

Evaluation of Aging Characteristics of Asphalts by Using TFOT and RTFOT at Different Temperature Levels

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The aging characteristics of 20 asphalts were investigated by using the thin film oven test (TFOT) and rolling thin film oven test (RTFOT) at three temperature levels. Infrared absorption spectroscopy and the Schweyer rheometer test as well as penetration and absolute viscosity tests were used to evaluate the characteristics of the asphalts before and after the TFOT and RTFOT. Data from the field were also used to compare with the laboratory results. On the basis of percent penetration retained and absolute viscosity ratio, the RTFOT was found to be a more severe aging process than the TFOT for oven temperatures of 285°F and 325°F. However, the two processes were not significantly different at an oven temperature of 365°F. On the basis of carbonyl ratio, a ratio of infrared absorbance at 1700 cm^{-1} and 1600 cm^{-1} used to express the level of oxidation in an asphalt binder, the effects of TFOT and RTFOT are not significantly different at oven temperatures of 285°F and 325°F. However, at 365°F, the TFOT is a more severe aging process than the RTFOT from the standpoint of carbonyl ratio. On the basis of low-temperature constant power viscosity, the effects of TFOT and RTFOT are not significantly different at any of the three levels of temperature. As a rough estimate, the TFOT or RTFOT procedure performed at 365°F, 3 months of natural weathering of compacted Marshall specimens, and 6 to 9 months of aging in a pavement would result in approximately the same hardening effects on a typical paving grade asphalt used in Florida. From the results of this study, it appears feasible to use TFOT or RTFOT at higher temperature to simulate the aging process on the asphalt binder in asphalt paving mixtures in service, as well as that of the hot-mixing process.

It has been recognized that the properties of asphalt binders play a major role in the performance of asphalt concrete pavements. It is important that the selected asphalt for paving not only have desirable properties at the time of placement but also have good long-term performance. Current asphalt binder specifications are not sufficient to ensure good long-term performance. The thin film oven test (TFOT) or rolling thin film oven test (RTFOT) at 325°F, adopted by almost all highway agencies, can only estimate the property changes of asphalt binders during the hot mixing process and do not provide adequate information on changes in properties during service in the pavement. It is necessary to have tests that can predict the properties of the asphalt binder during service in the pavement.

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The results of previous studies on aging characteristics of asphalts and asphalt mixtures indicate that it is possible to simulate the effects of aging during service as well as that of the hot mixing process by using the TFOT or the RTFOT at higher temperatures (1,2). The potential advantages of using the TFOT or the RTFOT at higher temperatures as compared with other long-term aging tests, such as the California tilt oven and the pressure oxidation vessel tests, are that existing standard equipment could be conveniently used and that the test would require much less time to complete. The results of a study on the aging characteristics of asphalts by using the TFOT and RTFOT at three temperature levels are presented. Infrared absorption spectroscopy and Schweyer rheometer tests as well as penetration and absolute viscosity tests were used to evaluate the aging characteristics of the asphalts before and after the TFOT and RTFOT. Data from the field were also used to compare with the laboratory results. Relationships between laboratory aging and field aging were established.

TESTING PROGRAM

Testing Program on Asphalt Binders

Twenty representative asphalts commonly used in Florida and its neighboring states were selected for a laboratory testing program to evaluate their aging characteristics. For each of the asphalts, the following tests were performed on the asphalts and the asphalt residues after the TFOT and RTFOT at 285°F, 325°F, and 365°F: penetration at 77°F, absolute viscosity at 140°F, infrared spectroscopy to determine the carbonyl ratio, and Schweyer rheometer at 41°F and 77°F.

Statistical Model for Asphalt Binder Tests

The test results from asphalt binder tests were analyzed as results of a factorial experiment composed of 20 types of asphalts (ASPHALT), 3 levels of temperature (TEMP), and 2 types of test (OVEN). The study is concerned only with these 20 asphalts, 3 temperatures, and 2 tests. Therefore, ASPHALT, TEMP, and OVEN are regarded as fixed effects. The following linear model was assumed for any single measurement in the experiment:

$$Y_{ijk} = m + A_i + T_j + O_k + (AT)_{ij} + (AO)_{ik} + (TO)_{jk} + \epsilon_{ijk}$$

where

- Y_{ijk} = the response of the i th ASPHALT, j th TEMP, and k th OVEN;
 m = the overall mean;
 A_i = the main effect of ASPHALT i ;
 T_j = the main effect of TEMP j ;
 O_k = the main effect of OVEN k ;
 $(AT)_{ij}$ = the interaction of ASPHALT $i \times$ TEMP j ;
 $(AO)_{ik}$ = the interaction of ASPHALT $i \times$ OVEN k ;
 $(TO)_{jk}$ = the interaction of TEMP $j \times$ OVEN k ; and
 ε_{ijk} = the experimental error.

The SAS/STAT computer software was used for the statistical analyses.

TEST PROCEDURES

Infrared Absorption Spectroscopy

Infrared spectroscopic technique was used to measure changes in molecular structures of the asphalts due to aging in terms of 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 since it contains the absorption bands for the functional groups of carboxylic acids, ketones, and anhydrides (3,4). Ketones and anhydrides are formed in asphalt on oxidative aging, whereas carboxylic acids occur naturally in asphalt but increase in amount on oxidative aging.

