A Review of the Fundamentals of Asphalt Oxidation

Chemical, Physicochemical, Physical Property, and Durability Relationships
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A Review of the Fundamentals of Asphalt Oxidation

Chemical, Physicochemical, Physical Property, and Durability Relationships

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Sponsored by
Characteristics of Bituminous Materials Committee
Transportation Research Board

October 2009
TRANSPORTATION RESEARCH CIRCULAR E-C140
ISSN 0097-8515

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Foreword

Oxidative aging of asphalt is of practical significance to the understanding of pavement service life. *Transportation Research Circular E-C140: A Review of Fundamentals of Asphalt Oxidation: Chemical, Physicochemical, Physical Property, and Durability Relationships* is a synopsis of current physicochemical understanding of the chemistry, kinetics, and mechanisms of asphalt oxidation and its influence on asphalt durability. The oxidative behavior of asphalt is thought to be one of the critical factors contributing to the performance of hot-mix asphalt (HMA) pavements. The content of this review reflects more than half a century of research work on the physicochemical consequences of oxidative aging and its effects on the fundamental rheological properties of the oxidized asphalt. Emphasis is made on how the component fractions of asphalt behave under oxidation, including a consideration of the effects of the mineral aggregate and metals contained in asphalts. A section of the Circular reviews recent data and offers further insight on pavement aging as a function of air-void content of the mixture, temperature, and pavement depth and how oxidative hardening contributes to decreasing pavement service life.

Civil engineers, chemists, and asphalt technologists developing fundamental pavement performance models will find this Circular to be of interest. Professionals in owner agencies will have at their fingertips a useful handbook to understand the subtleties of asphalt oxidation and how it contributes to distresses in an HMA pavement. Beginning students of asphalt technology will find this a welcome review with many references to original work. The review is paramount today as the HMA industry transitions to the new technologies of warm-mix asphalt (WMA) produced at lower temperatures.

It is hoped that this fundamental review on asphalt oxidation and its effects on pavement aging to practitioners of asphalt technology will further stimulate and revitalize applied research and further insights into the oxidation of asphalt at temperatures now used in WMA.

Finally, this Circular is a timely contribution to the field of asphalt chemistry. TRB’s Characteristics of Bituminous Materials Committee is grateful to J. Claine Petersen for this authoritative and valuable work and his ongoing commitment to the pursuit of asphalt chemistry and its effect on pavement performance.

—Delmar Salomon

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Introduction

The two major uses of asphalt as a building material are in paving and roofing where the asphalt serves as the binding and waterproofing component. Materials engineers design paving and roofing materials to have physical properties that provide optimum service performance and durability. Optimum performance properties are highly dependent on the flow—or more precisely the rheological properties—of the asphalt; thus, changes in flow properties with time are usually highly undesirable, and often lead to reduced product performance or even failure. Because asphalt is a natural organic end product of ancient living organisms, it is subject to chemical oxidation by reaction with atmospheric oxygen. Asphalt oxidation is of pragmatic importance because it leads to the hardening of the asphalt, resulting in a deterioration of desirable physical properties. In asphalt pavements, oxidative age hardening contributes significantly to pavement embrittlement, eventually resulting in excessive pavement cracking. In asphalt roofing materials, embrittlement from oxidative hardening can promote the loss of protective granules, substrate shrinkage, and cracking. Oxidative hardening is attributed primarily to the introduction of polar, oxygen-containing chemical functionalities on asphalt molecules causing increased molecular interactions. Some aromatization of asphalt molecules may also result from oxidation. These changes in chemical composition would be expected to increase asphalt hardening.

Much work has been done to identify the polar, strongly associating functional groups in asphalt, either naturally present or formed on oxidation, and in characterizing their association forces (1). This subject is discussed later in more detail. The sensitivity of asphalts to oxidative age hardening varies widely with asphalt source (chemical composition); thus, the durability and performance of asphalt is highly dependent on its chemical composition (1). The classic field demonstration of this dependency was the Zaca–Wigmore experimental road test conducted in California in the 1950s (2). In this field test, construction variables were held constant and asphalt source was intentionally varied. The performance of the experimental pavements in the test was evaluated on the basis of crack formation from oxidative aging. Results clearly demonstrated that asphalt source, and thus composition, was an important variable in pavement durability.

This review deals with the chemical and physicochemical characterization of asphalt oxidation, the effects of differences in asphalt composition on asphalt oxidation, and oxidative age hardening as it affects performance-related physical properties.

An explanation of what is meant by physicochemical characterization follows. Although asphalts have many physical properties that are quite similar to polymers, the chemical forces at the molecular level that are responsible for these properties are differ significantly. A simple polymeric material is composed of large molecules of similar chemical composition. The molecular weights of its molecules do not change with environmental temperature changes. Asphalt, on the other hand, is composed of relatively small molecules compared with polymers. Further, it is a complex mixture of molecules, ranging from rather nonpolar hydrocarbons similar in composition to waxes to highly polar or polarizable hydrocarbon molecules containing condensed aromatic ring systems that incorporate heteroatoms such as oxygen, nitrogen, and sulfur. Thus, asphalt gets its “polymeric” properties from the molecular association of polar components in the asphalt that forms molecular agglomerates at the nanoscale level. These agglomerates (microstructure) are of a size relatively similar to polymer molecules, and thus
impart to asphalt its “polymeric” properties. However, unlike polymers, the molecules in the molecular agglomerates are bonded together, not by primary chemical bonds but by polar association forces such as hydrogen bonding and dipole interactions. The strength of these bonding forces is highly dependent on temperature. Thus, as the temperature increases, these reversible bonds are broken and the sizes of the agglomerates are reduced. It is the reversible nature of these interactions that gives asphalts their unique high-temperature viscosity susceptibility. The study of these molecular interactions at the nanoscale level, and their affect of physical and chemical properties measured at the macro level, is what is meant by physicochemical characterization. This is asphalt’s “black box” in which its most guarded secrets are kept.

Chemical and physical property data and methods for their determination are cited in this review primarily to illustrate the fundamental effects of oxidation on asphalt properties. A review of asphalt chemistry and the physical properties and methods used for their determination are beyond the scope of this document.
Oxidation Characteristics of Asphalt Component Fractions

Asphalt is composed of an extremely large number of chemically diverse organic molecules; therefore, chemists have not seriously considered attempts to separate them and determine their individual molecular identities. Considerable progress, however, has been made in the study of asphalt composition by component separation and characterization based on the reactivity and/or polarity of the various molecular types present. Because asphalts are the product of the maturation of natural products of biological origin over millions of years, the different molecular class types present are limited in number in spite of asphalt’s extreme molecular complexity.

Based on long-used classical separation methods, the molecules in asphalt can be conveniently separated or grouped into molecular types or fractions with a narrower range of properties based on their chemical functionality. The separation and classification of molecular types has been useful in providing chemically definitive component fractions for further characterization, thus aiding in determining how different molecular types affect the physical and chemical properties of the whole asphalts, and how asphalts differ chemically from one another. A more detailed discussion of the fractionation of asphalts into various “generic” fractions is found elsewhere (1).

SENSITIVITY OF ASPHALT COMPONENT FRACTIONS TO OXIDATION

Although a variety of fractionation schemes have been used to separate asphalts into generic fractions, perhaps the scheme most widely used in the past has been the procedure developed by Corbett (3). Fractions from other separation schemes of general use can be chemically related to the so-called Corbett fractions, since all of the schemes generally produce fractions of progressively increasing molecular polarity, aromaticity, and heteroatom content. Relationships between fractions from different separation schemes have been discussed by Petersen (1).

The four fractions produced by the Corbett separation scheme in the order of their increasing molecular polarity are saturates, naphthene aromatics, polar aromatics, and asphaltenes. The saturates fraction is generally a light straw-colored oil, primarily hydrocarbon in nature, with little aromaticity and a low heteroatom content except for sulfur. Because of the low chemical reactivity of the saturates fraction, it is highly resistant to ambient air oxidation. A study by Corbett and Merz (4) of a group of asphalts from 18-year-old Michigan state test roads showed no measurable loss of the saturates fraction due to oxidation during the 18-year service period.

The changes in the remaining three Corbett fractions on oxidation were generally observed to be a movement of components from the more nonpolar fractions to the more polar fractions as oxygen-containing functional groups are formed in the asphalt molecules. Because the various fractions have different reactivities toward oxidation, the result is usually a net loss of naphthene aromatics, and possibly a net loss in polar aromatics, with a corresponding increase in the asphaltenes fraction. Relative percentage changes in only the amounts of the Corbett fractions on oxidation provide limited fundamental understanding, and chemical changes are hard to interpret. This is because mass changes alone provide limited information about the actual chemical changes taking place within the fractions.
To provide additional chemical insight, several investigators have studied the uptake of oxygen by the generic asphalt fractions and the formation of oxygen-containing functional groups formed by reaction with the oxygen. Studies by King and Corbett (5), using thin films at 150°C, and by Knotnerus (6), using dilute toluene solutions at ambient temperature, showed that the saturates fraction was relatively inert to reaction with oxygen as measured by oxygen uptake. The naphthene aromatics (5) and aromatics (6) fractions showed slight and no reactivity, respectively. However, the Corbett polar aromatics fraction and the Knotnerus resins and asphaltenes fractions were highly reactive with oxygen. Corbett’s asphaltenes fraction showed intermediate reactivity. The comparison of the King and Corbett fractions with the Knotnerus fractions is only relative because the two studies used different temperatures and oxidation conditions (film versus solution), different asphalts and different separation techniques; however, the results of both studies show how reactivity increases with increasing fraction polarity. Direct measurement of ketone formation on oxidation of Corbett fractions (thin films, 130°C) derived from a Wilmington (California) asphalt by Petersen et al. (7) ranked the relative reactivity with atmospheric oxygen of the saturates, naphthene aromatics, polar aromatics, and asphaltenes fractions as 1:7:32:40, respectively. The production of ketones in asphalt has practical significance because it has been shown (8–12) that the amount of ketones formed on oxidation is linearly related to the increase in log viscosity of the asphalt—the viscosity being an important performance-related property. The sensitivity of a given asphalt to viscosity increase as a function of ketone formation, however, is highly asphalt source (composition) -dependent.

The asphaltenes fraction has been considered by some (13) to be chemically inert; however, the data presented earlier indicate that the asphaltenes are inherently quite reactive with oxygen. This apparent contradiction is explained by the fact that isolated asphaltenes at ambient temperature are brittle solids and are quite unreactive with atmospheric oxygen at ambient temperatures. This lack of reactivity is attributable to their highly structured (associated) state, which reduces molecular mobility. On the other hand, when the asphaltenes are separated and melted (as in the 130°C oxidation) or in solution in solvents, their molecular mobility is increased and thus so is their apparent chemical reactivity.

RELATIONSHIPS BETWEEN ASPHALT COMPONENT FRACTIONS AND ASPHALT DURABILITY

For the purposes of this discussion, asphalt durability is defined as the resistance of asphalt to the detrimental effects of oxidative age hardening on its performance properties. Because the different generic fractions of asphalt have different solubility characteristics and reactivity with atmospheric oxygen, various investigators have attempted to use relationships between these fractions to predict asphalt oxidative aging characteristics. In this section, several of these relationships are discussed.

It is evident from the results of component fractionation, as previously described, that a wide spectrum of molecular types is present in asphalt. The most nonpolar saturates fraction, in the absence of the more aromatic resinous components, is so unlike the polar asphaltenes fraction that the two fractions are not mutually soluble; yet, these extremes in molecular types must coexist in neat asphalt as a microscopically homogeneous mixture. This is made possible by the interaction of the components of the various fractions of the asphalt with each other to form a stabilized or compatible system of dispersed molecular agglomerates. A good balance of
fractions from nonpolar to polar is necessary to produce a compatible asphalt with good durability. The role of the various asphalt fractions in contributing to asphalt component compatibility, and thus durability, will next be considered.

It has long been recognized that asphalts exhibit properties that deviate from those of a true solution. Nellenstyn was first to describe asphalt as a colloidal system (14, 15). He considered asphalt as a dispersion of micelles in an oily medium. The asphaltenes fraction was considered essentially equivalent to the dispersed or micellar component (16). It was also recognized that the relative inability of the resinous components to keep the highly associated asphaltenes components well dispersed in the oily medium largely determined the gel or non-Newtonian flow characteristics of the asphalt (17, 18). Rostler and White (13) described the asphaltenes fraction as the component of the asphalt primarily responsible for asphalt viscosity and colloidal behavior because of its limited solubility in the remaining components of the asphalt. They concluded that the asphaltenes are kept dispersed by the peptizing ability of the nitrogen bases fraction (the major resinous generic fraction identified by his fractionation technique). The peptized asphaltenes are in turn solvated by the somewhat less polar resinous acidiffin fraction (another Rostler fraction) and gelled by the paraffins fraction (Rostler’s equivalent to the Corbett saturates fraction). Corbett (19) described the effects on physical properties of the four generic fractions separated by his procedure as follows: the asphaltenes function as thickeners; fluidity is imparted by the saturates and naphthene aromatics fractions which plasticize the polar aromatics and asphaltenes fractions; the polar aromatics fraction imparts ductility to the asphalts, and the saturates and naphthene aromatics in combination with the asphaltenes produce complex flow properties in the asphalt. In summary, he concluded that “each fraction or combination of fractions perform separate functions with respect to physical properties, and it is logical to assume that the overall physical properties of one asphalt are thus dependent upon the combined effect of these fractions and the proportions in which they are present.”

A proper balance in the amounts of the different chemical components is necessary to produce asphalt that is durable and resistant to detrimental physical property changes on oxidative aging (20–27). Asphaltenes that are not properly dispersed by the resinous components of the maltenes (the nonasphaltene fraction of asphalt and referred to by Corbett as petrolenes), will have reduced compatibility and thus reduce asphalt durability (13, 26).

Rostler and others (20, 27, 28) showed that the balance of the component fractions from the Rostler analysis, as indicated by the ratio of the amounts of the most reactive fractions (nitrogen bases plus first acidiffsins) to the least reactive fractions (paraffins plus second acidiffsins), was important to the resistance of pellets composed of asphalt and Ottawa sand to abrasion loss in laboratory testing. The rationale for the Rostler durability ratio is that the nitrogen bases and first acidiffsins (the resinous components) are the dispersing or peptizing components of the asphalt, and the paraffins and second acidiffsins are the gelling components; the gelling components produce incompatibility in the asphalt if present in too large of an amount. Incompatibility in an asphalt in turn increases its sensitivity to deleterious physical property changes on oxidative aging. Thus, asphalts with a low durability ratio were deemed undesirable. Although the Rostler fractionation scheme was used by many materials laboratories in years past, and correlations with field performance attempted (29, 30), it has generally not been accepted as an accurate predictor of field performance and is presently receiving little attention.
In field tests conducted in California (30), the Heithaus parameter, P, (state of peptization), which is reportedly a measure of the internal compatibility of an asphalt (26), was found to correlate better with pavement oxidative field hardening than the Rostler durability parameter. The Heithaus parameter is a mathematical relationship between the peptizability of the asphaltenes and the dispersing power of the maltenes. The parameter is determined by titration with heptane of solutions of several asphalt samples at different concentrations in a good asphalt solvent (toluene) while observing the first appearance of asphaltenes precipitation. More recently, there was renewed interest in the Heithaus method during the SHRP. Pauli and coworkers at Western Research Institute developed equipment to automate the procedure (31). The automated procedure has gone through several stages of development, the most novel modification being the so-called “reversible” procedure (32). Using this procedure, measurements can be made at several asphalt concentrations, as required to calculate Heithaus and related parameters, while requiring only one initial test solution.

Traxler (33) found a correlation between his coefficient of dispersion (resins plus cyclics divided by asphaltenes plus saturates) and the rate of hardening during laboratory oxidative aging. The better-dispersed asphalts (those with the larger coefficient of dispersion) hardened more slowly. As with the Rostler parameter, the ratio represents the amount of dispersing components divided by those components that must be dispersed or made compatible. Traxler also suggested that the degree of dispersion of the asphalt components was inversely related to the complex (non-Newtonian) flow properties of the asphalt, and is indicative of the asphalt’s colloidal characteristics.

