

Effects of Physicochemical Factors on Asphalt Oxidation Kinetics

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Oxidative aging of asphalt is a primary cause of asphalt hardening in pavements, thus contributing to various forms of pavement cracking. Although the changes in asphalt physical properties on oxidative aging are primarily the result of the formation of oxygen-containing functional groups in the asphalt, the sensitivity of an asphalt to these oxidation products varies widely with asphalt source (composition). An understanding of the kinetics of oxidation in the pavement temperature range is confounded by both the complex composition of asphalt and its thermally reversible microstructure. To better understand the mechanisms of age hardening, the kinetics of asphalt oxidation were investigated from the pavement temperature range [60°C (140°F)] through the higher temperature range of commonly used accelerated laboratory tests [130°C (266°F)]. It was found that asphalts with different component compatibilities may exhibit similar age hardening kinetics at the low end of the pavement temperature range, but quite different kinetics at the high end of the range. This is because the aging kinetics become highly dependent on how temperature affects the molecular microstructure. A new microstructural model of the age hardening of asphalt cement is presented that proposes that the kinetics of aging in the pavement temperature range is largely governed by physicochemical factors related to the state of dispersion of the molecular microstructure rather than the inherent reactivity of the molecular components with oxygen. The model is supported by results of past and present research.

The oxidative hardening of asphalt contributes significantly to the embrittlement of asphalt pavements. This hardening is attributed primarily to the introduction of polar, oxygen-containing chemical functionality that increases interactions among asphalt molecules. Much work has been done in identifying the polar, strongly associating functional groups in asphalt, either naturally present or formed on oxidation, and characterizing their association forces (1). The sensitivity of an asphalt to the oxidation products varies with asphalt source. These and related phenomena are discussed elsewhere in a detailed review (1). A new model for asphalt oxidation has been proposed (2,3) suggesting that physicochemical factors dominate the kinetics of oxidative age hardening of most asphalts. This model proposes that potentially reactive polar asphalt molecules associate to form microstructure. This molecular association immobilizes the inherently reactive components, thus reducing their ability to react with atmospheric oxygen.

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Because molecular association of polar asphalt components plays a major role in determining aging characteristics (2,3), and because it is well known that molecular association is reversible and highly temperature sensitive, it becomes obvious that the kinetics of aging as a function of temperature must be examined to understand the age hardening characteristics of asphalt. The importance of such a study is underlined by the results of the field aging study of Kemp and Predoehl (4), in which pavement mixtures were aged in different climates. Although void content of a mixture is well known to influence pavement hardening, the California study showed that age hardening was much more dependent on climate temperature than void content. Thus, an understanding of the age-hardening kinetics as a function of temperature is important to the design of a realistic aging test. Aging indexes calculated from single-point viscosity measurements at one test temperature provide little or no information regarding the overall kinetics and limited information about the expected aging of asphalts in pavements.

The research results and data interpretation in this paper further define the physicochemical aging model and provide additional insight into the compositional factors governing the age hardening of asphalts at pavement temperatures. In addition, they provide kinetic information useful for the design of a realistic aging test.

MODEL OF ASPHALT OXIDATION KINETICS

The earlier work on the microstructural aging model (2,3) provided evidence that physicochemical factors are primarily responsible for (a) the lack of correspondence among asphalts between the concentration of oxidation products and viscosity increase on aging, and (b) the differences between low- and high-temperature age-hardening kinetics. This is illustrated in Figure 1 by a refinement of the earlier aging model. For simplicity, the four asphalt generic fractions are used in the illustration. This illustration is not intended to depict the exact spatial arrangement of molecules of the generic fractions because this is unknown, but is presented only for the purpose of illustrating the principles involved. The molecular polarity and inherent reactivity of the fractions with oxygen have been shown (1) to be asphaltenes > polar aromatics > aromatics > saturates. In some asphalts, over 85 percent of the easily oxidizable hydrocarbon moieties may reside in the asphaltene and polar aromatic fractions (3). In highly dispersed asphalts, the polar molecules are "solvated," thus they retain consid-

erable molecular mobility. On the other hand, the more polar molecules in a highly associated asphalt interact to form microstructure that significantly reduces molecular mobility. The assumption that molecular immobility decreases reactivity with oxygen is not without support. For example, the asphaltene fraction, although highly reactive in solution, is virtually inert to air oxidation at ambient temperature in its dry, powdered state.

Because the inherently reactive polar components (represented in Figure 1 by asphaltenes and polar aromatics) of a highly dispersed asphalt are highly mobilized at both high and low temperatures, the age-hardening kinetics are similar throughout a wide temperature range. The age-hardening kinetics of a highly associated asphalt, on the other hand, are highly temperature dependent. At low temperatures, the inherently reactive molecules are highly immobilized from association, which physically inhibits their oxidation. When the oxidation temperature is increased, the reactive polar molecules are mobilized by dissociation of microstructure, making more of them available for oxidation. The proposed model is supported by numerous examples in this paper.