The IR spectroscopy tests were run using a benchtop Perkin-Elmer Model 1600 Fourier transform infrared spectrophotometer. A 5 percent (weight/volume) solution in HPLC grade tetrahydrofuran (THF) was used in the tests. A sealed cell with 1-mm path length and sodium chloride windows was used. The background spectrum for the THF was first generated by scanning the pure solvent and stored in the 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.

Schweyer Rheometer Test

A Cannon Schweyer constant stress rheometer was used in this research. A comprehensive review of the theoretical background for the Schweyer constant stress rheometer and the application of rheological concepts proposed by Schweyer has been presented by Tia and Ruth (5). The rheometer consists of a gas-operated pneumatic cylinder that applied a specific force to the plunger in the sample tube. An LVDT measured the movement of the plunger, and the output voltage was digitized and acquired by a data acquisition and analysis system, which was operated on an IBM 9000 minicomputer.

In the rheometer test, a sample tube is filled to approximately 2 to 6 mm from the top. The plunger is inserted into the sample tube, and the entire assembly is placed into an insulated aluminum block, which has been cooled to the desired testing temperature. Once the temperature has stabilized, the gas pressure is preset and the gas cylinder activated to apply force to the plunger and asphalt sample. The defor-

mation versus time plot is recorded for each stress level until the response becomes linear. Tests are usually conducted at a minimum of five stress levels. The shear stress and shear rates obtained at the various stress levels are used to compute the shear susceptibility and the constant power viscosity at 100 w/m^3 of the asphalt.

TEST RESULTS

Penetration Test on Asphalt Binders

The results of the penetration tests are given in Tables 1 and 2. To increase the data base, data from a previous research study (1) were included in the analyses. Table 3 gives the data from the previous study.

Since the tested asphalts had a variety of penetration values in the original state, the percent penetration retained is more appropriate for comparison. Results of ANOVA on the percent penetration retained are given in Table 4. From Table 4, it is seen that all three main effects and the interaction effects except ASPHALT*TEMP are significant. The significance of the interaction between OVEN and TEMP means

TABLE 1 TFOT AND RTFOT EFFECTS ON PENETRATION

ASPHALT	TEST	ORIGINAL	PENETRATION AT 77°F OVEN TEMPERATURE (°F)		
			285	325	365
MA30A	TFOT	65	-	-	-
	RTFOT				
MA30B	TFOT	62	-	-	-
	RTFOT				
MA30C	TFOT	58	-	-	-
	RTFOT				
MA30D	TFOT	63	-	-	-
	RTFOT				
MA30E	TFOT	60	-	-	-
	RTFOT				
MA20T	TFOT	72	60	52	42
	RTFOT		56	51	42
MA20C	TFOT	70	53	45	35
	RTFOT		44	41	35
MA20V	TFOT	84	69	59	46
	RTFOT		64	52	45
TL20	TFOT	72	52	40	32
	RTFOT		42	34	30
TN20	TFOT	56	43	35	28
	RTFOT		41	34	29
BJ30A	TFOT	61	47	39	32
	RTFOT		41	34	28
BJ20	TFOT	70	53	43	33
	RTFOT		46	37	34
CJ30A	TFOT	66	54	45	37
	RTFOT		45	39	33
MT30	TFOT	53	44	37	31
	RTFOT		37	33	29
CT30	TFOT	57	-	-	-
	RTFOT		42	38	32
TB30A	TFOT	74	58	51	42
	RTFOT		56	45	42
SA20	TFOT	65	51	41	34
	RTFOT		41	37	33
AS30	TFOT	65	52	43	35
	RTFOT		44	39	32
BF30	TFOT	55	41	36	28
	RTFOT		36	31	28
MA30	TFOT	61	49	42	34
	RTFOT		47	38	33

TABLE 2 TFOT AND RTFOT EFFECTS ON PERCENT PENETRATION RETAINED

ASPHALT	TEST	% PENETRATION RETAINED OVEN TEMPERATURE(°F)		
		285	325	365
MA30A	TFOT	-	-	-
	RTFOT	-	-	-
MA30B	TFOT	-	-	-
	RTFOT	-	-	-
MA30C	TFOT	-	-	-
	RTFOT	-	-	-
MA30D	TFOT	-	-	-
	RTFOT	-	-	-
MA30E	TFOT	-	-	-
	RTFOT	-	-	-
MA20T	TFOT	83.3	72.2	58.3
	RTFOT	77.8	70.8	58.3
MA20C	TFOT	75.7	64.3	50.0
	RTFOT	62.9	58.6	50.0
MA20V	TFOT	82.1	70.2	54.8
	RTFOT	76.2	61.9	53.6
TL20	TFOT	72.2	55.6	44.4
	RTFOT	58.3	47.2	41.7
TN20	TFOT	76.8	62.5	50.0
	RTFOT	73.2	60.7	51.8
BJ30A	TFOT	77.0	63.9	52.5
	RTFOT	67.2	55.7	45.9
BJ20	TFOT	75.7	61.4	47.1
	RTFOT	65.7	52.9	48.6
CJ30A	TFOT	81.8	68.2	56.1
	RTFOT	68.2	59.1	50.0
MT30	TFOT	83.0	69.8	58.5
	RTFOT	69.8	62.3	54.7
CT30	TFOT	-	-	-
	RTFOT	73.7	66.7	56.1
TB30A	TFOT	78.4	68.9	56.8
	RTFOT	75.7	60.8	56.8
SA20	TFOT	78.5	63.1	52.3
	RTFOT	63.1	56.9	50.8
AS30	TFOT	80.0	66.2	53.8
	RTFOT	67.7	60.0	49.2
BF30	TFOT	74.5	65.5	50.9
	RTFOT	65.5	56.4	50.9
MA30	TFOT	80.3	68.9	55.7
	RTFOT	77.0	62.3	54.1