It is apparent from the above discussion of the relationships among asphalt components, that the component compatibility or state of dispersion of micellar components in neat asphalt is highly significant with regards to the tendency of asphalts to oxidatively age harden. While all the relationships cited above have been shown to correlate with asphalt age hardening, the correlations are not sufficiently good to warrant their routine use as predictors of the field performance of a given asphalt. It is highly probable that the poor correlations result primarily because only the weight percent of the fractions are used in the calculations; thus, the significant differences often found in the composition and solubility characteristics of the same generic fractions from different asphalt sources are not taken into account. In spite of this shortcoming, the apparent relationships between component ratios and property changes on oxidative aging, as determined by the relationships of the generic fractions, have been widely used in research studies, and have provided valuable insight into the chemical and physicochemical aspects of asphalt oxidative age hardening.
Changes in Asphalt Chemical Composition on Oxidation

For many years studies of the changes in asphalt composition that occur on oxidation focused largely on the use of elemental and fractional analyses to define these changes. More detailed chemical analyses were difficult because asphalt consists of a highly complex mixture of molecules varying in molecular weight and compound types. Such a complex mixture did not readily yield to experimental techniques then available.

ASPHALT FUNCTIONAL GROUP ANALYSIS

Asphalt fractional analysis as described in the previous section yields limited information regarding the types of chemical functionality present in asphalts. More recently, analytical techniques have been developed that have yielded considerable information on the chemical functional groups present in asphalt, particularly those containing heteroatoms, including those oxygen-containing functional groups formed on oxidation (34–40). The heteroatoms in asphalt are often associated with polar, strongly interacting chemical functional groups that have a disproportionately large influence on asphalt properties (1). Many asphalt molecules of different structural composition will have similar chemical functionalities, which in turn will produce similar effects on physical properties. When the different types of chemical functionalities that dominate the properties of the various asphalt molecules are considered the number of types of functionalities that need to be considered narrows to a manageable number. Examples of chemical functionalities that are integral parts of large asphalt molecules are shown in Figure 1.

Since the 1960s, research has been conducted in the author’s laboratory related to the identification and characterization of the polar, heteroatom-containing chemical functionalities in asphalts. Infrared spectrometry has been a rewarding technique in this research because it can be applied to the whole asphalt or complex mixtures without prior separation into molecular components. Early research to explore infrared spectrometry for the characterization of asphalts showed the technique to be useful in identifying general chemical structural types present (41); however, the strongly associating polar functionalities present were never adequately identified and characterized. Attempts to use standard infrared spectral scans to characterize these polar functionalities were frustrated by such inherent problems as overlapping and ill-defined absorption bands, and shifting and broadening of absorption bands from association such as hydrogen bonding. Hydrogen bonding is a dipole interaction phenomenon in which a nonionic association exists between the residually positive hydrogen of weakly acidic components and residually negative (basic) moieties of molecules containing such polar atoms as oxygen and nitrogen.

These inherent problems have been overcome by the combined use of selective chemical reactions, differential infrared spectrometry, and the use of a selective solvent to break up hydrogen bonding and thus eliminate its complicating effects on the infrared spectrum. This scheme made possible a qualitative and quantitative infrared spectroscopic method for asphalt functional group analysis (FGA). The development and application of the FGA technique (36, 38) and a comprehensive experimental procedure, including examples of applications, have been reported (40).
The chemical functional groups quantitatively or semiquantitatively determined using the functional group analysis as described (40) are carboxylic acids (and independently their salts), anhydrides, ketones, 2-quinolone types, sulfoxides, pyrrolic types, and phenolic types. Structural formulas for these functional group moieties of asphalt molecules are shown in Figure 1. With the exception of basic nitrogen compounds in asphalts (predominantly pyridine types), which do not readily yield to infrared analysis, these functionalities make up the important polar heteroatom-containing functionalities initially present in asphalts or formed during oxidative aging.

The theory of the FGA will next be described. Those interested in the detailed experimental methodology and additional information on the technique are referred to in the literature (35, 36, 38, 40). The most polar and strongly interacting functional groups in asphalts occur in relatively small amounts and their infrared absorption bands are complicated by

![Chemical functionalities in asphalt molecules](image-url)

(1) Naturally occurring
(2) Formed on oxidative aging

FIGURE 1 Chemical functionalities in asphalt molecules normally present or formed on oxidative aging (1).
hydrogen bonding and overlap with other strong absorption bands, making their detection difficult and their quantitative assessment virtually impossible without the use of special techniques. Phenolic, pyrrolic, carboxylic acid, and 2-quinolone-type functional groups are naturally occurring in asphalts and are hydrogen bonding functionalities. In neat asphalts or in solutions of asphalts in typical nonpolar infrared spectral solvents, a concentration-dependent equilibrium exists between the free and hydrogen bonded states of these functional groups; thus, the absorption bands of both free and hydrogen bonded functional groups are present in the spectrum.

The infrared absorption bands of the phenolic and pyrrolic functional groups are illustrated in Figure 2a for carbon disulfide (CS₂) solutions of a Wilmington (California) asphalt. This figure is reproduced from the author’s original publication (40). Spectrum A for the unoxidized asphalt shows the phenolic and pyrrolic functional group absorption bands at 3610 cm⁻¹ and 3480 cm⁻¹, respectively. These two functional groups strongly hydrogen bond with polar chemical functionality formed in the asphalt on oxidation to produce overlapping hydrogen bonding bands in the 3100 to 3300 cm⁻¹ region. The relative amounts of the functional groups represented by the free and bonded species are dependent on their concentrations, the characteristics of the solvent if spectra are obtained on solutions, and the basicity of the asphalt components with which the acidic hydrogen interacts.

The two naturally occurring, hydrogen-bonding functionalities that present the greatest challenge for infrared analysis are the carboxylic acids and 2-quinolone types. Not only do they form dimers in neat asphalt and nonpolar spectral solvents such as carbon tetrachloride and carbon disulfide, but they also interact strongly with each other to form a mixed dimer. The net result is six infrared absorption bands of which five overlap and become virtually indistinguishable (42). The overlapping of these absorption bands is illustrated in spectrum A, Figure 2a, by the broad absorption in the 1700 to 1600 cm⁻¹ region centering at about 1655 cm⁻¹. The region at about 1700 cm⁻¹ represents dimerized, hydrogen bonded carboxylic acids.

The infrared spectra in the carbonyl region are further complicated in oxidized asphalts because the intense ketone band formed at 1700 cm⁻¹ (spectrum B, Figure 2a) is at the same absorption frequency as the carboxylic acid dimer, making the two indistinguishable. The free (nonhydrogen bonded) absorption band of the carbonyl group of the carboxylic acids (1730 cm⁻¹) is also virtually lost in the shoulder of the strong ketone band. Dicarboxylic anhydrides are also formed on oxidative aging by reaction of oxygen with two alkyl chains attached to adjacent bridgehead carbons on aromatic rings (35). Their absorption bands at 1725 cm⁻¹ and 1765 cm⁻¹ are also virtually impossible to observe in typical infrared scans because they are also masked by the strong ketone absorption band.

The infrared absorption band at 1030 cm⁻¹, shown in spectrum B of Figure 2a, is useful for determining the sulfoxides formed on oxidation. The other major absorption bands shown in spectrum B in the 3000 cm⁻¹, 1400 cm⁻¹, and 900 to 700 cm⁻¹ regions arise from absorption of aliphatic and aromatic hydrocarbon components of the asphalt.

To overcome the problems of band overlap from hydrogen bonding and to obtain spectra suitable for quantitative analysis, several specialized techniques and procedures were developed. In the analysis, the solvent tetrahydrofuran (THF) is used to eliminate interference from hydrogen bonding in the carbonyl absorption region for the determination of ketones, carboxylic acids, anhydrides, and 2-quinolone types. THF is a cyclic ether having a strongly electronegative oxygen within the molecule. Because of its electron donating properties, THF associates with acidic hydrogens of carboxylic acids and 2-quinolone types, thus preventing the previously
FIGURE 2  (a) Infrared spectra of CS₂ solutions of unoxidized and oxidized asphalt (all spectra solvent compensated) and (b) examples of infrared spectra used in FGA: C = untreated, D = TPTH treated, E = untreated, F = TPTH treated, G = NaOH treated (all spectra solvent compensated).

(continued on next page)
FIGURE 2 (continued) (c) examples of differential infrared spectra used in FGA:
H = TPTH treated versus untreated, I = silylated versus untreated, J = silylated versus TPTH treated, K = NaOH treated versus TPTH treated, L = NaOH treated versus solvent, M = untreated versus solvent.

described dimer and mixed dimer formation. The unassociated carbonyl groups are therefore made available for characterization.

With the problems of hydrogen bonding eliminated, the problem of overlapping bands in the carbonyl region (about 1800 to 1600 cm\(^{-1}\)) is addressed by using selective chemical reactions and differential infrared spectrometry. The techniques applied are as follows.

To reveal the absorption band of the chemical functionality of interest, and to eliminate from the spectrum all other bands with interfering (overlapping) absorption bands, the asphalt sample is treated with a selective chemical reagent that reacts with and eliminates, or shifts to another frequency, the absorption band of interest. A differential spectrum is then taken with the treated sample in one sample beam and a corresponding untreated sample in the other sample beam of a double beam infrared spectrometer [the procedure has been subsequently successfully modified at Western Research Institute to use Fourier transform infrared spectroscopy (43)]. This procedure reveals the absorption band of the functionality of interest and nulls (cancels out) all unreactive and interfering absorption bands in the region, including the solvent. The area of the band of interest is then used for quantitative analysis to determine the concentration of the desired chemical functionality. The selective chemical reagents that are used individually to react with the acidic, hydrogen-bonding functionality to prepare the different asphalt sample combinations for differential infrared analysis are sodium hydroxide (NaOH), triphenyltin hydroxide (TPTH), and a silylating reagent consisting of a mixture of hexamethyldisilazane and trimethylchlorosilane.

The application of these techniques is illustrated by the infrared spectra in Figures 2b and 2c. These spectra are also reproduced from the author’s original publication (40). The THF
solvent breaks up hydrogen bonding to produce the free carboxylic acid band at 1730 cm⁻¹ in spectrum C, Figure 2b. Treatment of the asphalt with TPTH reagent forms silyl esters of the carboxylic acids, shifting their carbonyl absorption out of the 1700 cm⁻¹ region and into the broad band area at 1600 cm⁻¹ (spectrum C). As previously mentioned, when asphalt is oxidized the carbonyl region is further complicated by the formation of ketones and carboxylic anhydrides. Reacting the asphalt with sodium hydroxide converts the acids and acid anhydrides to their sodium salts, shifting their absorption frequencies to form an intense, broad absorption band at about 1580 cm⁻¹ (spectrum G). The band area of the original 1700 cm⁻¹ region occupied by the carboxylic anhydrides is the area between spectra E and F; the area between spectra F and G represents carboxylic acids. The shaded area inside spectrum G represents the ketones formed on oxidation together with overlapping background absorption from the broad 1600 cm⁻¹ band from carbon-to-carbon and carbon-to-nitrogen double bonds in aromatic rings.

The silylation reaction mentioned earlier is used together with the selective reactions just described to prepare samples for quantitative analysis using differential infrared absorption techniques as previously described. Spectrum J shows the absorption band for free carboxylic acids. When asphalt is reacted with the silylating reagent, the carbonyl band of 2-quinolones is liberated; this is shown in the differential spectrum as the shaded area in spectrum I. The shaded area in spectrum J results from the silyl esters of carboxylic acids. This spectrum is less desirable for quantitative determination of acids because of negative interference from the 2-quinolone band centering near 1680 cm⁻¹. The doublet for carboxylic anhydride absorption is shown as the shaded region in spectrum K.

In the analyses of phenolic and pyrrolic functional groups, advantage is taken of the ability of the electronegative oxygen atom in THF to hydrogen bond with the electronegative hydrogen of these functionalities. Broad and intense hydrogen bonding bands are formed for both functional groups centering at about 3300 cm⁻¹ as shown in differential spectra M and L. Because both groups absorb at the same infrared frequency, sodium hydroxide treatment is used to destroy the phenolic band, thus differentiating the pyrrolic band (spectrum L) from the sum of the two bands (spectrum M).

CHEMICAL FUNCTIONAL GROUPS FORMED ON OXIDATION

The major oxygen-containing functional groups formed on aging (1, 37) for four asphalts from different crude sources and aged under identical laboratory conditions as thin films in air at 130ºC by the gas–liquid chromatography column oxidation procedure (44) are listed in Table 1. The data represent averages for four asphalts aged on four different mineral aggregates typical of those used in pavement construction. The level of oxidation shown in the table is judged to be in the range typically found for asphalts after 5 or more years of pavement service.

That the chemical functionality developed during the laboratory oxidation at 130ºC is similar to that developed during normal pavement aging at ambient temperatures is supported by the data shown in Table 2 (45). Reasons for the lower levels of oxidation in some pavement samples when compared with laboratory oxidation relate to variability in the permeability of the different asphalt pavements to atmospheric oxygen because of variations in pavement void content, and to differences in maximum pavement temperatures in the different pavement environments.
TABLE 1  Chemical Functional Groups Formed in Asphalts During Oxidative Aging (1)

<table>
<thead>
<tr>
<th>Asphalt</th>
<th>Ketones</th>
<th>Anhydrides</th>
<th>Carboxylic Acids</th>
<th>Sulfoxides</th>
<th>Average Hardening Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-2959</td>
<td>0.50</td>
<td>0.014</td>
<td>0.008</td>
<td>0.30</td>
<td>38.0</td>
</tr>
<tr>
<td>B-3036</td>
<td>0.55</td>
<td>0.015</td>
<td>0.005</td>
<td>0.29</td>
<td>27.0</td>
</tr>
<tr>
<td>B-3051</td>
<td>0.58</td>
<td>0.020</td>
<td>0.009</td>
<td>0.29</td>
<td>132.0</td>
</tr>
<tr>
<td>B-3602</td>
<td>0.77</td>
<td>0.043</td>
<td>0.005</td>
<td>0.18</td>
<td>30.0</td>
</tr>
</tbody>
</table>

1B-2959, Mexican blend; B-3036, Arkansas Louisiana; B-3051, Bosan; B-3602, California.
2Naturally occurring acids have been subtracted from reported value.
3Ration of viscosity after oxidative aging to viscosity before oxidative aging.

TABLE 2  Comparison of Oxidation Products Formed in Laboratory and Pavement-Aged Asphalts (45)

<table>
<thead>
<tr>
<th>Asphalt</th>
<th>Concentration, mol/L</th>
<th>Column Oxidized</th>
<th>Pavement Aged</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ketones</td>
<td>Anhydrides</td>
<td>Ketones</td>
</tr>
<tr>
<td>60</td>
<td>0.76</td>
<td>0.024</td>
<td>0.53</td>
</tr>
<tr>
<td>25</td>
<td>0.70</td>
<td>0.025</td>
<td>0.53</td>
</tr>
<tr>
<td>30</td>
<td>0.64</td>
<td>0.027</td>
<td>0.64</td>
</tr>
<tr>
<td>61</td>
<td>0.64</td>
<td>0.022</td>
<td>0.44</td>
</tr>
<tr>
<td>67</td>
<td>0.43</td>
<td>0.013</td>
<td>0.32</td>
</tr>
<tr>
<td>71</td>
<td>0.76</td>
<td>0.026</td>
<td>0.51</td>
</tr>
<tr>
<td>72</td>
<td>0.82</td>
<td>0.033</td>
<td>0.68</td>
</tr>
<tr>
<td>73</td>
<td>0.49</td>
<td>0.013</td>
<td>0.35</td>
</tr>
<tr>
<td>74</td>
<td>0.72</td>
<td>0.027</td>
<td>0.43</td>
</tr>
</tbody>
</table>

1Laboratory thin film (~0.0015 cm) oxidation, 130°C, 24 h.
2Recovered from 11- to 13-year-old pavements.

