

Asphalt Hardening in Extraction Solvents

B. L. BURR, R. R. DAVISON, H. B. JEMISON, C. J. GLOVER, AND
J. A. BULLIN

Hardening occurs in asphalts during extraction and recovery, posing a serious problem for research into the properties of hot-mix and road-aged asphalts. Hardening appears to occur in all solvents and, to varying degrees, in all asphalts. The effects of light, oxygen, and temperature on this phenomenon were investigated. All are significant, and the data indicate that reflux methods of extraction should be avoided when the properties of the extracted material are to be investigated. The mechanism of the hardening is still unclear. Infrared spectra show definite chemical changes, but these are quite asphalt-dependent and do not relate clearly to changes in viscosity.

To study the changes that occur in asphalt as it ages during the hot-mix operation or on the road, asphalt must be extracted from the associated aggregate. Today, this is primarily accomplished by ASTM D2172 using either the centrifuge Method A or the reflux Method B.

Strong evidence exists that the present extraction and recovery methods are either inadequate or being performed improperly in the laboratories nationwide. AASHTO conducts interlaboratory proficiency tests periodically to determine the precision of the methods. It sends identical pavement samples to 50 to 100 laboratories. The laboratories extract and recover the asphalt, perform various tests, and send the results to AASHTO. In a February 1989 report, the coefficient of variance on recovered viscosities was about 25 percent. In earlier years, it has been as high as 42 percent (1).

Errors appear likely to stem from three main areas:

1. The solvent has some hardening effect on the asphalt that increases with temperature and time of exposure.
2. Solvent is often not completely removed from the asphalt during recovery. This results in viscosities that are lower than the true value.
3. Asphalt is not completely removed from the aggregate. The strongly adsorbed material left on the aggregate has a significantly different composition than the bulk asphalt.

PROBLEM AREAS

It is believed that the first two areas of error may be particularly serious. Very low viscosities for recovered asphalt are most likely the result of incomplete removal of asphalt as shown by Burr et al. (2). The rather widespread use of ASTM D2172 Method B, even though it is known that the reflux method hardens asphalt (ASTM D1856-79), probably accounts for many high viscosity values for recovered material.

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

Solvent Aging

It has been known for a long time that asphalts do harden upon exposure to solvents. However, little is known about the causes or extent of solvent aging.

Abson (3) dissolved a 156-penetration asphalt in benzene and let it sit at room temperature for different times. The penetration was down to 147 after 24 hr and 109 after 48 hr. For this reason, he advised that the extraction-recovery process should be completed within 8 hr. He did not study the effect of different solvents, concentration, or temperature. Bussow (4) found that his asphalts did not age when the solvent-asphalt mixture was left in the dark. He suggested that the hardening is due to a photochemical reaction. The literature makes no other mention of this phenomenon.

Abson and Burton (5) tested several chlorinated solvents and showed that some induced severe aging. The worst of these was CCl_4 . An 89-penetration asphalt was dissolved in 4 volumes of CCl_4 at room temperature for 2 to 4 hr before recovering. The residue had a penetration of 56. Another solvent, 1,1,1-trichloroethane, also caused severe hardening.

Abu-Elgheit et al. (6, p. 823) studied effects of different solvents on an asphalt's 77°F viscosity. After refluxing for 2 hr in 4 volumes of solvent, the viscosity-hardening indexes were 1.15 for benzene, 1.45 for benzene-ethanol, 1.9 for trichloroethylene (TCE), and 2.0 for 1,1,1-trichloroethane. Lottman et al. (7) reported a 140°F viscosity index of 1.4 for cold-extracted, Abson-recovered asphalt 16 hr after mixing with trichloroethylene. Bissett (8) contradicted this when he reported no aging after 7 days in trichloroethylene at room temperature. Almost certainly these results are incorrect and are affected by solvent contamination, as demonstrated by results of Noureldin and Manke (9). They experienced hardening after hot extraction in trichloroethylene and remedied it by reducing the recovery temperature to 311°F and time to 6 min. It is likely that they did not correct the aging that occurred in the extraction step, but corrected for it by leaving an amount of solvent that brought the penetration back to its original value. Currently, the safest way to avoid the solvent aging problem is to use a cold extraction method, as ASTM suggests.