EFFECTS OF TEMPERATURE AND ASPHALT COMPONENT COMPATIBILITY ON AGE-HARDENING KINETICS

Two laboratory aging tests were selected for the study of age-hardening kinetics. For the low temperature range, the pressure oxygen vessel (POV) technique developed by Lee (5) was selected. This method uses a 3.18 mm- ($\frac{1}{8}$ in.-) thick asphalt film in a thin film oven test (TFOT) pan exposed to oxygen at 2.07 MPa (300 psi). Pure oxygen and elevated pressure accelerates the rate of oxidative aging. The aging test selected to evaluate aging at higher temperatures was the thin

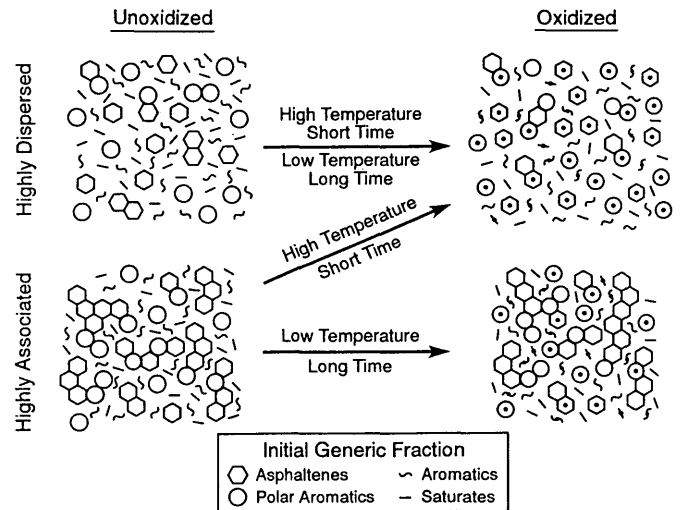


FIGURE 1 Model of Asphalt Oxidative Aging.

film accelerated aging test (TFAAT) (6). This test uses a 160- μ m (0.0063-in.) film of asphalt deposited on the inside of a rolling thin film oven (RTFO) bottle that is aged in an RTFO. The bottle contains a capillary opening to restrict volatile loss to an amount similar to that of pavement service. The asphalts studied were the eight Strategic Highway Research Program (SHRP) core asphalts. In the SHRP core asphalts, the uses of both oxygen and air in the pressure vessel were evaluated.

In the pressure air vessel (PAV) test to simulate pavement aging, the asphalt is first aged using the TFO test to simulate asphalt changes that occur in the hot mixture plant. The viscosity-time plots for PAV aging of the SHRP core asphalts at 60°C (140°F), together with viscosity changes during TFO aging, are shown in Figure 2. Changes upon TFO aging varied

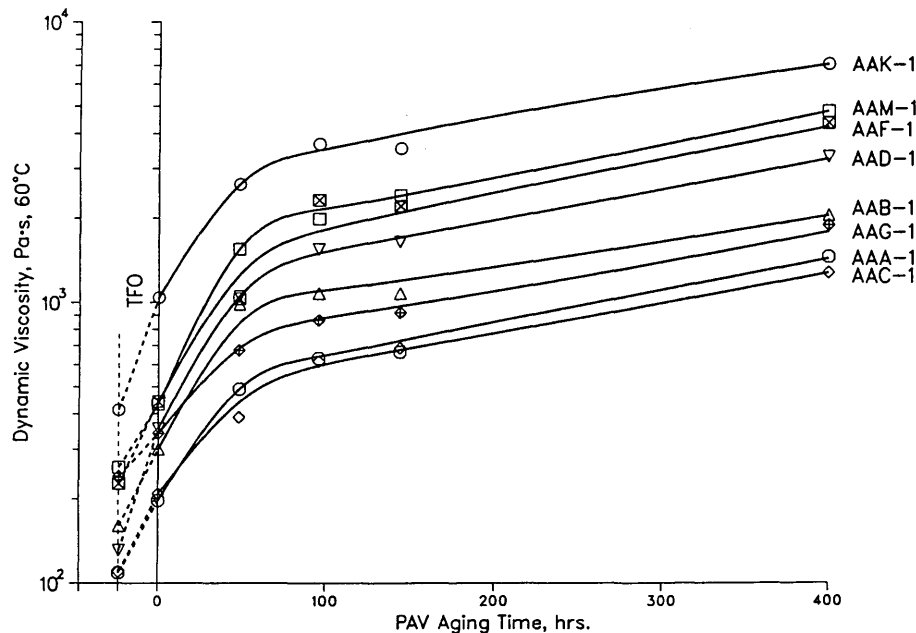


FIGURE 2 Kinetic aging plot of SHRP asphalts using PAV method at 2.07 MPa, 60°C.

considerably among asphalts; however, the PAV kinetic aging for the eight asphalts at 60°C (140°F) are surprisingly similar. All plots are distinctly parabolic, exhibiting a rapid viscosity increase during about the first 50 to 100 hr of aging followed by a rate decrease leading to a “steady state” viscosity increase in the plateau region beyond about 150 hr.

Prior TFO aging of the SHRP asphalts produced higher viscosity asphalts exhibiting the same subsequent POV aging kinetics as the original asphalt. This is illustrated in Figure 3

using asphalt AAD-1 aged at 60°C (140°F) in the POV. To better understand TFO aging, consider the weight versus viscosity changes during TFO aging of the SHRP asphalts at 163°C (325°F) as illustrated in Figure 4. Two factors dominate during TFO aging: (a) volatile loss producing a weight loss, and (b) oxidation producing a weight gain. The actual weight change is the net result of these two factors. If volatile loss dominates, the asphalt is found located on the right side of the zero weight change line; if oxidation dominates, it is on

