

FACTORS AFFECTING THE KINETICS AND MECHANISMS OF ASPHALT OXIDATION AND THE RELATIVE EFFECTS OF OXIDATION PRODUCTS ON AGE HARDENING

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ABSTRACT

The ketones and sulfoxides formed in asphalts are the major determinants of viscosity increase on oxidation. Asphalts initially exhibit a high reactivity with oxygen causing a rapid spurt in the formation of both oxidation products and viscosity increase. This spurt is followed by a slower rate of oxidation and hardening. Different oxidation mechanisms appear operative during these two periods. During the spurt, sulfoxides are the major oxidation product and determinant of viscosity increase, particularly at lower temperatures. Following the spurt, ketones are usually the major product and determinant of viscosity increase. Molecular moieties that are converted to ketones and sulfoxides compete for the reactive oxidant. The ratio of ketones to sulfoxides formed was found dependent on oxygen concentration (pressure), temperature and sulfur content. The relative amounts of sulfoxides and ketones formed under different internal and external environments, and their differing effects on viscosity, are rationalized by the microstructural model of asphalt.

INTRODUCTION

Asphalt oxidation is important because it is the major cause of asphalt hardening, resulting in the deterioration of many desirable asphalt performance properties. In asphalt concrete pavements, oxidative hardening contributes to pavement embrittlement and excessive pavement cracking. Factors affecting the rate of oxidative hardening and the mechanisms of asphalt oxidation are the subjects of this paper.

Oxidation produces polar functional groups in asphalt molecules; ketones (1) and sulfoxides (2) are the major oxidation products; only minor amounts of dicarboxylic anhydrides (3) and carboxylic acids (4) are formed during the advanced stages of oxidation. Methods for their quantification have been developed (5). Viscosity increase accompanies the introduction of the polar functional groups; however, the relative sensitivity to viscosity increase is highly asphalt source (composition) dependent and is related to the component compatibility of the asphalts (6). The more compatible asphalts show lower sensitivity to viscosity increase from oxidation (6-8). Component compatibility is defined as the relative amount of molecular aggregation of the polar asphalt components to form micellar structuring, often referred to as microstructure. The use of the term micellar with reference to asphalt does not imply well defined or spherical components as is common in aqueous systems. In fact, just the opposite is probably true in which irregular shaped molecular agglomerates with poorly defined boundaries and gradual polarity gradients exist within the asphalt matrix.

On oxidation, all asphalts exhibit a hyperbolic-like kinetic curve when log viscosity is plotted versus oxidation time, showing an initial rapid rate of viscosity increase (referred to in this paper as the spurt) followed by a slower, nearly linear rate of viscosity increase (8). Following the viscosity spurt, viscosity increase correlates directly with ketone formation (8-11), with each asphalt having its unique ketone-viscosity relationship. The formation of polar asphaltene components on oxidation also correlates with viscosity increase (12); thus, it follows that the rate of asphaltene formation should correlate with the rate of ketone formation, which relationship has been demonstrated (13,14).

The shape of the kinetic plot, and the effect of asphalt component compatibility on

oxidative aging are shown in Figure 1 for two asphalts studied in the Strategic Highway Research Program (SHRP). Asphalt AAG-1 is a highly compatible asphalt with well dispersed microstructure, while asphalt AAD-1 is at the other end of the compatibility spectrum. The time scales have been time-temperature shifted to offset the effect of temperature on the increase in oxidation rate so that changes in kinetics as a function of temperature can be visually compared. This procedure will be used throughout this paper. Data in Figure 1 are presented to illustrate the effects of component compatibility on oxidation kinetics. The data show that for the highly compatible asphalt AAG-1, there were no significant changes in microstructure on oxidation between 60°C and 80°C that affected the oxidation kinetics, presumably because the oxidation products were solubilized in the asphalt dispersed phase ("solvent" component) precluding their interaction to form significantly larger molecular agglomerates. Thus, the asphalt behaved more like a true solution. However, for the less compatible, more highly associated asphalt AAD-1, lowering the oxidation temperature from 80°C to 60°C significantly reduced the rate of oxidative hardening following the spurt. This lowering is believed the result of molecular immobilization from the formation of microstructure, reducing the reactivity of precursor molecules that form ketones. These effects are discussed in detail elsewhere (8).

In the present paper, the chemical and physicochemical factors that control the phenomena cited above are identified and their effects interpreted and rationalized by the microstructural model of asphalt. A new model for the chemical mechanisms of asphalt oxidation is also presented. Because of the large number of variables affecting asphalt oxidation kinetics, only selected examples can be presented within the scope of this paper. A sequence of papers are planned for future publication in which the subjects presented are discussed in more detail and on larger sets of asphalts.

RESULTS AND DISCUSSION

Oxidation Kinetics and Oxidation Products-Viscosity Relationships. As stated in the Introduction, ketones and sulfoxides are the major identifiable functional groups formed in asphalt on oxidation. Recent data of Liu, et al. (10) relating carbonyl formation with oxygen uptake for SHRP asphalts AAA-1 and AAG-1 were compared by us with total ketones plus sulfoxides formed in these same two asphalts oxidized at Western Research Institute (WRI) using the same oxidation method. Analysis of Liu's data showed that the ratio of oxygen uptake for AAA-1/AAG-1 was 1.32; the corresponding ratio of total ketones plus sulfoxides calculated from the WRI data was 1.31, confirming that ketones and sulfoxides account for essentially all of the oxygen that reacted with these asphalts. It therefore follows, that except for variable volatile loss in asphalt pavement mix plants, nonreversible age hardening of asphalts in pavements is a direct result of ketone and sulfoxide formation.

