to the following formula:

$$\text{TPI} = (\text{Pen at } 77°\text{F})/(\text{Pen at } 39.2°\text{F}) \quad (1)$$

Thus the greater the value of TPI, the more temperature susceptible was the material at low temperature.

Likewise, viscosity was measured at 39.2° and 77°F in a constant pressure (Schweyer) rheometer. The principle and operation of this device have been described by Schweyer et al. (10). The information from this test can be used to compute the viscosity of a material over a range of shear rates. High temperature viscosities were measured at 140° and 275°F in accordance with ASTM D 2171 and D 2170, respectively. The viscosities at 275°F were used to evaluate the differences in high temperature behavior of the materials.

The blends were subjected to conditioning in the RTFO as per ASTM D 2872 (9). After this treatment they were tested for penetration at 39.2° and 77°F, viscosity at 140°F, and ductility at 77°F. The penetration values were also expressed as percentages of the unaged penetration values. The aging index for the viscosity at 140°F was calculated according to the following formula:

$$\text{Aging index} = (\text{Viscosity at } 140°\text{F after RTFO}) \div (\text{Viscosity at } 140°\text{F before RTFO}) \quad (2)$$

CHEMICAL CHARACTERIZATION

Clay-Gel Composition

The clay-gel compositional analysis ASTM D 2007 (11) was used in this study. Basically, this procedure involves separation of the asphalt into the four generic fractions of asphaltenes, saturates, aromatics, and polars. Several modifications have been implemented in order to apply this procedure to a variety of asphaltic materials. These modifications are as follows:

1. Stripping the silica column with 70 percent toluene/30 percent methanol (vol. %),
2. Discarding the factor 0.88 in the calculations for polar compounds,
3. Solvent amount to separate asphaltenes,
4. Sample size,
5. Solvent percentages to strip the polar fraction,
6. Discarding use of separatory funnel and calcium chloride,
7. Stripping the polar fraction with additional polar solvent, and
8. Alternate solvent evaporation.

Repeatability is a question that has been raised with regard to the clay-gel compositional analysis. By using the modifications outlined, excellent repeatability has been obtained on a variety of asphaltic materials. With the exception of asphaltenes, the clay-gel procedure has produced results within ASTM limits. The ASTM procedure was originally developed for extender oils, which are very low in asphaltenes. The modifications outlined here have produced results within 0.6 percent in the asphaltene fraction.

Solution Properties

Heithaus (12) defined the solution properties of an asphalt system in terms of asphaltene peptizability (P_a), Maltene peptizing power (P_o), and the state of peptization (P). The properties defined by Heithaus are considered important in describing the mutual solubility of asphalt fractions. Waxman et al. (13) have correlated solubility parameters for asphaltic materials to solubility parameters of various solvents. They also observed that removing resins from an asphalt reduced the solubility characteristics of the asphalt.

Venable and Peterson (14) evaluated a series of fresh and aged asphalts as well as recycling agents by using Heithaus parameters. They found that variations in these parameters were dependent on the type of material and the conditions of the test. Venable and Peterson observed that asphaltene peptizability was inversely related to the polar functionality content of the asphalt system.

The solubility evaluation technique used in this study was designated the Heithaus/Waxman approach. This technique was chosen because the test procedures are similar, except for the following items.

1. The data handling and interpretation are different.
2. The nonpolar solvent used for titration is different. Heithaus used n-heptane and Waxman used n-dodecane. In this study n-dodecane was used.
3. The microscope magnification is 400X in the Heithaus procedure and 88X in the Waxman procedure. Observations in this study were made at 100 to 150X.

The Heithaus/Waxman procedure was generally the same as that used by Venable and Peterson (14) with some additional modifications. These modifications included reducing the sample size to 1.00 ± 0.05 g for five data points, weighing the samples to ±1 mg, and maintaining constant polar solvent (toluene) volumes throughout the test program. A finite and consistent wait time was instituted before testing. All testing was conducted at 77° ± 5°F. The modifications to the procedure by Venable and Peterson were made in order to conserve asphalt, reagents, and time without reducing the reliability of the results.

The Heithaus parameters are obtained from the following relationships (14):

$$\text{Flocculation ratio (FR)} = (\text{Volume of toluene}) \div [\text{Volume (toluene + n-dodecane)}] \quad (3)$$

$$\text{Dilution ratio (X)} = [\text{Volume (toluene + n-dodecane)}] \div (\text{Weight of asphalt}) \quad (4)$$

The calculations from these equations are presented graphically as FR versus 1/X. The extension of this plot leads to FR_{max} and $1/X_{min}$ as the ordinate and abscissa intercepts, respectively. These values are used to compute the Heithaus parameters:

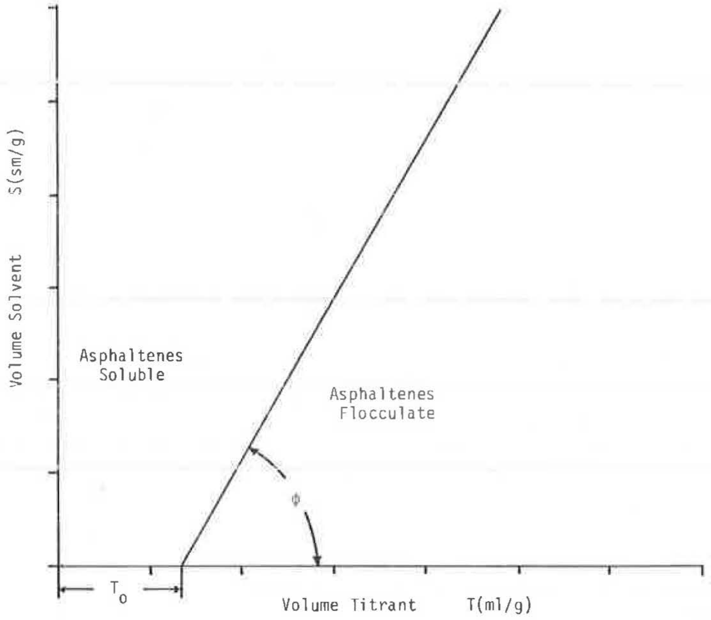

FIGURE 2 Schematic showing Waxman parameters.

$$P_a = 1.0 - FR_{max} \quad (5)$$

$$P_o = FR_{max}(1 + X_{min}) \quad (6)$$

$$P_a = P_o/(1 - P_a) = 1 + X_{min} \quad (7)$$

The Waxman parameters are shown in Figure 2. The cotangent of the angle ϕ is defined as:

$$\text{Cot } \phi = (T - T_o)/S \quad (8)$$

where

T = volume of titrant (mL) per gram of material,
T_o = volume of titrant per gram of material required for precipitation of the least soluble asphaltenes, and
S = volume of solvent per gram of material.

The value of T_o is considered to be a measure of the stability of the complex collodial micellar asphaltenes in the asphalt. It has the same function as the X_{min} term in the Heithaus procedure.

High Pressure Gel Permeation Chromatography

The high pressure gel permeation chromatography (HP-GPC) technique separates components of a sample based on molecular size. P.W. Jennings at Montana State University is currently involved in a 17-state project investigating this technique as a possible

TABLE 1 Modifier Properties

Modifier Designation	Clay-Gel Compositional Analysis, percent				P/S	Viscosity at 100°F, poises	Viscosity at 140°F, poises	Viscosity at 212°F, poises	Flash Point COC, °F
	Asphaltenes	Saturates	Aromatics	Polars					
MBD-1	0.25	84.34	12.68	2.74	0.03	0.77	0.25	0.07	420
MBD-2	20.35	20.78	23.19	35.48	1.72	15,300	490	14	555
MBD-3	9.78	15.96	24.34	49.87	3.12	20,000	540	9.7	535
MBD-4	0.73	50.49	43.95	4.97	0.10	0.19	0.08	0.03	325
MBD-5	0.20	23.46	49.02	27.73	1.18	16	2.8	0.25	435
MBD-6A	23.79	15.22	26.37	34.63	2.28	5,400	300	9.8	460
MBD-7A	0.24	22.17	62.40	15.55	0.70	6.2	1.0	0.15	445
MBD-8A	0.30	17.78	60.20	21.98	1.24	9.9	1.8	0.24	480
MBD-9	0.12	6.44	64.50	29.07	4.51	27	2.3	0.19	420

TABLE 2 Pope AFB Recovered Asphalt Properties

Property	Value
Penetration at 39.2°F, 200 g, 60 sec, 0.1 mm	11
Penetration at 77°F, 100 g, 5 sec, 0.1 mm	22
Viscosity at 39.2°F, 0.05 sec^{-1} (poises)	1.2×10^9
Shear susceptibility (c) at 39.2°F	0.71
Viscosity at 77°F, 0.05 sec^{-1} (poises)	2.4×10^7
c at 77°F	0.61
Viscosity at 140°F (poises)	56,800
Viscosity at 275°F (cSt)	1,413
Clay-gel composition (%)	
Asphaltenes	43.57
Saturates	10.79
Aromatics	12.78
Polars	32.82

tool in the evaluation of asphaltic materials. The samples in this study were sent to Jennings for analysis.

The results of the initial work by Jennings et al. (15) suggest that molecular size distribution is characteristic of each asphalt and may be a valuable tool in designing pavement recycling projects, as well as defining excellent to poor pavements. Jennings suggests that HP-GPC analysis along with physical tests and additional chemical tests such as compositional analysis may lead to a reasonable explanation for the performance of pavements.

The HP-GPC chromatograms are divided into three regions: large molecular size (LMS), medium molecular size (MMS), and small molecular size (SMS). The calculated areas are based on elution time and a standard asphalt sample. Jennings has stated that the LMS region along with the asphaltene content is significant in predicting pavement performance. This was based only on data from the Montana study.

MATERIALS

Materials used in this study included nine compositionally different modifiers and one field-sampled aged asphalt. Figure 1 shows that two highly paraffinic oils and two soft asphalts were included along with five commercially available recycling agents. The compositions and physical characteristics of the selected modifiers are given in Table 1. The level of aromatics ranged from 12.7 percent for MBD-1 to 64.5 percent for MBD-9. MBD-1 also had the lowest P/S value (0.03). MBD-9 had the highest P/S level (4.51). Although MBD-3 is marketed as a recycling agent, it exhibits viscosities comparable to the soft asphalts included in the study.