Data in Table 1 show that ketones and sulfoxides are the major oxidation products formed during oxidative aging as identified by FGA. Dicarboxylic anhydrides and carboxylic acids are formed in much smaller amounts. In some asphalts, the summed concentrations of the oxidation products approach 1 mole/L. If a molecular weight of 1,000 Daltons is assumed for an average asphalt molecule, then on the average, one functional group per molecule is formed. Of course, not all molecules of asphalt have the same reactivity, as has been discussed. Less reactive molecules in the nonpolar fractions may suffer no oxidation, while more than one functional group per molecule might be formed in the more reactive fractions such as the polar aromatics.

The types of oxidation products formed (but not concentrations) are consistently similar among asphalts from different sources, and are in good agreement with what is known about the hydrocarbon and sulfur-containing molecular types in asphalt and the general oxidation chemistry of these molecular types. The oxidation of asphalts is apparently complicated by different mechanisms of oxidation, which dominate at different stages of the oxidation reaction. Dorrence et al. (34) obtained strong evidence that the ketones are formed at the benzylic carbon position (the first carbon of an alkyl chain attached to an aromatic ring). A tertiary benzylic
carbon (one having two alkyl groups and one hydrogen atom attached to the carbon adjacent to aromatic ring) is likely to be the most reactive ketone precursor. The lone hydrogen on the tertiary benzylic carbon is very reactive and is easily removed during oxidation. Using nuclear magnetic resonance spectrometry, Mill and Tse (46) found that most of the benzylic hydrogen (6% to 11% of the total hydrogen in the four asphalts tested) is of this tertiary (methine) type. This type of carbon–hydrogen bond is orders of magnitude more reactive toward oxidation than the carbon–hydrogen bond of unbranched aliphatic hydrocarbons.

On certain aromatic molecules, which have two adjacent benzylic carbon moieties, a highly stable dicarboxylic anhydride can result from the oxidation of these adjacent benzylic carbons followed by the condensation of intermediates that would otherwise form ketones (35). These anhydrides form without prior formation of carboxylic acids. Only trace amounts of new carboxylic acids and no measurable amounts of esters (35) have been found in laboratory- or pavement-aged asphalts. It appears that the hydrocarbon oxidation reaction, except for the anhydride formation reaction, almost always stops with ketone formation at pavement aging temperatures.

The formation of sulfoxides, the other dominant oxidation product, has been shown to result from the oxidation of organic sulfides that are functional moieties of many asphalt molecules (39). Many of these sulfides are highly reactive and initially form sulfoxides at a much faster rate than ketones are formed. The sulfide types that most readily oxidize in asphalt are believed to be of the dialkyl or alkylaromatic types, and undoubtedly form sulfoxides by reaction with hydroperoxide intermediates from oxidation of asphalt hydrocarbons (39).

It is instructive to reconsider the data in Table 1 with regard to the relative effects of the amounts of oxidation products formed on oxidation and the effects of differences in asphalt chemical composition and compatibility on oxidative age hardening. In the table are shown the chemical changes that occurred in the asphalts on oxidation and also their hardening indexes. Note that asphalts B-3036 and B-3051 show the formation of about the same amounts of ketones and sulfoxides; yet, asphalt B-3051 showed the highest level of oxidative hardening and asphalt B-3036 the lowest level of all the four asphalts. On the other hand, asphalts B-2959 and B-3602, which showed the formation of widely differing amounts of ketones and sulfoxides, had nearly the same level of oxidative hardening. These results demonstrate that the sensitivity of an asphalt to the oxidation products, as governed by the asphalt’s component compatibility, may be more important to the level of asphalt age hardening than is the actual amount of oxidation products formed. Thus, it should not be surprising that the ratios of asphalt generic fractions, based only on the weight percent of the generic fractions, as previously discussed, might not be an accurate predictor of asphalt durability when used to compare asphalts from different sources having significant differences in chemical composition.

EFFECTS OF MINERALS, METALS, AND ANTIOXIDANTS ON ASPHALT OXIDATION

Effects of Minerals on Oxidation

Because asphalts are used in conjunction with mineral aggregates in both pavements and roofing, the possibility that these minerals might act as catalysts for asphalt oxidation is of pragmatic concern. To investigate this possibility, the oxidation of asphalts and asphalt fractions was
Changes in Asphalt Chemical Composition in Oxidation

To investigate this possibility, the oxidation of asphalts and asphalt fractions was studied \((7, 47)\) by oxidizing thin films on mineral aggregate surfaces using the inverse gas chromatographic technique \((44)\). When asphalt generic fractions (prepared by the Corbett separation procedure described earlier) were oxidized separately, mineral aggregate surfaces were found to catalyze the oxidation of the more nonpolar fractions. Infrared spectroscopic analyses of the extracted oxidized fractions \((7)\) showed that carbonyl compounds were formed in the saturates fraction oxidized on quartzite aggregate in concentrations 10 times greater than in the saturates fraction oxidized on an inert fluorocarbon substrate. The ratio was about 3:1 for the naphthene aromatics, with little or no effect of the aggregates on the oxidation of the polar aromatics or asphaltenes fractions. Oxidation of the whole asphalt on quartzite showed only a negligible effect of the aggregate on asphalt oxidation. It was proposed that the polar functional groups in the more polar fractions of asphalt are adsorbed on the catalytically active sites of the aggregate surface, thus “poisoning” their catalytic effect. Thus, it is believed that for most asphalts, the catalytic effect of mineral aggregate surfaces on asphalt oxidation is negligible relative to the amount of oxidation that occurs in the bulk asphalt in normal use applications.

Hydrated lime is widely used in asphalt pavements to increase pavement resistance to moisture damage. It was reported in 1971 by the Utah Highway Department \((48)\) that hydrated lime apparently reduced the rate of age hardening in a number of asphalt pavements. This phenomenon was later studied by others \((49–51)\). In a mechanistic laboratory oxidation study, Plancher and Petersen \((49)\) showed that the hardening rate of hydrated lime-treated asphalts was significantly reduced. This reduction was attributed to both the adsorption by lime of asphalt components that otherwise would have increased the sensitivity of the asphalt to the oxidation products, and to the reduction of the rate of formation of oxidation products. In this study, the hydrated lime was removed from the asphalt prior to laboratory oxidation. In a subsequent study \((51)\), the hydrated lime together with adsorbed asphalt components was left in the asphalt during the oxidative aging and similar results on age hardening rate were obtained.

**Effects of Metals on Oxidation**

It is well known that metals such as iron can catalyze the oxidation of asphalts. Metal salts such as ferric chloride have been used as catalysts in the air blowing of asphalt fluxes. In general, however, commercial asphalts for paving application do not contain sufficient amounts of contaminant metal salts to present a catalytic oxidation problem. However, some asphalts do contain significant amounts of naturally occurring vanadium, which in some forms, can be an active catalyst for hydrocarbon oxidation. Typical amounts of vanadium in asphalt range from near zero to about 1,300 ppm \((1)\).

Traxler and Scrivner \((52)\) proposed a direct correlation between asphalt hardening indexes and vanadium content based on laboratory oxidation studies. The data presented by Traxler and Scrivner were somewhat scattered, although the overall trend seemed clear. Their results were questioned by some as fortuitous because many asphalts that are high in vanadium also have high sensitivity to viscosity increase on oxidation because of reduced component compatibility from compositional differences as discussed previously.

To further clarify this question, Branthaver et al. \((53)\) studied the effects of metalloporphyrins on asphalt oxidation. It was concluded from this study that some vanadyl porphyrins naturally present promote asphalt oxidation as measured by ketone formation; others do not. The extent of the oxidation is not, however, a simple function of the vanadyl porphyrin...
concentration, but is also probably influenced by molecular aggregation involving the porphyrin and by differences in the porphyrin molecular structure. Nonporphyrin vanadium complexes and nickel porphyrins naturally present in petroleum appeared to be inactive in promoting oxidation. It should be noted, however, that many vanadium compounds (e.g., vanadium acetyl acetonate) and ions of other transition elements [e.g., Mn²⁺ as used in Chemcrete (54)] are active auto-oxidants for petroleum hydrocarbons.

Effects of Antioxidants and Related Materials on Oxidation

Because antioxidants have been successful in improving the resistance of polymers and related materials to oxidation and embrittlement, it was logical to investigate the potential use of antioxidants in asphalts. Martin (55) studied the ability of antioxidants to reduce age hardening in air-blown roofing asphalts when subjected to oxidation at 65°C both in the dark and under ultraviolet light. The dark oxidation was conducted in air at 300 psi. The antioxidants studied were examples from classes designated as ultraviolet absorbers, free-radical traps, and peroxide decomposers; these are classically hydroxybenzophenones, phenolic types, and sulfur compounds, respectively. Martin found that all types of additives reduced the hardening rate in the absence of light for at least one of the bitumens in the study, but the results were not consistent from one bitumen to another. Some additives increased asphalt hardening when heated in the absence of oxygen. Response to dark and ultraviolet oxidation was often different for a given additive; thus, if antioxidants were to be used, the optimum antioxidant would need to be determined experimentally for each bitumen involved. In a later study (56), Martin examined a larger group of 34 antioxidants in a single, partially blown Kuwait asphalt described as industrial waterproofing grade. All of the free-radical trap antioxidants and half of the peroxide decomposers showed antioxidant activity, the former class being much more effective against photo-oxidation than dark oxidation, and the effective species of the latter class being effective against both environmental conditions.

These early studies of antioxidants indicated that dithiocarbamates might be effective antioxidants. Lead and zinc dithiocarbamates were later investigated by Haxo and White (57). Santucci et al., evaluated zinc dithiocarbamates in laboratory aging studies (58). Oliver (59) evaluated these materials as antioxidants in sprayed asphalt seals for up to 10 years in the field. Both laboratory and field studies showed the dithiocarbamates to substantially reduce asphalt hardening, with the lead derivative being most effective. Evidence for the effectiveness of the dithiocarbamates in retarding the brittle failure point beyond 10 years in the field is uncertain. Santucci’s group (58) also compared the effectiveness of sodium hydroxide with that of zinc dithiocarbamates in reducing oxidative age hardening in three asphalts during laboratory oven aging at 113°C. They found that the caustic additive sodium hydroxide was more effective in reducing the age hardening rate than the dithiocarbamates. The present writer believes the effectiveness of this caustic additive resulted from its reaction with the native acids in the asphalt to form sodium salts, thus breaking up hydrogen bonding in the asphaltene agglomerates and increasing the dispersibility of the asphaltenes. This resulted in increased asphalt component compatibility and reduced sensitivity to oxidative age hardening. A word of caution is warranted at this point because experience has shown that acid salts produced by the addition of caustic to asphalts can often produce pavement mixtures with increased sensitivity to moisture damage.

Because the state of component dispersion (component compatibility) of an asphalt has a significant effect on asphalt oxidative hardening rate, as discussed in a previous section, the
possibility is suggested by this writer that some of the antioxidants used in the studies may have also reduced oxidative hardening by acting as a dispersant for the asphaltene-like components in the asphalt, thus improving component compatibility. Indeed, it has been reported by Dybalski (60) that cationic asphalt additives, commonly used as asphalt emulsifiers, augment the peptization of the asphaltene constituent and thus reduce the asphalt hardening rate. According to this report, of 82 asphalts tested, 81% were benefited by the additives, with a minimum of 15% and a maximum of 65% reduction in hardening rate during the rolling thin-film oven test (ASTM D2872-77). In another study (61), the hardening rate of a recycled pavement mixture during laboratory aging was reduced several fold by a high float emulsifying agent used to emulsify the recycling agent before recycling the pavement mixture in the laboratory.

Liquid antistripping agents added to asphalt mixtures to reduce moisture damage in pavements have also been widely observed by pavement technologists to sometimes reduce the viscosity of specification asphalts by a greater amount than what can be accounted for from dilution effects by the antistripping agent. It has been proposed that this may result because these highly polar additives may alter the dispersion of asphalt components. Such alteration of the state of dispersion could also alter the sensitivity of the asphalt to oxidative hardening. The phenomenon has been studied by Anderson et al. (62), and results showed that the antistripping agents not only altered flow properties, but also altered the oxidative hardening rates of asphalts. The phenomenon was highly dependent on both asphalt source and antistripping agent concentration, and as with the antioxidants, is not well enough understood to be pragmatically applied to alter the aging characteristics of asphalts.
Effects of Oxidation on Molecular Interactions and Physical Properties

Asphalt molecules are relatively large and of complex structure, and are highly diverse in their chemical composition. Many of the molecules are polyfunctional; that is, they contain more than one functional chemical moiety per molecule. For this and other reasons it is impractical, if not impossible, to separate asphalt into its individually different molecules for further analysis. A pragmatic compromise to this problem is to separate asphalt into group types having related chemical reactivity. Separation of asphalt into generic fractions using techniques such as the Corbett desorption chromatographic procedure have previously been described. More recently in SHRP, techniques such as ion exchange chromatography and size exclusion chromatography were adapted and used to separate asphalts into fractions containing functional groups with more definitive chemical functionality (63).

The interactions of the chemical functionalities in asphalt largely determine its physical properties and oxidative aging characteristics. For this reason, identifying these chemical functionalities and quantifying, to the extent possible, the magnitude of their interactions provides a fundamental approach to understanding and eventually predicting the effects of asphalt composition on physical properties and changes in these properties on oxidative aging.

FUNDAMENTALS OF MOLECULAR INTERACTIONS

Before discussing the asphalt molecular system, it is instructive to summarize a few fundamental concepts of molecular interactions in a somewhat simplistic manner. Molecules attract and interact with one another through a variety of secondary forces. These association forces are generally one or two orders of magnitude weaker than the covalent (primary) chemical bonding forces that hold the atoms in molecules together. The secondary association forces are significantly different from the stronger covalent bonding forces in that they form bonds that are generally reversible and are usually in dynamic equilibrium between the bonded and unbonded states. That is, they make-and-break under forces induced by such factors as temperature and external stress; and thus, they play a major role in determining the physical properties of the composite material.

To illustrate the principles involved, the familiar and classic example of the hydrogen bonding of water is considered. A simplistic schematic of the hydrogen bond formed between two water molecules is shown in Figure 3. The electronegative oxygen atom reduces the electron density of an attached hydrogen atom by attracting its electron field, thus creating an electropositive hydrogen atom. The polar water dipoles thus formed attract one another through dipole–dipole interactions between the hydrogen and oxygen of different water molecules. In reality in liquid water, all hydrogen and oxygen atoms of the water molecules interact through hydrogen bonding to form a three-dimensional network of associated water molecules. When water flows or is vaporized, the hydrogen bonds are the major association forces that must be overcome to allow the molecules to move with respect to one another or to escape as a vapor.
These are the major association forces controlling the properties of water. The dynamic formation and breakup of molecular structure via association forces is rapid, and for water, often of the order of nanoseconds.

To illustrate further the large influence of the electronegative oxygen atom (the atom also introduced into asphalt molecules during oxidative aging) on physical properties, consider replacing the oxygen atom of the water molecule with a sulfur atom (also the major heteroatom in most asphalts) to yield hydrogen sulfide ($\text{H}_2\text{S}$). Because sulfur is less electronegative than oxygen, the strength of the hydrogen bond with sulfur in $\text{H}_2\text{S}$ is much weaker than the hydrogen bond with oxygen in water. As a result, $\text{H}_2\text{S}$, even though of significantly higher molecular weight than water, is not a liquid, but rather a gas at ambient temperatures. Its boiling point is 163°C lower than that of water. Indeed, the molecular analogs of $\text{H}_2\text{S}$ in asphalts are organic sulfides in which the sulfur atom interactions have a negligible effect on physical properties. The effects of intermolecular forces, as illustrated by the hydrogen bond, are fundamental to understanding the effects of chemical composition and oxidative aging on asphalt properties because these intermolecular forces are the primary determinants of physical, and thus, performance properties.

It should not be implied from the forgoing example that the hydrogen bond is the most important interaction force in asphalt. Many other reversible interaction forces are at work in a material as complex as asphalt. These include a variety of dipole and induced dipole interactions. For simplicity in discussing molecular interactions in this chapter, all molecular structural types in asphalt that exhibit these forces are considered as chemical functionality. These functionalities include, but are not limited to, the more classical chemical functional groups such as carboxylic acids, ketones, sulfoxides, etc., as shown in Figure 1.