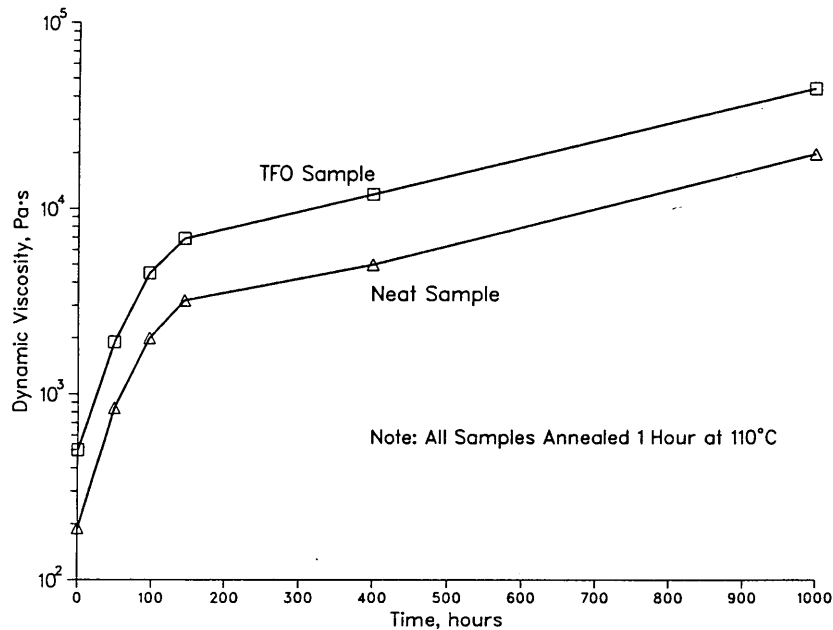


FIGURE 3 POV aging of asphalt AAD-1 at 60°C with and without prior TFO aging.

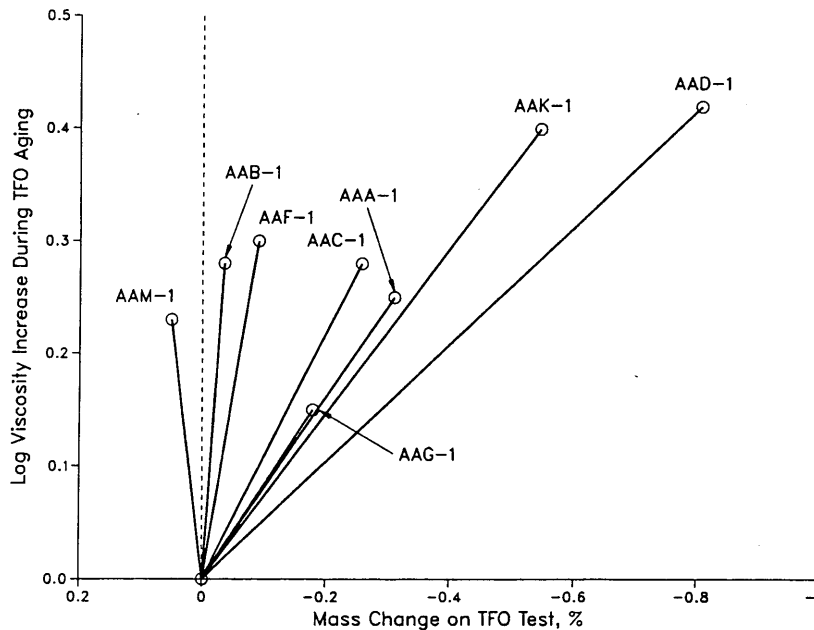


FIGURE 4 Mass change versus log viscosity increase during TFO aging.

the left. For asphalts AAD-1 and AAK-1, weight loss appears to dominate in increasing viscosity. On the other hand, for asphalts AAM-1, AAB-1, and AAF-1, changes from volatile loss are virtually offset by oxidative weight gain, indicating that oxidation contributes significantly to the viscosity increase.

More understanding of the TFO aging mechanism can be gleaned from Figure 5. The increase in viscosity with increasing carbonyl oxidation products during POV aging of AAD-1 with and without prior TFO aging is shown in this figure. The data points were obtained by analyzing a collection of samples of AAD-1 aged as a function of time at 60°C (140°F) for up to 1,000 hr. The data fit is within the expected precision of the experimental techniques. An excellent correlation exists between viscosity increase and carbonyl oxidation products formed. The relationship between carbonyl oxidation products [greater than 95 percent are ketones (1)] and viscosity increase has been previously reported (7,8) and will be discussed later in this paper. Of particular significance with regard to TFO aging, the data in Figure 5 imply that at any point in time on the POV kinetic plot (see Figure 3), the TFO aged asphalt has the same carbonyl content as the asphalt with no prior TFO aging. Thus, TFO aging apparently did not significantly alter the compositional factors responsible for the shape of the kinetic aging curve. This is not surprising because the volatiles lost are primarily nonpolar hydrocarbons. Similar shaped kinetic curves for the asphalt at different viscosities (Figure 3) also indicate that the shapes of the kinetic curves were not significantly influenced by viscosity increase during POV aging. The lack of significant ketone formation during TFO aging probably results from two factors: (a) the thick asphalt film that inhibits diffusion, and (b) the scavenging of oxygen by the highly reactive sulfides to form sulfoxides as air diffuses through the asphalt. At the TFO test temperature, the sulfoxides are thermally unstable (9,10) and subsequently decompose; thus few are found in the TFO res-

idue. The sulfoxide decomposition products (retention of oxygen) may possibly be largely responsible for the oxidation component of the weight change during TFO aging (see Figure 4).

Data in Figure 5 also strongly suggest that carbonyl compounds (ketones) formed during oxidative aging may be involved in the viscosity increase. To more fully understand the kinetics of asphalt aging as affected by temperature and composition, it was necessary to bridge the gap in the kinetic data between the low-temperature pressure vessel data and past data obtained at rather high temperatures. This was done using the TFAAT, which is fast and was designed to eliminate the confounding effects of volatile loss at higher temperatures. It was decided to first determine if the age hardening kinetics for both the pressure vessel and TFAAT aging methods were similar. Data confirming the similarity are shown in Figure 6 for POV and PAV aging at 60°C (140°F) and TFAAT aging at 65°C (149°F). The TFAAT aging was conducted at 65°C (149°F) because of equipment limitations.

