

Characterization of Age-Hardening Potential of Asphalts by Using Corbett-Swarbrick Asphalt Fractionation Test

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The use of the Corbett-Swarbrick fractionation procedure for characterization of age-hardening potentials of asphalts was studied. The fractionation procedure was used to separate asphalts into four different fractions (asphaltenes, saturates, naphthene-aromatics, and polar-aromatics), to identify trends in the changes of proportions of these asphalt fractions during aging. The technique of infrared spectroscopy was used to examine the changes in the characteristics of these fractions during aging. Analyses were performed to determine the relationship between the properties of these asphalt fractions and the hardening potential of the asphalts. The proportions of fractions in asphalts were found to change during aging: the proportions of the asphaltenes and polar-aromatics increase and the proportions of saturates and naphthene-aromatics decrease. For the asphalts tested, the higher the asphaltene content of an original asphalt, the higher the aging potential as determined by the absolute viscosity ratios after the thin film oven test (TFOT) or the rolling thin film oven test (RTFOT). The proportions of asphalt fractions in the original asphalts were found to correlate fairly well with the absolute viscosity ratios after the TFOT and moderately well after the RTFOT. The results of infrared spectral analyses on the asphalt fractions indicated that the characteristics of the fractions change as an asphalt ages. Anhydrides, carboxylic acids, and ketones develop in asphaltenes; carboxylic acids and ketones develop in polar-aromatics and naphthene-aromatics as a result of aging. No evidence exists that any functional group developed in saturates as a result of aging.

In the selection of an asphalt for paving, it is important to ensure not only that the asphalt has suitable properties at the time of placement but also that it retains these properties to achieve adequate long-term performance. One of the major factors affecting the durability of an asphalt is its rate of hardening in service. When an asphalt binder hardens excessively, it may cause the asphalt mixture to become too brittle, and the pavement will crack prematurely. The age hardening of an asphalt has been known to be caused by oxidation, loss of volatile fractions, and changes in chemical structure (such as polymerization) resulting from exposure to air, heat, and ultraviolet light. Although it is known that construction specifications such as plant mix temperature and compaction of the asphalt mixture have great effects on the hardening of the asphalt (1), it has also been recognized that the chemical

composition of the asphalt plays a great role in its hardening potential, and many studies have been devoted to this area (2-4).

The use of the Corbett-Swarbrick fractionation procedure for characterization of age-hardening potentials of asphalts has been studied. In this study, the Corbett-Swarbrick procedure (ASTM D4124-86, Method B), with modifications as recommended by Thenoux et al. (5,6), was used to separate asphalts into four fractions (asphaltenes, saturates, naphthene-aromatics, and polar-aromatics), to identify trends in the changes of proportions of these asphalt fractions during the aging process. The technique of infrared absorption spectroscopy was used to examine the changes in the characteristics of these fractions during aging. Analyses were performed to determine the relationship between the properties of these asphalt fractions and the hardening potential of the asphalts.

TESTING PROGRAM

Eight asphalts were selected and used to make Marshall specimens that were subjected to an artificial aging process. For each of the asphalts, the thin film oven test (TFOT) (ASTM D1754-78) and the rolling thin film oven test (RTFOT) (ASTM D2872-80) were performed at 325°F. The absolute viscosity at 140°F (60°C) of each asphalt was measured before and after the tests. Three fractionation analyses were performed for each asphalt under different aging conditions, namely, (a) the original asphalt, (b) the asphalt extracted from Marshall specimens that had not been subjected to any aging process, and (c) the asphalt extracted from Marshall specimens that had been aged in a forced-draft oven at 140°F (60°C) for 90 days. The absolute viscosity of each asphalt at these various conditions was also measured.

The infrared absorption spectroscopy was performed on the asphalt fractions from three of the asphalts to examine changes in the characteristics of these fractions during the aging process.

TEST PROCEDURES

Fabrication of Marshall Specimens

The Marshall specimens in this study were prepared using a limestone aggregate blend that meets the gradation speci-

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cation for a Florida Type S-1 asphalt concrete mix (dense-grade structural surface mix) with an asphalt content of 6.5 percent and compacted by the 50-blow Marshall compaction method. The Marshall specimens were aged in a forced-draft oven in which the temperature was maintained at 140°F (60°C) for 90 days. Results of a previous aging study indicated that aging in a forced-draft oven at 140°F (60°C) for 28 days simulated 1 to 2 years of field aging under Florida conditions (2). Aging in the forced-draft oven for 90 days would correspond to 3 to 6 years of field aging. The Abson method (ASTM D1856) was used to extract the asphalt from the Marshall specimens.

