Evaluation of Standard Oven Tests for Hot-Mix Plant Aging

H. B. Jemison, R. R. Davison, C. J. Glover, and J. A. Bullin

The thin film oven test and the rolling thin film oven test are widely used to simulate the asphalt hardening that occurs in hot-mix plants. Using nine road-collected hot-mix samples and the corresponding tank asphalts, a comparison is made between the oven tests and the hot mix. Comparisons are made on the basis of viscosity at 60°C and 135°C, penetration at 25°C, infrared analysis, and gel permeation chromatography. In general, the two oven tests are in close agreement for all parameters at standard test times. However, if the times are extended, they may diverge. The recovered hot-mix asphalt is generally more aged than the oven-aged material with respect to all parameters although less so with viscosity. The infrared spectra show much greater change in the hot-mix than in the oven-aged material. The hot-mix operation also produces highly oxidized material that is not usually removed from the aggregate in the extraction operation.

When hot asphalt and aggregate are combined in a hot-mix plant, considerable hardening occurs in the asphaltic material. Some of this is caused by a loss of volatile components, but the greater part is the result of oxidation. As the degree of hardening occurring in the hot-mix plant is an important property of asphalt, a number of tests have been devised to simulate this effect. By far the most commonly used are the thin film oven test (TFOT), ASTM D1754, and the rolling thin film oven test (RTFOT), ASTM D2872. The TFOT was designed by Lewis and Welborn (1, p. 14) and requires 5 hr. In 1963, Hveem et al. (2, p. 271) developed the RTFOT, which cut the time to 75 min and was designed to give results similar to the TFOT. On the basis of viscosity changes, these tests are generally in close agreement. Attempts to relate any test to hot-mix results are often marred by incomplete solvent removal and solvent hardening (3) and further complicated by hot-mix plant variability. Considering the variability in hot-mix plant operations, these tests probably reproduce viscosity changes reasonably well. Yet, it was noted many years ago (4) that this does not guarantee that what actually occurs in the hot-mix plant from a chemical standpoint is being simulated by the oven test.

Recently, Glover et al. (5), in a preliminary study, presented data on two asphalts indicating agreement between the two oven tests but divergence between the oven test asphalts and hot-mix asphalts, particularly with respect to infrared spectra. Chollar et al. (6) in a comparison of batch and drum plants also indicate greater hardening in hot-mix plants than usually occurs in oven tests. An ideal simulation should reproduce actual plant changes in every respect as closely as possible. To evaluate the oven tests as hot-mix plant simu-

Department of Chemical Engineering and the Texas Transportation Institute, Texas A&M University, College Station, Tex. 77843-3122.

lators, a variety of chemical and physical parameters for comparing extracted hot-mix and the corresponding oven-aged tank asphalts were employed.

OBJECTIVE

The objective of this study was to evaluate a more extensive and diverse set of asphalts than the earlier study of Glover et al. (5), thereby providing a better picture of the comparisons between the hot-mix and oven-aged materials.

EXPERIMENTAL DESIGN AND METHODS

Hot-mix samples were obtained along with the corresponding tank asphalts from nine plants, of which two were batch plants and seven drum plants. Six separate suppliers were represented, but the two asphalts designated "Cosden" are plainly from different sources.

The hot-mix asphalt samples were extracted from the aggregate using a modified ASTM D2172 Method A. The asphalt was recovered from the solvent using a modified ASTM D1856. Both of these procedures are described in Davison et al. (3); the recovery procedure is also described in Burr et al. (7). It has been shown using gel permeation chromatography (GPC) that the standard recovery procedure often failed to remove all the solvent. Time and temperature were increased to ensure complete removal and then confirmed by GPC. The major modification of the extraction procedure was to add 15 percent ethanol by volume to trichloroethylene. This considerably enhances removal of the last few percent of the asphalt. Agitation of the material was also increased, and care was taken to finish the entire extraction and recovery in 8 hr to minimize solvent hardening of the recovered material. Furthermore, filtration of the recovered solution with <5 μm filter paper was performed to remove residual fines material. In some cases, additional, very-hard-to-remove material was obtained by further agitation and soaking of the aggregate with a trichloroethylene/ethanol (15 percent) mixture for 2 days. This material was filtered, recovered, and analyzed separately from the material of the primary extraction.

The TFOT and RTFOT were performed on all tank asphalts. These tests were also run at extended times of 14.5 hr for the TFOT (ETFOT) and 3.5 hr for the RTFOT (ERTFOT). The tank and oven-aged asphalts provided a range in which the extracted hot mix would fall and give an indication of the ability of oven tests to predict the chemical and physical properties of the hot mix.

Penetrations (ASTM D5) and viscosities (ASTM D2171) at 140°F and 275°F were run on all samples of tank, oven-aged, and hot-mix asphalts. The samples were also analyzed chemically by GPC and Fourier transform infrared (FTIR) spectroscopy. GPC chromatograms give a molecular size distribution, and FTIR shows the presence of certain chemical groups.