Objective

The purpose of this study was to quantify solvent hardening with respect to time of exposure, temperature, and concentration of dissolved asphalt. A variety of solvents, as well as a number of asphalts, were included. Extraneous variables such as dissolved oxygen and light were also investigated.

EXPERIMENTAL METHODS

In general, asphalt was dissolved in solvent at various concentrations such as 20 g in 400 mL (5 percent) or in 800 mL (2.5 percent). These were allowed to stand for a specified period of time either at room temperature or at a controlled temperature. In most instances, the asphalt was recovered, although in some instances the solutions were injected directly into the gel permeation chromatograph (GPC).

A variety of conditions were used to assess the effect of oxygen, light, and preaging on solvent aging. In some instances the solution was deoxygenated by bubbling with CO₂ or N₂. This was either done to the solvent before dissolution or to the solution just after dissolving the asphalt. In some experiments, oxygen was bubbled through the solvent to achieve CO₂ saturation. In other experiments, solvents directly from the bottle were used (designated by "air"). Three levels of light were employed: dark, low hood light, and strong fluorescent light. Several experiments were performed on an Exxon AC-20 that had been air blown to 20,000 poises.

Most recoveries designated "hot" were in a roto-vap at atmospheric pressure. Those designated "cold" were under sufficient vacuum that the solvent temperature was near room temperature. The time and temperature were chosen to ensure complete solvent removal (2).

In the GPC analyses, a 500Å/50Å column combination was used. Tetrahydrofuran was used as a solvent with a flow rate of 1 mL/min. Injection volumes were 100 µL. The instrument was an IBM Model LC-9533 high-performance liquid chromatography- (HPLC-) equipped with a Waters refractive index detector.

Infrared analyses were made with a Nicolet 60 SX Fourier transform infrared (FT IR) single-beam spectrometer using an attenuated total reflectance method. In this procedure, the beam passes through a zinc selenide prism and is reflected

from the prism-asphalt sample interface back through the prism to the detector. The asphalt is softened and spread directly on the prism surface.

The primary measure used to monitor solvent hardening was the viscosity at 60°C, ASTM D2171.

RESULTS

It had been observed that GPC chromatograms tend to shift to larger molecular size on standing. It was thought that this might be used as a convenient solvent-aging tool. An American Petrofina AC-10 asphalt was dissolved in a variety of solvents at 7 percent by weight. Samples were aged for up to 5 days at room temperature, 50°C, and 100°C. The results were erratic, but it was clear that increasing temperature increased aging, in all solvents. Typical chromatograms at 100°C and 50°C are shown in Figures 1 and 2.

An extensive set of experiments, shown in Table 1, was conducted with a single asphalt at room temperature. A number of solvents were used, recovery was both hot and cold, and varying levels of light and oxygen exposure were studied. Viscosities at 60°C were run on the recovered asphalt and compared to the viscosity of the original asphalt. Some results for trichloroethylene and for trichloroethylene containing 15 percent ethanol are shown in Figure 3. The samples subjected to high levels of light or oxygen saturation are excluded. Except for one datum, there seems to be no effect from low light or using solvent directly from the bottle without degassing. Some rapid hardening apparently occurs in the beginning or during recovery, though with many asphalts and perhaps all tank asphalts, part of this is loss of volatiles during recovery.

Figure 4 shows the rest of the data. Prehardened asphalt still solvent hardens at about the same rate as tank asphalt. All the solvents appear about equal in hardening except CCl₄,