The kinetic data in Figure 6 for asphalts AAG-1 and AAK-1 are quite similar regardless of which test method was used. The plateau region for the POV aging curve has a steeper slope than that for PAV aging, undoubtedly because of a greater oxygen concentration. Asphalts AAG-1 and AAD-1 were chosen for test method comparisons because they represent extremes in asphalt component compatibility (2,3), AAG-1 having a highly dispersed polar phase and AAD-1 a highly associated polar phase. Data in Figure 6 show that a 60°C (140°F) aging test would rank asphalts AAD-1 and AAG-1 as having similar age-hardening characteristics. However, such a conclusion was found not valid for these two asphalts aged at higher temperatures (2,3). This will become apparent from the higher-temperature kinetic data that follow.

Kinetic data for the TFAAT aging of the SHRP asphalts at 85°C (185°F), 113°C (235°F), and 130°C (266°F) are shown

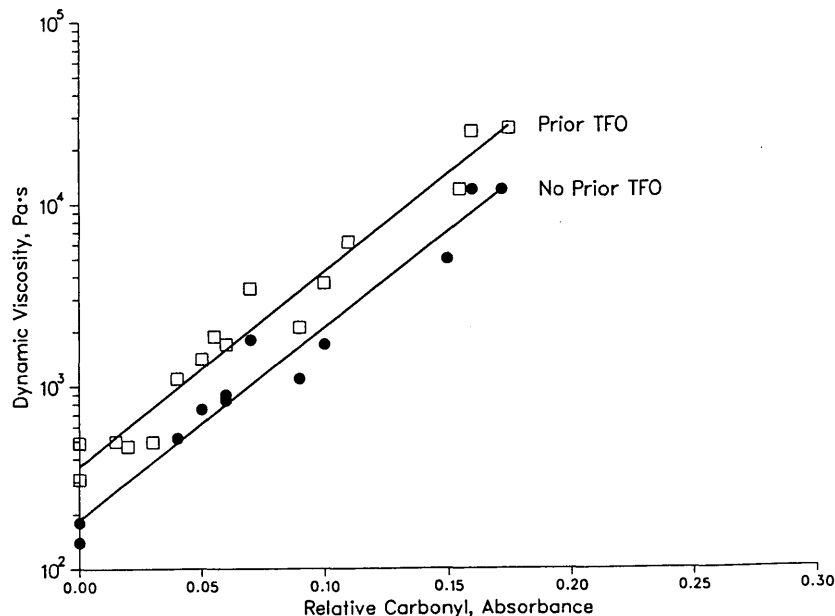


FIGURE 5 Relationship of viscosity change with carbonyl (ketone) formation on POV oxidation of asphalt AAD-1 with and without prior TFO oxidation.

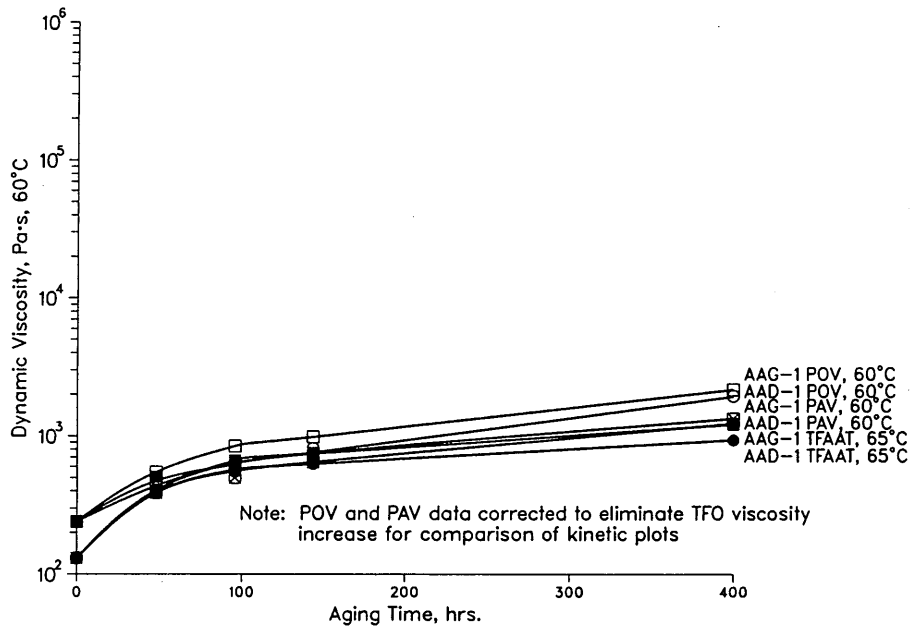


FIGURE 6 Comparison of low-temperature aging kinetics of asphalts AAD-1 and AAG-1 using POV, PAV, and TFAAT methods.

in Figures 7, 8, and 9, respectively. As seen in Figure 7, the kinetic plots at 85°C (185°F) show a greater rate of viscosity increase than at 60°C (140°F) (see Figure 6). Further, the similarity of kinetic data beyond the inflection point found for all asphalts aged at 60°C (140°F) (Figure 2) is no longer apparent. For example, kinetic plots for asphalts AAD-1 and AAG-1, which were similar at 60°C (140°F), now show disparity. The disparity among asphalts becomes even greater (Figure 8) at 113°C (235°F). Also, the time needed to reach

the inflection point of the kinetic curve (e.g., AAG-1) has decreased from about 100–200 hr (at 60°C) to 20–40 hr (at 113°C). Any single point aging test conducted, for example at 113°C (235°F) for 24 hr, would rank the asphalts and their differences quite differently than a test conducted for, say, 120 hr at the lower temperature. Finally, at 130°C (266°F) (Figure 9), large differences in the kinetic data are apparent. As judged by AAG-1, the inflection point now appears after about 5 hr of aging. For asphalts AAG-1 and AAD-1, whose