The rates (kinetics) of chemical oxidation and viscosity increase of asphalts are influenced by asphalt composition, oxidation products formed, temperature, oxygen partial pressure (concentration and/or diffusion rate) and physicochemical effects. These factors are demonstrated for selected asphalts in Figures 2-6. It has been shown (15, 16) that asphalts exposed to 100% oxygen or air at 300 psi (2.07×10^6 Pa) pressure are saturated with oxygen, thus eliminating the need to consider oxygen concentration (diffusion) as a variable in the oxidation kinetics. Elimination of this complicating factor greatly simplifies the study of the kinetics of the oxidation chemistry.

In Figures 2-4, the oxidation and age hardening kinetics of three selected SHRP asphalts having different sulfur contents are considered. The asphalts were aged at 60°C and 100°C using the SHRP TF0-PAV method (300 psi (2.07×10^6 Pa, air)). Data for AAF-1 (3.4% sulfur) are shown in Figure 2. Kinetic data are shown at the left of the figure and oxidation functional group-viscosity relationships at the right. The time scales are time-temperature shifted as explained for Figure 1. Note that during the initial oxidation spurt that sulfoxides are formed at a much faster rate than ketones. This has been found true for all asphalts studied. Further, the relative amounts of ketones and sulfoxides formed and viscosity increase during the spurt are nearly independent of temperature in the absence of oxygen diffusion effects. This was found to hold for all eight SHRP core study asphalts. Following the spurt, the rate of formation of ketones at 60°C is lower than at 100°C, resulting in a corresponding reduction in viscosity increase. These results are interpreted as follows based on the microstructural model

of asphalt (6-8).

First, it is proposed that the mechanisms of oxidation during and after the spurt are different. This is discussed later in the paper. The present discussion relates to oxidation following the spurt. Asphalt AAF-1 is of intermediate compatibility; therefore, as temperatures are decreased, polar, more aromatic components (related to the polar aromatics and asphaltenes generic fractions) associate into agglomerates, thus reducing their molecular mobility and reactivity with oxygen from physicochemical effects (7, 8). That is, the effective concentrations of mobile reactants are reduced by being buried in the microstructure. This is somewhat analogous to what has been observed in micellar catalysis where reaction sites on whole molecules can be buried in the micelle (17). Because the reactive components that form ketones (benzylic carbons, (1, 6)) are highly concentrated in the polar, more aromatic fractions (6), ketone formation is inhibited in the less compatible asphalt AAF-1 at lower temperatures. Lin, et al. (14) recently showed that the new asphaltenes which form on oxidation are produced primarily from the maltenes fraction. Based on the known composition of the precursors to ketone formation, the new asphaltenes are probably formed primarily from the polar aromatics fraction. The new asphaltenes are reported (14) to have the same effect of viscosity as original asphaltenes, although chemically quite different.

Next, consider the relative effects of ketones and sulfoxides on viscosity increase from data at the right in Figure 2. Note that the ketones formed correlate with viscosity increase as previously mentioned. During the oxidation spurt, for which limited data points are available, it is difficult to assess the relative contribution of sulfoxides and ketones to viscosity increase. However, the linear ketone-viscosity plot and major change in the slope of the sulfoxide-viscosity plot at the point corresponding to the end of the spurt indicate that the ketones are the major determinants of viscosity increase in asphalt AAF-1 oxidized between 60°C and 100°C. The lower concentration of sulfoxides at 60°C following the change in direction of the sulfoxide plot at the point corresponding to the end of the spurt in the kinetic plots could result from either greater thermal instability of the sulfoxides at 100°C and/or the depletion of highly reactive sulfides which form sulfoxides. Obviously, there is no additional contribution to viscosity increase by the sulfoxides formed during 100°C oxidation past the change in slope of the curve represented by about 0.25 mol/L sulfoxides, since the concentration of sulfoxides remains constant. Note also that the slope of the ketone plot is steeper (viscosity increase more sensitive to ketone formation) for 100°C oxidation than for 60°C oxidation, even in the absence of sulfoxide formation. This is evidence that at the higher temperature, ketones are formed deeper in the microstructure because their precursors are liberated for reaction by thermal dissociation of the microstructure.

Before discussing the remaining figures, the following hypothesis based on the microstructural model is presented to explain how ketones and sulfoxides produce viscosity increase. Sulfoxides and ketones are both polar, containing an electronegative oxygen producing a dipole that can interact or associate with other dipoles or induced dipoles. From a polarity standpoint, the sulfoxide functional group is probably as polar or more polar than the ketone. Yet, the ketones formed beyond the oxidation spurt show the major effect on viscosity increase. Thus, it is concluded that the polar nature of the ketones and/or sulfoxides alone is not the fundamental factor responsible for the significant effects on viscosity increase. It is proposed that the size of the associated molecular agglomerates on which these function groups are formed is the primary reason for their profound effects on viscosity. It is well known that the viscosity of polymers is directly related to molecular weight. The ketones are formed predominantly on molecules of the polar, aromatic components where the benzylic carbons are concentrated (6). These ketone precursors are also the molecules believed to be associated in molecular agglomerates in asphalt. As previously mentioned, the maltenes (which contain the polar aromatics) have been shown (14) to be involved in asphaltene formation and viscosity increase. Thus, it logically follows that the ketones, which are most likely formed on already associated molecular species, cause much larger molecular agglomerates to form through their association with other large associated species. As a result, the formation of a single ketone moiety could cause the formation of a much larger agglomerate with significantly greater effective molecular weight, and thus a significant effect on viscosity increase.

