

# Softening of Asphalts in Dilute Solutions at Primary Distillation Conditions

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Softening of asphalts in dilute solutions, often by as much as 50 percent, occurred in several instances during experiments using a modified Roto-vap recovery technique. The softening is caused by a mechanism that is characterized by Fourier transform infrared spectroscopy spectral growth near the traditional carbonyl region associated with oxidative hardening, as well as other minor changes. Gel permeation chromatograms of solvent-softened asphalts show formation of one and sometimes two new narrow peaks, suggesting that the reactions produce a very narrow range of products. Reaction rates vary considerably with asphalt source, solvent, and solution conditions. The rates also increase considerably with Roto-vap oil bath temperature from 102°C to 149°C. Reaction rates decrease with concentration, being almost nonexistent at 0.12 g/mL but generally significant at 0.06 g/mL. Reactions proceed faster in more polar extraction solvents, such as trichloroethylene with 15 percent ethanol (TCE/EtOH), than in toluene with 15 percent ethanol. Inhibitors such as butylated hydroxy toluene slow the reactions but do not appear to affect the extent of reaction. Compatible asphalts (such as SHRP AAG-1) react fastest at lower temperatures, whereas incompatible but reactive asphalts (SHRP AAK-1) react fastest at higher temperatures. The reactions appear to be dependent on the solvent's ability to dissolve associated species. However, the reactions have also been detected in dissolved maltene fractions. Care should be taken to avoid exposing asphalts in dilute solutions (below 0.15 g/mL) to temperatures above 93°C, especially in polar solvents such as TCE/EtOH, for extended periods of time.

Recently, several new modifications of the SHRP extraction and recovery method (1) have been made that speed the procedure time and reduce the sample size. One of these is an In-can recovery flask, which allows for the recovery of asphalt directly into an asphalt tin. It leaves no asphalt residue on a round-bottom flask and therefore reduces the initial sample size from about 50 to about 25 g. Also, the continuous addition of extract into the Roto-vap during primary distillation stabilizes boiling. This improvement speeds distillation considerably, to about 2.5 L/hr, so long as the oil bath temperature is raised from 100°C to about 121°C to provide the necessary heat. With the advent of the In-can final recovery method, frequent instances of asphalt softening began to occur within this laboratory. During verification of a new extraction and recovery procedure (called the Auto method in this paper), asphalts often had about half the viscosity of other identical asphalts using the SHRP method and ASTM D-2172A (Method A). During calibrations with Method A using portions of Asphalt Materials Reference Library (AMRL) test mixtures, the Auto method yielded much softer asphalts and the Fourier transform infrared (FT-IR) spectra showed a new peak at 1735 cm<sup>-1</sup> just to

the left of the carbonyl peak associated with oxidative hardening (2). Large-scale Corbett fractions (3) being similarly concentrated from heptane solutions were often soft and had the mysterious FT-IR peak at 1735 cm<sup>-1</sup>. When these softening phenomena started to appear within a short period of time, it was not clear whether the cause was some sort of contamination through the In-can flask's O-ring seal or a new form of reaction that occurs in solution under In-can recovery conditions.

## BACKGROUND

In prior studies of different extraction and recovery methods, reactions of asphalts in extraction solvents have been reported; such reactions raise the recovered asphalt viscosities by up to 100 percent. These reactions may occur at different rates in different solvents. Chlorinated extraction solvents were suspected of participating in these reactions (4), but it was also shown later that the reactions occur in nonchlorinated solvents with the rates being more a function of a solvent's ability to dissolve an asphalt (5). The susceptibility of SHRP asphalts to harden in extraction solvents was shown to correlate reasonably well with RTFO aging. However, the reaction mechanisms are not identical because carbonyl growth does not consistently follow solvent hardening as in oxidative aging (5). These solvent hardening reactions occur at temperatures as low as room temperature. The rates increase as the asphalt concentration in solution is lowered from about 0.4 to about 0.1 g/mL. Below 0.1 g/mL, solvent hardening becomes difficult to reproduce (5). The SHRP extraction and recovery procedure was designed to avoid solvent hardening by using low recovery temperatures and maintaining high asphalt concentrations (1).

The literature has no mention of reactions that soften asphalt while in high temperature or dilute solutions or of the strange FT-IR peaks near the oxidative aging carbonyl region.