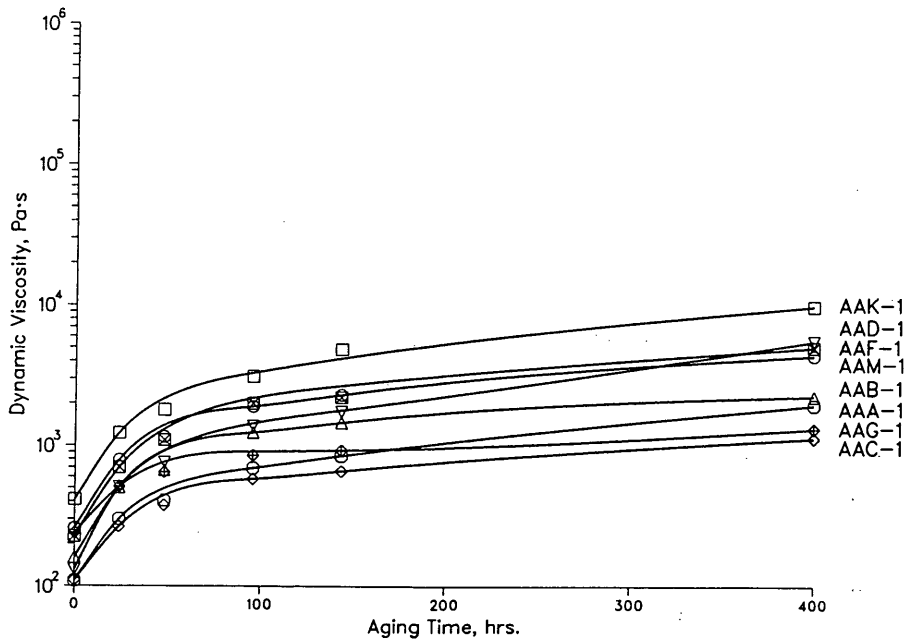


FIGURE 7 Aging kinetics of SHRP core asphalts using TFAAT method at 85°C.

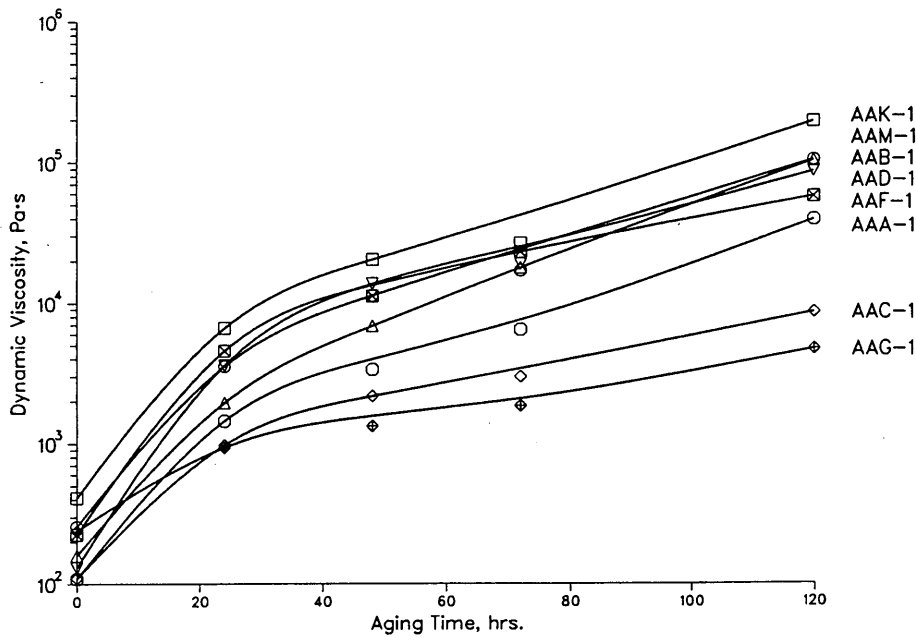


FIGURE 8 Aging kinetics of SHRP core asphalts using TFAAT method at 113°C.

plots were similar at 60°C (140°F), the plots are significantly different from each other, with AAD-1 showing a much greater age-hardening rate at 130°C (266°F) than AAG-1.

It is instructive for the further evaluation of age-hardening kinetics to examine the kinetics of the formation of the dominant oxidation products. The kinetics of ketone and sulfoxide formation during 113°C (235°F) TFAAT aging are shown in Figure 10 for asphalt AAG-1. Sulfoxides form rapidly during the first 5 hr followed by the familiar pseudo-steady-state concentration as their rate of formation and rate of subsequent thermal decomposition become equal (9,10). The rate of ke-

tone formation, also initially rapid, reaches a plateau in about 5 hr, after which the rate of formation remains constant.

That asphalt AAG-1 is a highly dispersed asphalt and AAD-1 is a highly associated asphalt is evidenced by the reduced specific viscosity data in Figure 11. Reduced specific viscosity, $\langle \eta \rangle$, as here applied to asphalts, is defined as follows (11).