Fractionation Test

The Corbett-Swarbrick procedure of asphalt fractionation (ASTM D4124-86, Method B), with modification recommended by Thenoux et al., was used to separate the asphalt into four different fractions (5,6). The procedure is briefly described here. The first step involves the separation of the asphalt into a n-heptane-insoluble asphaltene and the n-heptane-soluble petrole. The petrole is then adsorbed on a calcined F-20 alumina and further fractionated into the saturate, naphthene-aromatic, and polar-aromatic fractions by downward solvent elution in a glass chromatographic column. Eluted fractions are recovered by solvent removal before final weighing. The column feed volumes used in this test are shown in Table 1.

According to the ASTM D4124-86, the single operator precision of the fractionation test for asphaltene, saturates, naphthene-aromatics, and polar-aromatics are 0.32, 0.44, 1.03, and 0.78 percent, respectively.

Infrared Absorption Spectroscopy

Infrared spectroscopic technique was used to measure changes in the structures of the asphalts and asphalt fractions because

TABLE 1 COLUMN FEED VOLUMES

Eluant Solvent	ml	Fraction Received	Approximate ml
n-Heptane	65	Saturates	100
Toluene	35		
Toluene	100	Naphthene-Aromatics	200
Methanol/Toluene (50/50)	100		
Trichloroethylene	200	Polar-Aromatics	200+
		Cleaning Solvent	

of aging, in terms of the changes in the amount of certain functional groups in them. The infrared absorption spectrum between 1600 cm^{-1} and 1900 cm^{-1} is of particular interest, because it contains the absorption bands for the functional groups of carboxylic acids, ketones, and anhydrides (4,7). Ketones and anhydrides are formed in asphalt on oxidative aging, although carboxylic acids occur naturally in asphalt but increase in amount in oxidative aging.

The infrared spectroscopy tests were run on a Nicolet 60 SX research-grade Fourier transform infrared (FTIR) spectrophotometer system in the Materials Science and Engineering Laboratory of the University of Florida. The system offers a resolution of 0.25 cm^{-1} throughout the standard range of 5000 to 400 cm^{-1} . The components of the FTIR system are arranged into two main groups: the data acquisition system, consisting of the computer, disk drives, and terminal; and the spectrometer, consisting of the optical bench and washer control. Figure 1 depicts a typical 60 SX system configuration.

A 5 percent (wt/vol) solution in high-performance liquid chromatography- (HPLC-) grade tetrahydrofuran was used in the tests. A sealed cell with 1 mm path length and sodium chloride windows was used. The background spectrum for tetrahydrofuran was generated by scanning the pure solvent and stored in computer. Then the spectrum for the solution was generated. Using the computer software of the system, the background spectrum was ratioed out, yielding the spectrum of the sample.

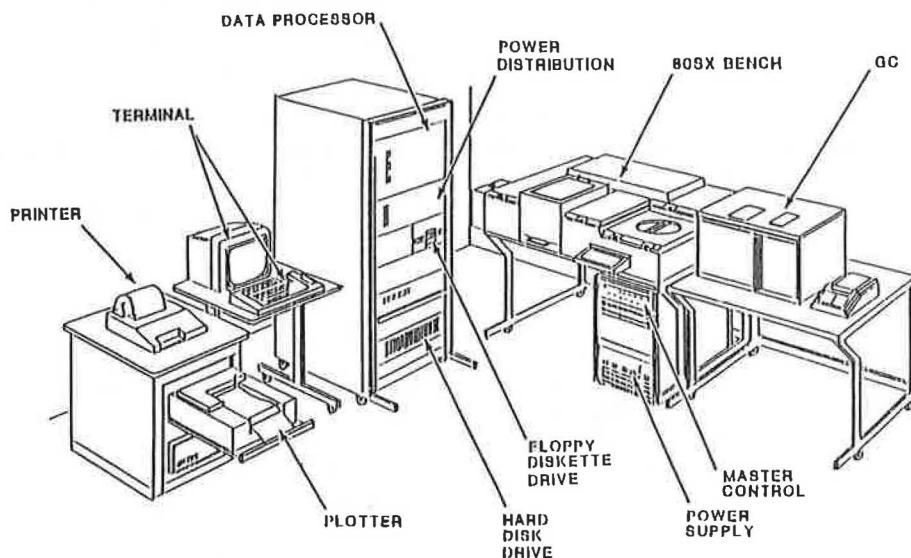


FIGURE 1 Typical 60 SX FTIR spectrophotometer system.

RESULTS

Results of Absolute Viscosity Test

The results of the absolute viscosity test on the eight asphalts at different aging conditions are shown in Table 2. Table 3 displays the viscosity ratios of these asphalts after the TFOT and RTFOT. It can be seen that the RTFOT procedure produced a slightly higher viscosity ratio than the TFOT procedure.