On the other hand, the sulfides which are precursors of sulfoxides should be found in

relative abundance in the weakly associated dispersing phase of asphalt, thus sulfoxides formed following the spurt could be concentrated in the dispersing phase. Also, if the sulfide moieties are located in the physical vicinity of the associated phase, the molecules of which they are a part may not have sufficient polarity or aromaticity to cause them to be strongly associated with larger agglomerates. Once sulfoxides are formed, they may then interact with polar constituents present in either the weakly or strongly associated components. However, in either case, they would have limited effect on effective molecular weight increase, and thus viscosity increase, for the following reasons. If the association of sulfoxides occurred in the dissociated (solvent) phase, the association of the sulfoxide with otherwise weakly associated molecules would only about double the effective molecular weight. For typical asphalt molecules, this might be a molecular weight increase from 1000 to 2000 Daltons. If a sulfoxide-containing molecule with no additional highly polar molecular components were to associate with a large agglomerate in the dispersed phase, for example and agglomerate with an effective molecular weight of 30,000 Daltons, this would only increase the effective molecular weight to 31,000 Daltons --- as rather insignificant relative increase. Thus, oxidation of sulfides to form sulfoxides under the conditions just described should have a relatively small effect on viscosity increase. Of course, another reason for the reduced effect of sulfoxides on viscosity following the spurt in some asphalts might be that the concentration of reactive sulfides in the vicinity of the ketone-forming precursors for which they compete to form sulfoxides might simply be depleted.

With the theory presented, consider the data for asphalt AAM-1 and AAA-1 in Figures 3 and 4, respectively. Asphalt AAM-1 (Figure 3) is a compatible asphalt with low sulfur content (1.2%). Because the polar components of this compatible asphalt are well dispersed, the lowering of the oxidation temperature from 100°C to 60°C does not significantly change the state of dispersion (immobilization of the aromatic molecules containing the ketone-forming benzylic carbons) of the asphalt. As a result, no significant physicochemical effect is seen in the kinetic plot at the left in Figure 3 for AAM-1 between 60°C and 100°C, as was seen for the more incompatible asphalt AAF-1 (Figure 2). The similarities of the ketone kinetics at both the high and low temperatures is also reflected in the viscosity plots, again confirming the relationship between ketone formation and viscosity increase. The decrease in sulfoxides with time following the oxidation spurt is unique for asphalt AAM-1 among the asphalt studied to date and is as yet unexplained.

The relatively large increase in viscosity with ketone formation as seen for AAM-1 is not typical for compatible asphalts (compare with the much-studied compatible asphalt AAG-1 (Figure 2)). Asphalt AAM-1 has a very low heptane asphaltenes content and its molecules are inherently much larger than those of most other asphalts (16). Recent solid state NMR measurements at WRI (18) indicate that asphalt AAM-1 has much larger condensed aromatic ring structures than the other SHRP asphalts. The authors propose that these large polarizable condensed ring structures provide for increased molecular association in this asphalt, and thus its high sensitivity to viscosity increase with ketone formation.

A change in slope of the ketone-viscosity plot at the right in the figure corresponding to the end of the spurt is evident. The combined effect of ketones and sulfoxides on viscosity during the spurt (below 0.15 mol/L ketones) is less than that of the ketones alone following the spurt. This is believed to result from the different oxidation mechanisms operating during the spurt, with the initial major oxidation product being sulfoxides. Further, the spurt oxidation mechanism proposed later on would dictate that during the spurt, oxidation products may be formed on molecules having a different state of dispersion than molecules on which they are formed after the spurt, thus having differing effects on viscosity increase.

Data on the high sulfur (5.5%) asphalt AAA-1 are shown in Figure 4. It is apparent when one compares the relative amounts of ketones and sulfoxides formed in the low sulfur asphalt AAM-1 (Figure 3) with those formed in asphalt AAA-1 (Figure 4), that a much higher ratio of ketones to sulfoxides are formed in the high sulfur asphalt. Note also, except for a slight lowering of the rate of ketone formation at 60°C from physicochemical effects, that the relative amounts of ketones to sulfoxides are almost the same at both high and low temperatures. This has been found to be true for the eight SHRP core asphalts during PAV oxidation, again confirming that the kinetics and

mechanisms of oxidation are similar at all temperatures studied and are not dependent on oxygen concentration, as previously mentioned.