## EXPERIMENTAL PROCEDURES

### Softening Experiments Simulating Solvent Recovery

To find conditions where solvent softening of asphalt occurred during solvent removal, asphalts were dissolved at various concentrations in several solvents and boiled in a 1000-mL round-bottom flask attached to a rotary evaporator. Distillate was continuously drawn and fresh solvent continuously charged to simulate real recovery conditions. Aliquots of solution were re-

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moved after each hour for 3 hr. The dissolved hourly samples were measured by FT-IR using a film casting technique. The asphalts in the bulk solution were recovered for subsequent GPC and viscosity analysis.

The temperature of the bulk solution was primarily determined by the solution's boiling point under the applied vacuum of 660 mm Hg. This is about 38°C for trichloroethylene with 15 percent ethanol (TCE/EtOH) and 60°C for toluene with 15 percent ethanol (Tol/EtOH). However, as the temperature of the solution film approaches the oil bath temperatures, the reaction rates are affected, as will be shown later. The reason oil bath temperatures were used in this analysis is that they best describe recovery conditions in which these reactions are pertinent.

### Longer-Term Solvent Softening Experiments

Asphalt samples (0.05 g/mL of TCE) were mixed with varying levels of the oxidation inhibitor, butyl-hydroxytoluene (BHT). Solutions were held at 70°C for several days. About 500-mL aliquots were removed after each day and recovered using the In-can procedure. The recovered asphalts were analyzed by viscometry, GPC, and FT-IR.

### Property Analyses

FT-IR spectra were obtained using a Mattson Galaxy Series 5000 spectrometer. Most of the recovery simulation samples were still in solution and had to be film-cast onto the prism. The other samples were applied as melts (6). In film-casting, a few drops of the asphalt solution are placed on the zinc selenide prism, and the solvent is driven off by evaporation and final drying with a hot air gun. This results in a several-micron layer of asphalt on the prism surface, which is free of solvent. The use of the hot air gun does not appear to affect asphalt properties. Viscosities of recovered samples were taken with the Carri-Med 500 CSL rheometer. GPC analyses were performed on a Waters HPLC system fitted with 1000 and 500 Å Ultrastaygel columns and a 50 Å PL Gel column using tetrahydrofuran flowing at 1 mL/min as the carrier solvent.

### Samples and Materials

Exxon AC-20 tank asphalt was used in the recovery simulation tests. Apparently, the Exxon AC-20 used in one series of tests was different from that used in some later experiments because common tests showed extreme differences in reaction rates. Therefore, these asphalts will be designated Exxon 1 and Exxon 2. Unfortunately, reasons for these differences are unknown. SHRP Asphalts AAG-1 and AAK-1 were mixed with the oxidation inhibitor and held at 70°C for longer periods. AMRL Asphalt Concrete Samples 37 and 38 were extracted using the Auto method with TCE/EtOH as the solvent and compared with Method A extractions. Extraction or solvent-softening reaction solvents were toluene and TCE with and without 15 percent ethanol additions. Pure BHT from DuPont Petroleum Chemicals was added in varying levels to solutions aged at 70°C.

## RESULTS AND DISCUSSION

### AMRL Proficiency Samples

To determine how the Auto extraction method performed against a large sample of extractors nationwide, two AMRL proficiency samples (37 and 38) were extracted. These were 500-g portions of the samples sent to the asphalt materials group at the Texas Transportation Institute. Unfortunately, the viscosities of the Auto extracted samples 37 and 38, respectively, were 5,700 and 3,600 poise (570 and 360 Pa·s), whereas the Method A extracted viscosities were 10,200 and 7,500 poise (1,020 and 750 Pa·s). The FT-IR spectra of the Auto and Method A extracted AMRL 37 asphalts were also quite different, as shown in Figure 1. There are four spectral regions where serious differences arise. From 1697 to 1770  $\text{cm}^{-1}$  (Peak 1), just to the left of the carbonyl peak that tracks oxidative aging, is a large, sharp peak. The peak is as large as the carbonyl peaks found in asphalts aged to several million poise. Another range of growth in the spectrum occurs from 1213 to 1329  $\text{cm}^{-1}$  (Peak 2). This area contains a region from 1300 to 1329  $\text{cm}^{-1}$ , which had previously shown signs of correlating with viscosity and oxidation. Another region that increases during solvent softening is from 1098 to 1150  $\text{cm}^{-1}$  (Peak 3). Absorbance in sulfoxide region, from 985 to 1051  $\text{cm}^{-1}$ , decreased during solvent softening.