The aged asphalt used in this study was extracted from pavement samples obtained at Pope Air Force Base (AFB), North Carolina. The pavement feature was a taxiway that had been constructed in 1941. The taxiway was so severely fatigued that it was recycled immediately after sampling. The aged paving mixture had the characteristics of high void content and a large amount of fine material in the gradation. The properties of the extracted asphalt are given in Table 2.

RESULTS AND DISCUSSION

Physical Properties of Asphalt-Modifier Blends

The physical properties of the unaged blends are given in Table 3. Some of these data are shown in Figures 3-5 with respect to the P/S in the modifiers. This parameter appeared to have more of an influence on the physical behavior of the blends than did the level of aromaticity in the modifiers.

Figure 3 shows the effect of modifier P/S on the temperature-penetration index of the blends. The effect of modifier P/S is greatest at the low level of aromatic fractions ranging from 1.40 at a P/S of 0.03 to 3.05 at a modifier P/S of 3.12. Modifiers in the medium level of aromaticity (<50 percent) showed a less dramatic increase in blend TPI. Blends made with high aromatic modifiers (>50 percent) showed no difference in TPI according to the modifier P/S. Therefore, at modifier aromatic contents of less than 50 percent, the low-temperature susceptibility of the blends increased with the increasing P/S's of the modifiers.

Shear susceptibility of the blends at 39.2°F, in general, decreased with an increasing P/S, as shown

TABLE 3 Physical Properties of Unaged Blends

Blend	% Modifier	Pen at 39.2°F 200 gm, 60 sec, 0.1 mm	Pen at 77°F 100 gm, 5 sec, 0.1 mm	η at 39.2°F, 0.05 sec^{-1} x 10^7 poises	"c" at 39.2°F	η at 77°F, 0.05 sec^{-1} x 10^6 poises	"c" at 77°F	η at 140°F, poises	η at 275°F, cSt
MBD-1	16	50	70	3.3	0.43	3.3	0.53	3,970	277
MBD-2	65	35	65	11	0.62	3.6	0.53	3,340	414
MBD-3	36	19	58	68	0.96	3.7	0.86	3,470	426
MBD-4	10	37	63	5.8	0.52	3.0	0.64	3,500	350
MBD-5	13	37	68	13	0.66	3.2	0.73	3,990	405
MBD-6A	43	34	73	8.9	0.65	2.3	0.76	3,420	497
MBD-7A	13	37	71	10	0.68	2.7	0.72	3,260	350
MBD-8A	16	36	68	13	0.68	2.6	0.75	3,760	405
MBD-9	12	36	74	16	0.79	2.4	0.80	3,500	424
Control	0	11	22	120	0.71	24	0.61	56,800	1413

η = Viscosity

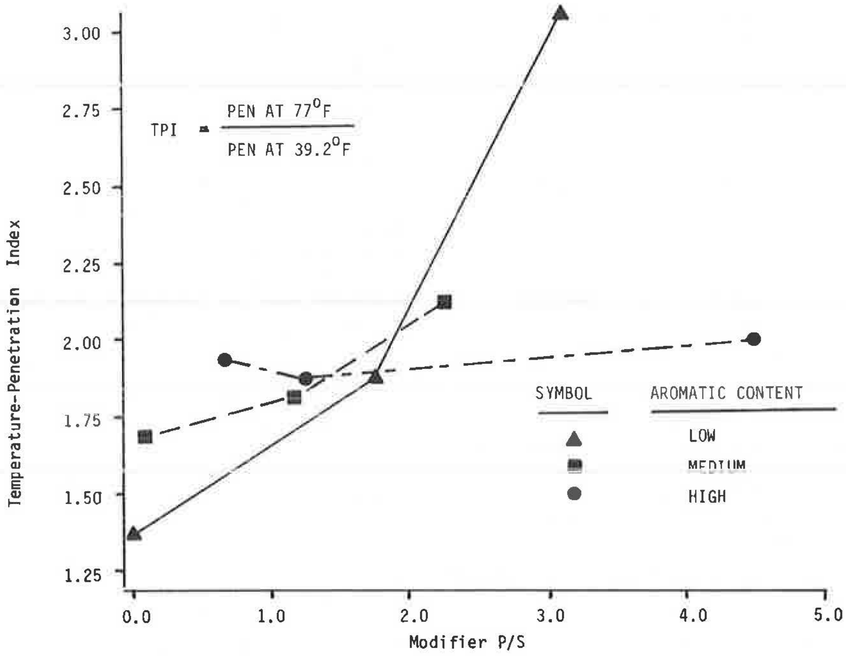

FIGURE 3 Effect of modifier P/S on temperature-penetration index.