In this work, an IBM LC-9533 liquid chromatograph with a refractive index detector was used in the GPC analyses. Tetrahydrofuran at 1 mL/min was used as the solvent. A 500Å/50Å column combination was used. The injected volume was 100 μL, and the asphalt concentration was 7 percent. The percent large molecular size (LMS), as suggested by Jennings (8), was used to characterize each asphalt, and in this work it was defined as the fraction of the chromatogram area between 20 and 25 min.

The infrared analyses were made with a Nicolet 60 SX FTIR single-beam spectrometer using an attenuated total reflectance method (9). In this procedure, the asphalt is coated on a zinc selenide prism. The infrared beam passes into and through the prism and is reflected at the sample interface surface back to the detector.

The area under the carbonyl peak around a wave number of 1700 cm^{-1} was used to characterize each asphalt. The height at 1820 cm^{-1} was arbitrarily chosen as the base and the carbonyl peak area was the area above this level from 1820 to 1650 cm^{-1}. Hard-to-remove material was obtained for analysis by allowing the previously extracted hot mix to soak in trichloroethylene/15 percent ethanol overnight and then evaporating the solvent.

RESULTS

The complete experimental results are given in Table 1 along with calculated viscosity-temperature susceptibility (VTS). The times for the two extended tests were chosen because they both approximately doubled the increase in viscosity for a particular asphalt relative to the standard test. It is interesting that, although the viscosities resulting from the two tests are in approximate agreement for the standard times, at the extended times there is close agreement for some asphalts and wide divergence for others.

Chromatograms obtained from the GPC show the shifts in molecular size associated with the oxidative aging of the asphalt. The average molecular size increases with aging, resulting in an increase of the percentage of LMS (Table 1). Some hot-mix samples gave chromatograms that not only differ in molecular size, but also show significantly different shapes. This can not be easily explained, and apparently no amount of oven aging can reproduce the shapes of some hot mixes.

The spectra obtained from the FTIR indicate a definite increase in carbonyl absorption with oxidative aging (Table 1). Changes also occur in other regions representing increases in carbon-oxygen bonds. The sulfoxide absorbance area at a wave number of 1030 cm^{-1} is of interest, but it could be masked by the presence of micron-size dust and aggregate particles whose silicon oxide bands absorb at approximately the same location. This could be the cause of the radically different absorbance of some hot mixes in the sulfoxide region

compared with the oven tests. Throughout the rest of the spectrum, however, the changes in chemical compositions attributed to the hot-mix procedure seemed to be proportional to the changes resulting in the oven tests. Using the parameters given in Table 1, a comparison is made between the TFOT and the RTFOT and then between these tests and the hot-mix results.

Oven Test Comparisons

The two oven tests are similar in design and the temperatures are identical. The RTFOT yields a more homogeneous product than the TFOT because of its constantly renewed surface. The exposure times of the tests differ significantly; the RTFOT's shorter time is generally more desirable. Because these methods were designed to accomplish the identical task of simulating the changes of asphalt properties occurring during the hot-mix process, they would be expected to produce at least similar outputs with identical inputs.

The data in Table 1 and Figures 1-6 show that the TFOT and RTFOT chemical and physical properties are indeed comparable. The diagonal lines represent lines of equality on each plot. The plots of the viscosities at 275°F (135°C), the percentage LMS, the penetration values, and the viscosities at 140°F (60°C) (Figures 1, 2, 3, and 4, respectively) appear to characterize the RTFOT as being a slightly more severe aging test. These differences are small, however, and the carbonyl area and the VTS values shown in Figures 5 and 6 indicate that one test could not be considered different from the other.

Examples of GPC and FTIR may be seen in Figures 7 and 8. Figure 7 shows the identical GPCs for the two oven tests with Ampet AC-20. Figure 8 exhibits almost identical infrared spectra for both tests with the Cosden AC-10.

Considering the inherent error in the oven tests and analysis techniques, and the variability of asphalt samples, the apparent differences between the two oven tests are small and probably insignificant. Indeed, their possible subtle differences do not warrant the use of both tests. Therefore, it is concluded that the TFOT and RTFOT methods are interchangeable and cannot be considered independent.

Hot-Mix and Oven Test Comparisons

For many years, the TFOT and RTFOT have been used to simulate and predict the chemical and physical changes of asphalt during the hot-mix process. Many factors during plant operation and in sample handling can complicate the comparison, however. Examples of these include solvent aging and insufficient removal of the asphalt from the aggregate during the extraction, as well as incomplete solvent removal and volatiles loss during the recovery. Other variables arise at the hot-mix plant such as different hot-mix plant types, fuels, and operating conditions.

The same parameters that were used to compare the oven tests are used to investigate the hot-mix performance. The hot-mix data are considerably more scattered because, at least in part, of the previously mentioned error contributions. Figures 9-14 show that the hot-mix and oven test data do not show nearly as good agreement as the two oven test comparisons exhibit.