Examination of the data in the kinetic plot at the left in Figure 4 suggests that the relatively small increase in the rate of ketone formation between the 60°C and 100°C may not be sufficient to account for the larger rate of viscosity increase between the two temperatures. These results suggest that the sulfoxides have a greater effect on viscosity increase at the higher temperature in this higher sulfur, less compatible asphalt than in the two asphalts previously considered. An explanation for this is found in the microstructural model. A relatively greater proportion of the reactive sulfides that are precursors to sulfoxides should also be found in more associated species in this less compatible asphalt. Therefore, their formation on more associated molecular agglomerates should have a greater effect of viscosity. Also, since sulfoxides compete with ketones for hydroperoxide precursors to form sulfoxides, the molecular dissociation occurring at the higher temperature would make sulfoxides "deeper" in the associated phase more available for reaction. Therefore, if the sulfoxides were formed deeper in the associated phase at 100°C than at 60°C, then when the viscosity of the 100°C sample is measured at 60°C, sulfoxides would be buried deeper in the associated phase and have a greater effect on viscosity increase. The greater sensitivity of viscosity increase to ketone formation at 100°C than at 60°C (right side of figure) could also be explained using the same argument for ketones as was just presented for sulfoxides, in that at higher temperatures ketones are formed deeper in the microstructure, thus having a greater relative effect on viscosity. Probably physicochemical effects involving both sulfoxides and ketones are responsible for the larger increase in viscosity sensitivity during oxidation at the higher temperature.

Effects of Oxidation at Atmospheric Pressure on Oxidation Kinetics. As previously discussed, high pressure oxidation (PAV procedure) produced sulfoxides and ketones at nearly the same ratios, independent of temperature. However, in a diffusion controlled system at atmospheric pressure in which oxygen concentration within the asphalt is low, the ratio of sulfoxides to ketones produced following the spurt are highly dependent on oxidation temperature. This temperature sensitivity can be seen by comparing the data in Figure 5 for asphalt AAF-1 with the PAV aging data for the same asphalt shown in Figure 2. Aging data for AAF-1 in Figure 5 were obtained using the Thin Film Accelerated Aging Test (TFAAT) in which the asphalt was oxidized as a 160 micrometer film at ambient air pressure. In general, as the oxidation temperature is lowered, the ratio of sulfoxides to ketones increases. Space do not permit comparison of the data for the other seven SHRP core asphalts, but a comparison is planned in a future publication.

The sensitivity to temperature of the ratio of sulfoxides to ketones appears to be related to the degree of molecular association at a given temperature. This is evidenced by the fact that those asphalts which exhibited a reduction of ketone formation and viscosity increase from the physicochemical effects of molecular association at the lower 60°C temperature in the PAV oxidations, as discussed earlier, are more sensitive to an increase in the sulfoxide-to-ketone ratio as temperature is lowered. The effect is pronounced during TFAAT oxidation at 85°C, but almost disappears above 113°C where molecular dissociation is high as indicated by similar ratios (not shown) for a given asphalt at both 113°C and 130°C oxidations. It was also found, and also not shown, that 65°C TFAAT oxidation data obtained on SHRP asphalts AAD-1 (6.9% sulfur) and AAG-1 (1.3% sulfur) oxidation kinetics were quite similar to those for 85°C TFAAT oxidation. Thus, the large change in the TFAAT oxidation kinetics attributed to physicochemical effects occurs between 85°C and 113°C. This is in contrast with results from PAV oxidation where the change occurs between 60°C and 80°C. Although not shown in graphical form, ketone and sulfoxide concentrations at 400 hours of TFAAT oxidation at 85°C for the highly compatible asphalt AAG-1 are 0.15 and 0.21 mol/L, respectively. Corresponding data for ketone and sulfoxide concentrations after a comparable oxidation of 120 hours at 113°C are 0.33 and 0.14 mol/L, respectively. Thus, at higher temperatures and low oxygen concentrations, ketones seem to be formed to some extent at the expense of sulfoxides; however, the total ketone plus sulfoxide concentration is higher at 113°C (0.47 mol/L) than at 85°C (0.36 mol/L). The known thermal instability of sulfoxides at higher temperatures and the dissociation of

more reactive ketone precursors, thus increasing their concentration in the dissociated phase, are possible contributors to this difference.

At the right in Figure 5, note also the large difference between the slopes of the ketone-viscosity plots for oxidation at 85°C and 113°C. As previously discussed, this is again evidence that at higher temperatures ketone precursors dissociate deeper in the asphalt microstructure, and when oxidized to ketones, have a relatively greater influence on viscosity increase. Comparison of Figures 2 and 5 show that this effect is greatly amplified at atmospheric pressure oxidation compared with PAV oxidation.

While theorizing on the mechanism is difficult, the fact remains that the large change in the ratio of sulfoxides to ketones as a function of temperature is primarily influenced by a change in the oxygen pressure (concentration) in the asphalt. Since oxidation in pavements is diffusion controlled at ambient pressures, and oxidative aging characteristics of asphalts may be evaluated using the SHRP procedure at high pressures in which the asphalt is saturated with oxygen, the correspondence between aging at low and high oxygen pressures needs to be rationalized.

Related to the above discussion, Liu and coworkers (10) found a significantly lower level of carbonyl absorption (CA) versus time in asphalts oxidized at 0.2 atmospheres oxygen pressure than at 20 atmospheres pressure at the same temperature for asphalt AAF-1. Linear extrapolation of the CA versus time plot to zero oxidation time (roughly corresponding to the oxidation level at the end of the spurt) shows significantly lower levels of CA (ketones) in the low pressure oxidation. Since CA correlates directly with log viscosity for a given asphalt, there is some question, as Lin, et al. also point out, that aging characteristics predicted from PAV aging may not always correspond well with aging predicted from aging tests run at lower pressures. Our results regarding the effects of temperature on the aging kinetics using high and low pressure aging, particularly for less compatible asphalts, seem particularly germane.