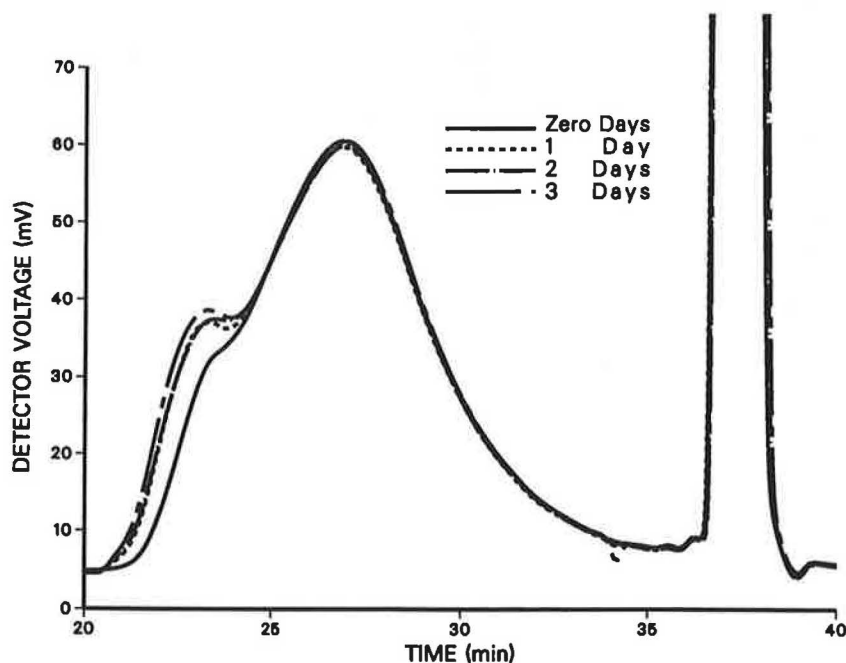


FIGURE 1 GPC chromatograms accompanying asphalt solvent hardening: 7 percent Ampet AC-10 in toluene at 100°C.

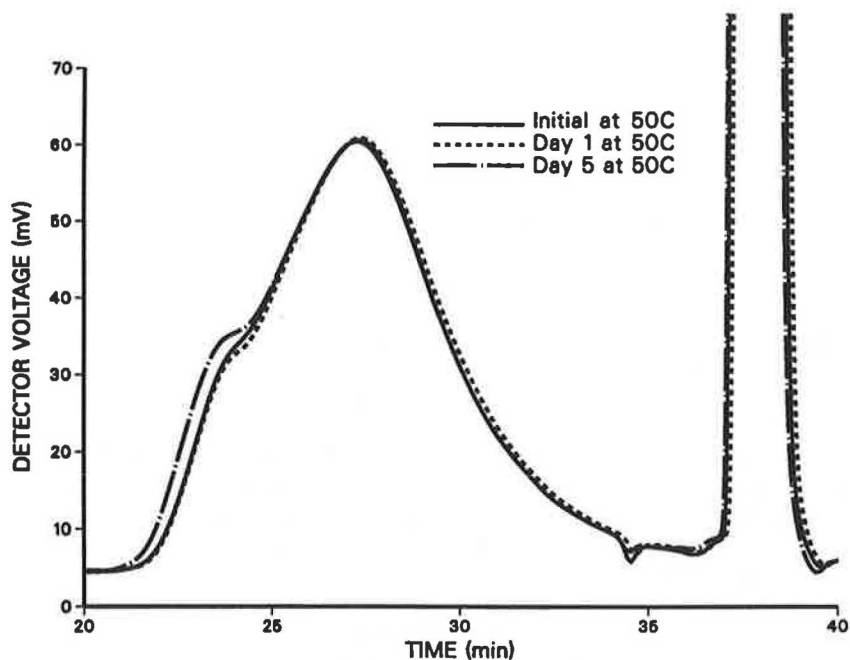


FIGURE 2 GPC chromatograms accompanying asphalt solvent hardening: 7 percent Ampet AC-10 in toluene at 50°C.