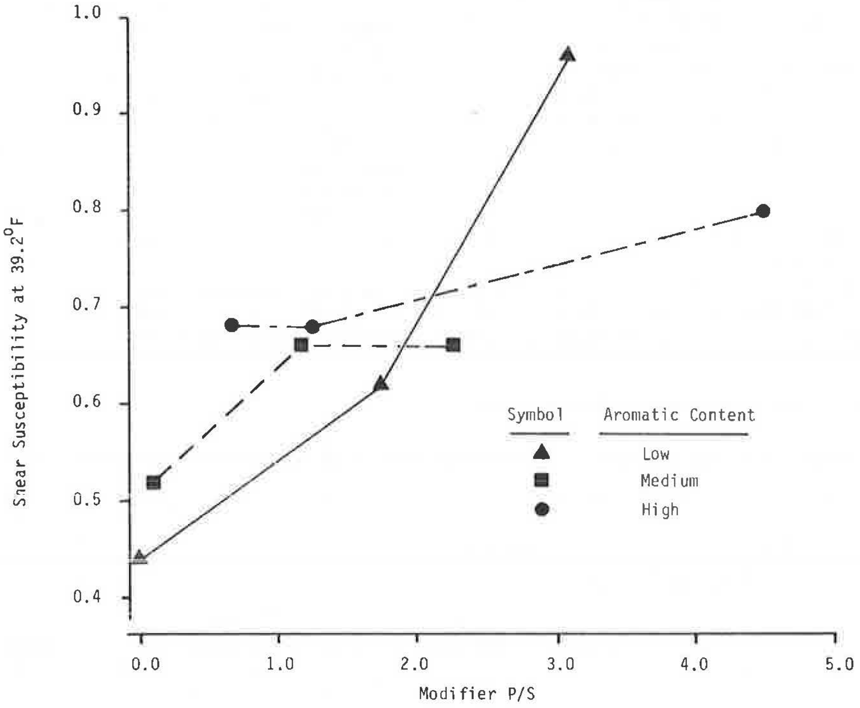

FIGURE 4 Effect of modifier P/S on shear susceptibility at 39.2°F.

in Figure 4. As the value of c approaches 1, the flow becomes more Newtonian. As c decreases from 1, the nature of the material is more psuedoplastic (shear susceptible). Again, those blends that have modifiers low in percent aromatics showed the most dramatic differences, ranging from a c value of 0.43 at a low P/S level to 0.96 at a high P/S. These same trends were noted for the shear susceptibility values at 77°F.

Figure 5 shows that the viscosities at 275°F for blends made with low P/S modifiers all had values less than 400 cSt. Increasing P/S's in the modifiers led to increased viscosities at 275°F.

The properties of the blends after conditioning in the RTFO are given in Table 4. Some of these data are presented in Figures 6-8. The P/S's of the modifiers had even greater effects on the aged blends than on the unaged blends.

The percent of penetration retained after the RTFO increased with increasing modifier P/S at 77°F, as can be seen in Figure 6. In this test the level of aromaticity in the modifiers did not have the dampening effect on the modifier P/S as noticed for the unaged blends. At 77°F the percentage of retained penetration ranged from a low of 24 percent for MBD-4 to 57 percent for MBD-2 and MBD-3.

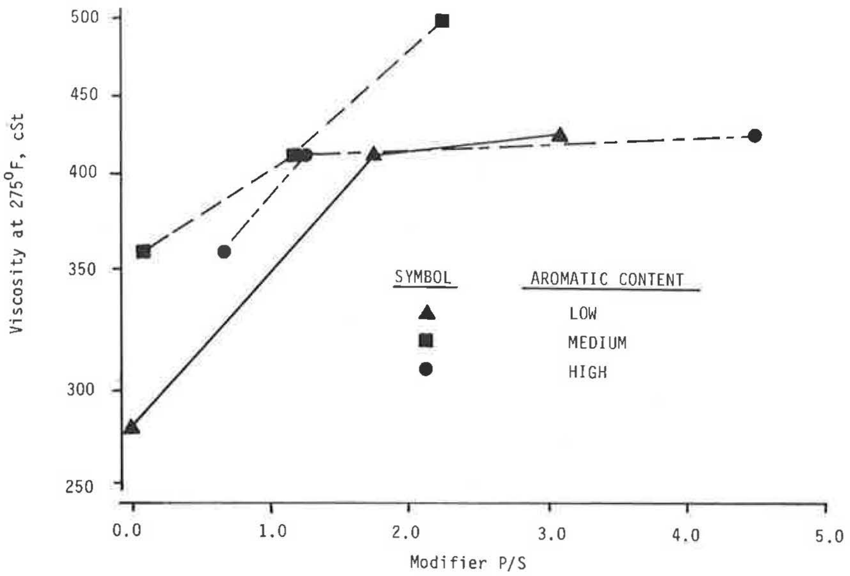

FIGURE 5 Effect of modifier P/S on viscosity at 275°F.

TABLE 4 Physical Properties of Blends After RTFO

Blend	Pen at 39.2°F, 200 gm, 60 sec		Pen at 77°F, 100gm, 5 sec		Viscosity at 140°F		Ductility at 77°F,
	0.1 mm	Percent of Unaged	0.1 mm	Percent of Unaged	Poises	Aging Index	cm/min, cm
MBD-1	19	38	28	40	118,700	29.9	4
MBD-2	17	48	37	57	23,620	7.1	10
MBD-3	14	74	33	57	10,220	2.9	100+
MBD-4	5	14	15	24	222,000	63.4	4
MBD-5	8	22	20	29	57,470	14.4	8
MBD-6A	20	59	38	52	13,520	4.0	100+
MBD-7A	9	24	21	31	43,020	13.2	9
MBD-8A	21	58	39	53	14,040	3.7	59
MBD-9	18	50	37	51	12,420	3.5	100+
Control	3	27	8	36	534,000	9.4	4

Figure 7 shows that as the P/S of the modifiers increased, the aging index decreased in a logarithmic fashion. The aging index was highest for the blend made with MBD-4 at 63 and lowest for the MBD-3 blend at 3. This appears to be a useful parameter for evaluating recycled blends, as does the ductility after RTFO, as shown in Figure 8. It is shown that blends with high P/S modifiers all exceeded 100 cm in the ductility test at 77°F. Blends made with low and medium P/S modifiers had ductilities considerably less than 100 cm.