TABLE 1 PROPERTIES OF HOT-MIX STUDY ASPHALTS

| Names	Asphalts	Penetration	Viscosity @ 60°C	Viscosity @ 135°C	%LMS	Carbonyl	VTS
AMPET AC-20	Tank	69.7	1835	3.91	15.7	0.392	3.49
1989	RTFOT	47.3	3287	4.58	18.2	0.445	3.59
Batch	TFOT	47.9	3100	4.61	18.0	0.493	3.56
	Hot Mix	28.7	4792	5.75	20.0	0.703	3.56
	ERTFOT	35.0	5437	5.60	20.8	0.553	3.62
	ETFOT	29.7	7533	6.73	22.0	0.695	3.60
COASTAL	Tank	57.7	1998	4.19	19.4	0.522	3.47
AC-20 1987	RTFOT	39.2	5722	6.58	23.2	0.607	3.52
	TFOT	41.1	5374	6.33	22.0	0.614	3.52
	Hot Mix	32.1	9227	6.83	26.2	0.763	3.66
	ERTFOT	29.5	15644	12.05	25.8	0.739	3.44
	ETFOT	27.1	27095	9.64	26.5	0.828	3.78
COSDEN	Tank	89.0	970	2.61	11.4	0.364	3.57
AC-10 1989	RTFOT	47.0	2571	3.33	15.2	0.488	3.76
	TFOT	50.7	2193	3.18	14.3	0.462	3.73
	Hot Mix	27.5	9854	4.40	19.7	0.894	4.03
	ERTFOT	27.0	7442	6.39	19.1	0.679	3.64
	ETFOT	29.0	7078	4.94	18.6	0.773	3.82
COSDEN	Tank	76.7	2061	3.85	26.3	0.497	3.55
AC-20 1989	RTFOT	46.0	5763	5.96	29.6	0.624	3.60
	TFOT	50.5	4695	5.25	28.6	0.605	3.62
	Hot Mix	47.0	5945	4.98	29.7	0.751	3.75
	ERTFOT	33.2	12533	7.94	32.5	0.788	3.66
	ETFOT	32.7	16620	8.80	32.8	0.793	3.68
EXXON	Tank	61.2	1974	3.64	13.4	0.450	3.58
AC-20 1987	RTFOT	38.8	4372	4.91	15.9	0.544	3.64
	TFOT	38.0	4195	5.02	15.2	0.552	3.61
	Hot Mix	45.9	3304	4.13	18.3	0.571	3.68
	ERTFOT	26.4	8539	6.58	18.5	0.641	3.66
	ETFOT	23.5	11347	7.82	19.6	0.760	3.64
EXXON	Tank	62.8	1809	3.12	10.9	0.377	3.67
AC-20 1987	RTFOT	46.6	2846	3.76	13.1	0.500	3.70
BATCH	TFOT	49.6	3004	3.68	13.0	0.517	3.74
	Hot Mix	41.8	2902	4.02	15.6	0.521	3.65
	ERTFOT	31.8	5056	4.69	15.6	0.607	3.74
	ETFOT	31.1	6564	5.24	16.6	0.715	3.74
EXXON	Tank	64.6	1864	3.43	10.9	0.421	3.60
AC-20 1988	RTFOT	47.6	3203	4.22	13.4	0.469	3.65
	TFOT	47.5	3204	4.28	13.3	0.517	3.64
	Hot Mix	46.6	3615	4.29	16.9	0.683	3.68
	ERTFOT	34.6	5733	5.51	15.9	0.601	3.66
	ETFOT	31.8	7529	6.17	17.1	0.721	3.67
TEXACO	Tank	86.6	2070	4.24	19.3	0.411	3.47
AC-20 1989	RTFOT	58.4	4372	5.66	21.7	0.460	3.53
	TFOT	52.0	4646	5.70	21.8	0.490	3.55
	Hot Mix	44.7	5547	6.23	23.8	0.543	3.55
	ERTFOT	39.1	9651	7.60	24.3	0.569	3.60
	ETFOT	40.4	13678	8.77	25.0	0.641	3.62
TEXAS GULF	Tank	78.4	2209	3.58	16.5	0.472	3.64
AC-20 1989	RTFOT	40.1	6496	5.39	19.7	0.578	3.72
	TFOT	47.1	5610	5.00	19.2	0.583	3.72
	Hot Mix	34.8	8607	5.99	21.4	0.653	3.74
	ERTFOT	29.3	18902	7.68	22.2	0.710	3.83
	ETFOT	28.9	29344	9.07	23.6	0.830	3.85
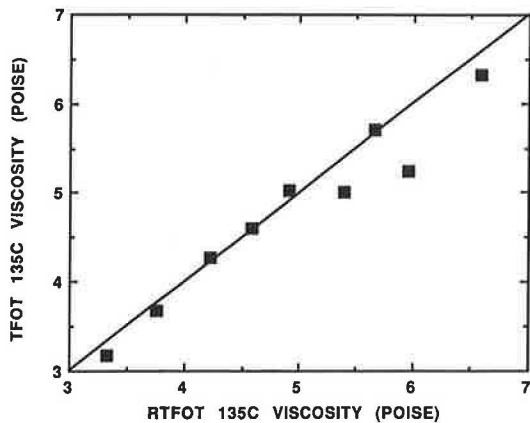
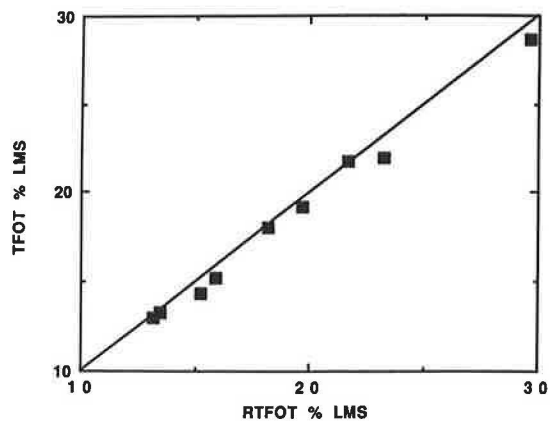FIGURE 1 Comparisons of TFOT and RTFOT viscosity at 135°C.