TABLE 2 ABSOLUTE VISCOSITY OF ASPHALTS AT DIFFERENT AGING CONDITIONS

Asphalt	Absolute Viscosity at 140°F (Poisies)				
	Original	After TFOT	After RTFOT	Zero day ⁽¹⁾ aging	90 days ⁽²⁾ aging
A AC-30	3301	9760	10451	7334	374433
B AC-30	3100	9748	14389	11322	132900
D AC-30	2967	7613	8489	7096	47893
E AC-30	2753	8894	11321	8906	100829
F Air blown 85-100 pen.	1931	3588	3426	2392	8928
G 85-100 pen.	1064	2327	2499	2345	11466
H 85-100 pen.	3810	17910	19090	11315	73359
I 25-35 pen.	17885	38309	48601	34021	2400000

NOTE:

(1) asphalt extracted from Marshall specimens which were not aged.

(2) asphalt extracted from Marshall specimens which were aged for 90 days.

TABLE 3 VISCOSITY RATIO OF ASPHALTS AFTER TFOT AND RTFOT PROCEDURES

Asphalt	Absolute Viscosity Ratio	
	After TFOT	After RTFOT
A	2.96	3.17
B	3.14	4.64
D	2.57	2.86
E	3.23	4.11
F	1.86	1.77
G	2.19	2.35
H	4.70	5.01
I	2.14	2.72

Results of Fractionation Test

The results of the fractionation test are shown in Table 4. Average percentages of the fractions for paving asphalts (excluding Asphalt I) are shown in Table 5 (Asphalt I is excluded because it is a roofing asphalt). Some trends can be easily identified from the results. The percentage of asphaltenes does not change much between the original and 0-day asphalt, and increases more significantly during the aging process. The

TABLE 4 RESULTS OF ASPHALT FRACTIONATION TEST

Asphalt	Condition	Asp (%)	Sat (%)	N-A (%)	P-A (%)
A AC-30	Original	23.31	9.77	44.74	22.18
	Zero day	25.47	6.64	37.64	30.25
	90 days	38.23	8.54	26.62	26.61
B AC-30	Original	22.22	14.93	45.14	17.71
	Zero day	22.89	11.25	40.16	25.70
	90 days	30.14	10.96	33.22	25.68
D AC-30	Original	15.25	10.64	48.22	25.89
	Zero day	14.28	8.22	43.57	33.93
	90 days	26.14	7.57	35.61	30.68
E AC-30	Original	23.48	13.77	45.75	17.00
	Zero day	22.54	10.56	40.85	26.05
	90 days	31.61	9.63	32.64	26.12
G 85-100 pen.	Original	12.75	27.49	38.25	21.51
	Zero day	12.64	10.03	39.78	37.55
	90 days	16.77	10.32	34.84	38.07
F Airblown 85-100 pen.	Original	7.41	23.61	43.52	25.46
	Zero day*	6.72	25.21	33.62	34.45
	90 days	17.36	23.02	31.32	28.30
I 25-35 pen.	Original	17.41	14.58	42.51	25.50
	Zero day	24.14	11.73	37.24	26.89
	90 days	29.93	12.41	31.02	26.64
H 85-100 pen.	Original	25.83	10.23	45.78	18.16
	Zero day	24.00	8.00	39.33	28.67
	90 days	33.58	7.66	29.93	28.83

Asp: Asphaltenes

Sat: Saturates

N-A: Naphthene-Aromatics

P-A: Polar-Aromatics

* The amount of asphalt used was only 1.24 grams.

TABLE 5 AVERAGE PERCENTAGES OF ASPHALT FRACTIONS

	Asp %	Sat %	N-A %	P-A %
Original	18.61	15.78	44.49	21.12
Zero day	18.36	11.42	39.28	30.94
90 days	27.69	11.10	32.03	29.18

NOTE: Asphalt I is excluded in the computation.

saturates' fraction decreases slightly after the mixing process and remains steady during the aging process. The naphthene-aromatics' fraction decreases during both the mixing and the aging process. The percentage of polar-aromatics increases during the mixing process, but no significant change occurs after that.

Relationship Between Asphalt Fractions and Absolute Viscosity

The plots of absolute viscosity at 140°F of the seven paving asphalts versus the percentages of the asphalt fractions present are shown in Figures 2–5. From Figure 2, it can be seen that the absolute viscosity increases when the asphaltenes content is higher. On the contrary, an asphalt with a higher content of saturates has a lower absolute viscosity value (see Figure 3). The trends in naphthene-aromatics and polar-aromatics are not clear. This agrees with the findings reported by Corbett (8), which state that asphaltenes contribute much toward temperature susceptibility and to high viscosity.