TABLE 3 PENETRATION RESULTS FROM PREVIOUS RESEARCH

Asphalt	Test	% Penetration Retained Oven Temperature(°F)		
		285	325	365
VB	TFOT	76.5	66.2	51.5
AC-30	RTFOT	69.1	60.3	48.5
VE	TFOT	79.1	64.2	50.7
AC-30	RTFOT	68.7	56.7	50.7
VA	TFOT	75.3	61.6	46.6
AC-30	RTFOT	68.5	56.2	46.6
VD	TFOT	75.8	66.1	56.5
AC-30	RTFOT	74.2	61.3	56.5
VC	TFOT	73.8	61.5	49.2
AC-30	RTFOT	66.2	56.9	47.7
VJ	TFOT	74.7	62.7	58.7
AC-20	RTFOT	70.7	57.3	52.0
VJ	TFOT	82.4	71.6	56.9
AC-20 Mod.	RTFOT	74.5	58.8	55.9
VG	TFOT	73.9	58.0	44.3
85-100	RTFOT	68.2	54.5	48.9
VF	TFOT	85.4	76.8	63.4
85-100	RTFOT	84.1	78.0	69.5
VI	TFOT	88.9	81.5	74.1
25-35	RTFOT	88.9	77.8	66.7
VH	TFOT	71.1	57.9	40.8
85-100	RTFOT	71.1	55.3	42.1

TABLE 4 RESULTS OF ANOVA ON PENETRATION RETAINED

Source	DF	Mean Square	F Value	Pr > F
ASPHALT	25	193.30075	46.53	0.0001
TEMP	2	6056.51418	1457.87	0.0001
OVEN	1	847.64310	204.04	0.0001
ASPHALT*TEMP	50	5.60310	1.35	0.1500
ASPHALT*OVEN	24	14.04473	3.38	0.0002
TEMP*OVEN	2	128.80673	31.01	0.0001

R-Square: 0.989

that the difference between the TFOT and the RTFOT also depends on oven temperature. From Tables 2 and 3, it is seen that the RTFOT is a more severe aging process than the TFOT for oven temperatures of 285°F and 325°F. However, the two processes are not significantly different from each other at an oven temperature of 365°F.

TABLE 5 TFOT AND RTFOT EFFECTS ON ABSOLUTE VISCOSITY

ASPHALT	TEST	ORIGINAL	VISCOSITY AT 140°F (Poises) OVEN TEMPERATURE (°F)		
			285	325	365
MA30A	TFOT	3245	5068	6924	11776
	RTFOT		5789	8712	12135
MA30B	TFOT	3258	5421	8968	13237
	RTFOT		6614	9622	16243
MA30C	TFOT	3549	5229	7991	16384
	RTFOT		6762	10649	17149
MA30D	TFOT	3290	5883	9474	19796
	RTFOT		7688	13515	23200
MA30E	TFOT	3053	4941	7693	14110
	RTFOT		5877	9394	14435
MA20T	TFOT	2606	3631	4996	7496
	RTFOT		4082	5571	7714
MA20C	TFOT	2861	4731	7148	13420
	RTFOT		5995	8699	13597
MA20V	TFOT	2563	4113	7223	13105
	RTFOT		4870	7302	13673
TL20	TFOT	1863	3676	6961	15884
	RTFOT		5184	9211	16838
TN20	TFOT	2028	3221	4586	7516
	RTFOT		3497	4959	7559
BJ30A	TFOT	3335	5043	7848	15501
	RTFOT		6782	11893	24079
BJ20	TFOT	1976	3367	5290	11727
	RTFOT		4691	7291	10783
CJ30A	TFOT	2965	4856	6836	11648
	RTFOT		6498	8535	13681
MT30	TFOT	3410	5740	8472	16429
	RTFOT		8148	11965	17832
CT30	TFOT	2890	4973	6996	10599
	RTFOT		6423	9228	12285
TB30A	TFOT	3175	5842	9594	19253
	RTFOT		7174	12089	17734
SA20	TFOT	2057	3583	5618	9878
	RTFOT		4804	6964	9786
AS30	TFOT	3421	5247	8192	13493
	RTFOT		6384	9414	13504
BF30	TFOT	4130	5482	7924	12267
	RTFOT		6793	9998	12267
MA30	TFOT	3202	4756	6958	10583
	RTFOT		5923	8511	11492

Absolute Viscosity Test on Asphalt Binders

The results of the absolute viscosity tests are given in Tables 5 and 6. To have a larger data base, data from previous research (1) were included in the analysis. Data from the previous research are given in Table 7.

Since the original viscosities of the asphalts are quite different from each other, it is more appropriate to use viscosity ratios than absolute viscosities in the analysis. Results of ANOVA on the absolute viscosity ratios are summarized in Table 8, which indicates that all three main effects and the interaction ASPHALT*TEMP are significant.

Comparison of the two types of oven was done at three different temperatures by means of Duncan's multiple-range test at a level of significance of 0.05. The results of the Duncan's test are given in Table 9, which indicates that the RTFOT is a more severe aging process than the TFOT for oven temperatures of 285°F and 325°F. However, for an oven temperature of 365°F, the two processes are not significantly different from one another.