FIGURE 2 Comparison of %LMS for TFOT and RTFOT aged asphalts.
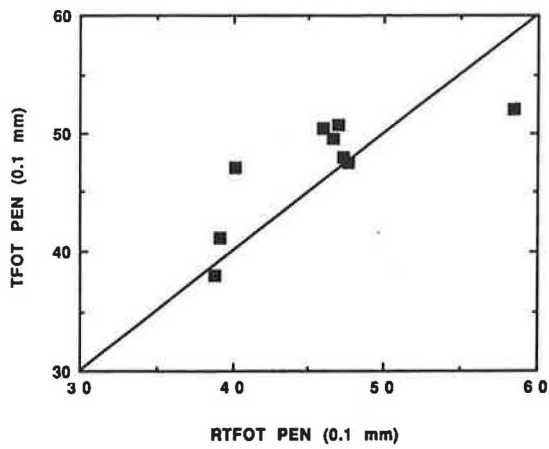
FIGURE 3　Comparison of the penetrations of
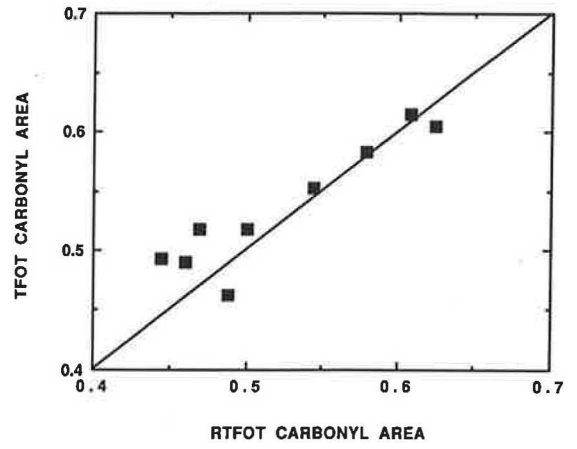TFOT and RTFOT aged asphalts.

FIGURE 5　Comparison of carbonyl areas of IR
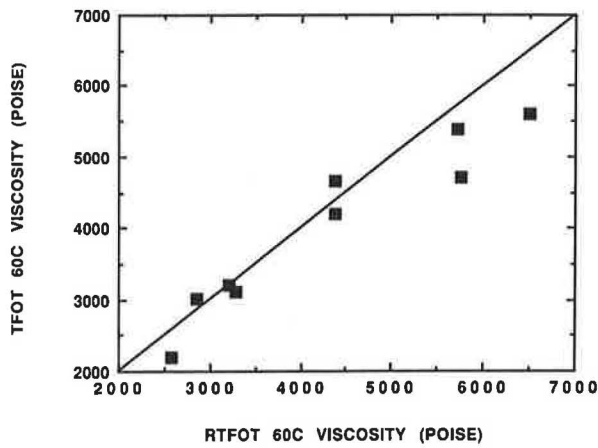spectra of TFOT and RTFOT aged asphalt.

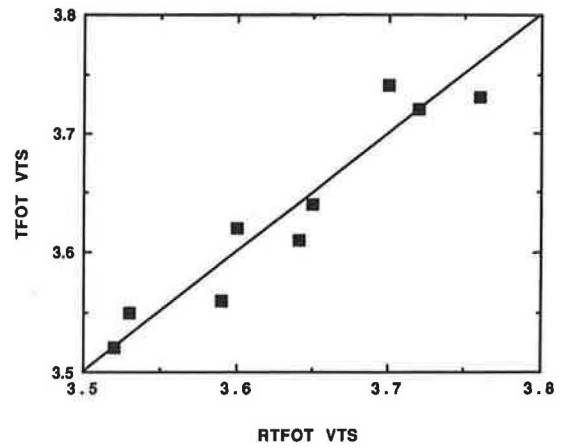FIGURE 4　Comparison of the 60°C viscosities of TFOT
and RTFOT aged asphalts.