### Recovery Simulations with Solvent Softening

After several attempts to detect oil leakage through the In-can recovery flask O-ring, it seemed probable that the new peaks were caused by reactions in solution rather than contamination. If it were a reaction, peak growth rates should change with temperature or asphalt concentration. Exxon 1 (30 g) samples were dissolved in TCE/EtOH to give 0.06 g sample/mL solution and refluxed under 660 mm Hg vacuum (100 mm Hg absolute) at oil bath temperatures of 102°C, 124°C, and 149°C. After each hour of refluxing, a 10-mL aliquot of solution was removed for analysis. After 3 hr, the asphalt was recovered. Figure 2 shows the FT-IR spectra from 700 to 1900  $\text{cm}^{-1}$  for the batch run at 149°C. Growth

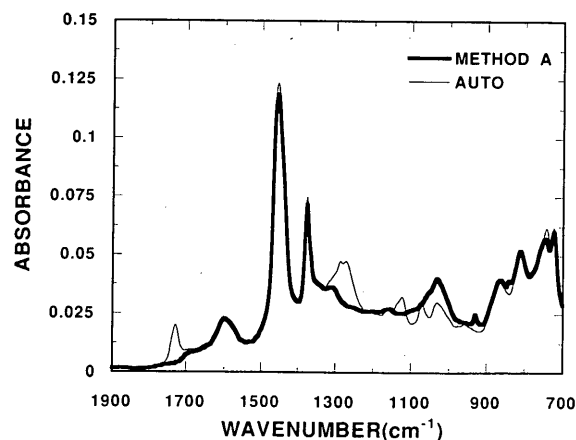


FIGURE 1 Comparison of FT-IR spectra for an asphalt binder extracted and recovered from aggregate by two methods.

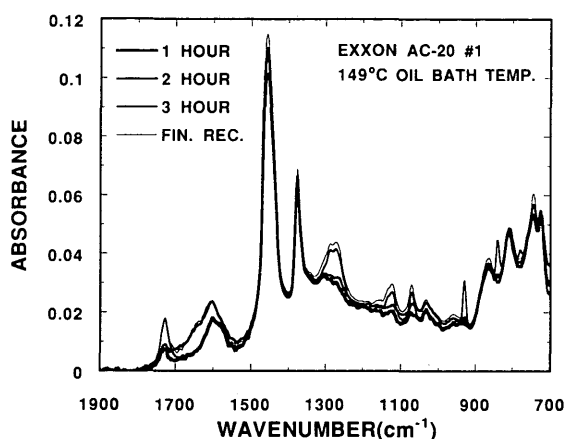


FIGURE 2 Effect of incubation time on the FT-IR spectra of Exxon AC-20 (0.06 g/mL TCE/EtOH, 149°C oil bath).

over time is apparent for Peaks 1, 2, and 3, but the sulfoxide region does not show a decrease as in the AMRL samples. However, there was a large amount of initial sulfoxide in the AMRL samples, whereas there was very little in the Exxon AC-20. Sulfoxides may be eliminated in the solvent softening process, but their presence does not appear necessary for the other peaks to form. Figure 3 shows the region from 1500 to 1800  $\text{cm}^{-1}$  and growth of Peak 1. Here there is a steady growth during the refluxing stage over time but no real growth during the final recovery step. Figures 4 through 6 show the growth in the peaks of interest (1, 2, and 3) at the three oil bath temperatures for the 0.06-g/mL solutions. For Peaks 1, 2, and 3, the peaks increase with time at each temperature and the growth rates increase with temperature. The sulfoxide region has small and random changes suggesting that there is no significant reaction occurring in this region. The oil bath temperature is not representative of the bulk solution temperature. The solvent and system pressure determine the boiling temperature. The oil bath temperature only affects the boiling rate and the temperature gradient in the solution film near

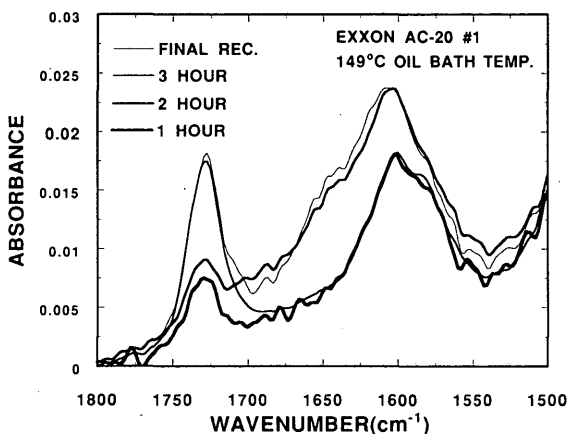


FIGURE 3 Effect of incubation time on the FT-IR carbonyl region of Exxon AC-20 (0.06 g/mL TCE/EtOH, 149°C oil bath).