TABLE 1 SOLVENT HARDENING EXPERIMENTS

Asphalt	Solvent % Asphalt	Recovery	Gas	Light	Time(hrs)	%Diff Visc
1 EXXON AC-20	TCE 5%	HOT	AIR	LOW	96.000	66.900
2 EXXON AC-20	TCE 5%	HOT	AIR	NO	7.000	21.500
3 EXXON AC-20	TCE 5%	HOT	AIR	NO	20.000	26.800
4 EXXON AC-20	TCE 5%	HOT	AIR	NO	49.000	34.300
5 EXXON AC-20	TCE 5%	HOT	AIR	NO	116.000	43.400
6 EXXON AC-20	TCE 5%	HOT	AIR	NO	1032.000	105.000
7 EXXON AC-20	TCE 5%	HOT	AIR	LOW	1.000	18.600
8 EXXON AC-20	TCE 5%	HOT	AIR	LOW	0.250	13.700
9 EXXON AC-20	TCE 5%	COLD	AIR	LOW	0.250	9.800
10 EXXON AC-20	TCE 5%	HOT	O ₂	BRIGHT	48.000	71.600
11 EXXON AC-20	TCE 5%	HOT	N ₂	NO	48.000	37.800
12 EXXON AC-20	TCE 5%	COLD	N ₂	BRIGHT	48.000	35.000
13 EXXON AC-20	TCE 5%	COLD	O ₂	NO	48.000	26.000
14 EXXON AC-20	TCE 5%	HOT	DEGASSED	BRIGHT	48.000	74.700
15 EXXON AC-20	TCE 5%	HOT	DEGASSED	NO	48.000	39.100
16 EXXON AC-20	TCE 5%	HOT	O ₂	BRIGHT	48.000	86.800
17 EXXON AC-20	TCE 5%	HOT	O ₂	NO	48.000	60.900
18 EXXON AC-20	CHCL ₃ 5%	HOT	AIR	LOW	48.000	38.700
19 EXXON AC-20	CH ₂ CL ₂ 5%	HOT	AIR	LOW	48.000	33.000
20 EXXON AC-20	111 TCE ane	HOT	AIR	LOW	48.000	34.300
21 EXXON AC-20	TCE/ETOH	HOT	AIR	LOW	48.000	34.700
22 EXXON AC-20	TCE 5%	HOT	AIR	NO	48.000	34.300
23 EXXON AC-20	CCL ₄ 5%	HOT	AIR	LOW	48.000	91.200
24 EXXON AC-20	TOLUENE	HOT	AIR	LOW	48.000	36.900
25 EXXON AC-20	12 DCE	HOT	AIR	LOW	48.000	39.600
26 EXXON AC-20	TCE/ETOH	HOT	AIR	NO	0.250	10.800
27 EXXON AC-20	TCE/ETOH	HOT	AIR	NO	1.300	15.700
28 EXXON AC-20	TCE/ETOH	HOT	AIR	NO	4.750	20.100
29 EXXON AC-20	TCE/ETOH	HOT	AIR	NO	6.670	17.800
30 EXXON 20kP	TCE 5%	HOT	AIR	NO	69.000	45.200
31 EXXON 20kP	TCE 2.5%	HOT	AIR	LOW	0.250	17.200
32 EXXON 20kP	TCE 2.5%	COLD	AIR	LOW	0.250	7.990
33 EXXON 20kP	TCE 5%	COLD	AIR	LOW	0.250	17.700

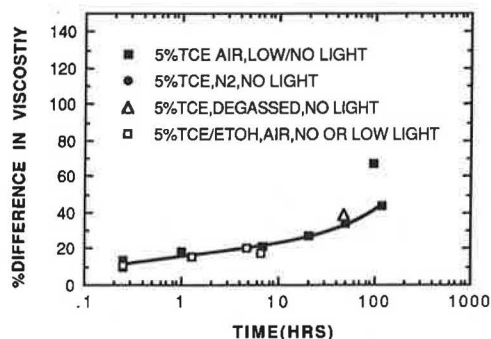


FIGURE 3 Solvent Hardening (60°C viscosity increases): 5 percent asphalt in trichloroethylene without oxygen or strong light.

which causes much greater hardening. As would be expected, some of the oxygen-containing samples hardened considerably. Light also seems to accelerate hardening both with and without oxygen. However, Runs 12 and 13 appear inconsistent. There is no proof here that cold recovery under vacuum reduces aging, but it appears logical and needs further study.

The next set of experiments used a single asphalt from the core asphalts of the Strategic Highway Research Program (SHRP) to investigate the effect of asphalt concentration on solvent aging. In addition, the effect of degassing was further explored, and one experiment was conducted at 0°C. Also, a direct comparison is made between the hardening properties of trichloroethylene/15 percent ethanol and toluene/15 percent ethanol.

The solvent aging (hardening index, viscosity at 60°C) results for 48-hr incubation times for SHRP asphalt AAK-1 (Boscan) in a variety of solvent systems and over a range of concentration are shown in Figure 5. For comparison, a result is shown that was obtained at an AAK-1 asphalt concentration of 0.05 g/mL in trichloroethylene/ethanol with zero incubation time. This point is actually three experiments that produced exactly the same result, approximately 11 percent hardening. All other steps of the procedure followed were the same. Based on our results for other asphalts, this is a normal amount of hardening, apparently due to volatiles loss from the virgin or unaged materials.