FIGURE 6　Comparison of viscosity temperature
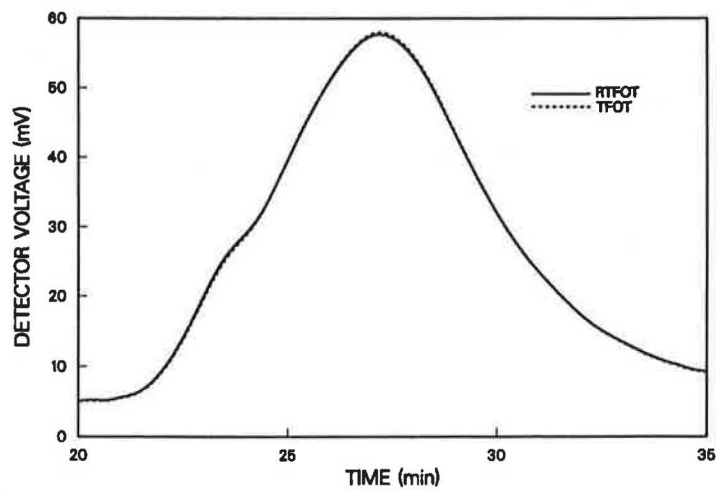susceptibility of TFOT and RTFOT aged asphalts.

FIGURE 7　GPC chromatograms for TFOT and RTFOT of 1989
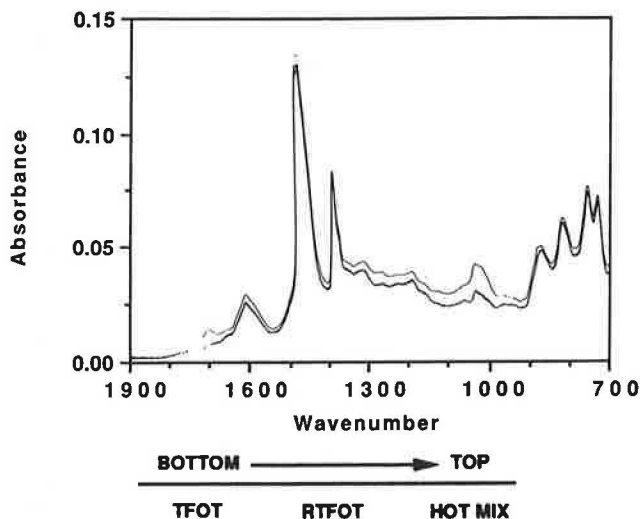Ampet AC-20.

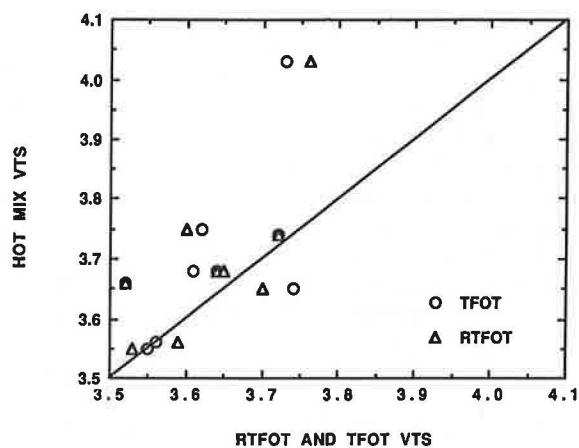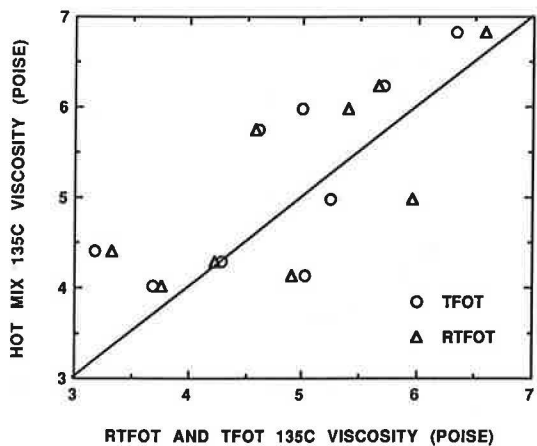FIGURE 8   Comparison of 60°C viscosities of hot-mix and oven-aged asphalts.

FIGURE 11   Comparison of IR carbonyl areas of hot-mix and oven-aged ashpalt.

FIGURE 9   Comparison of 135°C viscosities of hot-mix and oven-aged asphalt.
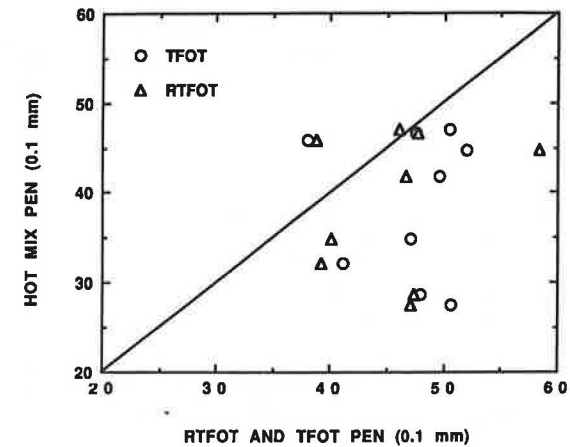
FIGURE 12   Comparison of IR carbonyl areas of hot-mix and oven-aged ashpalt.