Relationship Between Asphalt Fractions and Absolute Viscosity Ratio

The plots of the viscosity ratio (after the TFOT and RTFOT) versus the asphaltenes content of original asphalt are shown

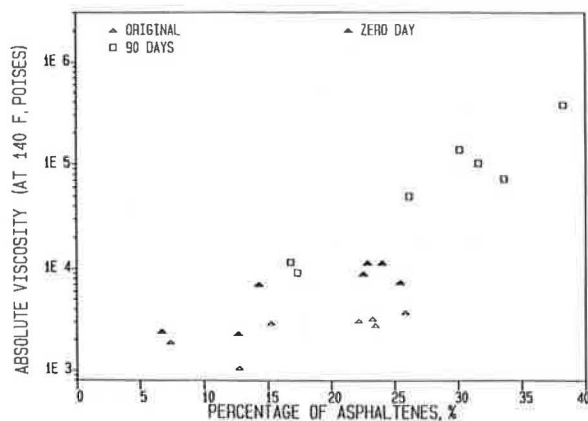


FIGURE 2 Asphaltenes content versus absolute viscosity.

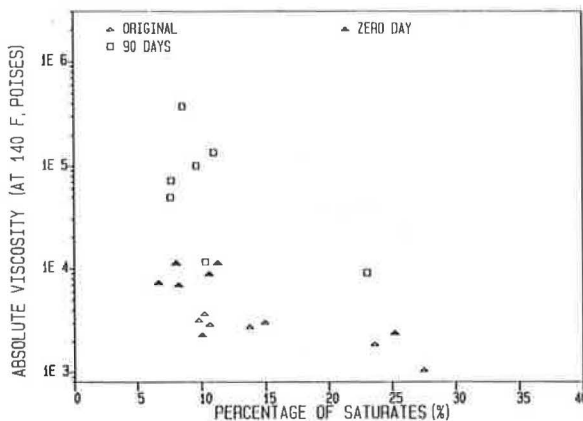


FIGURE 3 Saturates content versus absolute viscosity.

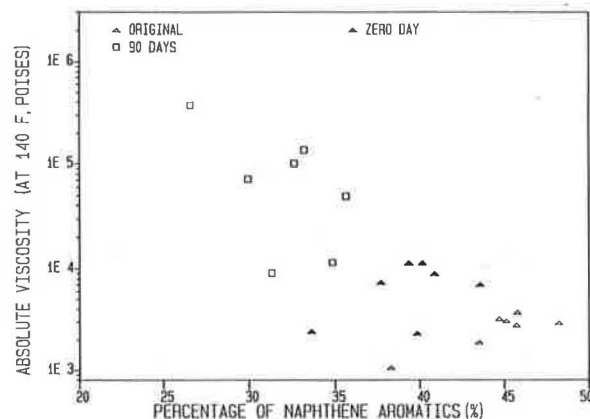


FIGURE 4 Naphthene-aromatics content versus absolute viscosity.

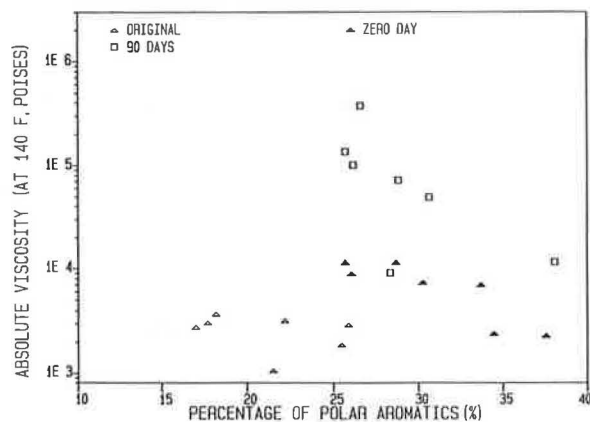


FIGURE 5 Polar-aromatics content versus absolute viscosity.

in Figures 6 and 7. In both cases, the viscosity ratio increases as the asphaltenes content increases. This indicates that an original asphalt with a higher asphaltenes content tends to produce a higher viscosity ratio after the TFOT or RTFOT (especially the RTFOT). The relationship between the viscosity ratio (after the TFOT and RTFOT) and the other fractions is not so clear.

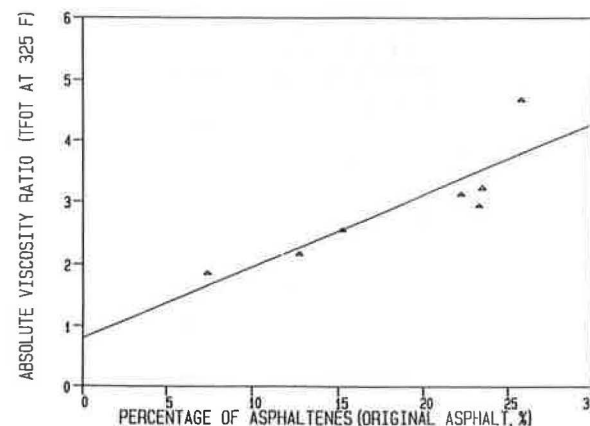


FIGURE 6 Relationship of asphaltenes content of original asphalt and absolute viscosity ratio (TFOT at 325°F).