Nonpolar hydrocarbon components in asphalt such as those dominant in the saturates fraction exhibit only weak interaction forces, which accounts for the fluid nature of the saturates fraction. Unoxidized sulfur atoms in asphalt molecules also exhibit very weak interaction forces, as typified by the comparison above of the hydrogen bonding properties of water and hydrogen sulfide. On the other hand, asphalt molecular components containing highly condensed (multi-ring) aromatic ring systems and chemical groups containing oxygen and nitrogen atoms are usually highly polar or polarizable and thus interact strongly with each other. These strong interaction forces largely account for the fact that asphaltenes, even though they are for the most part not significantly different in molecular weight than the other asphalt fractions (64), are high melting solids. The molecules of asphaltenes appear to cluster upon interacting by close packing of their planar aromatic ring systems. This molecular structuring is evidenced by x-ray diffraction patterns and is reported to have association energies of the order of 14 kcal/mole (65).
EFFECTS OF MOLECULAR INTERACTIONS ON ASPHALT FLOW PROPERTIES

The data in Table 3 were abstracted by the writer from data obtained by Griffin et al. (22) to illustrate the effects of different types of molecular interactions on viscosity. Griffin et al. separated the nonasphaltene fraction of asphalt into component fractions followed by molecular distillation of the fractions. They then determined the molecular weight versus viscosity profiles for the fractions. The data in Table 3 were selected from these profiles to represent the viscosity of each of the three fractions at the same true molecular weight. The saturates fraction had a viscosity of only 10 Pa-s. The saturates do not contain chemical functionality of significant polarity and the molecular interactions are weak. Molecular interactions of increased intensity are exhibited by the aromatics fraction, the viscosity of which was 1,000 Pa-s. Finally, the resins that contain polarizable aromatic systems and heteroatom functionality exhibited even more intense molecular interactions, producing a viscosity for this fraction of 1,000,000 Pa-s. Because the true molecular weights of each fraction are the same, the differences in viscosity result primarily from differences in the type and strength of the molecular interactions. The association forces among asphalt molecules give asphalts many of the properties of high molecular weight polymers.

Considerable research has been done in identifying the polar, strongly associating functional groups in asphalts, either naturally present or formed on oxidation, and characterizing their association forces (34–36, 38–40, 42, 63, 66–74). Structural formulas of important chemical functional moieties of asphalt molecules were shown in Figure 1. Nitrogen, which occurs in asphalts in concentrations ranging from about 0.2% to 1%, is present in several forms from the slightly acidic pyrrolic types to the more basic, strongly interacting pyridine types (74). The nitrogen types in asphalt are not known to be significantly altered on oxidative aging. The sulfur in asphalts (usually ranging from about 1% to 6%) is present primarily as sulfides (39, 63); these are illustrated in Figure 1. The organic moieties attached to the sulfur atom may be alkyl, cycloalkyl or aromatic (39). Cyclic sulfur molecules exist primarily as thiophene homologs (63) and are quite unreactive during oxidative aging. Alkyl substituted sulfur, on the other hand, is quite reactive toward oxidative aging, yielding sulfoxides (39), and generally accounts for about one-fourth to one-fifth of the sulfur present in the asphalt (39, 63). Phenolics are also present (74). Carboxylic acids and 2-quinolone type functionalities, although present in relatively small amounts, are highly polar and strongly associate (69).

TABLE 3 Effect of Molecular Polarity on the Viscosity of Asphalt Fractions of the Same Molecular Weight

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Molecular Weight</th>
<th>Viscosity, Pa-s, 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturate</td>
<td>500</td>
<td>10</td>
</tr>
<tr>
<td>Aromatic</td>
<td>500</td>
<td>1,000</td>
</tr>
<tr>
<td>Resin</td>
<td>500</td>
<td>1,000,000</td>
</tr>
</tbody>
</table>

Source: Adapted from data in Griffen et al. (22).
EFFECTS OF POLAR GROUPS FORMED ON OXIDATION ON ASPHALT FIELD PERFORMANCE

Asphalts vary considerably in their susceptibility to adverse effects from oxidative aging. If during oxidative aging, the concentration of polar functional groups becomes sufficiently high to immobilize an excessive number of molecules through intermolecular association, the molecules or molecular agglomerates lose sufficient mobility to flow past one another under thermal or mechanical stress. The resulting embrittlement of the asphalt makes it susceptible to fracturing or cracking and resistant to healing.

To illustrate the effect of polar functional groups on the cracking tendency of asphalt pavement, consider the data in Figure 4. The asphalts used in this laboratory study (66) were from the California Zaca–Wigmore experimental road test (2) previously mentioned, in which construction variables were kept as constant as possible in order to evaluate the effects of differences in asphalt composition (source) on pavement durability.

Data in the figure show the relationship between the amount of strongly interacting polar functional groups naturally present plus those formed in the asphalts during controlled laboratory oxidative aging, and the resistance to failure from cracking in pavements in which these asphalts were used. In the laboratory study, the asphalts were coated as thin films on inert fluorocarbon

FIGURE 4  Relationship between phenol interaction coefficient and pavement surface performance rating (66).
particles and aged in a gas chromatographic (GC) column at 130°C for 24 h by passing air through the column (44). This procedure oxidizes asphalt to a level equivalent to about 5 or more years in a typical pavement. Following column aging, the polar test compound, phenol, was passed through the GC column using an inert carrier gas, and its interaction with the polar functional groups in the asphalt determined from the retention time of the phenol. As phenol passes through the column, it is in dynamic equilibrium with the asphalt; thus, those asphalts having a greater concentration of polar functional groups interact more strongly with the polar functionality of phenol, giving a larger phenol interaction coefficient. In Figure 4, the phenol interaction coefficient is plotted versus the cracking density of the pavements after 51 months of service as determined from visual inspection by an independent rating panel (2). As can be seen in the figure, an excellent correlation was found between the total asphalt polarity, as measured by the phenol interaction coefficient after aging, and the service performance rating based on the crack density of the Zaca–Wigmore pavements. Those asphalts that had a higher concentration of polar functionality after GC column oxidative aging failed sooner from fatigue cracking in the road.

In the laboratory study of the Zaca–Wigmore asphalts, a number of different test compounds with widely differing chemical functionality were evaluated in addition to phenol; however, the excellent correlation was found only with phenol. It is theorized that the phenol molecule contains the three fundamental types of strongly interacting functionalities found in oxidized asphalts: (a) the acidic hydrogen of the phenol OH group, which hydrogen bonds through its residually positive dipole, (b) the residually negative dipole of the oxygen of the phenolic OH, and (c) the polarizable pi electrons of the phenolic aromatic ring. The polar interacting moieties in the asphalt molecules are analogous to one of these types of functionalities, and thus the phenol interaction coefficient is postulated to reflect the sum of all of the above types of interactions between the phenol and the asphalt as the phenol moves through the stationary GC column.

In Figure 5 is shown a similar correlation developed using 20 roofing asphalts (66), the weatherability of which was determined by resistance to cracking when aged in a carbon-arc Weather-Ometer. Thus, strong evidence exists relating polar functional groups in asphalts with failure from embrittlement and cracking.

EFFECTS OF POLAR ASPHALT COMPONENTS ON VISCOSITY

The significant influence of polar constituents, in this case asphaltenes, on asphalt viscosity is shown in Figure 6. In the study cited (37), Plancher et al. used four asphalts all meeting the same pavement grade specifications. These asphalts were oxidized in the laboratory both before and after treatment with hydrated lime. The asphalts were aged using four different laboratory aging methods to achieve different levels of oxidation. Following aging, both asphaltenes content and viscosity at 25°C were determined. Each data point in the figure represents a separate level of oxidation. The unusual behavior of asphalt B-3602 before and after lime treatment is attributed to the fact that this asphalt had been treated with sodium hydroxide prior to distillation. This converted the acids to sodium salts. These were converted to calcium salts and subsequently removed during the laboratory aging studies, changing the dispersibility of the asphaltenes.
FIGURE 5  Relationship between phenol interaction coefficient and durability of 20 roofing asphalts (66).

FIGURE 6  Relationship between viscosity at 25°C and asphalene content of untreated and lime-treated asphalts aged by four different laboratory methods (37).
Although each asphalt displayed a unique relationship, a good correlation exists between asphalt viscosity and asphaltenes content for each of the asphalts. Several important points can be inferred from the data in Figure 6. First, the asphaltenes fraction is the dominant component controlling asphalt viscosity. Second, the asphaltenes, or at least their effects on viscosity, are quite different from one asphalt to another. This could result from differing asphaltenes composition and/or from different solubility or dispersive powers of the maldenes fraction among the different asphalts. This is a necessary condition in order for these asphalts with widely differing asphaltenes contents to meet the same viscosity specification.

The effects of polar functionality on oxidative age hardening are further illustrated by the data in Table 4, which show the effects of hydrated lime treatment on reducing the hardening rate of asphalt during laboratory GC column oxidation. During lime treatment, about 4% of the asphalt was irreversibly adsorbed on the lime, which was removed with the lime prior to conducting the age hardening experiments. The material adsorbed on the lime was identified as predominantly carboxylic acids and 2-quinolone analogs. Note that except for asphalt B-3602 (the most compatible asphalt in the group), the lime treatment reduced the hardening indexes of the asphalts by more than 50%. Asphaltenes formation was also reduced by about 50% in the lime-treated asphalts. Functional group analyses, however, showed that the oxidation reaction, as measured by ketone formation, was reduced only 10% by lime treatment. What was concluded in addition to decreasing the oxidation rate was that lime also removed carboxylic acids and other polar functionality that reduced the viscosity sensitivity of the asphalts to the oxidation products formed. Putting it another way, removal of the highly polar constituents removed chemical functionality that would otherwise have remained in the asphalt and reacted with oxygen or interacted with the oxidation products to increase viscosity. Separate studies have shown that carboxylic acid functional groups introduced onto asphalt molecules by an unambiguous synthetic route caused a significant increase in the viscosity of an asphalt maldenes fraction.

As discussed in the previous paragraph, lime treatment in the laboratory significantly reduced the rate of asphalt oxidative hardening by both reducing the rate of oxidation and removing the strongly associating, and thus viscosity building, carboxylic acids and 2-quinolone types. Removal of these viscosity-building components increase the component compatibility of lime-treated asphalt, particularly in the pavement temperature range. As a result, the possibility exists that the reduced molecular associations in the lime-treated asphalt from the adsorption of the viscosity-building components on the lime surface might also delay the onset of the

<table>
<thead>
<tr>
<th>Asphalt</th>
<th>Untreated</th>
<th>Lime Treated</th>
<th>Reduction, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-2959</td>
<td>37</td>
<td>17</td>
<td>54</td>
</tr>
<tr>
<td>B-3036</td>
<td>27</td>
<td>10</td>
<td>63</td>
</tr>
<tr>
<td>B-3051</td>
<td>132</td>
<td>35</td>
<td>73</td>
</tr>
<tr>
<td>B-3602</td>
<td>29</td>
<td>18</td>
<td>39</td>
</tr>
</tbody>
</table>

1Viscosity after aging divided by viscosity before aging.
2B-2959, Mexican blend; B-3036, Arkansas Louisiana; B-3051, Boscan; B-3602, California.
“quenching” effect of reduced molecular mobility that results from increased association of oxidation products during the oxidation reaction. However, lime-treated asphalts in pavements might continue to oxidatively harden over time until they eventually reach a viscosity similar to that of untreated asphalts. This possibility was suggested from results of an unreported study by the author and coworkers in which asphalts extracted from lime-treated pavement sections in a Montana road study, although less hardened than an untreated control section after 3 years of service, reached an oxidative hardening level similar to the control section after 5 years. Similar results by Oliver (59) showed that after 10 years, lime treatment showed no apparent beneficial effect on the age hardening of asphalt extracted from an Australian pavement.

In all of these field studies, however, it was necessary to extract the asphalt from the road samples using powerful solvents prior to obtaining physical property measurements on the asphalt. In doing so, any lime-induced molecular structuring which might be beneficial to pavement properties would be destroyed by the solvent. Furthermore, the solvent most likely extracted polar, viscosity-building asphalt components from the lime, thus recombining them with the recovered asphalt.

In a more recent kinetic study (75), this problem was addressed by pressure vessel oxidative aging of asphalt in air (2.07 x 10^6 Pa, 300 PSI) near upper pavement temperatures (60°C) for times up to 2,000 h. This produced a level of oxidation typically beyond that normally encountered during the useful life of an asphalt pavement. In this study it was found that for an asphalt normally sensitive to oxidative aging, that after the 2,000-h aging period, the lime-treated asphalt had better ductile flow properties than its untreated counterpart as evidenced by a larger phase angle at the same stiffness modulus. That is, at the same stiffness modulus, the ratio of the loss (flow) modulus to the storage (elastic) modulus was greater for the lime-treated asphalt. This suggests more resistance to fatigue and low-temperature cracking in pavements using lime-treated asphalt. These laboratory results are supported by a Peruvian pavement study (76) that showed lime-treated asphalt pavements to be more resistant to crack development on aging.

The well-recognized superior performance of hydrated lime in reducing moisture-induced damage in asphalt pavements, thus increasing wet strength resulting in reduced fatigue cracking and rutting, together with the potential of lime to reduce the rate of oxidative hardening and improve ductile flow properties at the same stiffness as untreated asphalt, is ample justification for its use in pavements.

In more recent studies, the amount of ketones formed in asphalt on oxidative aging has been shown to correlate with the increase in viscosity (9–11, 63); however, each asphalt exhibits its unique relationship.

Data in Figure 7 (11) illustrate this relationship. Oxidations were carried out at 60°C using a pressure aging vessel (PAV) (11, 63); and at 85°C, 113°C, and 130°C using the thin film accelerated aging test (TFAAT) (63, 77). The asphalts were aged for various time periods at each temperature to develop the data in the figure. Although the data obtained in both the pavement aging temperature range (60°C) and in the higher temperature ranges generally fit the same plot, the data for some of the asphalts suggest a slightly smaller slope for the lower temperature (60°C) PAV aging. The different viscosity sensitivities of the different asphalts to the amount of ketones formed, as evidenced in Figure 7, are undoubtedly related to the dispersibility of the asphaltenes and to the dispersive (solvating) power of the asphalt maltenes fraction. Moon-Sun-Lin et al. (78) have shown that asphaltenes formed on oxidative aging have similar effects on rheological properties as the asphaltenes originally present in the asphalt. It is instructive to consider further the possible implications of the correlations just presented (Figures 6 and 7) with
FIGURE 7  Relationships between carbonyls formed and dynamic viscosity increase during PAV (solid points) and TFAAT (open points) oxidative aging (II).

regard to molecular association or aggregation (microstructure). It follows that if both ketones and asphaltenes are linearly related to log viscosity, that they are related linearly to each other. This strongly implies that the ketones formed on aging are responsible for the formation of additional asphaltenes. Therefore, it is likely that most of the ketones are formed on molecules from the Corbett polar aromatics fraction as evidenced by the fact that the polar aromatics fraction shows the greatest mass loss on oxidation.

EFFECTS OF POLAR ASPHALT COMPONENTS ON ASPHALT COMPONENT COMPATIBILITY AND AGING CHARACTERISTICS

Reference has been made in previous sections of this chapter to the need for a good balance among asphalt components of differing polarities to yield an asphalt with good aging characteristics and durability. The purpose of this section is to examine the relationships between component compatibility and asphalt aging characteristics in more detail.

Compatibility in asphalts deals with the mutual solubility or dispersibility of a variety of components with widely differing solubility characteristics and solvent powers. Early workers in
the field considered compatibility in terms of the state of peptization of the asphaltenes. Heithaus (26) stated that asphaltenes are the most polar and aromatic components of asphalt and are present in asphalts as rather concentrated solutions (10% to 40%). To obtain optimum solvency or dispersion for these polar, strongly associating species in asphalts, the polarity of the solvent (maltenes) must be matched to the materials being dispersed (asphaltenes). For example, more polar asphaltenes or larger relative amounts of asphaltenes require maltenes with greater solvent power to effectively disperse them.