Effects of Oxidation at Low Temperatures and at Atmospheric Pressure.

Several years ago the principle author and coworkers (G. Miyake, H. Plancher, and P.M. Harnsberger) at WRI oxidized a series of asphalts as thin films (5 wt%) in Ottawa sand briquettes. These asphalts were the unmodified control samples prepared in connection with a kinetic study to evaluate an oxidation accelerator in asphalt. Oxidations were performed at 45°C. The data obtained on extracted samples for one of these asphalts are shown in Figure 6. Since this oxidation was performed at a relatively low temperature, reaction rates were slow and oxidation during the spurt could be looked at in more detail because a number of data points were obtained during the spurt. When comparing these data with data in the previous figures, it should be noted that very little oxidation occurred following the spurt at the 45°C temperature during the 100 day aging period. Ketone levels never exceeded about 0.025 mol/L. This level is below ketone levels reached at the first data point near the end of the spurt during oxidation at the higher temperatures. It should be noted that although the oxidation temperature was low, the viscosity measurements were made at the same temperature (60°C) as was used for the kinetic studies at the higher temperatures, making these data comparable for interpretation with the higher temperature data.

Important information regarding oxidation during the spurt is apparent in Figure 6. First, the formation of sulfoxides is extremely rapid, even at 45°C, with the virtual exclusion of ketone formation. This is in agreement with the work of Huh and Robertson (19) in which it was shown that the slope of the Arrhenius plot for sulfoxide formation was smaller than that for ketone formation, thus indicating that the activation energy for sulfoxide formation is less sensitive to temperature change than is the activation energy for ketone formation. In the absence of ketone formation, one can conclude that the initial oxidation mechanism during the spurt under near ambient conditions is not a typical hydrocarbon free radical chain reaction which always produces ketones and more free radicals. This result is consistent with the observation of van Gooswillen, et al. (20) who oxidized asphalt in solution and measured the reaction rate by oxygen uptake. They noted no induction period in the oxidation kinetics which is characteristic of classical hydrocarbon chain reactions; they concluded that asphalt oxidation was not of the classical hydrocarbon type.

What is most revealing in Figure 6 is that the viscosity increase corresponds with the

formation of sulfoxides with virtually no ketones being formed. This shows that under the conditions of this experiment, that viscosity increase during the spurt is largely controlled by the formation of sulfoxides, suggesting that the sulfoxides are being formed on associating molecules deep in the polar, highly associated components during the spurt and not in the dispersing phase as may occur for sulfoxide formation following the spurt. In times past at WRI, samples taken from the surface of asphalt stored for and extended periods in sample cans at ambient temperatures have been observed to have sulfoxide concentrations of over 0.3 mol/L with no ketones having been formed.

A Proposed Two-Stage Mechanism for Asphalt Oxidation. As discussed above, sulfoxides were the primary oxidation product formed during the spurt with the virtual exclusion of ketones. The reaction of sulfides to form sulfoxides was also very rapid, yet sulfides in an inert solvent do not react with atmospheric oxygen under these conditions. A highly reactive precursor inherent in the asphalt that reacts with oxygen to form a hydroperoxide intermediate which then reacts with the asphalt sulfide to form sulfoxides (16) is proposed. Sulfides are well recognized to be very reactive hydroperoxide scavengers and react with hydroperoxides to form sulfoxides with no free radical products. Sulfides are used commercially in hydrocarbon plastics such as polypropylene as hydroperoxide scavengers to prevent the further reaction of hydroperoxides in promoting further hydrocarbon chain reactions. It has recently been proposed by Mill (21) that oxygen initially reacts with a highly reactive hydrocarbon in asphalt such as a hydroaromatic. This type of moiety can be exemplified by saturated, nonaromatic bridgehead carbons fused between aromatic ring structures to form a strained ring between the aromatic rings. Because of the steric strain imposed on the saturated carbon atoms, the hydrogens on these carbons are highly reactive toward abstraction by the oxygen to form hydrogen peroxide and/or hydroperoxides (as proposed by Mill), resulting in aromatization of the nonaromatic ring component. Thus, hydroperoxides are generated which then react with the asphalt sulfides with little or no production of ketones, consistent with the observed asphalt oxidation during the initial stages of the spurt. Then, as the oxidation continues toward the end of the spurt, initiation of a hydrocarbon chain-reaction begins with abstraction of a hydrogen from a benzylic carbon, which is a precursor to ketones, forming benzyl free radicals. These radicals can then compete with the sulfides for the available hydroperoxides. These radicals can also begin to react with oxygen to form peroxy radicals, and then continue on to form hydroperoxides with the generation of more benzylic carbon free radicals. Thus, in the latter case, a free radical hydrocarbon chain reaction has begun. Many reaction paths are possible; however, one route is for the hydroperoxide to decompose to form ketones or react with sulfides to form sulfoxides. Once the supply of the highly reactive hydrocarbon precursors previously described is exhausted, the spurt is over, explaining the rapid reduction in the oxidation rate and viscosity increase following the oxidation spurt. After the spurt, ketones form at a much slower, but nearly constant rate via typical hydrocarbon free radical chain reactions. Such chain reactions have previously been proposed (6). Reactive sulfides, as long as available, compete with the hydroperoxide ketone precursors to form sulfoxides.