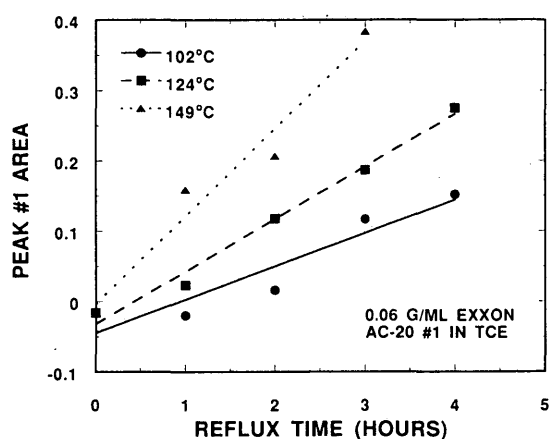


FIGURE 4 Growth of Peak 1 (1770 to 1697  $\text{cm}^{-1}$ ) in Exxon AC-20 at three oil bath temperatures (0.06 g/mL TCE).

the flask surface. Since there are definite changes in reaction rates due to the oil bath temperature, which is approached only in a small portion of the system, the rates in a true isothermal system at these temperatures are expected to be much higher.

Chemical reactions follow an Arrhenius relationship between reaction temperature and the log of the rate constant. The growth rates can be estimated by calculating the slopes of the curves in Figures 4 through 6. These slopes represent the rate of peak area growth,  $d(\text{peak area})/dt$ , for each peak at each temperature. The sulfoxide rates exhibited almost random variation and are not shown. The logs of the growth rates are plotted against inverse temperature to form an Arrhenius plot in Figure 7. Peaks 1, 2, and 3 all follow the Arrhenius relationship and have the same slope. Common slopes indicate that they are all participating in the same reaction.

Since growth stopped upon final recovery, the reactions may not occur at higher asphalt concentrations. Several similar batches having asphalt concentrations of 0.12 g/mL were run at 102°C, 124°C, and 149°C. At 124°C, peak growth was only negligible

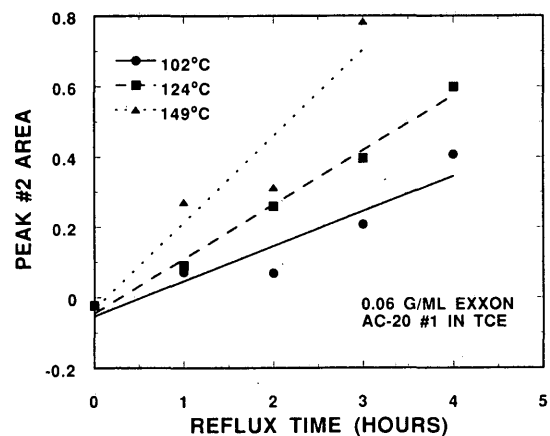


FIGURE 5 Growth of Peak 2 (1329 to 1213  $\text{cm}^{-1}$ ) in Exxon AC-20 at three oil bath temperatures (0.06 g/mL TCE).

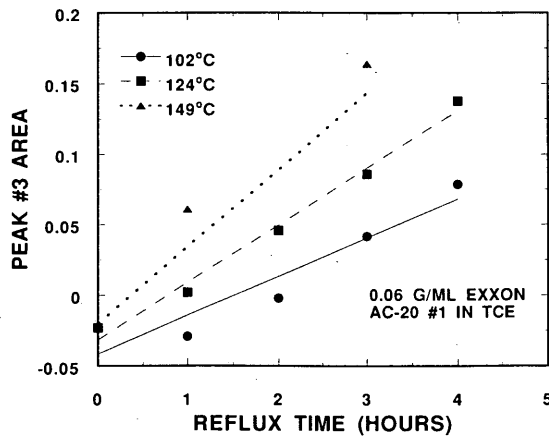


FIGURE 6 Growth of Peak 3 ( $1150$  to  $1098\text{ cm}^{-1}$ ) in Exxon AC-20 at three oil bath temperatures ( $0.06\text{ g/mL TCE}$ ).