A number of studies have addressed the dispersibility of asphaltenes and methods to measure dispersibility and compatibility (21, 26, 63, 78–81). Altgelt and Harle (80) convincingly showed, using reduced specific viscosity measurements, that selected asphaltenes from different asphalt sources produced dispersed asphaltene agglomerates of different effective sizes when added at the same weight percent to a common maltenes fraction. In the technique used, the reduced specific viscosity is a measure of the relative thickening power of the asphaltenes. More fundamentally, it is related to the hydrodynamic volume occupied by the proposed agglomerated asphaltenes. The technique is widely used to determine molecular weights of polymers. Altgelt’s work further showed that maltenes derived from asphalts of different sources had different solvency power for asphaltenes, thus producing dispersed asphaltenes agglomerates of different effective sizes from the same asphaltene fraction.

To illustrate the application of reduced specific viscosity to the study of the effects of asphalt oxidation on the compatibility and oxidative hardening characteristics of asphalt, consider the data in Figure 8 (11) in which two of the core study asphalts (63) from SHRP were used. These asphalts represent the extremes in component compatibility of the eight SHRP core study asphalts. Reduced specific viscosity is defined in the figure, and data were calculated from viscosity measurements made at 45ºC on maltenes fractions containing various amounts of asphaltenes below and above the natural abundance levels of the neat asphalts. Because asphaltenes once separated from the asphalt are not readily dispersed when added back to the maltenes fraction, special techniques were used to prepare the samples with different asphaltene contents from the unoxidized and oxidized parent asphalts. To prepare samples with an asphaltene content less than natural abundance levels, maltenes previously separated from the same asphalt were added back to neat asphalt so as to least disturb the structural morphology of the native asphaltenes present. For samples with asphaltene contents greater than natural abundance, the appropriate amounts of maltenes and asphaltenes were dissolved in dichloromethane followed by solvent removal.

Because the reduced specific viscosity is related to the apparent molecular size of the asphaltenes component in the asphalt mixture, the tendency of the asphaltene molecules to associate into molecular agglomerates, and thus form microstructure appears to be observable. If the reduced specific viscosity remains constant as the asphaltene content is increased, this is evidence that the asphaltene agglomerates are remaining well dispersed in the maltenes phase with no significant increase in their apparent size as asphaltene concentrations increases. However, if the reduced specific viscosity increases as the concentration of asphaltenes is increased (Figure 8), this is evidence that the size of the asphaltene agglomerates is increasing with asphaltene content. Extrapolation of the asphaltene content to zero is defined as the intrinsic viscosity. It is highly likely that this strongly associated, “hard core” asphaltene agglomerate, at near zero concentration, is the smallest structural unit of the dispersed asphaltenes. This agglomerate would most likely consist of a relatively stable configuration or cluster of a number of individual asphaltenes molecules (65, 82, 83).
FIGURE 8 Reduced specific viscosity data from measurements at 45°C for asphalts AAD-1 and AAG-1 before and after oxidative TFAAT aging at 113°C for 72 h (11).

Interpretation of the data in Figure 8, as discussed, shows that the asphaltenes in unoxidized asphalt AAG-1 are well dispersed, and are highly mobile at their natural abundance level of 5%. Of particular interest are the data in Figure 8 showing reduced specific viscosity measurements for asphalt AAG-1 that had previously been oxidized at 113°C for 72 h using the TFAAT. Although oxidation did reduce the compatibility of the asphaltenes in the maltenes, the size of the asphaltenes agglomerates increased only modestly. This indicates that this asphalt is highly compatible and can quite effectively solubilize or disperse the oxidation products formed on normal oxidative aging.

On the other hand, data in Figure 8 for unoxidized asphalt AAD-1 show that its asphaltene agglomerates at their natural abundance level of 20% are much less compatible and of much larger size than the agglomerates in AAG-1 at their natural abundance level of 5%. As will be discussed later, with increasing asphaltenes concentration the asphaltene microstructure of AAD-1 increases rapidly in size thus immobilizing molecules that would otherwise be inherently reactive toward oxidation (84). It is also seen that oxidation had a much greater effect on microstructure formation in the less compatible AAD-1 than in the more compatible AAG-1.
Also shown in Figure 8 are the asphalt aging indexes and the amounts of ketones formed on aging for the two asphalts AAD-1 and AAG-1. Note that although asphalt AAD-1 aged at a much more rapid rate than asphalt AAG-1, as evidenced by the aging indexes, only about half the amount of viscosity-inducing ketones were formed in AAD-1 compared with AAG-1. These results again demonstrate the importance of asphalt component compatibility on oxidative age hardening characteristics. Even though asphalt AAG-1 was more chemically reactive in forming ketones than AAD-1, it was much more resistant to oxidative age hardening, again demonstrating the important role of physicochemical factors on asphalt age hardening. Because of the good solvent power of the maltenes in AAG-1, and the asphalt’s low concentration of asphaltenes, it was able to solubilize and/or disperse the oxidation products to a much greater extent, thereby reducing their effect on viscosity increase.

Consider next the reduced viscosity data presented in Figure 9. Instead of presenting the asphaltene concentration as percent of natural abundance, it is presented as actual percent asphaltenes. What becomes apparent is that the new asphaltenes formed on oxidation form molecular agglomerations with essentially the same effective size at a given concentration as the asphaltenes naturally present in the asphalt. Putting it another way, the new asphaltenes formed on oxidation have the same effect on viscosity and viscosity increase as the native asphaltenes. Although not shown in Figure 9, blends of asphaltenes from oxidized AAG-1, when added incrementally to the maltenes fraction produce reduced viscosity values similar to those of AAD-1 until concentrations reach about 12% asphaltenes. Beyond 12%, the AAG-1 reduced viscosity values are smaller than those at corresponding concentrations of AAD-1 asphaltenes. This indicates that the asphaltene agglomerates in AAG-1, when concentrations become large enough.
to form larger associated species, are smaller in size and better dispersed than the agglomerates of AAD-1.

Considering together the chemical, physicochemical and physical property data presented, an important conclusion suggested earlier is tentatively confirmed; that is, that the extraordinary effect of the ketones formed on oxidation to increase asphalt viscosity results because they cause the formation of increasing amounts of asphaltenes which form molecular agglomerates; these agglomerates increase significantly in size with increasing asphaltene concentrations above approximately 12%.
Asphalt Oxidation Kinetics and Mechanisms of Oxidation

The rheological data presented in this section were obtained at Western Research Institute (WRI) using a Rheometrics mechanical spectrometer (Model RMS-605). This instrument was a research grade dynamic shear rheometer. All dynamic viscosity data cited were obtained in the linear viscoelastic region, thus the viscosity data presented are at or near zero shear viscosity. Shear rates used were 1.0 radians/s or less unless otherwise noted, and temperature measurements were made at 60ºC. Earlier studies on asphalts oxidatively aged both in the laboratory and in the field (54) showed that under these shear conditions and at this temperature complex dynamic shear viscosities were in the linear viscoelastic region until they reached about $2 \times 10^4$ Pa-s ($2 \times 10^5$ poise).

EFFECTS OF COMPOSITION AND TEMPERATURE ON AGE HARDENING CHARACTERISTICS

The kinetics of asphalt oxidation and oxidative age hardening are important because they yield quantitative information on the rate of change in asphalt properties on oxidation as a function of aging time. Such information is necessary to more accurately predict the useful life of asphalt in service under varying environmental conditions. Unfortunately, oxidative aging data most frequently obtained in laboratory aging tests, and used to aid in predicting asphalt long-term performance, are single-point determinations at some point on the oxidation time scale, and at aging temperatures much higher than actual pavement temperatures. Such data provide little useful information on what the properties of the asphalt might be at some other point on the time-temperature scale. Unless aging tests are run at different temperatures, one is never assured as to how the asphalt properties might change when aged at temperatures different for those used in the laboratory test. Thus, kinetic data as a function of time and temperature are important to assist in the development of more reliable aging tests for predicting long-term asphalt performance.

To illustrate this problem, it is instructive at this point to consider the kinetic data for the oxidative hardening of the two SHRP core asphalts AAD-1 and AAG-1, whose widely different component compatibilities were discussed in the previous section of this report. These asphalts were oxidized in air at 60ºC and 80ºC as a function of time in a pressure aging vessel (PAV) at 2.07 MPa (300 PSI). The kinetic data were abstracted from a WRI semiannual report (85) and are presented in Figure 10. The aging time scale at the lower temperature has been scaled and shifted to offset the doubling of the chemical reaction rate for each 10ºC increase in temperature. This makes possible the visual comparison of the kinetics at the two temperatures as they are affected by physicochemical factors.

An interpretation of the data in Figure 10 is suggested by the data in the reduced specific viscosity plots in Figures 8 and 9, together with additional compositional data. It was discussed previously that a major part of the ketone oxidation that occurs in asphalt takes place in the polar aromatics fraction, unless sufficiently high temperatures are used that the asphaltene fraction is dissociated. The polar aromatics contents of asphalts AAD-1 and AAG-1 are 41% and 51%, respectively; the asphaltenes contents are about 20% and 5%, respectively. First consider asphalt
AAG-1. The reduced specific viscosity data show that the asphaltenes are well dispersed and mobilized in the maltenes phase; and on oxidation the oxidation products are probably also somewhat solubilized and mobilized. Since the total asphaltenes fraction is only a small percentage of the total reactive components of AAG-1, and only small amounts of oxidation products are immobilized by association upon oxidation, the concentration of reactive, mobile species is not significantly changed during oxidation at both temperatures.

However, in the case of the less compatible asphalt AAD-1, a rather large percentage of the high asphaltenes content of this asphalt may be immobilized through molecular association, and thus rendered less reactive toward atmospheric oxygen. Further, the total amount of polar aromatics is lower in AAD-1 than in AAG-1, and is likely more strongly associated. As these polar aromatics oxidize, they become less compatible in the maltenes phase and associate to form a significantly larger population of immobilized, less reactive, associated species. Thus, the concentration of the more reactive components that remain mobile is significantly reduced during oxidation. Because molecular associations are temperature sensitive and increase as temperature decreases, the lower time-temperature adjusted rate of oxidative hardening of AAD-1 at 60°C than at 80°C is a logical result, when compared with the similar aging data for AAG-1.

**FIGURE 10** Effects of temperature and component compatibility on oxidative aging characteristics (85).
at both temperatures. The kinetics of oxidative age hardening as affected by temperature and differences in asphalt composition will be discussed in greater detail in a later section.

Data in Figure 10 also have pragmatic implications with respect to laboratory aging tests designed to simulate the effects of pavement aging. If single-point oxidation tests are to be used, the oxidation should be carried out at least to a level significantly beyond the inflection point on the kinetic plot to a point on the flat or linear portion of the plot to yield reproducible and meaningful results (11, 86). Further, if single-point aging determinations are made, they should be made as near the use temperature as possible, and measurements made at more than one temperature within the use-range window.

**KINETICS OF ASPHALT OXIDATION CHEMISTRY**

In the previous section, the effects of asphalt composition on physical property changes during oxidative aging were considered. Because these physical property changes are a direct result of changes in the chemical composition of asphalt, the kinetics of the formation of chemical functional groups during oxidation will next be considered. Figure 10 shows the rates of formation of the four identifiable chemical functionalities formed in a Boscan asphalt on oxidation (87). The aging procedure used was the gas chromatographic column oxidation procedure (44) in which the asphalt was aged at 130°C as a 15-micron thick film coated on an inert fluorocarbon column packing in a GC column. Functional group analyses (FGA) were performed using the technique based on differential infrared spectroscopy and selective chemical reactions (36, 38, 40) discussed earlier. Ketones and sulfoxides are the major oxidation products, with minor amounts of carboxylic acids and dicarboxylic anhydrides (35) being formed in the later stages of oxidation. (Note that the concentration scale for the minor components has been expanded fourfold). Anhydrides are not formed from the condensation of carboxylic acids, but result from the condensation of oxidation product intermediates on adjacent side chains of aromatic ring systems (35).

The level of oxidation reached in this rather high temperature procedure (Figure 11) is greater than normally seen in an asphalt pavement throughout its thickness; however, oxidation near the pavement surface may approach these levels. Significant amounts of ketones and anhydrides have been found in older pavements (Table 2). Ketones and sulfoxides are formed more rapidly during the initial stages of oxidation, with sulfoxides being the most easily formed oxidation product. After the initial oxidation spurt; however, ketone and sulfoxide formation proceed at a much slower rate as was previously noted.

Because of the high temperature of the aging test used in this experiment, and the tendency of the polar components of the Boscan asphalt to further associate during oxidation, the inflection point in the ketone plot between the higher initial and subsequent lower rate of ketone formation is not well defined. Figure 12 (63) shows the oxidation at 113°C for the highly compatible SHRP asphalt AAG-1, in which changes in the state of dispersion of the polar components during oxidation are minimum. The inflection points for both the ketone and sulfoxide plots at about 5 h of oxidation are readily apparent. The hyperbolic kinetic oxidation plot with an initial rapid rate of ketone and sulfoxide formation followed by their formation at a lower, rather constant rate, together with the hyperbolic viscosity plot, is typical of all asphalts and has been amply demonstrated (10–12, 63, 86).
FIGURE 11 Oxidation products formed as a function of time in a Boscan asphalt during thin-film laboratory aging at 130°C (87).

FIGURE 12 Kinetic oxidation data for TFAAT oxidation of SHRP asphalt AAG-1 at 113°C (63).
Herrington and coworkers (88), in kinetic studies of paving asphalts at different temperatures, have also reported that the increase in viscosity was a hyperbolic function of oxidation time, and that asphalts had a limiting viscosity on oxidation that was different for each temperature. The quenching effects of molecular association of the oxidation reaction, as was proposed in this writer’s previous study (84), is also supported by their work. They attributed these temperature related effects in part to differences in the availability of reactive species due to temperature-dependent structural effects.

Liu et al. (86) reported in a study of 14 asphalts that the activation energy for ketone formation in the temperature range of 60ºC to 80ºC following the initial oxidation spurt varied from 64 to 109 kJ/mole, and the reaction order was 0.6.

The very rapid rate of formation of sulfoxides during the initial stages of oxidation at higher oxidation temperatures levels off to a somewhat constant concentration with time (39). This apparent pseudo steady state sulfoxide concentration depends upon the environmental parameters affecting the asphalt sample (63, 87). This steady concentration level apparently is the result of the depletion of reactive sulfides only for those asphalts low in sulfur. In most asphalts (generally those with sulfur contents over 1% or 2%), this apparent sulfoxide steady state concentration appears to be the net result of sulfoxide formation from oxidation and sulfoxide loss through thermal decomposition (63, 89).

When thermal decomposition of sulfoxides is occurring during oxidation, the absolute level of sulfoxides in the asphalt in the steady state condition is highly dependent on aging temperature (which determines the rate of decomposition) and the diffusion rate of oxygen into the asphalt (largely controlled by sample film thickness). These conclusions are demonstrated in Table 5 for a Boscan asphalt (~5.5% sulfur) in which both film thickness and temperature were varied during ambient pressure oxidation (89). In both thin- and thick-film oxidation, as temperature was increased while holding film thickness constant, the steady state sulfoxide concentration decreased, thermal decomposition being effected more by temperature changes than the rate of oxygen diffusion into the asphalt. However, as film thickness varied at the same temperatures, the sulfoxide steady state concentration was higher in the thin film than the thick film because of the increased diffusion rate of oxygen into the thin film, while the rate of sulfoxide thermal decomposition remained constant in both thick and thin samples.