FIGURE 10   Comparison of viscosity temperature susceptibility of hot-mix and oven-aged asphalt.
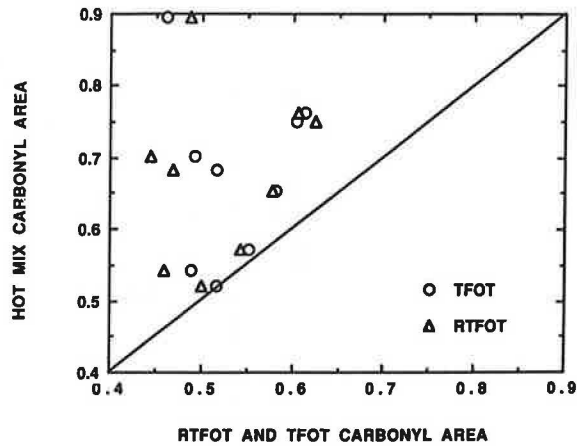
FIGURE 13   Comparison of %LMS for hot-mix and oven-aged asphalts.

Figure 9 indicates that the 60°C (140°F) viscosity is being fairly reproduced for more than half of the samples, but several were badly hardened in the plant. The viscosity at 275°F (135°C), Figure 10, shows better agreement than most properties but has considerable scatter. Both the penetration comparison, Figure 12, and particularly the carbonyl area comparison, Figure 13, show greater change in the hot-mix plant than in the oven tests. In general these comparisons suggest that the hot-mix process is more severe than the oven test.

Only the percent LMS, Figure 14, shows linear variation, but it is displaced to higher hot-mix values. Some of this may be solvent aging. Also percent LMS alone does not reflect all of the aging changes that occur in the GPC chromatograms. Consider the case of the Texaco AC-20. The data in Table 1 show that the percent LMS for the hot mix and the ERTFOT are close, but in Figure 15 the chromatograms are seen to be quite different. The infrared spectra in Figures 8, 16, and 17 are particularly instructive. In Figure 8, the good agreement of the oven tests and their gross disagreement with the hot mix is clearly evident with greater hot-mix aging across the spectrum. Figure 16, however, shows fair agreement in the
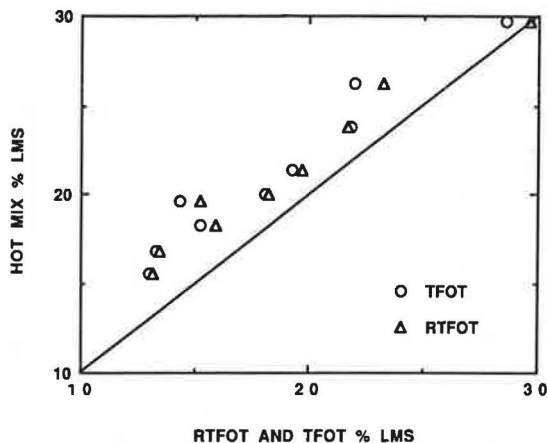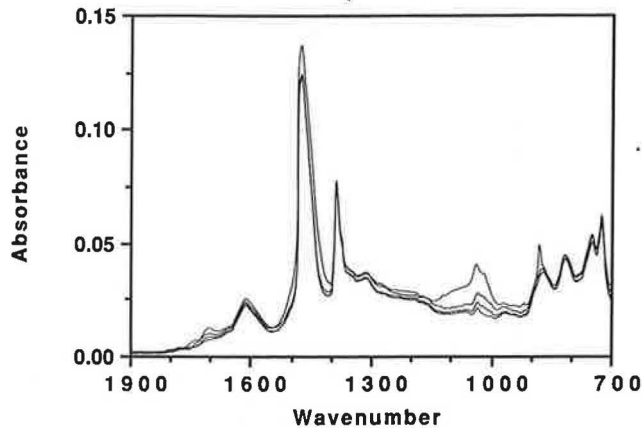

SELECTED WAVENUMBERS	BOTTOM	⟶		TOP
1700	TANK	RTFOT	HOT MIX	ERTFOT
1200	TANK	RTFOT	HOT MIX	ERTFOT
1100	TANK	RTFOT	ERTFOT	HOT MIX
1030	TANK	RTFOT	ERTFOT	HOT MIX

FIGURE 16 Comparison of IR spectra RTFOT, ERTFOT, and hot-mix: 1989 Cosden AC-20.