after the 4 hr. There was no direct level indication or control in the boiling flask, but evaporative analysis of asphalt concentrations in the aliquots showed variation from  $0.10\text{ g/mL}$  for the 3-hr sample to  $0.17\text{ g/mL}$  for the 2-hr sample. This poor concentration control leaves the possibility that the concentration dropped low enough to initiate reaction.

In light of these results, it was decided that future extractions would be run such that the boiling flask liquid level was kept at around  $150\text{ mL}$ , yielding a concentration at  $0.2\text{ g/mL}$  during extraction of a  $600\text{-g}$  mixture containing 5 percent asphalt. This is more in line with concentrations found in earlier extraction and recovery methods. However, it makes operation of the Auto method more tedious, since the boiling flask level must be monitored more closely.

#### Long-Term Solvent Softening with Inhibitor

There were questions whether these reactions would respond to the presence of oxidation inhibitors. This might give some clue

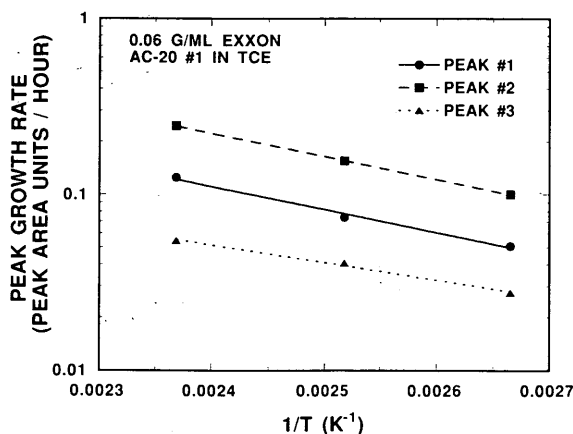


FIGURE 7 Peak 1, 2, and 3 Arrhenius curves for an Exxon AC-20 at three oil bath temperatures ( $0.06\text{ g/mL TCE}$ ).

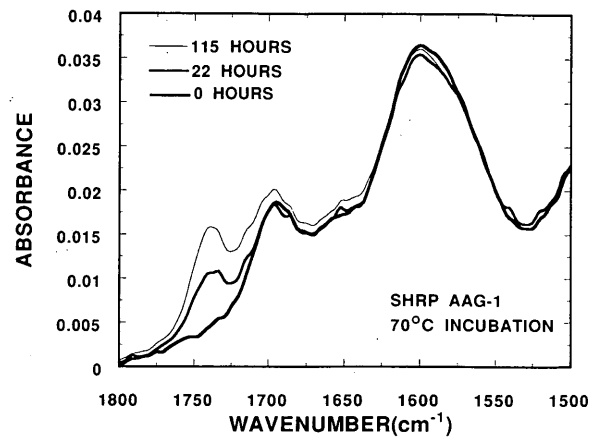


FIGURE 8 Effect of extended incubation times on solvent-softening peak growth for SHRP AAG-1 ( $0.07\text{ g/mL TCE}$ ,  $70^\circ\text{C}$ ).

as to the nature of the reactions. SHRP AAG-1 and AAK-1 tank asphalts were dissolved in TCE at  $0.07\text{ g/mL}$  and spiked with 0, 1, or 2 wt percent BHT. These solutions, about  $1000\text{ mL}$  each, were stored at  $70^\circ\text{C}$  in an oven for several days. About 200- to 300-mL aliquots were removed after 0, 22, and 115 hr of incubation. Figure 8 shows the carbonyl region ( $1500$  to  $1800\text{ cm}^{-1}$ ) where Peak 1 grows in the samples having no BHT. This is similar to what is seen in the Exxon AC-20, though it is much slower because the temperature is lower. Figure 9 shows the effect of BHT concentration on the growth of Peak 1 for the 22-hr samples. The effect is less dramatic on the 115-hr samples because, eventually, the BHT-treated samples' peaks reach the same equilibrium level of peak growth that the untreated samples reach. This suggests two things. First, the reaction is a free-radical transfer mechanism (which is what oxidation inhibitors can slow). Second, the peak growth inhibition in the BHT-treated samples is only temporary, since after 115 hr, all samples have comparable softening peaks. This may be due to depletion of softening reactants at the lower temperature or depletion of inhibitor. GPCs of these sam-