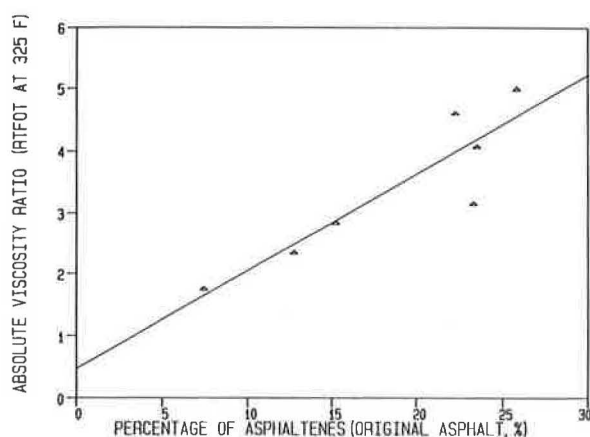


FIGURE 7 Relationship of asphaltenes content of original asphalt and absolute viscosity ratio (RTFOT at 325°F).

Regression analyses were performed to relate the percentages of the asphalt fractions present in the original asphalt to the viscosity ratio after the TFOT and RTFOT. The SAS/STAT computer software was used for this purpose. A regression equation of the following form was used:

Viscosity ratio (after RTFOT or TFOT)

$$= \beta_0 + \beta_1 (\text{Asp } \%) + \beta_2 (\text{Sat } \%) + \beta_3 (P - A \%) + \text{error}$$

The *R*-square values for the model above were found to be .7531 for TFOT and .9193 for RTFOT. The regression coefficients for the RTFOT case are as follows:

$$\beta_0 = 13.5444$$

$$\beta_1 = -0.0709$$

$$\beta_2 = -0.1229$$

$$\beta_3 = -0.3252$$

It is to be noted that only the percentages of three of the four fractions are needed in this prediction equation. Using the percentage of the fourth fraction in the prediction equation would be redundant, because it is dependent on the percentages of the other three fractions (they add up to 100 percent).

Although the three regression coefficients— β_1 , β_2 , and β_3 —are all negative, β_1 is less negative than the other two coefficients. An increase in asphaltenes content (Asp %) will result in an increase in viscosity ratio, because an increase in asphaltenes content is accompanied by a decrease in the other fractions, whose corresponding coefficients are more negative than that for the asphaltenes.

Table 6 shows the comparison between the actual and predicted viscosity ratios if this regression equation were used to predict the viscosity ratios after the RTFOT from the percentages of the fractions of the original asphalts. It can be noted that the predicted values are fairly close to the actual ones with a maximum error of 0.55. This indicates that the composition of an asphalt (in terms of the proportions of the four fractions) might be used to predict the hardenability of

TABLE 6 COMPARISON BETWEEN ACTUAL VISCOSITY RATIOS (AFTER RTFOT) AND THOSE PREDICTED BY REGRESSION EQUATION

Asphalt	Actual	Predicted	
		Value	Residual
1	4.64	4.3758	0.2642
2	4.11	4.6600	-.550011
3	3.17	3.4795	-.309531
4	2.86	2.7375	0.1225
5	2.35	2.2673	.0827177
6	1.77	1.8384	-.068374
7	5.01	4.5515	0.4585

the asphalt. The effects of asphalt composition on predicted hardenability are depicted in Figure 8. In this plot, percentage of asphaltenes and percentage of polar-aromatics are used as abscissa and ordinate, respectively. For specified fixed percentages of saturates (10, 15, 20, and 25 percent), lines that represent combinations of percentages of asphaltenes and polar-aromatics that would give a predicted viscosity ratio of 4 are drawn. For a specified saturates content (such as 15 percent), the area above the line represents combinations of percentages of asphaltenes and polar-aromatics that would give a predicted viscosity ratio of less than 4. If the combination of percentages of these two fractions falls below the line, the predicted viscosity ratio would be greater than 4.

Results of Infrared Absorption Spectroscopy

Fractions from Asphalts A, E, and F at different conditions were used in the infrared absorption spectroscopy test. The characteristic changes of fractions caused by aging are similar for these three asphalts.

Figures 9–12 display the infrared absorption spectra for fractions of Asphalt A in the region between 1900 cm^{-1} and 1500 cm^{-1} . Three spectra in each figure are for three different conditions, that is, original 0-days, and 90-days aging. From Figure 9, which shows the spectra of the asphaltenes, anhydrides can be identified at about 1730 cm^{-1} and 1780 cm^{-1} .