TABLE 5 Steady State Concentrations of Sulfoxides in a Boscan Asphalt Under Different Oxidation Conditions (89)

<table>
<thead>
<tr>
<th>Oxidation Method</th>
<th>Oxidation Temperature, ºC</th>
<th>Steady State Sulfoxide Concentration, mol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin film on Teflon™ (~0.0015 cm)</td>
<td>25</td>
<td>&gt;0.46*</td>
</tr>
<tr>
<td></td>
<td>113</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>163</td>
<td>0.16</td>
</tr>
<tr>
<td>Thick-film rolling thin-film oven (~0.5 cm)</td>
<td>113</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>163</td>
<td>0.15</td>
</tr>
</tbody>
</table>

*No steady state concentration was reached at the conclusion of the experiment because sulfoxide decomposition is negligible at 25ºC.
In a separate experiment (89), it was found that 90% of the sulfoxides in oxidized Boscan asphalt were thermally decomposed by treatment of the sample in an inert atmosphere for 10 h at 163°C. During this thermal treatment, no new oxygen-containing absorption bands or baseline changes appeared in the infrared spectra. Similar results were also found by Herrington (90). These findings suggest that neither stable oxygen-containing sulfur compounds nor hydrocarbon oxidation products are formed during the sulfoxide thermal decomposition. This loss of oxygen from the sulfoxide functional group together with its apparent loss from the asphalt sample during thermal decomposition needs further study.

The relative stability of the sulfoxides in a Boscan asphalt is shown in Figure 13. These data were obtained in the SHRP research (91) during annealing experiments to determine an appropriate sample conditioning protocol prior to conducting physical property measurements.

Below about 50°C, the rate of sulfoxide thermal decomposition appears negligible for the Boscan asphalt, but as temperature increases, the rate becomes significant. Since there were no

![Graph](image_url)

**FIGURE 13** Thermal stability of sulfoxides in oxidized SHRP asphalt AAD-1 and effects of their decomposition on rheological properties (91).
changes in the infrared spectra during sulfoxide thermal decomposition except for the loss of the sulfoxide band, the physical property data in Figure 13 indicate that the sulfoxides in this asphalt contributed to asphalt viscosity. The tan delta data in Figure 13 (ratio of loss modulus to storage modulus during dynamic shear rheological measurements) show that the sulfoxides also contributed significantly to the storage (elastic) modulus of the asphalt. Infrared spectroscopy studies by the writer have indicated that sulfoxides hydrogen bond with pyrrolic NH groups in asphalt.

The sensitivity of sulfoxides to thermal decomposition is not the same for all asphalts. In fact, Boscan asphalt seems to be an asphalt in which the rate of sulfoxide thermal decomposition is on the high side. Thermal treatment of oxidized SHRP study asphalt AAF-1 in a similar manner to the Boscan asphalt described above decomposed only 58% of the sulfoxides. Mill (63) and Herrington (90) have also reported variable reactivity to sulfoxide thermal decomposition of asphalts from different sources.

KINETICS OF OXIDATIVE AGE HARDENING

The kinetics of oxidation at higher temperatures typically used in laboratory accelerated aging tests was shown for a Boscan asphalt in the previous section (Figures 11, 12). In fact, prior to the SHRP program, virtually all laboratory testing used to evaluate asphalt oxidative age hardening characteristics was conducted at temperatures much higher than pavement temperatures. However, the paving community is becoming increasing aware that the laboratory aging characteristics obtained at high temperatures are not representative of the aging that occurs at field temperatures. Therefore, understanding how kinetic aging data are affected as a function of aging temperature is vital. In the field temperature range, oxidation reactions become significantly affected by the physicochemical state (degree of molecular association and immobilization) of the polar, more chemically reactive components. The degree of association or agglomeration of the polar species, as discussed in previous sections, is highly temperature dependent. The temperature can also change the relative amounts of the major oxidation products formed. It has been repeatedly observed (63, 87, 92, 93) that at ambient temperatures, the rate of sulfoxide formation during the initial oxidation spurt is much more rapid than ketone formation. At lower temperatures during this initial oxidation spurt, sulfoxides are formed initially with the virtual exclusion of ketones. As a result, oxidative age hardening characteristics are altered.

PAV Versus Atmospheric Pressure Aging

During the 1980s there was an increased interest in the use of polymer-modified asphalts in asphalt pavements. Many of these modified asphalts, e.g., those modified with styrene-butadiene rubber or polyethylene, possessed a two-phase morphology in which the polymer existed as a separate dispersed phase in the asphalt. When these asphalts were subjected to the high-temperature laboratory aging tests then currently in use, the morphology of the polymer phase was seriously altered, thus having a detrimental effect on physical properties. In an attempt to overcome this problem in work being conducted at WRI on polymer-modified asphalts, this writer decided to try the low-temperature pressure vessel aging technique developed by Day-Yinn Lee at Iowa State University (94). Using this procedure, the standard thin-film oven pan containing the sample is aged in a pressure vessel in an oxygen atmosphere at 60ºC and at a
pressure of 20 atmospheres. It was found that at this relatively low temperature, the asphalt was sufficiently viscous to preserve the morphology of the polymer dispersion during the oxidative aging process. In developing his procedure, Lee experimented with different pressures to determine what pressure was necessary to get uniform oxidation throughout the thickness of the 1/8 in. (3.1 mm) asphalt sample. The 20-atmosphere pressure selected satisfied this condition, thus eliminating oxygen diffusion as a problem in studying the aging kinetics. The lack of significant diffusion effects under these aging conditions was further verified at WRI.

PAV was later selected for use in development of the long-term aging test for the SHRP asphalt composition research being conducted at WRI. Conditions selected initially for aging were 6 days in oxygen at 60ºC and at 20 atmospheres pressure. The 60ºC temperature was chosen to be more representative of field aging temperatures. About 2 years into the research program, air was substituted for oxygen because of concerns about the safety of using pure oxygen. At this time, conditions were found to be borderline regarding sufficient oxygen partial pressure to eliminate problems with diffusion of oxygen into the sample. About the same time, industry became concerned that a 6-day aging test was unacceptably long, and a decision was made, without the benefit of time to do kinetic studies, that the temperature of the test would be raised to 100ºC and the time reduced to 20 h so that the test could be completed in 1 day. These conditions produced an aged asphalt with about the same consistency as the 60ºC, 6-day test.

Unlike at 60ºC, however, during PAV aging at 100ºC, the rate of oxidative aging in the 1/8 in. (3.1 mm) asphalt sample was significantly affected by the effects of limited diffusion of oxygen into the sample (95). This problem was discussed in more detail in the presentation made by the author at the 2006 WRI–FHWA Symposium in Laramie, Wyoming (96). The author concluded that when the temperature was raised from 60ºC to 100ºC, two additive effects greatly increased the rate of oxygen consumption by the asphalt. First, the reaction rate of organic compounds approximately doubles with every 10ºC increase in temperature. Second, as will be discussed in detail later on, molecular structuring (microstructure) of the polar, most oxidation-reactive species, which inhibits oxidation at 60ºC, is mostly broken up at 100ºC. This disruption of the microstructure greatly increases the effective concentration of mobile reactive species at 100ºC. Thus, the compounding effects of these two phenomena increase the rate of oxygen consumption faster than oxygen can diffuse into the sample. Therefore, the PAV kinetic data obtained at 100ºC cannot be quantitatively compared with the corresponding data obtained at 60ºC because of the unknown effects of oxygen diffusion on the results (96). For this reason, most of the kinetic data as a function of temperature that are subsequently discussed in detail will be reported only on atmospheric pressure aging using the TFAAT aging procedure. In this procedure, diffusion problems are of limited concern because of the thin film (0.0063 in., 0.16 mm) used.

Effects of Temperature on Oxidative Aging Hardening Kinetics

Early in the SHRP program, age hardening kinetic studies for the eight SHRP core study asphalts was conducted at 60ºC (near pavement aging temperature) using oxygen in the pressure vessel at 20 atmospheres pressure in which diffusion effects were inconsequential. The dynamic shear viscosity measured at 60ºC as a function of aging time is shown in Figure 14 (63).
The results of these studies were quite unexpected. It is apparent that after the initial fast reaction (about the first 50 h of aging), that the long-term aging rates for all of the SHRP asphalt are quite similar. This is apparent, in spite of the fact that these asphalts have very different aging rates when aged using typical laboratory aging tests at temperatures above 100°C. Also shown in the figure are the ketones produced during the aging period. Note that their concentration varies widely, with a low of 0.07 mol/L for asphalt AAA-1 to a high of 0.18 mol/L for asphalt AAG-1. It was shown earlier (Figure 7) that ketones produced in more compatible asphalts with low levels of microstructure have less effect on producing viscosity increase than ketones in less compatible asphalts having higher levels of microstructure. The interpretation of the data in Figure 14 is that the molecular association (microstructure) caused a reduction of molecular mobility, and thus the rate of chemical oxidation, in the less compatible asphalts, so that their rate of increase in viscosity at 60°C nearly matched the rate of viscosity increase in the more compatible asphalts.

These results have significant implications with regard to using higher temperature laboratory aging tests to predict the aging characteristics of asphalts in pavements. The 60°C temperature used in the pressure aging vessel data shown in Figure 14 is in the range of temperatures experienced in actual pavement aging. The laboratory data in Figure 14 are not significantly affected by diffusion effects of oxygen into the test sample as explained earlier; thus, they show the actual inherent oxidative aging hardening characteristics of the asphalts at 60°C. It is also noteworthy that the aging during the TFO test plus the aging during the rapid
oxidation spurt had a greater influence on the aging indexes at 60°C than did the steady-state long-term aging after 400 h.

The proposed effects of breaking up microstructure by increasing the temperature on the hardening characteristics of the eight SHRP asphalts during PAV in oxygen are illustrated in Figure 15 (63). These data show the aging indexes (viscosity aged–viscosity unaged, measured at 60°C) after 144 h of aging at 60°C, 70°C, and 80°C (a more-detailed discussion on the effects of temperature on oxidative age hardening will be presented in a later section).

For the highly compatible asphalt, AAG, a relatively constant rate of increase in the aging index is seen throughout the aging temperature range. This is interpreted as primarily the influence of temperature only on reaction rate, with changes in the microstructure having little influence. This should be expected because this asphalt has few asphaltenes (about 5%) and lots of polar aromatic asphaltene dispersants. Most of the oxidation-reactive species are mobilized in the maltenes phase, and increases in the amount of associated microstructures on oxidation have a limited effect on viscosity because they are too far apart to interact. On the other hand, as previously explained, at 60°C many of the reactive components in the less compatible, high asphaltene asphalts are immobilized by absorption in the microstructure (it will be shown later that this microstructure begins to break up just above 60°C). However, as temperature increases, this microstructure is disrupted, mobilizing these reactive components and making them much more reactive with oxygen. As a result, as evidenced in Figure 15, their aging indexes increase.

**FIGURE 15** Effect of thermal disruption of asphalt microstructure on oxidative age hardening.
exponentially with temperature. Note the disparity between asphalt AAD and the other asphalts. These data agree with field experience for this California asphalt, which often produces pavements that fail prematurely from embrittlement and cracking when used in hot climates.

**Kinetic Relationships Between Viscosity Increase and Oxidation Chemistry**

In most use applications, asphalt is exposed to the oxygen in air at ambient pressures. Kinetic data for the ambient pressure oxidation of asphalt AAF-1 are displayed in Figure 16 together with relationships between viscosity increase and ketone and sulfoxide formation (92). The ambient pressure oxidations were conducted using the thin film accelerated aging test (TFAAT) in which the asphalt was oxidized as a 160-micrometer thick film at both 85°C and 113°C. The data shown for asphalt AAF-1 are typical of most asphalts, although relationships among the variables differ for asphalts from different sources.

At the lower temperature of 85°C, as shown in the left plot in Figure 16, a larger concentration of sulfoxides were formed during the initial oxidation spurt at the expense of ketone formation when compared with the relative amounts of these two functional groups formed at the higher 113°C temperature. As will be discussed in detail in the later section on the chemical mechanisms of asphalt oxidation, the initial fast reaction spurt initially results from the reaction of oxygen with highly reactive perhydroaromatic hydrocarbons to form hydroperoxides. These can then either react with asphalt sulfides to form sulfoxides, or decompose to form free radicals. When free radicals are formed the can initiate and/or intensify a subsequent oxidation.

![Figure 16](image)

**FIGURE 16** Oxidative aging kinetic data and viscosity–functional group relationships for SHRP asphalt AAF-1 after TFAAT oxidation as a thin film at atmospheric pressure (92).
reaction involving the benzylic carbon on aromatic rings to form ketones. Thus, as temperature is increased, more free radicals are produced and less sulfoxides are formed because the hydroperoxides are thermally unstable. If the asphalt has a lower sulfur content, this temperature effect will favor a lower ratio of sulfoxides to ketones at higher temperatures. Another factor that undoubtedly contributes to the rapid change in the ratio of sulfoxides to ketones with temperature change is the high sensitivity of the molecular agglomerates to dissociation with temperature increase. This would mobilize benzylic carbon-containing aromatic molecules that at lower temperatures are locked up in the associated molecular agglomerates.

It should be noted that the total concentration of sulfoxides-plus-ketones at the end of the initial oxidation spurt is about the same at both high and low temperatures regardless of the relative amounts of each that are produced. This fact suggests that both ketones and sulfoxides are produced as a result of a common precursor. When the reactive precursor is exhausted, the oxidation spurt is over. This produces a leveling off of the kinetic curve. The ratio of sulfoxides to ketones following the initial oxidation spurt varies considerably as a function of asphalt sulfur content. Higher sulfur content produces more sulfoxides and less ketones. Also, the sensitivity of sulfoxides to thermal decomposition following their formation also significantly affects the sulfoxide content during the long-term aging following the initial oxidation spurt.

Data on the right side of Figure 16 show the relationships between viscosity increase and the formation of ketones and sulfoxides. It should be noted that this is not a kinetic plot. As has been previously discussed, for any given asphalt source, the concentration of ketones formed on oxidation correlates linearly with log viscosity increase. This is apparent from the data on the right side in Figure 16. Also note that after the rapid oxidation spurt is compete at about 0.15 mol/L ketones, the viscosity increase is more sensitive to ketone formation during the high temperature, 113ºC oxidation. This is not apparent for the 85ºC oxidation. Additional data on the effects of oxidation on viscosity sensitivity to ketones will be presented later. Note that sulfoxide concentration shows less correlation with log viscosity increase for the 113ºC aging temperature because of thermal decomposition of sulfoxides during the long-term oxidation reaction following the rapid oxidation spurt. During the rapid oxidation spurt, however, sulfoxide formation is very large at both temperatures.

The SHRP core asphalt AAF-1 used to develop the data shown in Figure 14 has an intermediate level of component compatibility and sulfur content. The reader is referred to the literature (92, 97) for similar data on other SHRP core asphalts with higher and lower levels of component compatibility and sulfur content. Kinetic data for the oxidation of all eight of the SHRP core asphalts have been published (87, 93).

The effects of oxidation temperature on the kinetics of ketone and sulfoxide formation become even more apparent when one considers the data in Figure 17. These data were obtained by the author (87) from oxidizing briquettes of asphalt-coated Ottawa sand at 45ºC. Asphalt film thickness on the sand was about 15 micrometers. When comparing these data with the data in Figure 15, it should be kept in mind that oxidation level did not progress significantly beyond the initial oxidation spurt during the 45ºC oxidation because of the slow rate of oxidation at 45ºC and the termination of the experiment after 100 days of oxidation time. Because of the slow rate, it was possible to obtain a number of samples for analysis during the initial oxidation spurt, thus more clearly defining the relative rates of ketone and sulfoxide formation during this unique period. Of pragmatic importance is the fact that a temperature of 45ºC is within the pavement temperature range.
What is most striking about the data in Figure 17 is that the initial oxidation spurt is virtually complete after about 20 h with sulfoxides being formed at a much greater rate than ketones. Apparently most of the hydroperoxides formed during the initial spurt are scavenged by the naturally occurring asphalt sulfides to form sulfoxides. Unlike the apparent hyperbolic nature of the kinetic plot for ketone formation at higher temperatures, the ketone plot is almost linear with time during the oxidation spurt reaction at 45°C. This fact suggests a possible induction period for ketone formation at yet lower temperatures.