TABLE 7 ABSOLUTE VISCOSITY RESULTS FROM PREVIOUS RESEARCH

Asphalt	Test	Absolute Viscosity Ratio Oven Temperature (°F)		
		285	325	365
VB	TFOT	1.98	3.14	7.33
AC-30	RTFOT	2.49	4.64	10.60
VE	TFOT	2.03	3.23	8.42
AC-30	RTFOT	2.41	4.11	7.86
VA	TFOT	1.77	2.96	7.15
AC-30	RTFOT	2.11	3.17	5.47
VD	TFOT	1.72	2.57	4.57
AC-30	RTFOT	1.96	2.86	4.76
VC	TFOT	1.90	3.19	7.98
AC-30	RTFOT	2.54	3.94	8.73
VJ	TFOT	1.85	2.93	6.02
AC-20	RTFOT	2.07	3.93	4.78
VJ	TFOT	1.48	1.91	3.94
AC-20 Mod.	RTFOT	1.97	3.53	4.74
VG	TFOT	1.51	2.19	3.80
85-100	RTFOT	1.78	2.35	3.06
VF	TFOT	1.37	1.86	3.07
85-100	RTFOT	1.48	1.77	2.47
VI	TFOT	1.47	2.14	3.93
25-35	RTFOT	1.60	2.72	6.49
VH	TFOT	2.36	4.70	21.40
85-100	RTFOT	2.38	5.01	13.95

TABLE 6 TFOT AND RTFOT EFFECT ON ABSOLUTE VISCOSITY RATIO

ASPHALT	TEST	ABSOLUTE VISCOSITY RATIO OVEN TEMPERATURE (°F)		
		285	325	365
MA30A	TFOT	1.56	2.13	3.63
	RTFOT	1.78	2.68	3.74
MA30B	TFOT	1.66	2.75	4.06
	RTFOT	2.03	2.95	4.99
MA30C	TFOT	1.47	2.25	4.62
	RTFOT	1.91	3.00	4.83
MA30D	TFOT	1.79	2.88	6.02
	RTFOT	2.34	4.11	7.05
MA30E	TFOT	1.62	2.52	4.62
	RTFOT	1.92	3.08	4.73
MA20T	TFOT	1.39	1.92	2.88
	RTFOT	1.57	2.14	2.96
MA20C	TFOT	1.65	2.50	4.69
	RTFOT	2.10	3.04	4.75
MA20V	TFOT	1.60	2.82	5.11
	RTFOT	1.90	2.85	5.33
TL20	TFOT	1.97	3.74	8.53
	RTFOT	2.78	4.94	9.04
TN20	TFOT	1.59	2.26	3.71
	RTFOT	1.72	2.45	3.73
BJ30A	TFOT	1.51	2.35	4.65
	RTFOT	2.03	3.57	7.22
BJ20	TFOT	1.70	2.68	5.93
	RTFOT	2.37	3.69	5.46
CJ30A	TFOT	1.64	2.31	3.93
	RTFOT	2.19	2.88	4.61
MT30	TFOT	1.68	2.48	4.82
	RTFOT	2.39	3.51	5.23
CT30	TFOT	1.72	2.42	3.67
	RTFOT	2.22	3.19	4.25
TB30A	TFOT	1.84	3.02	6.06
	RTFOT	2.26	3.81	5.59
SA20	TFOT	1.74	2.73	4.80
	RTFOT	2.34	3.39	4.76
AS30	TFOT	1.53	2.39	3.94
	RTFOT	1.87	2.75	3.95
BF30	TFOT	1.33	1.92	2.97
	RTFOT	1.64	2.42	2.97
MA30	TFOT	1.49	2.17	3.31
	RTFOT	1.85	2.66	3.59

TABLE 8 RESULTS OF ANOVA ON ABSOLUTE VISCOSITY RATIO

Source	DF	Mean Square	F Value	P r > F
ASPHALT	30	8.7368643	19.12	0.0001
OVEN	1	6.3215274	13.84	0.0004
TEMP	2	216.2998651	473.40	0.0001
ASPHALT*TEMP	60	3.9948567	8.74	0.0001
ASPHALT*OVEN	30	0.6934641	1.52	0.0848
OVEN*TEMP	2	1.3043145	2.85	0.0654

R-Square: 0.972

TABLE 9 COMPARISON OF TFOT AND RTFOT AT THREE TEMPERATURES ON THE BASIS OF VISCOSITY RATIO

TEMP.	Duncan Grouping	Mean	N	OVEN
285°F	A	2.0645	31	RTFOT
	B	1.6748	31	TFOT
325°F	A	3.2626	31	RTFOT
	B	2.6148	31	TFOT
365°F	A	5.538	31	RTFOT
	A	5.470	31	TFOT

* Means with the same letter are not significantly different.