$$\langle \eta \rangle = \frac{\eta_s - \eta_o}{\eta_o c} \quad (1)$$

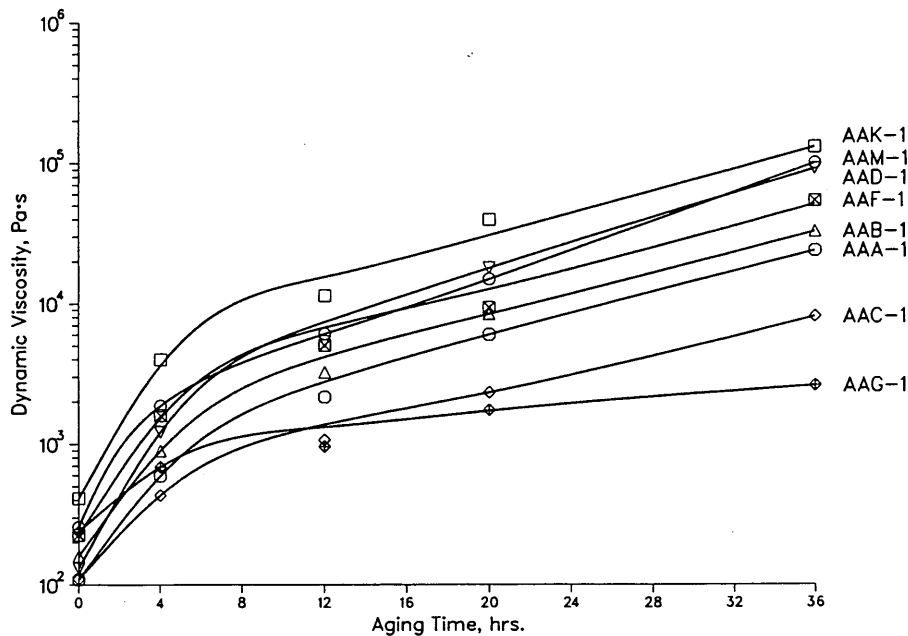


FIGURE 9 Aging kinetics of SHRP core asphalts using TFAAT method at 130°C.

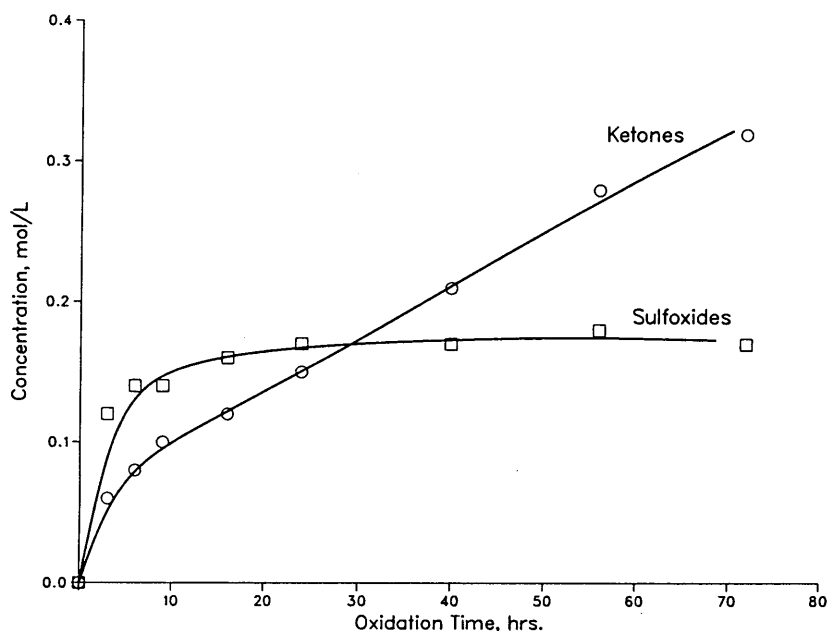


FIGURE 10 Chemical kinetic data for TFAAT oxidation of asphalt AAG-1 at 113°C.

where

- η_o = viscosity of the maltenes (solvent),
- η_s = viscosity of a maltene-asphaltene mixture, and
- c = concentration of asphaltenes (solute) in maltenes in gms/100 gms.

Viscosity measurements were made at 45°C (113°F) on maltene fractions of asphalts AAG-1 and AAD-1, which contained asphaltene concentrations below and above their nat-

ural abundance levels. Data on TFAAT-aged asphalts were obtained from asphalts aged for 72 hr at 113°C (235°F). This aging procedure produces an oxidation level significantly greater than POV and PAV aging (compare Figures 6 and 8). Reduced specific viscosities of the mixtures were then calculated. This technique is advantageous because it allows the asphaltene association to be studied in its natural environment in the absence of solvent. Because the $\langle \eta \rangle$ is related directly to the apparent molecular weight of the solute (asphaltenes) in

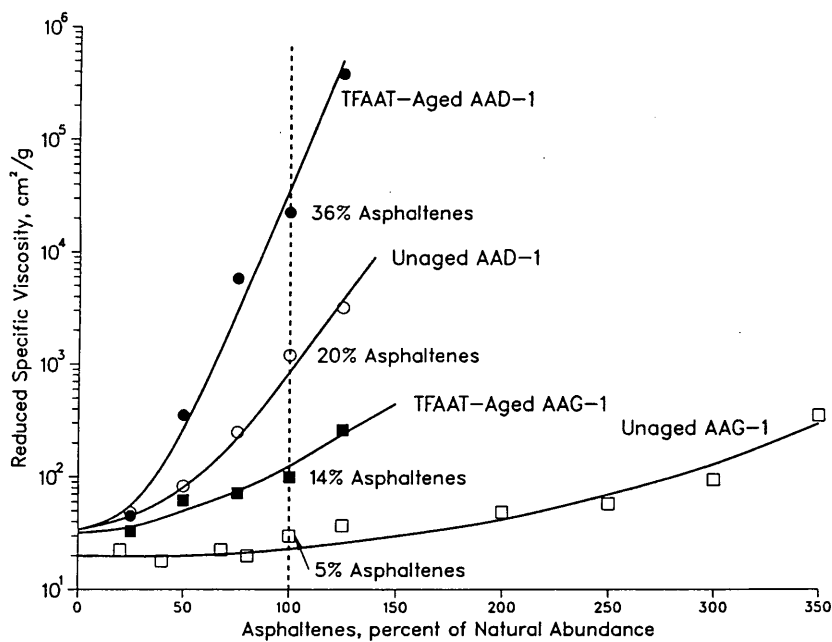


FIGURE 11 Reduced specific viscosity measurements at 45°C for asphalts AAD-1 and AAG-1 before and after TFAAT aging at 113°C, 72 hr.

the solvent (maltenes), the relative tendency for the asphaltene to associate and form microstructure is directly observable. If the $\langle\eta\rangle$ remains constant as asphaltene content is increased, this is evidence that the asphaltene are soluble and are highly dispersed in the maltene phase. If the $\langle\eta\rangle$ increases with increasing asphaltene concentration, this shows that the size of the asphaltene agglomerates is increasing through molecular association. At zero concentration, the asphaltene are at their smallest divisible size at 45°C (113°F).