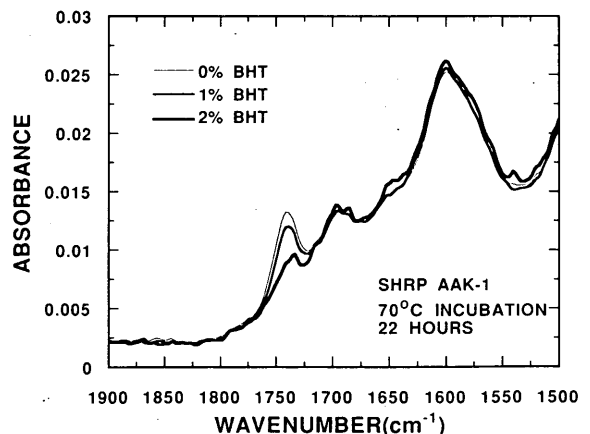


FIGURE 9 Effect of BHT inhibitor on FT-IR spectra changes due to solvent softening of SHRP AAK-1 ( $0.07\text{ g/mL TCE}$ ).

ples show formation of two narrow peaks, one of which is lower in molecular weight than the bulk of the asphalt (Figure 10). Viscosities are strongly affected by solvent softening for SHRP AAG-1 and AAK-1 (Figure 11). SHRP AAG-1 softens considerably at first and somewhat less at later times. More relative softening occurs for the uninhibited sample, as is expected. SHRP AAK-1 softens considerably in the uninhibited material but hardens at later times. Inhibited SHRP AAK-1 just hardens very gradually. It is probable that both hardening and softening reactions are occurring, with softening being most responsive to inhibitors. The softening possibly arises from the presence of the low-molecular-weight reaction product seen on the GPC chromatogram.

### Effects of Solvent and Asphalt Source

Solvent softening rates vary considerably with the source of asphalt and extraction solvent. In Figure 12, solvent softening rates for Exxon 1 and 2 in TCE/EtOH and Exxon 2 in Tol/EtOH are shown at several temperatures and concentrations. It is clear that TCE/EtOH promotes solvent softening more than Tol/EtOH. In fact, Tol/EtOH stimulates softening in only the most severe recovery conditions (high temperature and very low concentration). Even though Tol/EtOH is a slightly poorer solvent for extracting strongly adsorbed material from the aggregate (7), its superior resistance to solvent softening makes it the solvent of choice. Also, it can be seen that two asphalts, which were thought to be identical, have very different solvent softening susceptibilities. Exxon 1 has softening rates that are roughly three times that of Exxon 2. Exxon 1, which reacted fastest of all asphalts tested, might have shown signs of softening in Tol/EtOH at typical conditions, but it was depleted by the time those experiments were performed.

Table 1 gives softening rates for Exxon 1, Exxon 2, SHRP AAG-1, and SHRP AAK-1 under identical conditions. Exxon 2 is comparable to SHRP AAK-1 at high temperatures with SHRP AAG-1 being much less reactive. However, at lower temperatures, SHRP AAG-1 is nearly as reactive as SHRP AAK-1. This is not surprising, since this relative rate switching also occurs during oxidative aging for the two asphalts. At low temperatures, the

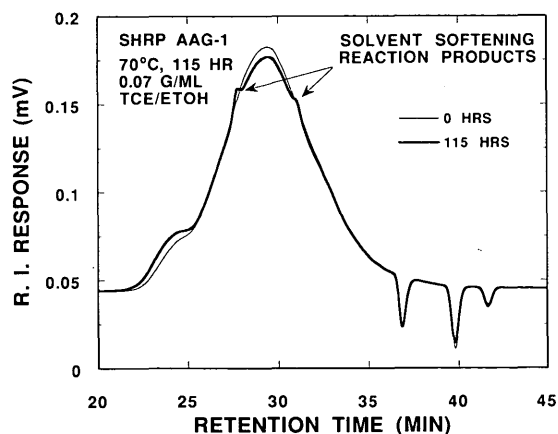


FIGURE 10 Formation of two unique GPC peaks during solvent softening of SHRP AAG-1 without BHT (0.07 g/mL TCE, 115 hr, 70°C).