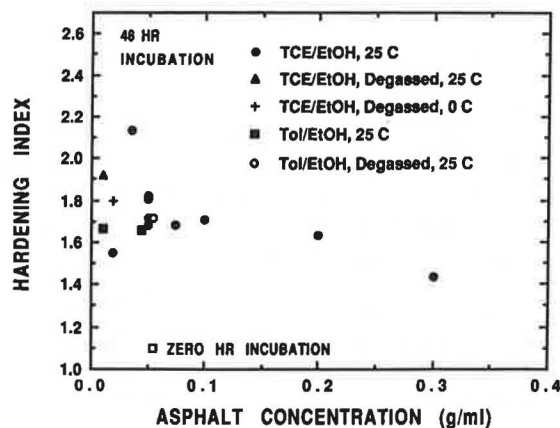


FIGURE 5 Solvent aging of asphalt AAK-1 in dilute solution.

The trichloroethylene/15 percent ethanol solvent systems showed gradually increasing hardening with decreasing asphalt concentration over the range of asphalt concentration up to 0.3 g/mL. The increase with decreasing concentration was not great, however; the total range in hardening index rose from about 1.45 to about 1.8. However, the low concentrations may be less reproducible than the higher concentrations. The degree of hardening for the 48-hr incubation time is very significant, much greater than that attributed to volatiles loss.

The comparisons between trichloroethylene/ethanol and toluene/ethanol were made at an asphalt concentration of 0.05 g/mL and at 0.01 g/mL. No significant difference between the toluene system and the trichloroethylene system is observed for these two experiments. The solutions degassed before incubation show no difference from those that were not degassed. Also, the solution that was incubated at 0°C rather than at 25°C shows no difference. These results are somewhat puzzling.

It is interesting to speculate as to what this reveals about the mechanism of solvent hardening. Figures 1 and 2 show that solvent hardening is accompanied by an increase in large molecular size material. If this occurs from multibody collisions, one would expect the hardening to decrease with concentration, but Figure 5 suggests the opposite.

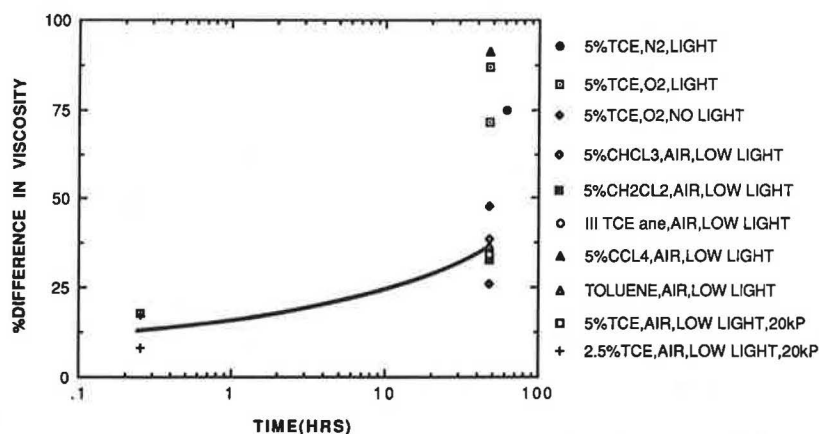


FIGURE 4 Solvent hardening in various solvents and the effect of oxygen and strong light.

Figure 6 shows the large molecular size (LMS) region (defined as the fraction of the chromatograph area that elutes before 25 min) plotted as a function of asphalt concentration in tetrahydrofuran. A large number of asphalts were analyzed in this way, and all but the one, which has no asphaltene, showed the positive slope as in Figure 6. The samples were run immediately following dissolution, so little solvent hardening has occurred. Figure 6 indicates a partial dissociation of LMS material to be occurring at high dilution that evidently increases the reactivity of this material but tells us nothing of the nature of the reactions.