carbonyl region between the standard oven test and the hot mix but gross divergence in the sulfoxide region. As mentioned earlier, some of this, at least, could be silica contamination, and this is supported by the sharp and unusual peak at about 900, which is probably carbonate. In Figure 17, we see good agreement in the carbonyl region between hot mix and oven test but in the sulfoxide region agreement is best between the ETFOT and the hot mix. The upper curve shows the great hardening for material that is not normally extracted and that is absent from the hot-mix spectra. If this material could be extracted with the rest, the divergence between oven tests and hot mix would be greater.
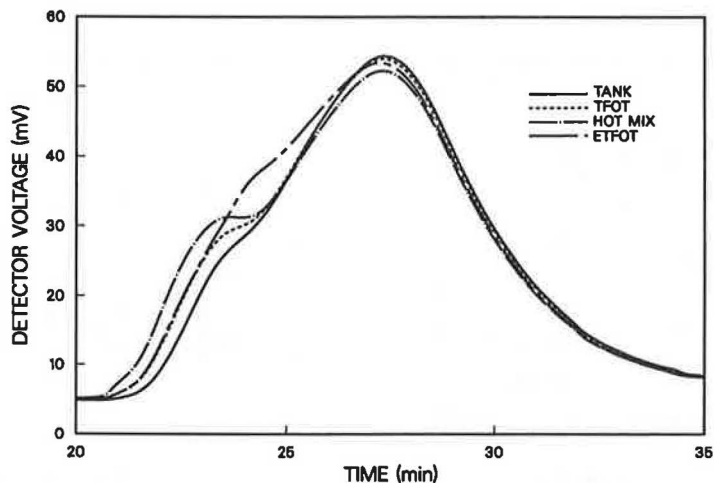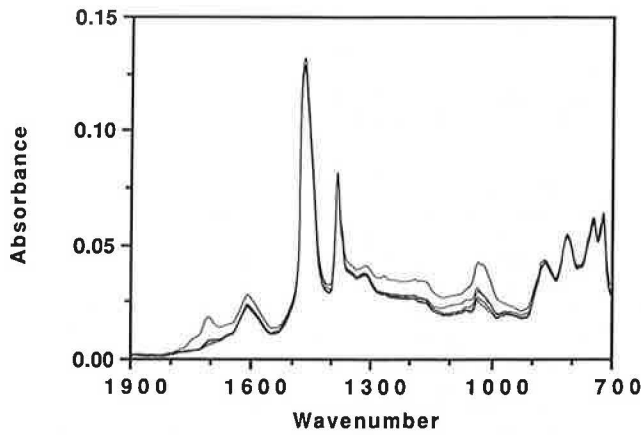

FIGURE 14 GPC chromatograms of tank, TFOT, ETFOT, and hot-mix: 1989 Texaco AC-20.

FIGURE 15 Comparison of IR spectra for TFOT, RTFOT, and hot-mix: 1989 Cosden AC-10.

FIGURE 17 Comparison of IR spectra for oven test and extended oven test with hot-mix and hard-to-remove material: 1987 Exxon AC-20 (drum).

Relation Between Carbonyl Area and Viscosity

Martin et al. (*10*) obtained a very strong correlation between FTIR carbonyl peak height and the viscosity of asphalt extracted from road cores. For a given asphalt, log viscosity varied linearly with the carbonyl peak. A similar correlation was attempted with log viscosity at 60°C and carbonyl area data given in Table 1. The results for all three Exxon asphalts are shown in Figure 18. Even though these asphalts are not identical, being produced at different times, the agreement for the tank and oven-aged samples is not bad. The hot-mix samples appear to form a different population. The same thing is seen in Figure 19 where a very good relation exists for all but the hot-mix point. To a varying degree, this was true for
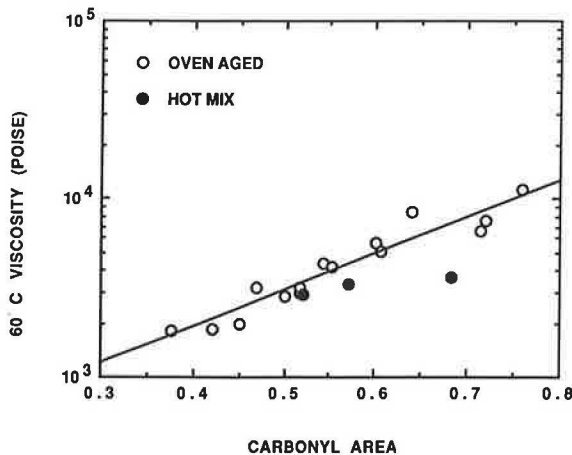

FIGURE 18 Correlation of 60°C viscosity with IR carbonyl area for hot-mix and oven-aged Exxon AC-20.
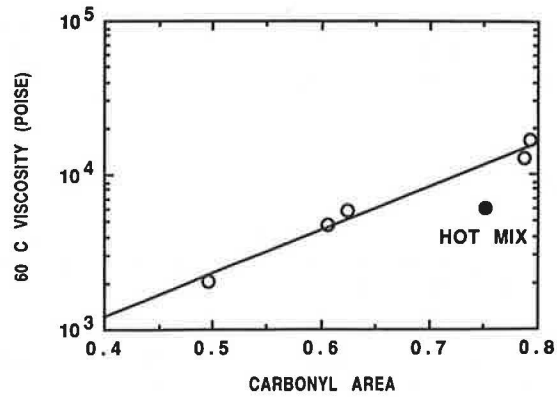

FIGURE 19 Correlation of 60°C viscosity with IR carbonyl area for hot-mix and oven-aged Cosden AC-20.

all asphalts with the hot-mix point invariably below the least square fit of the remaining data.