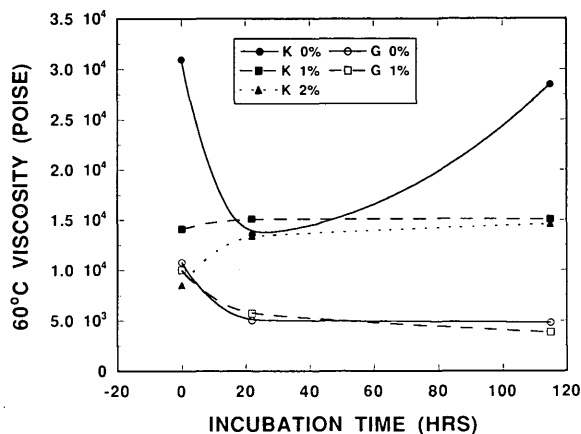


FIGURE 11 Effect of BHT on solvent softening of SHRP AAK-1 and AAG-1 (0.07 g/mL TCE).

poorer compatibility of SHRP AAK-1 probably keeps it from being as completely dissolved as SHRP AAG-1. This could hinder the reactive sites of SHRP AAK-1 and yield lower rates. SHRP AAK-1 may actually have more reactive sites than SHRP AAG-1 at high temperatures where SHRP AAK-1 is dissolved as completely as SHRP AAG-1.

### Solvent Softening Reaction Mechanism

There is not enough information available yet to explain mechanistically the phenomena occurring in these experiments. However, several things are known. First, the FT-IR peaks arise because of some reaction (or reactions) that does not involve dissolved free oxygen, since they occur in refluxing systems saturated with solvent. The reactions also respond to free-radical inhibitors, suggesting that they are initiated by free radicals existing naturally in the asphalt. There has been considerable speculation in the past that TCE reacts with dissolved asphalt. However, the occurrence of these reactions in other solvents like heptane and

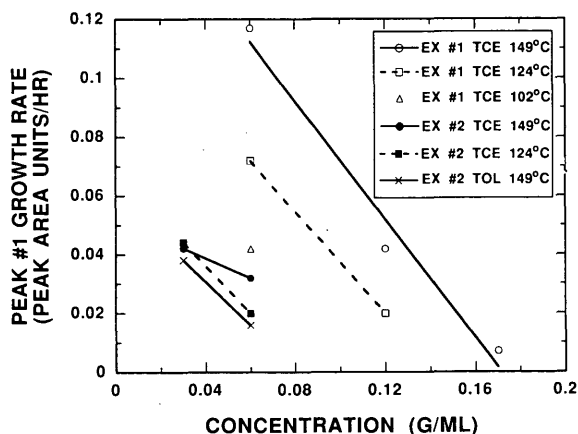


FIGURE 12 Solvent softening rates of Exxon 1 and 2 in TCE/EtOH and Exxon 2 in Tol/EtOH at several solution conditions.



been seen in other reactions of asphalt. Also, narrow molecular-weight products are formed during solvent softening. The one having low molecular weight could lower asphalt viscosities. The solvent softening reaction rates increase with recovery oil bath temperature. Within practical temperature ranges, there appear to be threshold asphalt concentrations, above which softening does not occur. In higher asphalt concentrations, solvent hardening dominates. Below threshold concentrations, softening rates increase as asphalt concentration decreases. Softening rates also increase with the strength of the extraction solvent. TCE/EtOH is better at removing strongly adsorbed material from aggregate but also promotes solvent softening more than Tol/EtOH. The softening reactions respond to oxidation inhibitors, suggesting that they are free radical-initiated reactions.

The importance of these reactions is their potential effect on asphalt properties during extraction and recovery. With the advent of new recovery techniques that use lower asphalt concentrations and higher oil bath temperatures during recovery, softening becomes a genuine concern. These reactions are more damaging to asphalt properties than solvent hardening because they can cause a reduction of viscosity of more than 50 percent during a recovery, whereas increases in viscosity due to hardening can easily be held to less than 15 percent. Solution conditions that minimize the risk of solvent softening can be specified. This may be done by using Tol/EtOH rather than TCE/EtOH, keeping oil bath temperatures below 110°C, and ensuring that recovery solutions have asphalt concentrations higher than 0.15 g/mL.

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