Figure 7 shows the ketone and sulfoxide concentrations in the eight SHRP core asphalts at the end of the spurt during PAV oxidation at 100°C. Except for the low sulfur asphalts, the concentrations of ketones plus sulfoxides are nearly constant, indicating that these asphalts all have about the same concentration of reactive hydrocarbon precursors. Asphalt AAM-1, which is low in aromatics, might be expected to have a smaller concentration of the highly reactive hydrocarbon precursor, thus explaining its low level of oxidation during the spurt.

As previously mentioned in the discussion of Figure 6, the sulfoxides formed during the spurt appeared to control the viscosity increase during this stage of oxidation. This is explained as follows. If the reactive hydrocarbon precursors are indeed hydroaromatics, as suggested by Mill, then they would be expected to be present in the highly associated molecular agglomerates in which the more aromatic components are found. The formation of a polar sulfoxide group in the microstructure should cause the association of relatively large molecular agglomerates, thus significantly increasing effective molecular weight, and thus viscosity. Sulfoxides formed after the spurt would have less effect on viscosity if they were formed in the weakly associated dispersing phase or on rather nonpolar molecules as previously explained.

The relative abundance of ketones and sulfoxides following the spurt should be a

function of sulfide (related to sulfur) content of the asphalt. Higher sulfide concentrations provide more competition for the hydroperoxide at the expense of ketone formation. This is illustrated by the data in Figure 8 for sulfoxide and ketone formation in asphalts following the spurt. Note the ketone and sulfoxide data in the figure for the high sulfur asphalts AAK-1 and AAD-1. They cease to follow the trend as a function of sulfur content. More ketones begin to be formed at the expense of sulfoxides. Data for 80°C are shown as solid data points to provide evidence that this change in product ratios occurs somewhere between 80°C and 100°C.

As confirming evidence for a dual, two-stage oxidation mechanism for asphalts, the data in Figure 9 are submitted. These unpublished data were obtained several years ago at WRI by H. Plancher in scouting experiments on potential antioxidants in asphalts. In this experiment, a Boscan asphalt was oxidized as a thin film at 130°C with and without 2% of a potential antioxidant, triphenyltin hydroxide (TPTH). It is apparent that the TPTH had no effect on sulfoxide formation during the spurt; however, following the spurt, ketone and sulfoxide formation rate were both significantly reduced, indicating that the reaction mechanism during and after the spurt were not the same.

The Pragmatic Benefit of Sulfur in Asphalts. It has been reported (22) that asphalt sulfur content correlates with asphalt component compatibility as defined by relative viscosity measurements. In general, the less compatible asphalts are more sensitive to oxidative age hardening. Further, it has been shown in this paper that the ratio of sulfoxides to ketones formed on oxidation increases with increasing sulfur content, with sulfoxides being formed at the expense of ketone formation. This is illustrated in Figure 8 for PAV oxidation. The increasing sulfoxide to ketone ratios with increasing sulfur content is further intensified in atmospheric, diffusion controlled oxidation, particularly as the temperature is lowered. This phenomenon was explained in connection with Figure 5, but is characteristic of the SHRP core asphalts. It has also been pointed out that oxidizable asphalt sulfides are potent hydroperoxide scavengers, and thus interfere with the production of free radicals in the hydrocarbon chain reaction following the oxidation spurt. Finally, it has been shown that following the spurt, ketones have a much greater effect on viscosity increase than sulfoxides.

The pragmatic conclusion to all this is that sulfides in asphalts are effective antioxidants and reduce the effect of oxidation on age hardening. Since sulfides compete with ketone precursors, increased sulfide content in the asphalt means that more sulfoxides and less ketones are formed, a favorable situation for reduction in the rate of viscosity increase. This increased sulfoxide content and reduced ketone content tends to offset the increased sensitivity to age hardening of the less compatible asphalts, particularly at low aging temperatures. The effect of temperature on this phenomenon is illustrated in Figure 1 for the low sulfur (1.3%), highly compatible asphalt AAG-1 and the high sulfur (6.9%), rather incompatible asphalt AAD-1. The above arguments could explain why asphalts made from some high sulfur crudes harden and become brittle so rapidly in hot climates, but perform quite well in more moderate climates. With regard to age hardening, it is our belief that the maximum pavement temperature reached during hot days is more critical to eventual age hardening than are the average temperatures. Careful analysis of the data from the extensive California simulated field study of Kemp and Prodoehl (23) seem to confirm this conclusion.