Note also, that while only a few ketones were produced during the spurt, the kinetics of viscosity increase parallels that of sulfoxide formation. This leads to the tentative conclusion that during the spurt, the sulfoxides and/or aromatics formed during the spurt (discussed in later section on oxidation mechanisms) are major contributors to viscosity increase during this low temperature oxidation. This conclusion is further evidenced by the excellent correlation between sulfoxide formation and viscosity increase during the spurt as shown in the plot at the right in Figure 17.

Relative Effects of Ketones and Sulfoxides on Viscosity Increase

The data in Figures 16 and 17 bring into focus questions regarding the relative effects of ketones and sulfoxides on viscosity increase during oxidative aging. Research has been discussed that report correlations between ketone formation and viscosity increase on aging, with sulfoxides generally showing little or no correlation with viscosity increase. However, many of these earlier studies used accelerated tests conducted at temperatures and/or pressures higher than normally experienced in most pavement applications. Also, because the reaction rate during the initial
oxidation spurt under these accelerated conditions was rapid, the kinetics during the spurt were not examined in detail.

The data shown in Figure 17 for oxidation at 45ºC show quite conclusively that the ketones formed were not significantly responsible for the viscosity increase during the initial reaction spurt, although ketones have been shown to correlate well with the log viscosity increase during the long-term oxidation that follows the oxidation spurt. These facts strongly imply that a different chemistry is occurring during of these two reaction periods.

That a unique hydrocarbon precursor is responsible for the initial oxidation spurt, as previously suggested, is supported by the following facts: (a) very few ketones are formed during the spurt during low temperature oxidation, limiting significant involvement of free radical-producing benzylic carbons, (b) sulfides do not oxidize to sulfoxides by direct reaction with oxygen, and (c) model sulfides will not oxidize in air at the temperatures used in asphalt oxidation tests when outside the asphalt (39, 63). Mill (98) has suggested that the reactive hydrocarbon precursor might be a perhydroaromatic moiety whose active hydrogen readily reacts with oxygen to form a hydroperoxide intermediate. This hydroperoxide intermediate could then react with an asphalt sulfide to form a sulfoxide, accompanied by the former perhydroaromatic moiety being converted to an aromatic moiety. Sulphides are well known to be active scavengers of hydroperoxides, the reaction being a non-radical, heterolytic reaction (99). The low temperature aging data in Figure 17 provide good evidence for such a reaction since few ketones were formed during the initial stages of the oxidation spurt. Ketones would be expected to be a major reaction product during the spurt if the initial reaction of oxygen was a free radical reaction involving the benzylic carbon to form a hydroperoxide.

Thus, the question still remains: what is the physicochemistry that is responsible for the rapid increase in viscosity during the rapid reaction spurt? Is it the polarity resulting from the formation of sulfoxides, or is it the aromatization of the perhydroaromatic ring that produces the viscosity increase? Kinetic data following the rapid spurt presented earlier suggest that sulfoxides cannot fully account for the viscosity during the spurt. It is, however, plausible that aromatization of perhydroaromatic rings might accomplish this. The perhydroaromatic ring system is non-planer and sterically strained. Aromatization of this ring system during oxidation would cause it to become planer. The aromatization of this ring should increase the planarity and polarizability of the aromatic ring system of which it was originally a part. The newly modified ring system could then associate with other highly aromatic and associated ring systems to form more and/or larger associated clusters, thus increasing viscosity without the formation of ketones.

Data in Figure 18 shed light on this question. In this experiment, a Boscan asphalt was oxidized at 130ºC as a function of time as a thin film using the Greater London Council column technique (7). FGA for ketone and sulfoxide contents were made on the oxidized asphalt at each oxidation level. The oxidized asphalts were then separated into asphaltenes and maltenes, and the same FGA analysis performed on the fractions. During the experiment, the maltenes decreased from 74% to 66%; thus the asphaltenes increased from 26% to 34%. Examination of the ketone and sulfoxide data shows that most of the ketones that were produced remained in the asphaltene phase when the fractions were separated. This is consistent with much data in the literature that show that the increase in ketone content correlates linearly with asphaltene content, which in turn correlates linearly with log viscosity increase. Thus, ketone formation produces asphaltenes, which in turn causes viscosity increase. On the other hand, examination of the data in the figure show that virtually all of the sulfoxides produced on oxidation remained in the maltenes fraction.
This becomes apparent when one considers that the increased concentration of sulfoxides in the maltenes compared with the neat asphalt roughly correlates with the weight difference between the maltenes and neat asphalt, which is considered in calculating concentrations.

Because the sulfoxides produced during the reaction spurt remained in the maltenes is evidence that they were not associated with polar fractions that produced the asphaltenes, and thus do not have the properties necessary to produce the rapid viscosity increase during the spurt observed in the data shown in Figure 17. This is further evidence supporting the tentative conclusion that the rapid increase in viscosity during the oxidation spurt is strongly influenced by the aromatization of the perhydroaromatic ring.

These data together with much additional chemical data acquired at WRI on the formation of functional groups in asphalt lead to the logical conclusion that most of the ketones formed on oxidation arise from oxidation of components of the resinous fraction, consisting in large part of the polar aromatics as characterized by the Corbett fractionation. The sulfoxides, on the other hand arise primarily from oxidation of the sulfides in the less polar fractions that for the most part do not oxidize to form asphaltenes.

In summary, the preponderance of data strongly suggest that it is not the inherent polarity of the ketone or sulfoxide functional groups that has the most significant influence on viscosity increase in asphalts, but it is whether or not these functional groups are formed on molecules that can further associate into significantly larger agglomerated domains, and thus significantly increase the apparent molecular weight of the agglomerate. In fact, the inherent polarity of the sulfoxide functional group is probably greater than that of the ketone; however, the relatively
small effect of sulfoxides on viscosity increase after the initial oxidation spurt, as previously explained, is probably because most of the sulfoxides are formed on molecules identified with the less strongly associating components of the asphalt.

Chemical Oxidation Mechanisms

Kinetic studies of asphalt oxidation in dilute toluene solutions at room temperature by Knotnerus (100) showed that asphalts initially reacted rapidly with oxygen at low activation energy. Then, after a time, and at low bitumen concentrations, the oxidation reaction virtually stopped. He proposed that asphalt contained limited amounts of highly reactive hydrocarbons. He further proposed that hydroperoxides were formed on oxidation, which then further reacted. He suggested, based on his model compound studies, that the highly reactive asphalt components might be “partially hydrogenated polyaromatics” (referred to early in this chapter as perhydroaromatics).

In Knotnerus’ studies (selected data, Table 6), the perhydroaromatic 9,10-dihydroanthracene had a relative reaction rate of 800 compared with the benzylic carbon-

<table>
<thead>
<tr>
<th>Model Compound</th>
<th>Structure</th>
<th>Relative Rate of Oxygen Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octadecane</td>
<td>CH₃(CH₂)₁₆CH₃</td>
<td>Nil</td>
</tr>
<tr>
<td>Dodecylbenzene</td>
<td>H-C-(CH₂)₁₀-CH₃</td>
<td>4.3</td>
</tr>
<tr>
<td>1-Methyl-7-isopropyl-phenanthrene</td>
<td>CH₃-C-CH₃</td>
<td>16</td>
</tr>
<tr>
<td>9,10-Dihydroanthracene</td>
<td></td>
<td>800</td>
</tr>
<tr>
<td>Typical Road Bitumen</td>
<td></td>
<td>560</td>
</tr>
</tbody>
</table>
containing hydrocarbons dodecylbenzene and 1-methyl-7-isopropylphenanthrene, which had relative reaction rates of 4.3 and 16, respectively. The typical road bitumen (asphalt) that he examined had a relative reaction rate of 560, 35 times more reactive than his most reactive benzylic carbon-containing model compound. This reactivity of the bitumen approached that of the dihydroaromatic, 9,10-dihydroanthracene. Knotnerus also noted that neither the asphalt nor the dihydroaromatic model compound exhibited and induction period on oxidation.

Mechanistic studies by van Gooswilligen et al. (101) led to their conclusion that asphalt oxidation did not proceed via a free radical chain reaction because the reaction was insensitive to added initiator (added free radicals). They showed an apparent wide range in reactivity of oxidizable components. They attributed the apparent absence of a free radical chain reaction to a possible high concentration of natural inhibitors in asphalts. As did Knotnerus, they concluded that bitumens contain limited concentrations of highly reactive components that were depleted on oxidation. They found that oxidation catalyst poisons (KCN and NaN₃) greatly reduced the rate of oxidation, and thus suggested that oxidation might proceed mainly via metal catalysis, probably involving the metal porphyrin type.

King (102) has proposed an oxycyclic reaction mechanism as a unifying oxidation theory. This theory views the net chemical oxidation reaction as a series of two or more cyclic steps following pathways based on current chemical knowledge. King’s proposed oxycyclics mechanism could include the formation of a molecular complex between oxygen and asphalt, or an asphalt molecule and a metal as proposed by van Gooswilligen, but is much broader and includes mobile electrons as facilitators to lower the net energy barrier to oxygen transfer.

Martin (55, 56) and Petersen (1) have previously proposed free radical chain reactions to account for the hydrocarbon oxidation in asphalt. More recently, a dual sequential asphalt oxidation mechanism was proposed by Petersen (92) that has since been refined and described in more detail (87, 93). This dual mechanism, which rationalized the apparent conflict between the different oxidation mechanisms suggested in the earlier studies, is illustrated in Figure 19. More details can be found in the original literature.

Both Knotnerus (100) and van Gooswilligen (101) recognized the presence in asphalts of a finite amount of highly reactive hydrocarbons that was depleted on oxidation. Neither investigator, however, based on this author’s analysis of their papers, were apparently aware that different oxidation kinetics resulting from a different oxidation mechanism might exist beyond the exhaustion of these highly reactive components (near the end of the oxidation spurt as has been defined in this document). It is believed by this author that failure during earlier investigations to recognize the existence of two different reaction mechanisms contributed significantly to the earlier confusion regarding the chemical mechanisms of asphalt oxidation.

The dual mechanism proposed for the oxidation of asphalt (87, 93) will next be considered in detail. Oxidation during the spurt will first be discussed using dihydroanthracene as the model perhydroaromatic for the proposed oxidation of polycyclic perhydroaromatics in asphalt. This reaction, as illustrated in Figure 20, could produce either hydrogen peroxide (H₂O₂) or a perhydroaromatic hydroperoxide (III). This reaction has been shown (98) to have no induction period, which is typical of the kinetic plots for asphalt oxidation. Either one of the hydroperoxides formed in reaction 1 could, as shown in reaction 2, react with reactive sulfides in asphalt by well known mechanisms (99) to produce sulfoxides. The oxidation of perhydroaromatic hydrocarbons in asphalt would increase the aromaticity of the asphalt. Oxidation studies of road asphalts by Herrington et al. (88) support an increase in aromaticity during asphalt oxidation.
FIGURE 19 Typical kinetics of the dual oxidation mechanism.

\[
\begin{align*}
\text{I} + O_2 & \rightarrow \text{II} + H_2O_2 \quad \text{or} \quad \text{III} \\
\text{IV} & \rightarrow \text{Free Radicals (RO·, OH·, etc.)}
\end{align*}
\]

FIGURE 20 Reaction sequence for oxidation of proposed polycyclic perhydroaromatics in asphalt during oxidation spurt (illustrated for dihydroanthracene) \((87, 93)\).
During the oxidation spurt, some of the hydroperoxides formed likely decompose to produce free radicals (reaction 3, Figure 20), which could contribute to the initiation of, and increase the rate of, the reactions involving benzylic carbon and also form ketones during the spurt. Because the decomposition of hydroperoxides is highly temperature sensitive, their more rapid decomposition to free radicals at the higher temperatures could contribute to the more rapid rate of ketone formation at higher temperatures during the spurt. The relative insensitivity to thermal decomposition of hydroperoxides at lower temperatures could be largely responsible for the very small amount of ketones produced during the initial part of the oxidation spurt at lower temperatures (Figure 17).

Following the oxidation spurt, when most of the available proposed perhydroaromatics have been consumed, the rates of both ketone and sulfoxide formation are reduced. Ketones formed both during and after the spurt are produced from the same precursor, benzylic carbon (87, 93). It has been suggested (88) that some ketones might be formed from precursors other than benzylic carbon; however, based on the infrared absorption frequency of ketones at all levels of oxidation likely to be encountered in pavement aging, amounts of ketones that might be formed on nonbenzylic carbon are likely to be small (87). However, it is conceivable that higher oxidation temperatures could favor the formation of a relatively greater amount of nonbenzylic ketones.

Possible sequences for benzyl carbon oxidation are outlined in Figure 21. Initiation of the oxidation of benzylic carbon requires abstraction of an active hydrogen to form a benzyl radical (II) which then reacts with oxygen to form a peroxy radical (III). The inability to observe the inhibition period for the free radical oxidation of the benzylic carbons in asphalt probably results from a masking effect caused by the initial oxidation reaction of the asphalt perhydroaromatic hydrocarbons (87). Mushrush has reported (103) that the peroxy radical is the most stable free radical formed during typical hydrocarbon chain transfer reactions. It is probably the primary precursor to ketones (e.g., reaction c, Figure 21). Also Hiatt et al. (104) reported that secondary peroxy radicals undergo nonradical self-reaction to form ketones. Once a chain reaction has begun, it has been reported that formation of alkyl free radicals is usually rate controlling; however, at very low oxygen concentrations (ca. 1 ppm), reaction of oxygen with alkyl free radicals (reaction b) can be rate controlling (105).

The most probable route to sulfoxide formation following the oxidation spurt is the reaction of alkylarylhydroperoxides (VII) with asphalt sulfides (reaction g). This reaction has been studied in detail (99) and is promoted by the presence of acidic molecules. In addition, hydroperoxide (VII) decomposition might be an alternate route to ketone formation (reaction f). It has been reported (103) that hydroperoxide decomposition to yield carbonyl compounds can be induced by catalytic amounts of metal ions or a basic reaction medium. Additional experimental data and discussion supporting the oxidation mechanisms presented can be found elsewhere (87).

The dual oxidation mechanism just described is supported by independent studies of Herrington (106). His work showed that the rate of oxidation of bitumens can be accurately described by an equation derived assuming two simple first order reactions. His equation was successfully fitted to oxidation rate data for viscosity increase obtained at 300 psi in air at 60ºC, 70ºC and 80ºC. He concluded that bitumen oxidation can be generalized as consisting of a group of fast reactions obeying approximately first order kinetics and involving carbonyl and sulfoxide formation, and a much slower process involving carbonyl formation having a nearly constant rate over the experimental time frame.
Temperature Sensitivity of Asphalt Microstructure

It was discussed earlier in this report that two independent effects, one chemical and one physicochemical, can cause an increase in the oxidation reaction rate. The chemical effect is the doubling of the reaction rate with approximately every 10ºC increase in temperature. The physicochemical effect is the increased chemical reactivity of the potentially reactive species as their mobility is increased when the microstructure is broken up or disrupted with an increase in temperature. Because bimolecular reactions are involved, increased mobility increases the reaction rate. In this section, the contributions of these two factors will be quantitatively separated using kinetic data for SHRP core asphalts. The kinetic data used are those obtained from asphalts aged as a thin film at atmospheric pressure using the TFAAT test procedure (77).

Data in Figure 22 show the effects of temperature on the age hardening kinetics of two asphalts of differing component compatibility. These data include the combined effects of the two factors discussed in the previous paragraph. Important observations can be made from Figure 22 regarding the differences in the increase in reaction rates and levels of oxidation for asphalts AAG-1 and AAD-1 between 85ºC and 113ºC. Note, that the aging rates and levels of oxidation are quite similar for both asphalts between 65ºC and 85ºC. However, at 113ºC and 130ºC the rate and level of oxidation is much greater for the less compatible asphalt with high
microstructure (AAD-1) than for the more compatible AAG-1. This difference is attributed to the disruption of microstructure in AAD-1 as temperature increases beyond 85°C and breaks the weak molecular interaction forces that hold the microstructure together, thus increasing the effective concentration of reactive species.