TABLE 10 RESULTS OF INFRARED SPECTROSCOPY

ASPHALT	ORIGINAL	CARBONYL RATIO		
		TFOT 285°F	TFOT 325°F	TFOT 365°F
MA30A	0.3543	0.3480	0.3668	0.4066
MA30B	0.2548	0.2984	0.3231	0.3924
MA30C	0.2551	0.2530	0.2914	0.3561
MA30D	0.2737	0.3126	0.3479	0.4010
MA30E	0.3081	0.3619	0.3675	0.4070
MA20T	0.3775	0.3764	0.4320	0.4586
MA20C	0.3540	0.3861	0.4338	0.4983
MA20V	0.3512	0.3742	0.4075	0.4349
TL20	0.3250	0.3644	0.3924	0.4305
TN20	0.2444	0.2627	0.2958	0.3381
BJ30A	0.3370	0.2933	0.3256	0.3674
BJ20	0.3171	0.3321	0.3660	0.4048
CJ30A	0.3050	0.3468	0.3650	0.3910
MT30	0.3282	0.3126	0.3421	0.3869
CT30	0.3584	0.3975	0.4469	0.4622
TB30A	0.4314	0.4529	0.4971	0.5445
SA20	0.3178	0.3620	0.3980	0.4326
AS30	0.3971	0.3741	0.4114	0.4224
BF30	0.3673	0.3831	0.4279	0.4735
MA30	0.3277	0.3404	0.3678	0.4045
VB	0.2840	0.3410	0.3680	0.3950
VE	0.3210	0.3520	0.3670	0.4340
VA	0.2850	0.3310	0.3680	0.4240
VD	0.3130	0.3470	0.3820	0.4100
VC	0.3150	0.3600	0.3860	0.4450
VJ	0.2820	0.3190	0.3490	0.4010
VJM	0.2820	0.2960	0.3150	0.3600
VG	0.2540	0.2800	0.3100	0.3670
VF	0.7480	0.8050	0.8210	0.8850
VI	0.3590	0.3740	0.3870	0.4690
VH	0.3660	0.4030	0.4140	0.4700

ASPHALT	ORIGINAL	RTFOT 285°F	RTFOT 325°F	RTFOT 365°F
MA30A	0.3543	0.3545	0.3680	0.3711
MA30B	0.2548	0.2812	0.3206	0.3683
MA30C	0.2551	0.2030	0.2487	0.2868
MA30D	0.2737	0.3102	0.3443	0.3684
MA30E	0.3081	0.3207	0.3568	0.3867
MA20T	0.3775	0.3836	0.4236	0.4516
MA20C	0.3540	0.3995	0.4467	0.4736
MA20V	0.3512	0.3951	0.4121	0.4360
TL20	0.3250	0.3753	0.3920	0.4244
TN20	0.2444	0.2479	0.2726	0.3066
BJ30A	0.3370	0.3033	0.3359	0.3761
BJ20	0.3171	0.3421	0.3708	0.3931
CJ30A	0.3050	0.3653	0.3866	0.4073
MT30	0.3282	0.3286	0.3360	0.3577
CT30	0.3584	0.3807	0.3890	0.4288
TB30A	0.4314	0.4496	0.4512	0.4774
SA20	0.3178	0.3557	0.3791	0.4044
AS30	0.3971	0.3892	0.4373	0.4643
BF30	0.3673	0.3987	0.4366	0.4601
MA30	0.3277	0.3401	0.3607	0.3870
VB	0.2840	0.3240	0.3660	0.3920
VE	0.3210	0.3230	0.3490	0.4120
VA	0.2850	0.3530	0.3620	0.4260
VD	0.3130	0.3180	0.3600	0.3760
VC	0.3150	0.3370	0.3670	0.4110
VJ	0.2820	0.3240	0.3540	0.3630
VJM	0.2820	0.2930	0.3160	0.3580
VG	0.2540	0.2790	0.3260	0.3390
VF	0.7480	0.7930	0.8380	0.8580
VI	0.3590	0.3760	0.4090	0.4740
VH	0.3660	0.3930	0.4180	0.4580

Infrared Spectroscopy on Asphalt Binders

Study of the infrared absorption spectra indicates that there is a definite increase in the infrared absorbance in the 1700 cm^{-1} region as the level of oxidation increases. This is due to increasing concentration of ketones and anhydrides, which have infrared absorbances at about 1700 cm^{-1} , and carboxylic acids, which have infrared absorbance at about 1730 cm^{-1} . Ketones and anhydrides are formed on oxidative aging, and carboxylic acids occur naturally in the asphalt but increase on oxidation aging. Since these three functional groups are the most significant chemical functionalities that can be related to oxidative aging, examination of the spectra in this study was done with particular reference to them.

The spectra also indicate that the band centering at about 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 (6). Therefore, the carbonyl ratio, which is a ratio of absorbance at 1700 cm^{-1} and 1600 cm^{-1} , can be used to express the level of oxidation. All absorption measurements were with reference to the absorption at 1900 cm^{-1} .

The results of the infrared spectroscopy are given in Table 10. Results of ANOVA on the data are summarized in Table 11, which indicates that all three main effects and interaction effects are significant.

Comparison of the effects of OVEN was done at different temperatures by means of Duncan's multiple-range test at a level of significance of 0.05. The results are summarized in Table 12, which indicates that the effects of TFOT and RTFOT are not significantly different at oven temperatures of 285°F and 325°F. But at 365°F, the TFOT is a more severe aging process than the RTFOT from the standpoint of carbonyl ratio.

Schwyer Rheometer Test on Asphalt Binders

Table 13 gives the results of the Schwyer rheometer test on the original asphalts. Nine of the 20 asphalts were used in the Schwyer rheometer test. The results are given in Table 14. Results of ANOVA on the rheometer test are summarized in Table 15, which indicates that the OVEN effect is not significant.

When the constant power viscosity versus temperature relationships for the original and aged asphalts were plotted, it was observed that asphalts of the same grade (viscosity) at high temperature (60°C) could have very different properties at lower temperature. In addition, the asphalt constant power viscosity-temperature relationship is shifted parallel to the original relationship after TFOT. The degree of parallel shifting depends on the severity of the aging process; it shifts more for a higher oven temperature than for a lower oven temperature.