SUMMARY AND CONCLUSIONS

The oxidative hardening of asphalts is a direct result of the formation of ketones and sulfoxides. The relative amount of amount of hardening that they produce depends upon the state of dispersion of the molecules on which they are formed. When formed on a molecule in a highly associated molecular agglomerate, they produce, through association with other associated agglomerates, a much larger molecular weight entity, thus significantly increasing effective molecular weight. When formed on weakly associated molecules, as in highly compatible asphalts or on molecules in the dispersing phase, their association has minimal effect on molecular weight, and thus viscosity increase. The hyperbolic-like plot of property change versus time observed for asphalt oxidation kinetics is the result of two sequential and different oxidation mechanisms. The rapid increase at the onset of the kinetic plot is attributed to reaction of highly reactive hydrocarbon precursors of limited concentration which react with oxygen to form hydroperoxides. The hydroperoxides then react primarily with asphalt sulfides to form sulfoxides with the virtual exclusion of ketone formation during the

initial stages of the spurt. Sulfoxides are the major contributor to viscosity increase during the initial stages of the spurt, at least below 45°C at atmospheric pressure. Towards the end of the spurt, a classical free radical hydrocarbon chain reaction begins to take over. When all of the highly reactive hydrocarbon precursors are exhausted, the spurt is over, after which ketones are formed at a nearly constant rate and are the major determinants of viscosity increase. As asphalt sulfur content increases, the sulfoxide contribution to viscosity increases. Following the spurt, sulfides compete for the hydroperoxide ketone precursors. Thus, less compatible, high sulfur asphalts produce more sulfoxides and less ketones than highly compatible, low sulfur asphalts. Because asphalt viscosity increase is more sensitive to ketone than sulfoxide formation, the production of more sulfoxides and less ketones in high sulfur asphalts tends to offset their increased sensitivity to age hardening, particularly at low temperatures. Sulfides in asphalt are effective antioxidants. The ratios of sulfoxides to ketones produced at high oxygen concentrations, as during PAV aging, were found independent of oxidation temperature, indicating that the mechanism of oxidation does not change with temperature. The ratio of sulfoxides to ketones, however, increased as sulfur content increased. At lower temperatures, physicochemical effects inhibit ketone formation and thus viscosity increase. During atmospheric pressure oxidation (low oxygen concentrations), the ratio of sulfoxides to ketones is not independent of temperature, but increases as oxidation temperature is lowered. The effect is intensified as the asphalt sulfur content increases and could have pragmatic implications when PAV aging is used to predict pavement aging under atmospheric, diffusion controlled condition.

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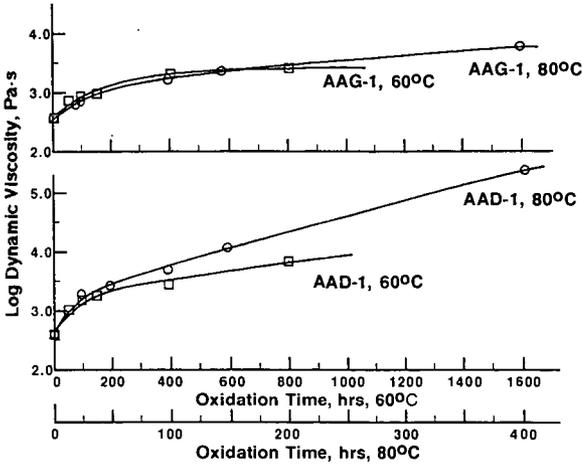


Figure 1. Effects of Temperature and Compatibility on Aging Characteristics

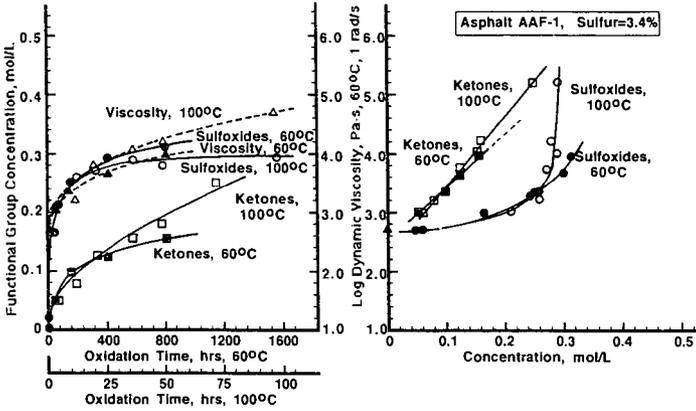


Figure 2. Kinetics and Viscosity-Functional Group Relationships, PAV Oxidation of Asphalt AAF-1

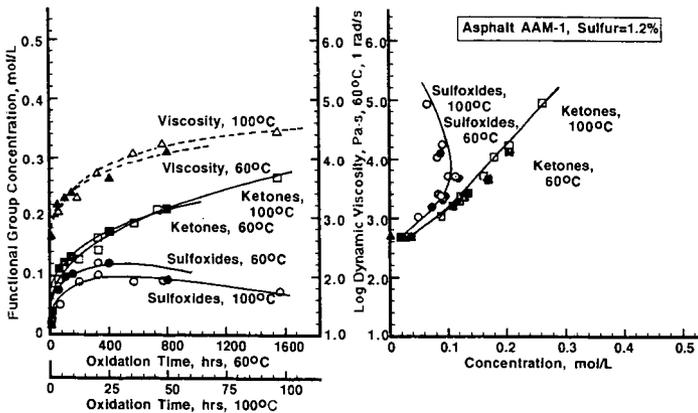


Figure 3. Kinetics and Viscosity-Functional Group Relationships, PAV Oxidation of Asphalt AAM-1