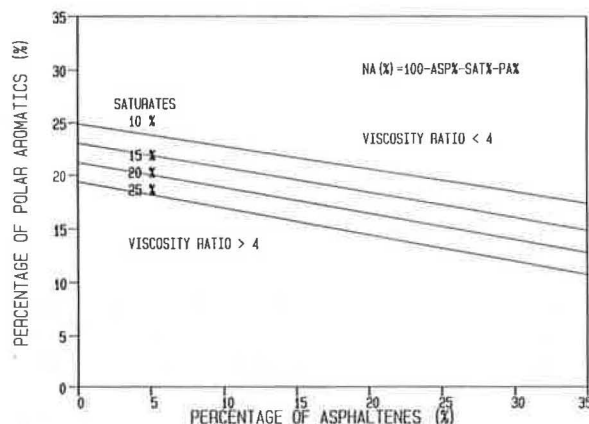


FIGURE 8 Relationship between compositions of original asphalt and viscosity ratio after RTFOT.

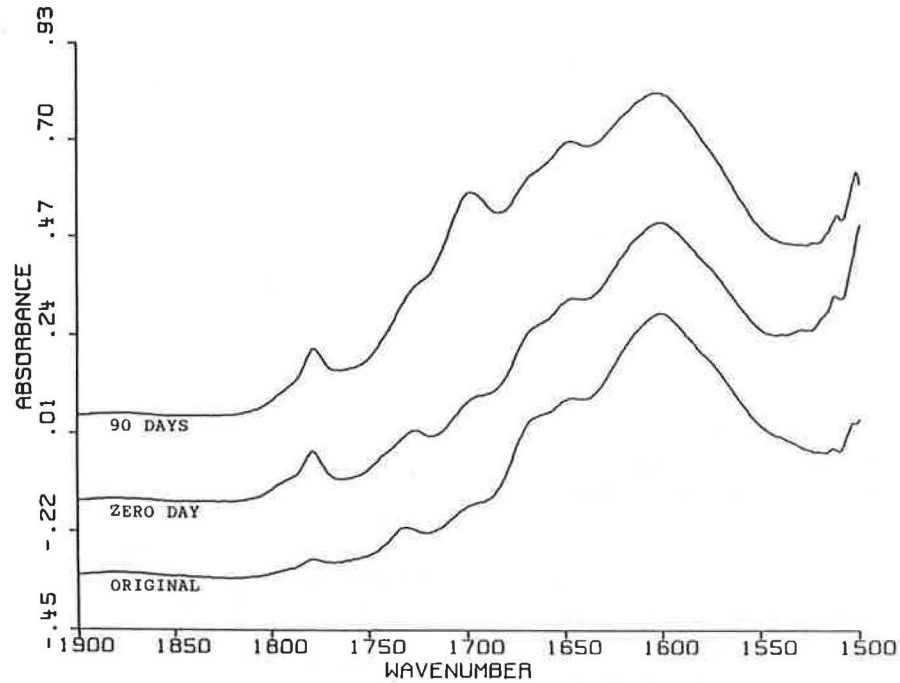


FIGURE 9 Infrared spectra of asphaltenes for Asphalt A at different conditions.

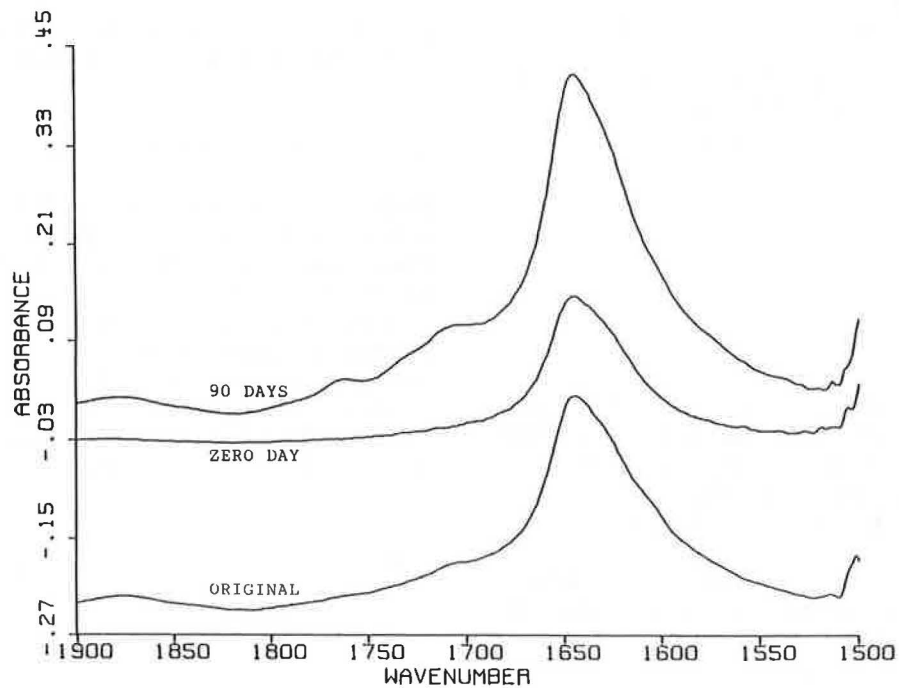


FIGURE 10 Infrared spectra of saturates for Asphalt A at different conditions.