Solvent hardening appears to occur to roughly the same degree in most solvents, so it is not a reaction between asphalt and solvent. It also occurs with all asphalts that have been investigated and is much more asphalt- than solvent-dependent. Figure 7 shows solvent hardening versus time for three asphalts. The contact was in trichloroethylene/15 percent ethanol at room temperature in the dark in contact with air followed by cold recovery. Again aging is rapid in the beginning, partly because of volatiles loss during recovery, and then the effect slows gradually with time. Most significant, however, is the much more rapid hardening of the California Coastal asphalt.

In the next set of experiments, all the SHRP asphalts were hardened for 48 hr in trichloroethylene/15 percent ethanol and toluene/15 percent ethanol at room temperature in the

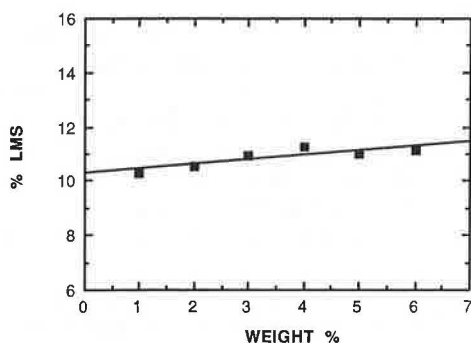


FIGURE 6 GPC percent LMS versus concentration for 1989 Exxon AC-20.

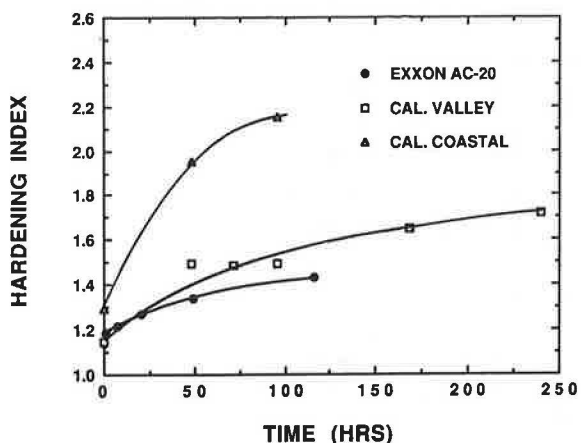


FIGURE 7 Effects of time on solvent hardening of various asphalts at 5 percent in trichloroethylene/ethanol solutions at 25°C.

dark in contact with air and cold recovered. Another identical set was recovered immediately. The results are shown in Figure 8, plotted versus SHRP (10) values for thin film oven (TFO) aging. The correlation coefficients are $r^2 = .65$ for trichloroethylene, .32 for toluene, and .097 for the instant recovery. Obviously, there is no apparent relation between initial solvent hardening and TFO aging, which is hardly surprising as this includes volatiles loss on recovery. Although there is considerable scatter, it appears that for most of these asphalts a relation exists between solvent and oxidative hardening. If it were not for two very low data for toluene, the correlations would be indistinguishable. Actually, one might expect somewhat lower hardening in toluene because it is a poorer solvent that leads to more aggregation or association in solution (11,12, p. 240).

Although solvent aging and oxidative aging must be by different mechanism, they may both be affected by some inherent reactivity of a given asphalt. To further explore the solvent aging mechanism, infrared spectra were run on the SHRP asphalts and a number of others, some of which had been subjected to light and oxygen. It has already been shown above that light and oxygen accelerate solvent hardening; furthermore, infrared changes accompany this hardening and are similar to those observed for oxidative oven aging.

The spectra of asphalts aged in the absence of light and oxygen corresponding to the asphalt aging in Figure 8 are far more interesting. Five of these are shown in Figures 9–13. On each figure, the spectra before and after hardening are shown. The results raise more questions than they answer. For instance, for asphalt AAA-1, Figure 9 shows almost no change in infrared but has a viscosity increase of 52 percent. Asphalt AAC-1 (Figure 10) hardened an almost identical 53 percent but shows a rise in the spectrum over a broad width. Asphalt AAG-1 (Figure 11) also hardened 50 percent but shows a spectral change similar to that of slight oxidative aging, that is, an increase in the carbonyl area at 1,700 and the sulfoxide region at 1,030. Asphalt AAK-1 (Figure 12) hardened 77 percent and shows a spectral change different from the above. The carbonyl area is shifted to about 1,735 and a distinct area appears at about 1,270. These bands correspond well to cyclic anhydrides or certain esters. Asphalt AAD-1 (Figure 13), on the other hand, shows a large change