Clay-Gell Analysis and Solution Properties

Based on the percent modifier added to the aged asphalt to prepare the blends used in this study, the respective percentages of asphaltenes, saturates, aromatics, and polars were calculated to see if the effect of the modifier was additive. Without exception, the actual percent asphaltenes was lower and the polar percentage was higher. This indicates that the effects of the modifiers were not additive. The modifiers increased the solubility of the maltene phase and redispersed the asphaltenes into the maltene phase. The data in Table 5 give three examples that illustrate this phenomenon. On RTFO aging, there was an increase in the asphaltene content and a decrease in the polar content. The saturate and aromatic fractions remained essentially the same. The clay-gel data for each blend unaged and aged are

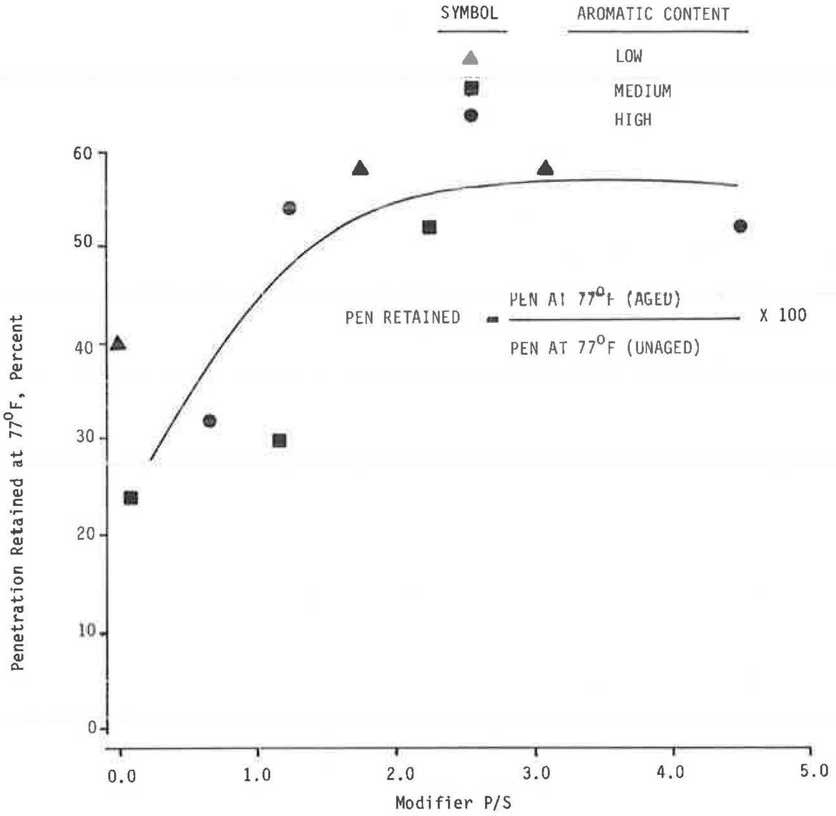

FIGURE 6 Effect of modifier P/S on percent penetration retained at 77°F after RTFO.

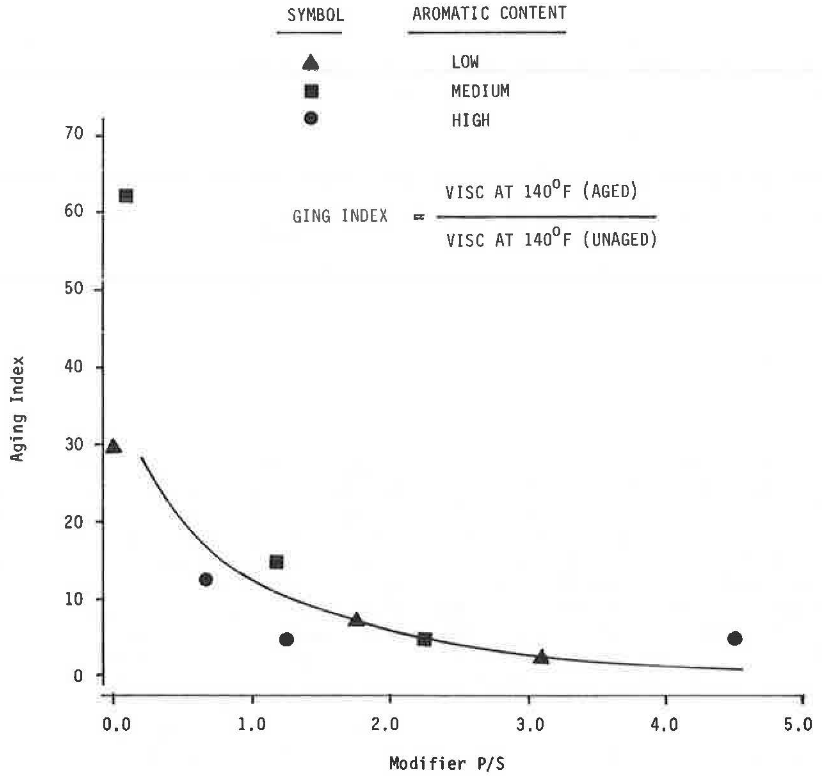

FIGURE 7 Effect of modifier P/S on aging index.