The peak at about 1700 cm^{-1} results from the presence of carboxylic acids, ketones, and aldehydes. Anhydrides exist in the asphaltenes of original asphalt and continue to develop during the mixing and aging process. Aldehydes exist in the original spectrum, and do not change much after that. Ketones and carboxylic acids are formed during the mixing and aging process.

The difference between the spectra of saturates at different conditions is primarily in the intensity of the peak at around 1645 cm^{-1} (see Figure 10). In Figure 11, which shows the spectra of the naphthene-aromatics, the peak at around 1700 cm^{-1} develops continuously during the mixing and aging process. It results from the forming of ketones and carboxylic acids. No evidence exists of the presence of anhydrides in

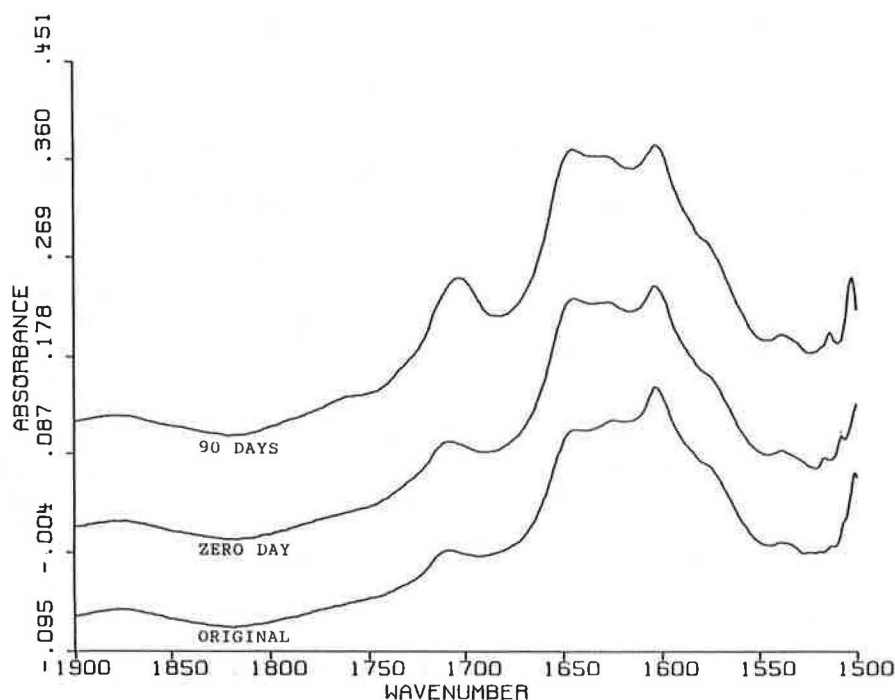


FIGURE 11 Infrared spectra at naphthene-aromatics for Asphalt A at different conditions.

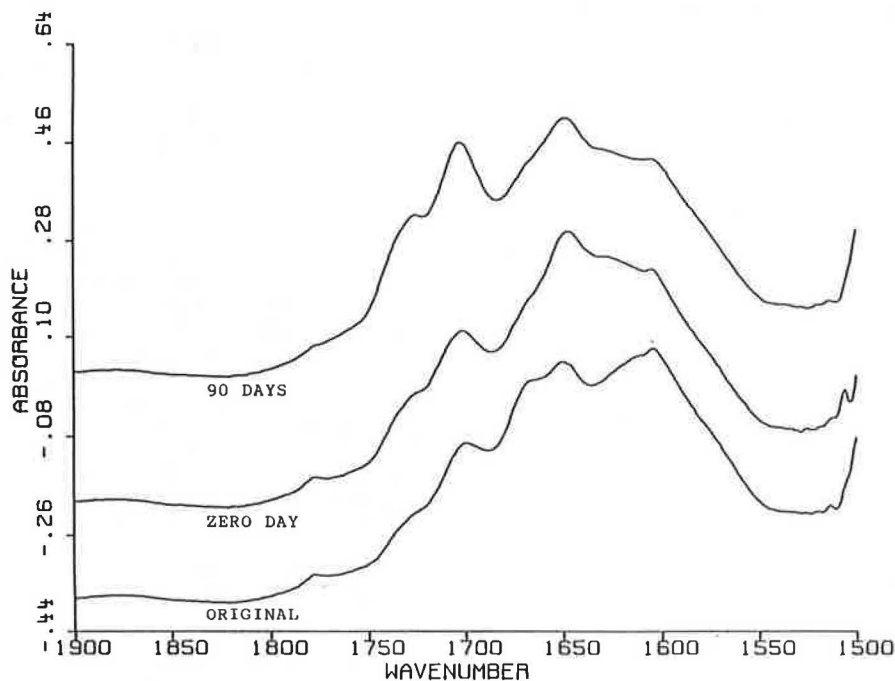


FIGURE 12 Infrared spectra of polar-aromatics for Asphalt A at different conditions.