ANALYSIS AND DISCUSSION

The TFOT and the RTFOT tests were adopted by AASHTO, ASTM, and almost all state highway departments and other

TABLE 11 RESULTS OF ANOVA ON INFRARED SPECTROSCOPY RESULTS

SOURCE	DF	ANOVA SS	F VALUE	PR > F
ASPHALT	30	1.57990015	646.54	0.0
TEMP	2	0.14249844	874.71	0.0
OVEN	1	0.00360800	44.29	0.0001
ASPHALT*TEMP	60	0.00950103	1.94	0.0055
ASPHALT*OVEN	30	0.01348053	5.52	0.0001
TEMP*OVEN	2	0.00223958	13.75	0.0001

TABLE 12 COMPARISON OF TFOT AND RTFOT BASED ON CARBONYL RATIO

TEMP.	DUNCAN GROUPING	MEAN	N	OVEN
285°F	A	0.359371	31	TFOT
	A	0.356042	31	RTFOT
325°F	A	0.389452	31	TFOT
	A	0.384955	31	RTFOT
365°F	A	0.434623	31	TFOT
	B	0.416023	31	RTFOT

* Means with the same letter are not significantly different.

TABLE 13 RESULTS OF SCHWEYER RHEOMETER TEST ON ORIGINAL ASPHALTS

ASPHALT	C VALUE		η_j (Pa s)	
	41°F	77°F	41°F	77°F
MA30A	0.78	0.99	105559000	225715
	0.83	1.00	89936900	188550
MA30B	1.11	1.02	74156400	342260
	1.09	1.09	89563200	278806
MA30C	0.63	0.89	226055000	416123
	0.72	0.90	159718000	359387
MA30D	0.61	0.92	136696000	386520
	0.57	0.85	244281000	394638
MA30E	0.87	1.16	153100000	202829
	0.93	1.10	116200000	210183
MA20T	1.17	1.01	63108600	102577
	1.14	1.00	62118000	159926
MA20C	0.99	0.90	78002200	515192
	1.05	0.87	45416900	691512
MA20V	0.89	0.99	54533000	220698
	0.86	0.95	60670800	192815
TL20	0.29	0.97	1778310000	281662
	0.28	1.01	1875600000	167020
TN20	0.79	0.92	487279000	951524
	0.82	1.07	482526000	536071
BJ30A	0.79	0.99	113312000	264961
	0.94	0.89	67216800	408088
BJ20	0.83	0.78	111734000	544280
	0.85	0.73	113379000	748936
CJ30A	0.62	0.99	286575000	349691
	0.61	1.03	278523000	301660
MT30	0.64	0.85	252477000	471541
	0.63	0.85	258437000	486388
CT30	0.78	0.87	105307000	408446
	0.68	0.82	176288000	677324
TB30A	0.72	0.64	36108400	836738
	0.57	0.64	62694200	876500
SA20	0.24	0.91	1638560000	239055
	0.26	0.92	1946950000	370852
AS30	0.47	1.06	1104530000	209811
	0.45	1.01	1111200000	256713
BF30	0.70	1.14	610784000	243592
	0.68	1.04	613913000	345046
MA30	0.68	0.94	230442000	482422
	0.78	0.92	254569000	521246

governmental agencies as specification tests (7). The AASHTO and ASTM standards state:

This method indicates approximate change in properties of asphalt during conventional hot-mixing at about 302°F (150°C) as indicated by viscosity, penetration or ductility measurements. It yields a residue which approximates the asphalt condition as incorporated in the pavement. If the mixing temperature differs appreciably from the 302°F level, more or less effect on properties will occur.

Results of the tests on asphalt binders presented in this paper have demonstrated that higher oven temperatures result in increased differentials in properties. For example, the change in viscosity ratio between 325°F and 365°F is greater than that between 285°F and 325°F. The higher test temperature of 365°F would magnify the asphalt properties change compared with the lower test temperature of 325°F. On the basis of percent penetration retained and absolute viscosity ratio, the effect of RTFOT is slightly more severe than that of TFOT for oven temperatures of 285°F and 325°F, whereas the difference is not significant at 365°F. On the basis of carbonyl ratio, the effects of TFOT and RTFOT are not significantly different for oven temperatures of 285°F and 325°F, whereas the TFOT is a more severe aging process than the RTFOT at 365°F. From the standpoint of low-temperature constant power viscosity, the effects of TFOT and RTFOT are not significantly different from each other at any of the three temperatures. Therefore, there is no reason to favor the RTFOT process over the TFOT process, especially if the oven temperature is raised to 365°F.

Comparisons were made between the residues after TFOT and RTFOT at 365°F, and recovered asphalts from specimens aged in a forced-draft oven and on the roof under natural weathering. Table 16 compares the different aging effects. It appears that the TFOT and RTFOT procedures performed at 365°F, 14 days aging at 140°F in the laboratory, and 3