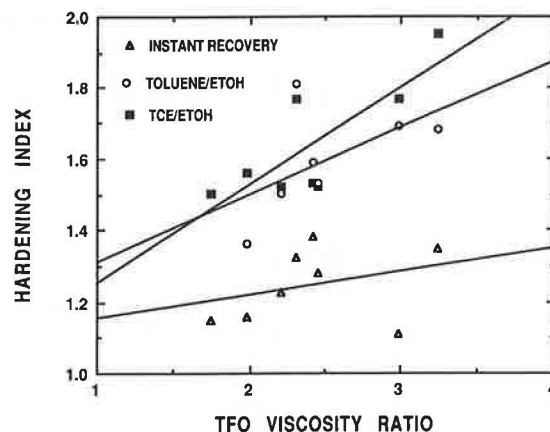


FIGURE 8 Comparison of SHRP asphalt's solvent aging and volatiles loss hardening to TFO aging.

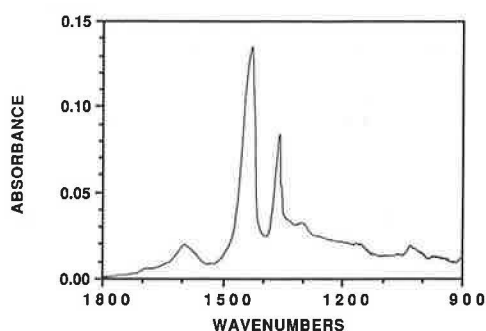


FIGURE 9 IR spectrum of SHRP AAA-1 asphalt aged at 5 percent in trichloroethylene/ethanol for 2 days at 25°C.

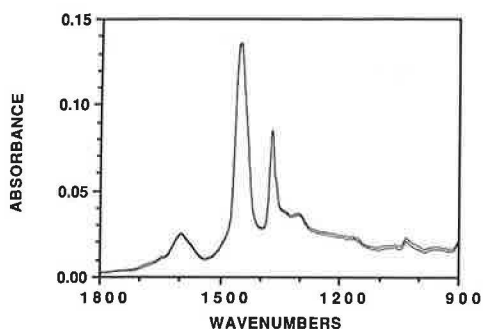


FIGURE 10 IR spectrum of SHRP AAC-1 asphalt aged at 5 percent in trichloroethylene/ethanol for 2 days at 25°C.

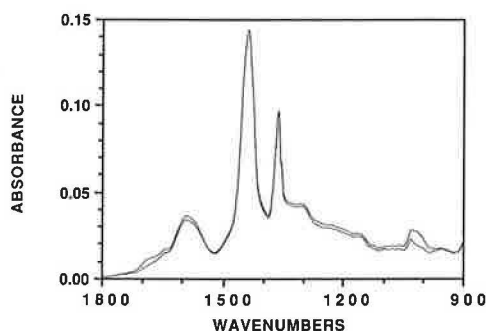


FIGURE 11 IR spectrum of SHRP AAG-1 asphalt aged at 5 percent in trichloroethylene/ethanol for 2 days at 25°C.

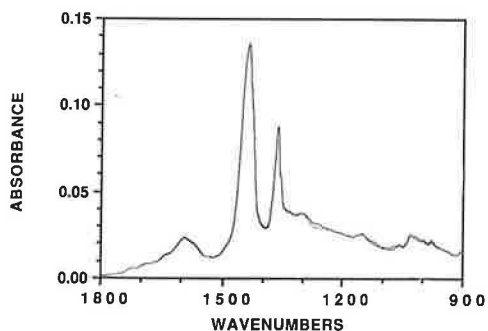


FIGURE 12 IR spectrum of SHRP AAK-1 asphalt aged at 5 percent in trichloroethylene/ethanol for 2 days at 25°C.

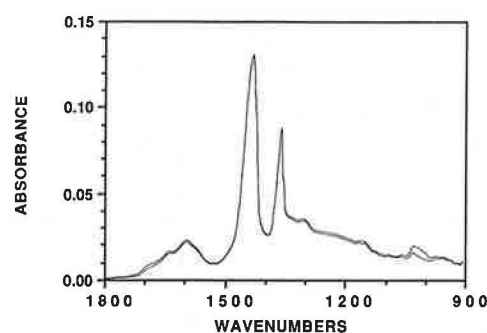


FIGURE 13 IR spectrum of SHRP AAD-1 asphalt aged at 5 percent in trichloroethylene/ethanol for 2 days at 25°C.

all across the spectrum and also exhibited the greatest viscosity change of 95 percent.