naphthene-aromatics. In the fraction of polar-aromatics (see Figure 12), anhydrides exist in each condition, but no change is found at the different aging conditions. The peak at 1700 cm^{-1} resulting from the ketones and carboxylic acids develops during the mixing and aging process.

The absorption band centering at 1600 cm^{-1} , which results primarily from aromatic carbon-carbon double bonds, can be

assumed to be fairly constant, because the group is present in highly condensed stable molecules (2,9). The absorption band centering at 1375 cm^{-1} , resulting primarily from carbon-methyl bond, is also fairly constant (2). Therefore, the carbonyl ratio, a ratio of absorbances at 1700 cm^{-1} and 1600 cm^{-1} (CR1) or a ratio of absorbances at 1700 cm^{-1} and 1375 cm^{-1} (CR2), was used as an indicator of the level of oxidation

(2). Table 7 presents the carbonyl ratio of each fraction of asphalts. All absorption measurements were with reference to the absorption at 1900 cm^{-1} . It is obvious, from the results, that the carbonyl ratios of asphaltene and polar-aromatics increase significantly during the mixing and aging process. The carbonyl ratios of the naphthene-aromatics increases also but not significantly. The trend of saturates is not clear.

SUMMARY

The major findings from the results of the study are summarized as follows:

1. The proportions of fractions in asphalts change during aging. The proportion of asphaltene does not change much during the mixing and increases during the aging process. The proportion of saturates decreases during mixing and changes very little during aging. The naphthene-aromatics content decreases during both mixing and aging. The polar-aromatics portion increases during mixing, but not much change occurs after that.

TABLE 7 CARBONYL RATIOS OF ASPHALT FRACTIONS

Asphalt	Condition	Carbonyl Ratio			
		Asphaltene	Saturates	Naphthene Aromatics	Polar Aromatics
Asphalt A	Original	CR1 0.2606	0.4756	0.2701	0.6290
		CR2 0.2034	0.0807	0.1099	0.4760
AC-30	Zero day	CR1 0.3606	*0.4055	0.3362	0.7296
		CR2 0.2761	*0.1368	0.1361	0.5253
	90 days	CR1 0.6871	0.6010	0.5163	1.0785
		CR2 0.5937	0.1323	0.2175	0.7144
Asphalt E	Original	CR1 0.2028	0.6273	0.2469	0.5482
		CR2 0.1552	0.0852	0.1447	0.4822
AC-30	Zero day	CR1 0.3701	*0.3183	0.2713	0.7085
		CR2 0.3692	*0.0884	0.1206	0.5624
	90 days	CR1 0.6241	--	0.3498	0.9644
		CR2 0.5517	--	0.1800	0.8032
Asphalt F	Original	CR1 --	0.6040	0.4619	0.8946
		CR2 --	0.0552	0.2580	0.9325
Airblown	Zero day	CR1 --	0.6239	0.5002	1.0530
		CR2 --	--	0.3081	0.9716
85-100 pen.	90 days	CR1 --	0.4735	0.4854	1.1986
		CR2 --	0.0642	0.3304	1.1444

CR1 = Relative Absorbance @ 1700 cm^{-1} /Relative Absorbance @ 1600 cm^{-1}

CR2 = Relative Absorbance @ 1700 cm^{-1} /Relative Absorbance @ 1375 cm^{-1}

* = 1% concentration

2. For the asphalts tested, the higher the asphaltene content of an original asphalt, the higher the viscosity ratio after the TFOT or RTFOT.

3. The proportions of asphalt fractions in the original asphalts correlate fairly well with the absolute viscosity ratios after the RTFOT (with an R -square value of .92) and correlate moderately well with that after the TFOT (with an R -square value of .75).

4. As noted from the results of infrared spectral analyses on the asphalt fractions, the characteristics of the fractions change as an asphalt ages. Anhydrides, carboxylic acids, and ketones develop in asphaltene as a result of aging. For naphthene-aromatics and polar-aromatics, carboxylic acids and ketones develop because of aging. No evidence exists for any functional group developed in saturates as a result of aging.

5. The change of the proportions of fractions in an asphalt alone may not be a simple indicator of the degree of oxidation in the asphalt, because not only do the proportions of fractions change but the characteristics of the fractions themselves also change during the oxidation process.

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