TABLE 14 TFOT AND RTFOT EFFECTS ON THE SCHWEYER RHEOMETER TEST

CONSTANT POWER VISCOSITY (Pa s)											
ASPHALT			OVEN TEMPERATURE			ASPHALT			OVEN TEMPERATURE		
			285°F	325°F	365°F				285°F	325°F	365°F
MA30	TFOT	77°F	1.206E+06	2.243E+06	4.390E+06	MA20C	TFOT	77°F	6.044E+05	1.182E+06	3.107E+06
MA30	TFOT	59°F	2.122E+07	2.620E+07	5.240E+07	MA20C	TFOT	41°F	9.972E+08	8.493E+08	2.073E+09
MA30	RTFOT	77°F	2.836E+06	3.729E+06	3.218E+06	MA20C	RTFOT	77°F	6.528E+05	6.850E+05	1.964E+06
MA30	RTFOT	59°F	4.069E+07	4.780E+07	7.040E+07	MA20C	RTFOT	41°F	6.697E+08	1.256E+09	2.473E+09
BF30	TFOT	77°F	1.135E+06	2.069E+06	6.168E+06	MA20T	TFOT	77°F	2.562E+05	2.644E+05	6.999E+05
BF30	TFOT	59°F	3.460E+07	4.523E+07	1.072E+08	MA20T	TFOT	41°F	3.216E+08	7.226E+08	9.109E+08
BF30	RTFOT	77°F	1.526E+06	3.113E+06	6.523E+06	MA20T	RTFOT	77°F	3.039E+05	6.675E+05	2.099E+06
BF30	RTFOT	59°F	4.820E+07	8.612E+07	1.253E+08	MA20T	RTFOT	41°F	4.513E+08	5.146E+08	7.916E+08
MT30	TFOT	77°F	9.139E+05	1.871E+06	2.730E+06	MA20V	TFOT	77°F	5.049E+05	5.465E+05	1.250E+06
MT30	TFOT	59°F	7.607E+07	5.210E+07	1.241E+08	MA20V	TFOT	41°F	6.767E+08	8.064E+08	2.084E+09
MT30	RTFOT	77°F	1.419E+06	1.682E+06	2.679E+06	MA20V	RTFOT	77°F	4.123E+05	6.310E+05	1.682E+06
MT30	RTFOT	59°F	6.424E+07	5.830E+07	6.512E+07	MA20V	RTFOT	41°F	4.757E+08	6.813E+08	2.054E+09
BJ30A	TFOT	77°F	6.918E+05	2.693E+06	4.878E+06	TL20	TFOT	77°F	1.737E+06	2.860E+06	6.806E+06
BJ30A	TFOT	59°F	2.661E+07	9.145E+07	1.523E+08	TL20	TFOT	41°F	1.133E+09	2.715E+09	7.570E+09
BJ30A	RTFOT	77°F	7.384E+05	3.357E+06	4.740E+06	TL20	RTFOT	77°F	2.267E+06	2.776E+06	8.567E+06
BJ30A	RTFOT	59°F	3.146E+07	6.007E+07	2.162E+08	TL20	RTFOT	41°F	2.123E+09	4.203E+09	5.028E+09
CT30	TFOT	77°F	2.240E+06	2.622E+06	4.091E+06						
CT30	TFOT	59°F	5.086E+07	8.103E+07	1.259E+08						
CT30	RTFOT	77°F	2.699E+06	2.618E+06	4.282E+06						
CT30	RTFOT	59°F	4.119E+07	6.083E+07	9.348E+07						

TABLE 15 RESULTS OF ANOVA ON RHEOMETER TEST RESULTS

41°F SOURCE	DF	ANOVA SS	F VALUE	PR >F
ASPHALT	3	3.587895479527E+19	17.76	0.0022
OVEN	1	8.045031317606E+14	0.00	0.9735
TEMP	2	1.710756580212E+19	12.71	0.0070
ASPHALT*OVEN	3	6.586750236695E+16	0.03	0.9913
ASPHALT*TEMP	6	1.034365879240E+19	2.56	0.1387
OVEN*TEMP	2	1.004507498132E+18	0.75	0.5136

59°F SOURCE	DF	ANOVA SS	F VALUE	PR >F
ASPHALT	4	8678182209014668.0	4.58	0.0322
OVEN	1	59330671960336.0	0.13	0.7325
TEMP	2	26348574128073500.0	27.83	0.0002
ASPHALT*OVEN	4	2976281389387996.0	1.57	0.2714
ASPHALT*TEMP	8	11600818804872336.0	3.06	0.0670
OVEN*TEMP	2	4348036038164.0	0.00	0.9954

77°F SOURCE	DF	ANOVA SS	F VALUE	PR >F
ASPHALT	8	70490652640426.259	30.01	0.0001
OVEN	1	1216989513771.125	4.14	0.0587
TEMP	2	67283685634763.368	114.57	0.0001
ASPHALT*OVEN	8	1917444626002.031	0.82	0.5994
ASPHALT*TEMP	16	30612108812535.961	6.52	0.0003
OVEN*TEMP	2	107356391528.258	0.18	0.8346