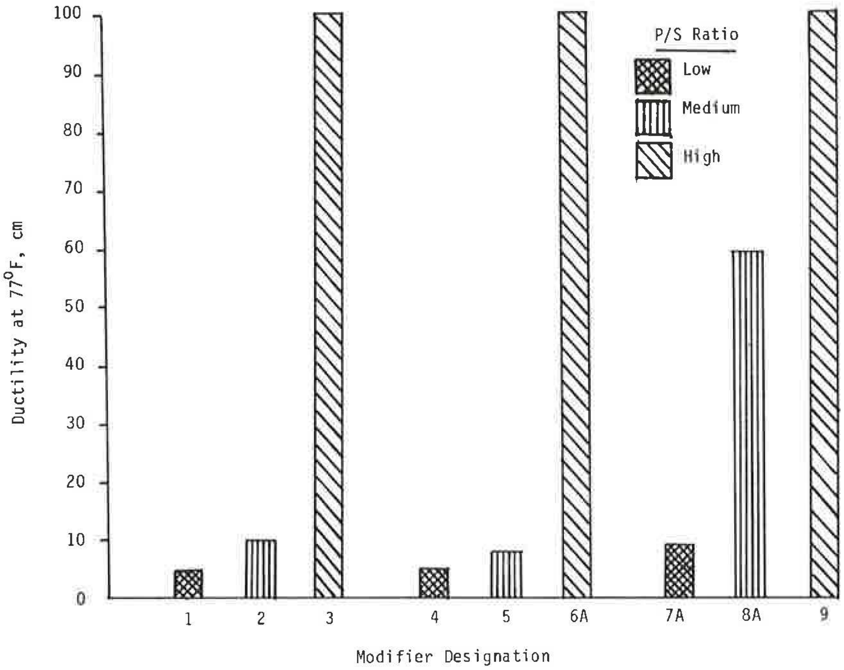

FIGURE 8 Ductility of blends after RTFO.

given in Table 6. The trends seen in the clay-gel analysis of the blends completed so far in this project correlate well with physical data obtained on aging.

The data in Tables 7 and 8 present the solubility data of the aged and unaged blends, respectively. The results for one of the blends, MBD-3, are shown in Figures 9 and 10. These figures show the curves for the control asphalt (Pope AFB), the unaged blend, and the RTFO-aged blend. Figure 9 is a Heithaus plot and Figure 10 is a plot of the Waxman data.

The results given in Table 7 reveal a decrease in asphaltene peptizability and cot ϕ values from the control sample in all blends except MBD-6A. According to Venable and Peterson (14), MBD-6A may have a lower polar functionality and a more homogenous molecular system than the other unaged blends. The general trend noted in these results was also observed by Venable and Peterson, even when modifiers were added to fresh asphalts. The state of asphaltene peptization and the maltene peptizing power were improved through the addition of the modifiers. This is further evidenced by the value of T_o and

TABLE 5 Examples of Compositional Effects of Modifiers on Aged Asphalt

	ASPHALTENES	SATURATES	AROMATICS	POLARS
POPE WHOLE AGED ASPHALT	43.57	10.79	12.78	32.82
MBD-1 16%	0.25	84.34	12.68	2.74
CALCULATED	36.64	22.56	12.76	28.01
ACTUAL	32.90	20.94	15.14	29.74
MBD-6A 43%	21.47	15.07	33.56	29.44
CALCULATED	33.71	12.80	22.33	31.45
ACTUAL	30.32	11.09	15.86	42.59
MBD-9 12.5%	0.12	6.44	64.50	29.07
CALCULATED	38.15	10.27	19.56	32.49
ACTUAL	32.68	10.09	17.00	39.90

TABLE 6 Clay-Gel Analysis of Blends

Blend	Asphaltenes		Saturates		Aromatics		Polars	
	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged
MBD-1	32.90	34.24	20.94	22.51	15.14	13.39	29.74	29.86
MBD-2	26.56	28.01	14.79	15.55	16.82	15.53	41.53	40.53
MBD-3	26.12	30.92	11.39	14.34	14.26	15.24	48.15	39.50
MBD-4	35.86	39.10	13.29	12.79	17.60	18.75	33.38	29.36
MBD-5	33.76	35.95	12.27	13.16	16.99	16.98	36.79	33.54
MBD-6A	30.32	33.15	11.09	12.38	15.86	16.06	42.59	38.41
MBD-7A	31.98	34.95	11.93	11.24	21.33	20.40	34.76	33.41
MBD-8A	30.81	33.69	10.60	11.56	22.31	23.86	36.28	30.90
MBD-9	32.68	33.20	10.09	11.42	17.00	18.65	39.90	36.68
Control	37.70	40.34	11.75	12.31	15.72	12.72	36.25	34.63

TABLE 7 Solubility Test Results (unaged)