Interpretation of the data in Figure 11 shows that the asphaltene in asphalt AAG-1 are solubilized, dispersed, and highly mobile. Even the asphaltene in the TFAAT-aged AAG-1 are quite well dispersed. The data for asphalt AAD-1 show that the asphaltene are much less compatible with their maltene phase, even in the unoxidized sample, at much less than their natural abundance concentration. With increasing asphaltene concentration, the asphaltene microstructure of AAD-1 increases rapidly in size, thus immobilizing reactive components (2,3). It is also seen that oxidation [at 113°C (235°F)] has a much greater effect on microstructure formation in AAD-1 than in AAG-1.

On the basis of the data presented thus far, it is appropriate to discuss the age-hardening kinetic data with regard to the aging model proposed in Figure 1. This will be done using the kinetic data in Figure 12 for the two asphalts with representative component compatibility extremes, asphalts AAG-1 and AAD-1. The time scale for the lower temperature aging [60°C (140°F)] was compressed to offset the increase in reaction rate at the high temperature [113°C (235°F)]. Because the most reactive components of asphalt AAG-1 are mobilized even at low temperatures, the kinetics of age hardening are similar at both low and high temperatures when the time scales are shifted to overlap the data. This behavior is illustrated in the top half of Figure 1. This result reveals important

information on the oxidation mechanism. It implies that the sharp decrease in the rate of age hardening near the inflection point of the kinetic curve for low temperature oxidation does not result from depletion of asphalt components reactive only at low temperatures. The rapid rate of viscosity increase during the initial period of AAG-1 aging is tentatively attributed to the reaction of a small population of more reactive hydrocarbon components and possibly to the formation of sulfoxides. Data in Figure 10 for the formation of sulfoxides and ketones support this view.

Kinetic data in Figure 12 for the low- and high-temperature aging of asphalt AAD-1 are quite different from one another. At 60°C (140°F), the kinetic data for AAD-1 are similar to those of AAG-1; however, at 113°C (235°F), AAD-1 shows a much greater increase in age hardening during the initial stages of oxidation and a more rapid rate of increase in the plateau region than at 60°C (140°F). This is interpreted as follows. During low temperature oxidation, the reaction rate decreases because a large part of the inherently reactive molecules are immobilized as depicted in the lower half of Figure 1. However, at higher temperatures, there is less microstructure, making greater amounts of reactive components available for reaction (arrow to the upper right corner of Figure 1). Also, as more reactive molecules become available at higher temperatures, more of the small, reactive hydrocarbon population in AAD-1 is made available, producing a significantly greater initial increase in viscosity during oxidation at 113°C (235°F) than at 60°C (140°F). Finally, evidence that the age-hardening kinetics for AAD-1 are different at high and low temperatures is provided by the inability to superimpose their kinetic plots by shifting the time scales as was done with AAG-1.

Because high oxygen or air pressure [2.07 MPa (300 psi)] is used in pressure vessel aging, it is important to know how oxidation proceeds through the sample thickness during ag-

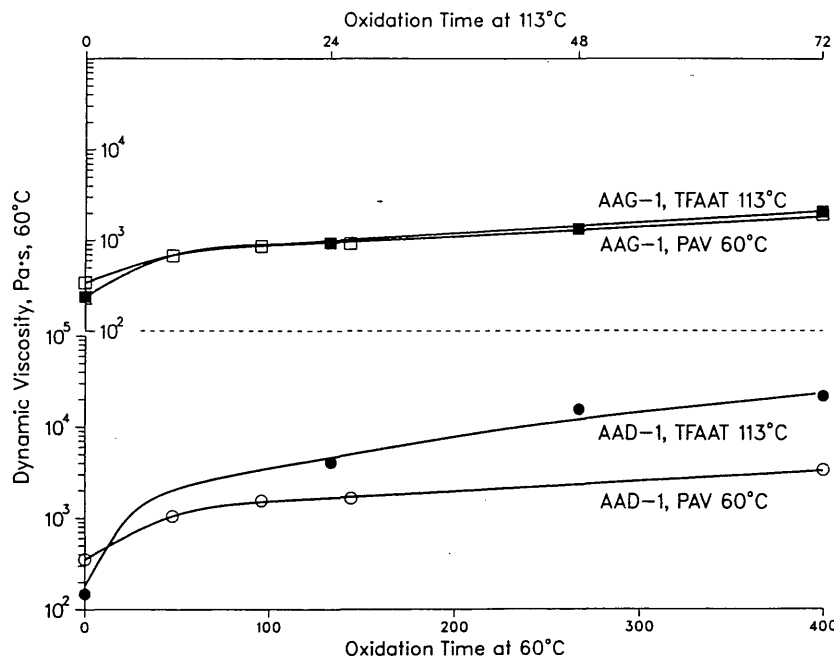


FIGURE 12 Effects of temperature on aging characteristics of asphalts AAD-1 and AAG-1.

ing. Lee (5) found that at 66°C (150°F) the viscosity through the sample thickness [3.18 mm (1/8 in)] approached a uniform value after about 250 hr at 200 kPa (29 psig) oxygen pressure and after about 50 hr at 847 kPa (132 psig). It was found that, after 96 hr in oxygen and 144 hr in air at 2.07 MPa (300 psi), the viscosity and the concentrations of carbonyls and sulfides were identical at both the top and bottom of the sample. Two important deductions can be made from these data. First, when the POV test is run near 60°C (140°F) at 2.07 MPa (300 psi), the oxidation should be nearly uniform throughout the sample thickness in much less than 50 hr, thus the oxidation should not be diffusion controlled after a short period of initial aging. Second, because more than 50 hr are needed to reach the plateau region of the kinetic aging plot during 2.07 MPa (300 psi) aging (Figure 3), it is highly unlikely that diffusion alone can account for the shape of the kinetic curve during the first 150 hr. This latter observation supports the previous proposition that the shape of the front end of the kinetic curve is largely controlled by reaction of a small population of highly reactive asphalt components.