TABLE 16 COMPARISON OF AGING EFFECTS

	TFOT (365°F)	RTFOT (365°F)	ROOF (MON.)		LAB (DAYS)	
			3	6	14	28
PENETRATION AT 25 °C						
MA	34	33	34	30	33	32
BF	28	28	32	24	30	26
BJ	32	28	30	28	28	27
CT	-	32	31	30	33	31
MT	31	29	26	26	29	27
ABSOLUTE VISCOSITY AT 140 °F (Poise)						
MA	10583	11492	10313	14171	9987	11426
BF	12267	12267	11310	16074	11150	15515
BJ	15501	24079	14959	20353	16136	20900
CT	10599	12285	20239	21931	16555	21399
MT	16429	17832	20225	22904	14251	19556
CARBONYL RATIO						
MA	.4045	.3870	.4979	.5140	.4551	.5014
BF	.4735	.4601	.5027	.5333	.4861	.5182
BJ	.3674	.3761	.3761	.4855	.5141	.4914
CT	.4622	.4288	.4643	.4944	.4371	.5010
MT	.3869	.3577	.4396	.4705	.4414	.4880
CONSTANT POWER VISCOSITY AT 77 °F						
MA	4.39E6	3.22E6	1.43E6	3.15E6	1.83E6	3.93E6
BF	6.17E6	6.52E6	2.23E6	2.82E6	2.40E6	3.35E6
BJ	4.88E6	4.74E6	1.69E6	8.15E6	4.12E6	7.18E6
CT	4.09E6	4.28E6	2.70E6	3.90E6	2.91E6	4.25E6
MT	2.73E6	2.68E6	7.30E6	8.29E6	2.31E6	4.73E6
CONSTANT POWER VISCOSITY AT 59 °F						
MA	5.24E7	7.04E7	4.00E7	4.75E7	6.64E7	6.71E7
BF	1.07E8	1.25E8	4.60E8	7.13E7	8.11E7	1.42E8
BJ	1.52E8	2.16E8	5.97E7	1.13E8	1.14E8	1.00E8
CT	1.26E8	9.35E7	6.77E7	8.49E7	6.59E7	6.69E7
MT	1.24E8	6.51E7	4.84E7	9.10E7	8.09E7	9.56E7

months of natural weathering would result in approximately the same hardening effects on a typical paving grade asphalt used in Florida.

From a previous study (8), it was found that Marshall specimens that were allowed to weather naturally for 6 months would harden approximately two to three times as much as the mixtures when placed and compacted in a pavement. Since the hardening effects of the TFOT or RTFOT at 365°F are about the same as those of 3 months natural weathering, the hardening effects of the TFOT or RTFOT at 365°F should be about the same as those of 6 to 9 months aging on the roads.

SUMMARY

The major findings of the tests on asphalt binders are as follows:

1. On the basis of percent penetration retained and absolute viscosity ratio, the RTFOT is a more severe aging process than the TFOT for oven temperatures of 285°F and 325°F. However, the two processes are not significantly different at an oven temperature of 365°F.
2. The carbonyl ratio, a ratio of infrared absorbance at 1700 cm^{-1} and 1600 cm^{-1} , can be used to express the level of oxidation in an asphalt binder.
3. On the basis of carbonyl ratio, the effects of TFOT and RTFOT are not significantly different from each other at oven temperatures of 285°F and 325°F. However, at 365°F, the

TFOT is a more severe aging process than the RTFOT from the standpoint of carbonyl ratio.

4. On the basis of constant power viscosity, the effects of TFOT and RTFOT are not significantly different from each other at any of the three temperatures.

5. Asphalts of the same grade at high temperature (60°C) can have very different properties at lower temperature.

6. Higher oven temperatures result in increased differentials in properties (i.e., the change in viscosity between 325°F and 365°F is greater than that between 285°F and 325°F).

7. The constant power viscosity-temperature relationship of asphalt is shifted parallel to the original relationship after aging process. The relationship shifts more for higher oven temperature than for lower oven temperature.

8. As a rough estimate, the TFOT or RTFOT procedure performed at 365°F, 3 months of natural weathering of Marshall specimens, and 6 to 9 months of aging in a pavement would result in approximately the same hardening effects on a typical paving grade asphalt used in Florida.

9. From the results of this study, it appears feasible to use TFOT or RTFOT at a higher temperature to simulate the aging process on the asphalt binder in service as well as that of the hot-mixing process.

REFERENCES

1. M. Tia, B. E. Ruth, C. T. Chari, J. Shiau, D. Richardson, and J. Williams. *Investigation of Original and In-Service Asphalt Properties for the Development of Improved Specifications—Final Phase*

- of Testing and Analysis*. Final report. UF Project 4910450420812. Department of Civil Engineering, University of Florida, Gainesville, 1988.
2. C. T. Chari, B. E. Ruth, M. Tia, and G. Page. Evaluation of Age Hardening on Asphalts and Mixtures. *Proc., AAPT*, Vol. 59, 1990, pp. 176–239.
 3. K. O. Anderson, B. P. Shields, and J. M. Dacyszyn. Cracking of Asphalt Pavements due to Thermal Effects. *Proc., AAPT*, Vol. 35, 1966, pp. 247–262.
 4. R. J. Schmidt. The Relationship of the Low Temperature Properties of Asphalt to the Cracking of Pavements. *Proc., AAPT*, Vol. 35, 1966, pp. 263–269.
 5. M. Tia and B. E. Ruth. Basic Rheology and Rheological Concepts Established by H. E. Schwyer. *Asphalt Rheology: Relationships to Mixtures*, ASTM STP 941, 1987, pp. 118–145.
 6. A. C. Edler, M. M. Hattingh, V. P. Servas, and C. P. Marais. Use of Aging Test To Determine the Efficiency of Hydrated Lime Additions to Asphalt in Retarding Its Oxidative Hardening. *Proc., AAPT*, Vol. 54, 1985, pp. 118–139.
 7. O. K. Kim, C. A. Bell, J. E. Wilson, and G. Boyle. Development of Laboratory Oxidative Aging Procedures for Asphalt Cements and Asphalt Mixtures. In *Transportation Research Record 1115*, TRB, National Research Council, Washington, D.C., 1987, pp. 101–112.
 8. M. Tia, B. E. Ruth, J. Shiau, S. Huang, and D. Richardson. *Evaluation of Criteria for Improved Durability of Asphalt*. Final report. Department of Civil Engineering, University of Florida, Gainesville, 1990.

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