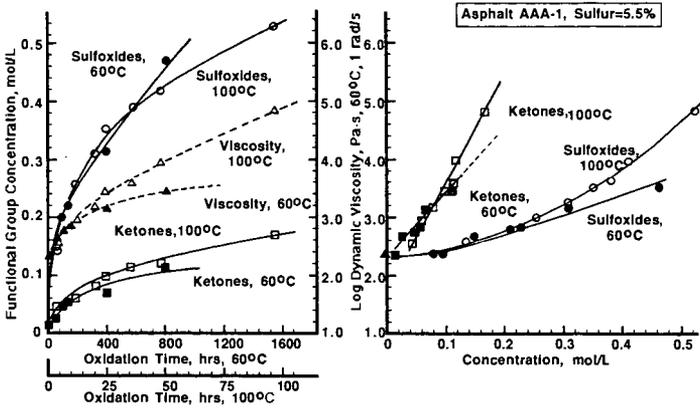


Figure 4. Kinetics and Viscosity-Functional Group Relationships, PAV Oxidation of Asphalt AAA-1

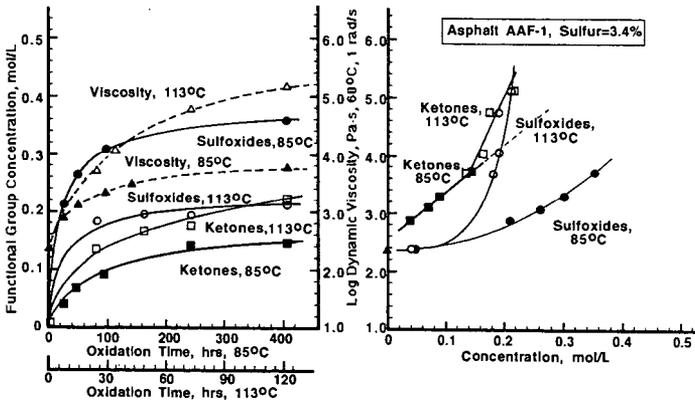


Figure 5. Kinetics and Viscosity-Functional Group Relationships, TFAAT Oxidation of Asphalt AAF-1

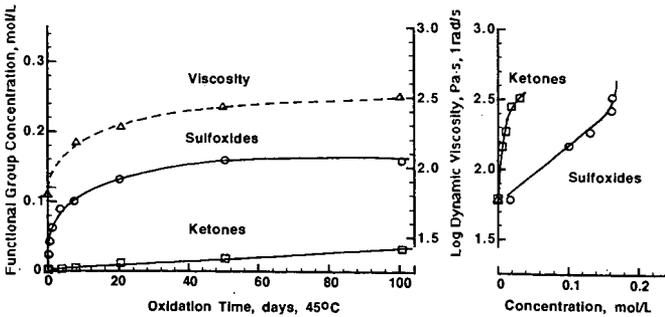


Figure 6. Kinetic Data and Viscosity-Functional Group Relationships for Shell Wood River Asphalt Oxidized at Atmospheric Pressure as a Thin Film on Ottawa Sand at 45°C

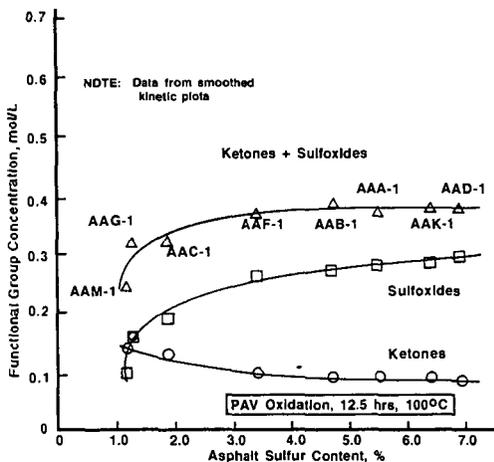


Figure 7. Ketone and Sulfoxide Concentrations at End of Oxidation Spurt

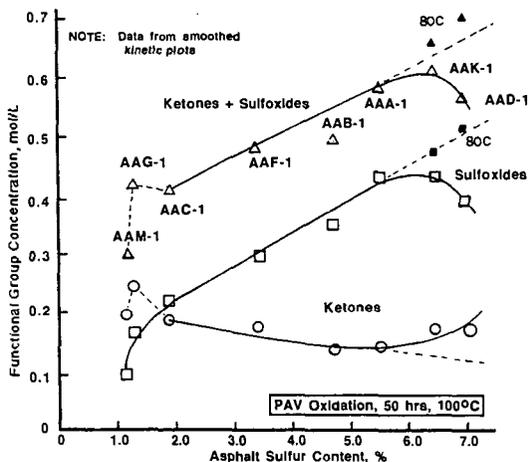


Figure 8. Ketone and Sulfoxide Concentrations at a Moderate Oxidation Level

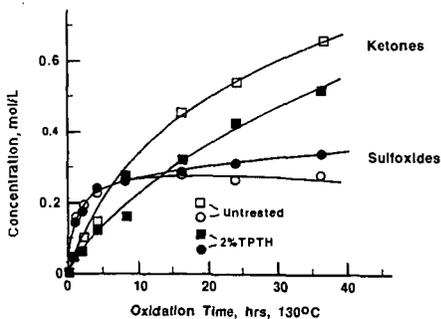


Figure 9. Effect of the Potential Antioxidant Triphenyltin Hydroxide on Oxidation Kinetics of a Boscan Asphalt