EFFECTS OF OXIDATION REACTIONS ON AGE-HARDENING KINETICS

The relationship between carbonyls formed on oxidation and viscosity increase is shown in Figure 13. The data points include PAV aging at 60°C (140°F) for 48, 96, 144, and 400 hr; TFAAT aging at 85°C (185°F) for 24, 48, 96, 144, and 400 hr; TFAAT aging at 113°C (235°F) for 24, 48, 72, and 144 hr; and TFAAT aging at 130°C (266°F) for 4, 12, 20, and 36 hr. The correlation for each individual asphalt is good. These

data include the entire temperature range of concern from 60°C (140°F) to 130°C (266°F), and the data imply that the mechanism of hydrocarbon oxidation of asphalts is essentially the same from the pavement temperature range through the temperature range of common laboratory tests. Because both PAV and TFAAT data fit the same plot, evidence is provided that the hydrocarbon oxidation mechanism is the same for both atmospheric pressure and pressure vessel aging.

The different sensitivity of the asphalts to the oxidation products is evident from the data in Figure 13. More carbonyls are formed in asphalt AAG-1 than in any of the other asphalts; however, it is much less sensitive to the oxidation products, undoubtedly because of its high degree of dispersion. The highly structured asphalt, AAK-1, is highly sensitive to oxidation, suggesting that the oxidation products formed, rather than being solubilized, participate in strong association interactions.

IMPORTANT CONSIDERATIONS FOR A PRESSURE VESSEL AGING TEST

Several technical recommendations for test method development seem justified from this study. First, because of the high sensitivity of highly associated asphalts to age harden with increasing temperature, it is recommended that any single-point aging test be conducted as near as practical to the actual maximum pavement temperature. Second, the test aging time should be sufficient to move the measurement point beyond the inflection point of the kinetic plot. Finally, aging indexes that include viscosity changes that occurred during prior TFO testing are not necessarily reflective of the changes that actually take place during pavement service.

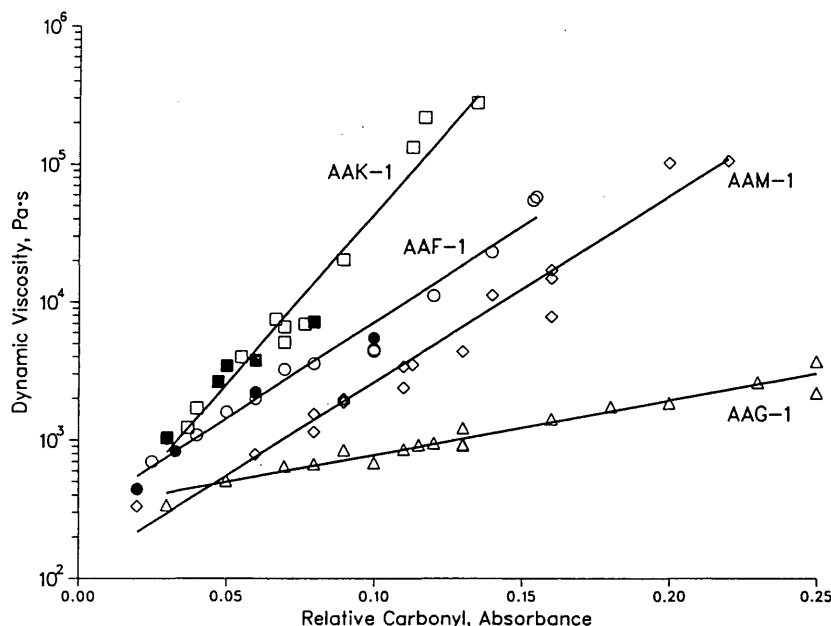


FIGURE 13 Relationship between carbonyls formed and dynamic viscosity increase using PAV (solid points) and TFAAT (open points) data.

CONCLUSIONS

The following conclusions are based on the data and interpretations presented in this paper.

1. The age-hardening kinetics at pavement temperatures of all but the most highly dispersed asphalts are dominated by the immobilization of polar, reactive asphalt molecules through microstructure formation.

2. The sensitivity of an asphalt to viscosity increase on oxidation is strongly influenced by its component compatibility. The more highly structured an asphalt, the more sensitive it is to viscosity increase with increasing temperature of oxidation.

3. TFO aging increases the viscosity of an asphalt but does not significantly affect its POV age-hardening kinetics.

4. The viscosity increase on oxidation correlates with the rate of oxidation of asphalt hydrocarbon moieties, however the viscosity sensitivity to the oxidation varies greatly among asphalts.

5. The hydrocarbon oxidation chemistry is similar for both ambient and pressure vessel aging of asphalts, and is also similar throughout the temperature range of 60°C (140°F) to 130°C (266°F).

In light of these conclusions, it seems advisable that the sensitivity of an asphalt to viscosity increase as a function of maximum pavement temperature should be carefully evaluated when selecting asphalts for use in different climates.

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