No identifiable source of error could have produced this. All extracted asphalts were solvent free, and either solvent hardening or fines contamination would tend to produce higher, rather than lower, viscosities. It seems reasonable to postulate that oxidation is occurring by a different mechanism in the hot-mix plant to give a different relation between carbonyl production and viscosity change.

CONCLUSION

As mentioned earlier, the TFOT and RTFOT run at specified standard times would appear to be identical, so that there is little point in running both. On the other hand, the data strongly indicate that the oven tests do not accurately predict the chemical and physical changes occurring in the asphalts during the hot-mix process and, in particular, the FTIR data indicate that different mechanisms may be involved during oxidation.

Problems sometimes arise because the properties of the extracted asphalt are changed during the extraction and recovery processes. Incomplete solvent removal or solvent hardening during extraction and recovery can affect the properties of the recovered hot-mix asphalt, but considerable care was exercised to minimize these effects. Leaving small amounts of asphalt on the aggregate during the extraction can affect the resulting bulk properties, because the asphalt closest to the aggregate surface tends to be more oxidized. The hot-mix properties may also be influenced by the source of the asphalt. In Figure 8, of the 60°C viscosities, the lowest three hot-mix values result from Exxon AC-20 asphalts with which the oven-test values coincide. For this asphalt, using the 60°C viscosity, the oven tests seem to predict the hot-mix properties, but this is not so for the other asphalts. Consequently, the hot-mix properties may be extremely difficult to simulate without accounting for differences in asphalts, the presence of aggregate, and in some cases, incomplete extraction.

ACKNOWLEDGMENTS

REFERENCES

1. R. H. Lewis and J. Y. Welborn. Report on the Properties of the Residues of 50–60 and 85–100 Penetration and Ductility at Plant Mix Temperatures. *Proc., Association of Asphalt Paving Technologists*, Vol. 12, 1940.
2. F. N. Hveem, E. Zube, and J. Skog. Proposed New Tests and Specifications for Paving Grade Asphalts. *Proc., Association of Asphalt Paving Technologists*, Vol. 32, 1963.
3. R. R. Davison, J. A. Bullin, C. J. Glover, B. L. Burr, H. B. Jemison, A. L. G. Kyle, and C. A. Cipione. *Development of Gel Permeation Chromatography, Infrared and Other Tests to Characterize Asphalt Cements and Correlate with Field Performance.* Report FHWA/TX-90/458-1F. Texas Department of Highways and Public Transportation, Austin, Nov. 1989.
4. E. H. Chipperfield, J. L. Duthie, and R. B. Girdler. Asphalt Characteristics in Relation to Road Performance. *Proc., Association of Asphalt Paving Technologists*, Vol. 39, 1970.
5. C. J. Glover, R. R. Davison, S. M. Ghoreishi, H. B. Jemison, and J. A. Bullin. Evaluation of Oven Simulation of Hot-Mix Aging by an FT-IR Pellet Procedure and Other Methods. In *Transportation Research Record 1228*, TRB, National Research Council, Washington, D.C., 1989, pp. 177–182.
6. B. H. Chollar, J. A. Zenewitz, J. G. Boone, K. T. Tran, and D. T. Anderson. Changes Occurring in Asphalts in Drum Dryer and Batch (Pug Mill) Mixing Operations. In *Transportation Research Record 1228*, TRB, National Research Council, Washington, D.C., 1989, pp. 145–155.
7. B. L. Burr, R. R. Davison, C. J. Glover, and J. A. Bullin. Solvent Removal from Asphalt. In *Transportation Research Record 1269*, TRB, National Research Council, Washington, D.C., 1990.
8. P. W. Jennings. *Chemical Composition of Commercial Asphalt Cement as Determined by High Pressure Liquid Chromatography.* Report FHWA-MT-7929. FHWA, U.S. Department of Transportation, Dec. 1977.
9. H. B. Jemison, B. L. Burr, R. R. Davison, J. B. Bullin, and C. J. Glover. Application and Use of the ATR FT-IR Method to Asphalt Aging Studies. Presented at 200th ACS National Meeting, Washington, D.C., Aug. 1990.
10. K. L. Martin, R. R. Davison, C. J. Glover, and J. A. Bullin. Asphalt Aging in Texas Roads and Test Sections. In *Transportation Research Record 1269*, TRB, National Research Council, Washington, D.C., 1990.