Material Type	Heithaus Parameters				Waxman Parameters	
	P_a	P_o	P	X_{min}	T_o	Cot ø
MBD-1	0.204	1.750	2.199	1.199	1.252	0.224
MBD-2	0.313	1.678	2.441	1.441	1.117	0.596
MBD-3	0.259	2.085	2.816	1.816	1.798	0.358
MBD-4	0.207	1.884	2.374	1.374	1.465	0.208
MBD-5	0.237	1.800	2.358	1.358	1.355	0.302
MBD-6A	0.370	1.673	2.655	1.655	1.274	0.760
MBD-7A	0.338	1.476	2.230	1.230	1.411	0.420
MBD-8A	0.290	2.179	2.691	1.691	1.757	0.191
MBD-9	0.419	1.070	1.842	0.842	0.911	0.713
CONTROL[a]	0.356	1.316	2.044	1.044	0.901	0.623

Note: Unaged = RTFC aging.

[a] Aged recovered asphalt treated in the same manner as the blends.

TABLE 8 Solubility Test Results (aged)

Material	Heithaus Parameters				Waxman Parameters	
Type	P_a	P_o	P	X_{min}	T_o	Cot ϕ
MBD-1	0.193	1.636	2.026	1.026	1.068	0.207
MBD-2	0.267	1.892	2.580	1.580	1.497	0.397
MBD-3	0.308	1.995	2.882	1.882	1.887	0.438
MBD-4	0.161	2.113	2.518	1.518	1.546	0.178
MBD-5	0.119	2.074	2.355	1.355	1.250	0.165
MBD-6A	0.215	2.197	2.797	1.797	1.814	0.264
MBD-7A	0.153	1.868	2.206	1.206	1.140	0.216
MBD-8A	0.392	1.019	1.676	0.676	1.438	0.318
MBD-9	0.193	2.213	2.742	1.742	1.711	0.248
CONTROL[a]	0.224	1.942	2.503	1.503	1.586	0.243

Note: Aged = RTFC aging.

[a] Aged recovered asphalt treated in the same manner as the blends.

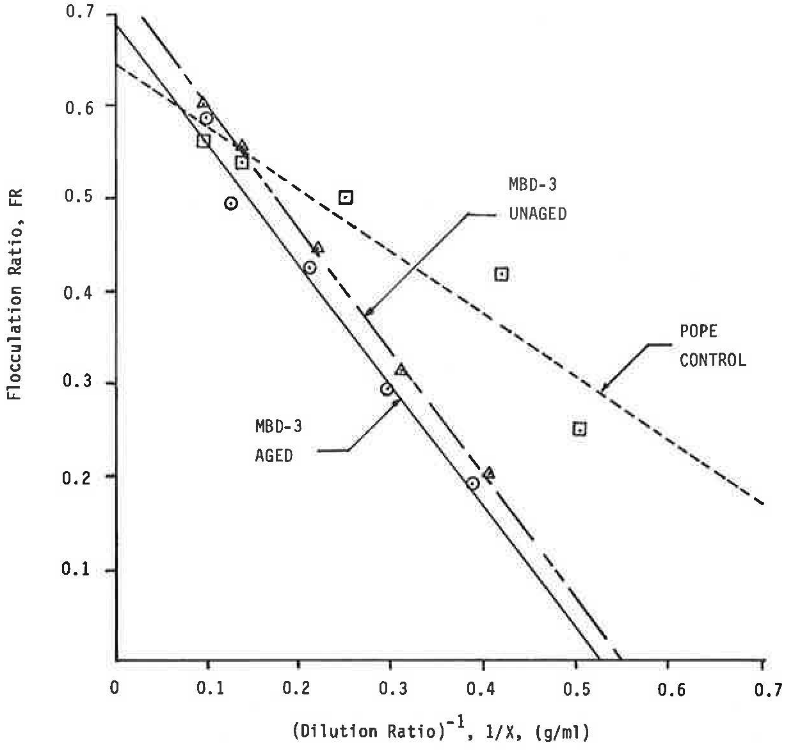

FIGURE 9 Heithaus solubility test results.

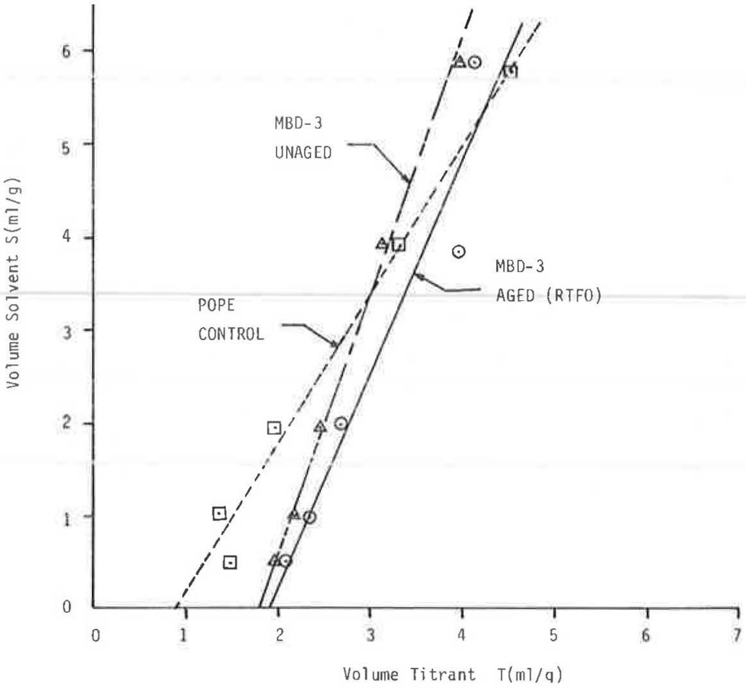

FIGURE 10 Waxman plot of S versus T.

the rightward shift of the curve for MBD-3 in Figure 10. The leftward shift of the curve for MBD-3 in Figure 9 further confirms this observation.