Chemical changes occur in most but not all asphalts during solvent hardening, and the changes vary with the asphalt. No obvious relation between these chemical changes and the viscosity change is yet evident. The only consistent datum is that the large infrared spectrum change did occur in the most hardened asphalt.

CONCLUSIONS

Solvent aging appears to occur in all solvents and is, to some extent, unavoidable when extracting asphalt from aggregate. It is definitely a concern when the asphalt is being extracted for a study of properties. It can be minimized by using cold extraction and completing recovery of the resulting solutions as rapidly as possible.

The mechanism is still unclear and is worthy of further study. Like oxidative aging, it involves changes that increase the fraction of large molecular size material, but the mechanism must be quite different, as it occurs in the absence of oxygen, but sensitivity by an asphalt to one seems to correlate with sensitivity to the other. The infrared spectra indicate chemical changes occur, but unlike oxidative hardening, the species formed vary from asphalt to asphalt and do not seem to be related necessarily to the hardening process.

ACKNOWLEDGMENTS

Support for this work by the Texas State Department of Highways and Public Transportation, in cooperation with FHWA, and by SHRP is gratefully acknowledged. Helpful discussions with Don O'Connor and Darren Hazlett and the technical contributions of Ana Laura G. Kyle are greatly appreciated.

REFERENCES

1. AASHTO Materials Reference Laboratory Report for Bituminous Concrete Proficiency Samples. Reports from 1987, 1988, 1989 tests. National Bureau of Standards, Gaithersburg, Md.
2. 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.

3. G. Abson. Method and Apparatus for the Recovery of Asphalt. *Proc., ASTM II*, 1933, pp. 704–714.
4. C. Bussow. Notes on a Method of Recovering Bitumen from Paving Materials. *Proc., Association of Asphalt Paving Technologists*, Vol. 7, 1936, pp. 160–164.
5. G. Abson and C. Burton. The Use of Chlorinated Solvents in the Abson Recovery Method. *Proc., Association of Asphalt Paving Technologists*, 29, 1960, pp. 246–252.
6. M. A. Abu-Elgheit, C. K. Hancock, and R. N. Traxler. Effect of Selected Solvents on the Viscosities and Oxygen Contents of Asphalts. *Analytical Chemistry*, 41, May 1969.
7. R. P. Lottman, S. K. Sonawala, and M. Al-Haboobi. Change of Asphalt Viscosity During Mixing with Hot Aggregates. *Proc., Association of Asphalt Paving Technologists*, Vol. 32, 1963, pp. 1–36.
8. J. R. Bissett. Changes in Physical Properties of Asphalt Pavement with Time. *Bulletin 41*, HRB, National Research Council, Washington, D.C., 1962, pp. 211–220.
9. M. S. Noureldin and P. G. Manke. Study of Transverse Cracking in Flexible Highway Pavements in Oklahoma. In *Transportation Research Record 695*, TRB, National Research Council, Washington, D.C., 1978, pp. 28–32.
10. *Properties of Materials Reference Library Asphalt Cements*, Strategic Highway Research Program, National Research Council, Washington, D.C., 1990.
11. G. R. Donaldson, J. A. Bullin, R. R. Davison, C. J. Glover, and M. W. Hlavinka. The Use of Toluene as a Carrier Solvent for Gel-Permeation Chromatography Analysis of Asphalt. *Journal of Liquid Chromatography*, Vol. 11, 1988, pp. 749–765.
12. K. H. Altgelt and O. L. Harle. The Effect of Asphaltenes on Asphalt Viscosity. *Industrial and Engineering Chemistry Product Research and Development*, Vol. 14, 1975.

The contents of the paper reflect the views of the authors, who are responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of FHWA, the Texas State Department of Highways and Public Transportation, or SHRP. This paper does not constitute a standard, specification, or regulation.

Publication of this paper sponsored by Committee on Characteristics of Bituminous Materials.