The solubility test results given in Table 8 reveal a decrease in asphaltene peptizability except for MBD-3 and MBD-8A. A similar trend may be noted in the cot ϕ values. According to Venable and Peterson (14), an increase in asphaltene peptizability after an oxidation process implies that the peptizing components from the maltenes are being converted to asphaltenes. This also implies that the maltene peptizing power decreases.

The result of T_o for MBD-3 indicates an overall improvement in the solvency characteristics after RTFO aging. It is interesting to note that MBD-3 also had the lowest aging index, the highest retained penetration, and a ductility value greater than 100 cm after aging. This blend also showed a large gain in its aromatic fraction and a lower P/S after aging.

Blend MBD-8A showed decreases in X_{min} and T_o on RTFO conditioning. This may indicate a degradation of the blend. The drastic decreases in X_{min} for MBD-8A is evidenced by a sharp decrease in the peptizing power of the maltenes.

HP-GPC Analysis

Jennings et al. (15) report that there are five features to examine in the HP-GPC chromatograms for interpretation:

1. Elution time of the largest molecules,
2. Height of the curve in the LMS region,
3. Elution time of the curve maximum,
4. Height of curve maximum relative to height in LMS and SMS regions, and
5. Height of the curve in the SMS region.

Figure 11 illustrates three overlayed chromatograms. The three curves represent Pope AFB whole asphalt, the modifier MBD-3, and the MBD-3 blend. It can be seen that the Pope AFB whole asphalt has a

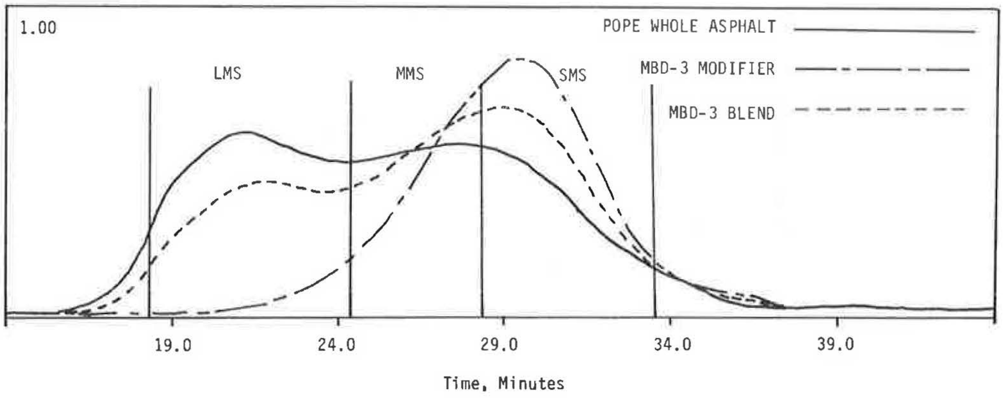

FIGURE 11 Effect of modifier on molecular size distribution of blend.

large amount of LMS material, whereas the modifier has little LMS. When the modifier is added to the whole asphalt, it reduces the area of the curve in the LMS region, which is a desirable effect. It is speculated that the modifier is breaking the aggregation of molecules that add to the LMS region and that separate as asphaltenes in the compositional analysis. This same trend is also evident in the compositional analysis. Currently, only a trend can be seen in the HP-GPC data, and that is a reduction of the LMS region when a modifier is added.

CONCLUSIONS

From the nine modifiers and one aged asphalt used in this study, the following conclusions are made.

1. As the modifier P/S increased at the low and medium levels of modifier percent aromatic content, the low-temperature susceptibility of the blends increased. However, as the level of aromatic content increased, P/S had less influence on the low-temperature susceptibility.
2. As the modifier P/S increased, less shear susceptibility was exhibited by the modified blends at 39.2° and 77°F.
3. As the modifier P/S increased, so did the blend viscosity at 275°F.
4. The penetration of the blends retained after RTFO increased and the aging index of the blends decreased with increasing modifier P/S. The ductility of the blends after RTFO increased with increasing modifier P/S.
5. Modifiers do not have a compositionally additive effect to aged asphalt fractions.
6. On RTFO aging of the blends, there were increases in the asphaltene contents and decreases in the polar fractions. The saturate and aromatic fractions did not change markedly.
7. Solution properties as determined by the Heithaus/Waxman procedure can be used to characterize the effects of modifiers on aged asphalts. The results of this test can be used to infer variations in polar functionality.
8. The most sensitive physical parameters with regard to the effects of modifiers on the aged asphalt cement were the aging index and ductility at 77°F after RTFO conditioning.

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