The effects of breaking up microstructure on the age hardening kinetics of five SHRP core asphalts having different levels of microstructure are shown in Figure 23. The time axis for the 113°C data has been scaled and shifted to offset the doubling of the reaction rate with every 10°C increase in temperature as previously described. Thus, the differences in data at 85°C and 113°C should represent only the effects of the microstructure on the hardening kinetics. Again, with regard to attempts to relate high-temperature laboratory tests to pavement aging kinetics, note how the spread between the aging kinetics among the asphalts becomes greater as the temperature increases. Data in the next two figures illustrate how the effects of microstructure on the kinetics can be quantified among the different asphalts.

Data from Figure 22 for asphalt AAD-1 are reproduced on the left side of Figure 24. If the time axis is scaled and shifted to offset the doubling of the chemical reaction rate for every 10°C increase in temperature, one obtains the plot on the right side of the figure. The next step is to pick a point on the time scale (illustrated by the solid vertical line) and calculate and aging index (aged viscosity–unaged viscosity) at this level of aging for the four temperatures.
FIGURE 23  Effects of microstructure on age hardening kinetics of five SHRP core asphalts.

FIGURE 24  Technique for quantifying effect of microstructure on viscosity.
This procedure was conducted on each of the SHRP core study asphalts and the data plotted in Figure 25. The resulting figure then shows the contribution to the aging index of microstructure only for the eight SHRP asphalts as a function of aging temperature and at atmospheric pressure. As pointed out in a previous section, the PAV kinetic data now obtained at 100°C using the standard SHRP procedure cannot be compared in this manner with corresponding PAV data obtained lower temperatures because of the severe diffusion-related problem (96).

At the risk of being overly redundant, it is again obvious from the figure that the aging kinetics of common high-temperature laboratory tests, including the current PAV test, are much different than the kinetics at pavement aging temperatures. Unlike most organic materials, the microstructure in asphalt makes its aging characteristics uniquely different than typical organic materials. The problem is compounded by the fact that asphalts from different sources have uniquely different characteristics.

It is worth noting at this point that aging characteristics, microstructure, and component compatibility seem to be generally related, although possibly fortuitously, to the sulfur content of the asphalt (107). Those asphalts higher in sulfur content generally are less compatible and are more susceptible to an increased rate of age hardening with an increase in temperature. This writer has often found it helpful to use sulfur content as a base parameter in correlating the chemical and physicochemical properties of asphalt (84, 87, 93).
What is apparent to this writer is that the effects of component compatibility and microstructure, and the effects of temperature on microstructure oxidation kinetics, must be quantitatively taken into account to successfully model the effects of oxidative age hardening on asphalt pavement performance characteristics.

CONSIDERATION OF TEMPERATURE AND COMPOSITION IN ASPHALT APPLICATIONS

It is apparent from the laboratory data presented that temperature and asphalt composition are important factors to be considered in the design of accelerated aging tests that are intended to mimic or predict the oxidative age hardening of asphalts, and in selecting appropriate asphalts for pavements, roofing and other applications. To emphasize the pragmatic importance of these considerations, it is helpful to examine selected results from a comprehensive California aging study conducted by Kemp and Predoehl (108). In their study, they field-aged laboratory-prepared briquettes of actual pavement mixtures in four climatic environments—coastal, low valley, high mountain, and low desert—where average temperatures ranged from 42ºF (5.5ºC) to 73ºF (27.3ºC). Asphalts derived from three different crude sources, and mixtures with void contents ranging from 3% to 12% were used.

They found that within the variable constraints of their study, that climate (temperature) had a greater effect on age hardening than did the void content (related to air permeability) of the mixtures. These results are illustrated in Figures 26 and 27. Data in these figures were derived from the Kemp and Predoehl report by averaging data for all samples used in the study. Further, when the data for the asphalts from different sources used in the Kemp and Predoehl study were averaged for the different climates, aggregates and void contents, and plotted as in Figures 26 and 27, the climatic (temperature) conditions were also found to have a greater impact on variations in oxidative age hardening than did asphalt source (composition). The data of Kemp and Predoehl vividly illustrate the large effects of temperature and asphalt source on oxidative age hardening in the field. Dickinson (109) has attempted to quantify the contributions of these variables to the field hardening of sprayed seals and thin hot-mix surfacing laid at sites covering most of the climatic conditions encountered in mainland Australia.

The following laboratory data are presented to illustrate the problems of obtaining data predictive of field performance from laboratory oxidative aging tests. Data in Table 7 are the slopes of the plots of log viscosity versus ketones formed during the hydrocarbon oxidation that follows the initial oxidation spurt for the eight SHRP core asphalts (93). Oxidations were carried out at two temperatures using both the SHRP PAV test procedure at 20 atmospheres air pressure (63) and the TFAAT technique at atmospheric pressure (77). The lower test temperatures used (60ºC for the PAV and 85ºC for the TFAAT) are in or near the temperatures experienced in pavements; the higher temperatures (100ºC for the PAV and 113ºC for the TFAAT) are typical of temperatures used in some present and past laboratory aging tests. The asphalts in Table 7 are listed in the order of their increasing sulfur content, and with the exception of asphalt AAM-1 (which has molecules of unusually high inherent molecular weight), in the approximate order of their decreasing component compatibility.
FIGURE 26 Effects of climate temperature on rate of oxidative hardening of pavement mixtures [data adapted from Branthaver et al. (107)].

FIGURE 27 Effects of pavement void content on rate of oxidative hardening of pavement mixtures [data adapted from Branthaver et al. (107)].
With the exception of asphalt AAK-1 that was PAV-aged at 100°C and the highly compatible asphalt AAG-1, viscosity sensitivity to ketone formation increases significantly with increasing oxidation temperatures. Thus, ketones formed in a higher temperature laboratory test would cause a relatively greater increase in viscosity than would the same amount of ketones formed at a lower temperature in a pavement. This viscosity difference increases with decreasing asphalt component compatibility. Data for 60°C PAV oxidation and 85°C TFAAT oxidation in Table 7 show a good correspondence except for asphalt AAD-1. Since TFAAT aging is at atmospheric pressure, this correspondence suggests that 60°C PAV data might effectively correlate with pavement aging characteristics. The disadvantage of the 60°C PAV aging procedure is that the oxidation time needed to obtain a suitable level of aging is at least 1 week compared with 20 h for the currently used 100°C PAV test. The 100°C PAV data in Table 7 deviate considerably from the 60°C PAV data.

Variations in the rate and amount of sulfoxides formed appear to have a minimal effect on the linear correlation between ketone formation and log viscosity increase as previously noted. This is believed to result because sulfoxide precursor molecules, probably primarily nonpolar and monofunctional, are concentrated in the asphalt dispersing phase and thus have a lesser influence on effective molecular weight increase than do ketones which are formed on polar associating, and often polyfunctional, molecules. In a sulfoxide thermal decomposition experiment (Figure 13) using 60°C PAV-oxidized AAK-1, the viscosity sensitivity to sulfoxide formation was found to be 1.3 log Pa-s/mol-L⁻¹ (91, 93); this value is small compared with 14.7 log Pa-s/mol-L⁻¹ (Table 7) for the viscosity sensitivity to ketones for the same asphalt. Based on the microstructural model, the viscosity sensitivity to sulfoxides for the more compatible SHRP asphalts such as AAG-1 should be even less than that for asphalt AAK-1.

Results summarized in Figure 25 for the effect of temperature on age hardening, and in Table 7 for viscosity sensitivity to ketone formation, underscore the pragmatic importance of the conclusion reached earlier during the SHRP research (63) that the maximum temperature, not the average temperature, that a pavement experiences in service is the major determinant of the ultimate level of oxidative age hardening that the pavement will experience in service. The data presented in this report also demonstrate the inappropriateness of making judgments on the level

### TABLE 7 Viscosity Sensitivity to Ketone Formation for SHRP Core Study Asphalts Oxidized by Both PAV and TFAAT Methods (93)

<table>
<thead>
<tr>
<th>Asphalt</th>
<th>Sulfur Content, %</th>
<th>60°C</th>
<th>100°C</th>
<th>85°C</th>
<th>113°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAM-1</td>
<td>1.2</td>
<td>9.1</td>
<td>12.5</td>
<td>8.7</td>
<td>13.3</td>
</tr>
<tr>
<td>AAG-1</td>
<td>1.3</td>
<td>4.5</td>
<td>4.5</td>
<td>5.4</td>
<td>5.4</td>
</tr>
<tr>
<td>AAC-1</td>
<td>1.9</td>
<td>6.9</td>
<td>10.0</td>
<td>8.0</td>
<td>11.8</td>
</tr>
<tr>
<td>AAF-1</td>
<td>3.4</td>
<td>8.7</td>
<td>10.0</td>
<td>10.0</td>
<td>20.0</td>
</tr>
<tr>
<td>AAB-1</td>
<td>4.7</td>
<td>10.5</td>
<td>14.8</td>
<td>11.1</td>
<td>18.2</td>
</tr>
<tr>
<td>AAA-1</td>
<td>5.5</td>
<td>10.5</td>
<td>21.0</td>
<td>10.0</td>
<td>28.5</td>
</tr>
<tr>
<td>AAK-1</td>
<td>6.4</td>
<td>14.7</td>
<td>9.1</td>
<td>15.1</td>
<td>19.2</td>
</tr>
<tr>
<td>AAD-1</td>
<td>6.9</td>
<td>12.5</td>
<td>18.2</td>
<td>18.2</td>
<td>23.3</td>
</tr>
</tbody>
</table>
Asphalt Oxidation Kinetics and Mechanism of Oxidation

of asphalt oxidative age hardening in pavements from the results of single data points obtained from accelerated aging tests performed at temperatures significantly higher than actual pavement temperatures.

CONSIDERATION OF PAVEMENT AGING AS A FUNCTION OF VOID CONTENT AND DEPTH

Although it has been recognized for decades that oxidative age hardening and embrittlement of the asphalt cement in asphalt pavements is one of the major contributors to the pavement failures, past studies dealing with the mechanisms by which the oxidation actually occurs within the pavement structure are limited. In the more recent past, there has been a renewed interest in being able to predict oxidative age hardening of asphalt pavements. A landmark paper in this area is that of Mirza and Witczak (110) in which attempts are made to predict the aging characteristics of asphalt cements in actual pavements based on properties of the asphalt cements, environmental factors and the morphological properties of the asphalt mixtures. Within the context of these efforts, the present writer will next examine data from selected past research (108, 110–112) which, when interpreted based on the more recent physicochemical models, are believed to be important in shedding additional insight on the fundamental mechanisms of pavement aging.

In the 1960s, Coons and Wright (111) took 6-in. cores from pavements that had been in service from 4 months to 13 years. The pavements with up to 4 years service were constructed with AC 6 asphalts, and those with 4 to 13 years of service with softer AC 8 asphalts. The cores were sectioned as a function of depth, the asphalts recovered from the sections, and viscosities determined on the recovered asphalts. In all, 14 projects were sampled, with all but two of the projects within locations near Atlanta, Georgia, and the remaining two from southern Georgia; thus, this study is of particular importance because virtually all of the pavements were exposed in the same geographic area and most likely the asphalts were obtained from the same source.

Shown in Figure 28 are plots of pavement aging as a function of depth that this writer has produced from the data in the Coons and Wright paper.

It is apparent, as might be expected, that oxidation proceeds from the surface down through the pavement as a function of time. In these studies only the top 2 in. of the cores were analyzed, but it is apparent that in the early stages of pavement life, that oxidation had only significantly penetrated the top ½ in. of the pavement.

An important tentative conclusion can be drawn regarding these data with respect to the past studies of pavement aging as a function on time. In most instances, asphalt to be characterized was extracted from whole cores. Thus, cores taken early in the study may have a thin layer of highly oxidized asphalt at the top of the core, while the remaining asphalt further down in the core may have little or no oxidation. As a result, the measured chemical and physical properties of the asphalt from the whole core was only an average of the levels of oxidation throughout the depth of the core. It then follows, that the hyperbolic kinetic plot of age hardening as a function of pavement service life generated from such data does not represent the actual level of oxidation of the asphalt cement in the pavement as a function of time, but in reality largely reflects the average aging of the asphalt cement in the pavement as oxidation proceeds deeper into the pavement mixture with time. It should also be recognized that some studies have
shown a differential level of aging of the pavement from the bottom up as well. This can happen if the sub-grade structures are more readily permeated by oxygen (air).

Because the rate of oxidative aging is highly dependent on temperature, the temperature profile within the pavement will also influence the age-hardening profile within the pavement. This phenomenon is suggested in the bottom right-hand plot in Figure 28. It is apparent from this plot that oxidation had proceeded significantly down through the top two inches of depth that was investigated; the horizontal line at the left side of the plot indicates the initial laydown viscosity. Based on the temperature effect, the question arises regarding how much of the decrease on hardening as a function of depth is due to decreasing maximum temperatures and how much is due to less exposure to oxygen because of diffusion effects. There is little question that temperature effects should contribute significantly to the viscosity–depth profile. Data reported from the National Center for Asphalt Technology test track when the 7-day high air temperature averaged 94.3°F showed that the maximum temperature reached two inches below the surface was over 10°F (5.5°C) lower than at the surface. At 10 in. below the surface, the temperature differential was about 32°F (18°C).

The hyperbolic nature of the age hardening profile, particularly in highly aged pavements raises another interesting question that could form the basis of future fundamental studies. The temperature profile within the pavement, while influenced by the effect of temperature on
oxidation rate, might also be influenced by a “quenching” or significant slowdown of oxidation as oxidation immobilizes the asphalt components that are potentially reactive with oxygen. The immobilization of reactive components by microstructure has been discussed in detail in earlier sections of this document. It is known that most of the reactive components that form ketones are contained within the polar aromatic fraction of the asphalt. As the viscosity of the asphalt is increased with oxidation, the reactivity of this fraction is greatly reduced both from the loss of reactive components from oxidation and immobilization. This phenomenon occurs at lower levels of oxidation as the temperature is lowered. This writer over the years has seen repeated evidence that at lower oxidation temperatures (about 60ºC and lower) oxidation tends to quench; and when the temperature is lowered below this quenching level, continued oxidation virtually ceases. Based on this reasoning, the maximum temperature that the pavement reaches throughout its depth is critical to the maximum level of hardening that can be expected.

Evidence for the quenching effect can be found in the data collected by Coons and Wright (111). In Figure 29, this writer has graphed the viscosity that they found in the top ¼ in. of pavement as a function of aging time. It is readily apparent that the average viscosity of the asphalt in the top ¼ in. of pavement after only 4 months of service was essentially the same as that found in the top ¼ in. after many years of service. The average limiting viscosity found for the asphalt in this top surface was approximately 22 megapoise (2.2 megapascals). Data are linear shear viscosity measurements at 25ºC and 0.05 reciprocal seconds. This limiting viscosity cannot be attributed to the exhaustion of potentially reactive components, since it is well known

![Graphic produced from Coons and Wright (111)](image)

**FIGURE 29** Viscosity in the top ¼ in. of pavement in Georgia roads as a function of time in service. [Graphic produced from Coons and Wright (111)].
that oxidative aging of asphalt at higher than ambient temperatures does not stop at this viscosity. It is noteworthy that this limiting viscosity is virtually the same as the dynamic shear viscosity (measured at 25°C and 0.01 rad/s in the linear viscoelastic region) found by this author and coworkers for limiting viscosity on oxidation at 45°C of a manganese catalyzed Chemcrete-modified asphalt, and also an asphalt recovered from an old abandoned section of US-30 between Laramie and Cheyenne Wyoming (54).

If indeed there is a temperature-dependent quenching effect that limits the level of oxidative age hardening in pavements, this phenomenon is of both fundamental and pragmatic importance, and should be an object of future research.

One might ask the question: if the phenomenon exists, why has it escaped apparent recognition over the years? To this question is suggested that first, detailed laboratory aging studies of asphalt have not been conducted at relatively low pavement temperatures because of the extremely long time it takes to oxidize the asphalt to the proposed quenching viscosity. Second, this phenomenon would begin to diminish at temperatures above about 60°C at which temperature-dependent microstructure begins to break up, based on the kinetic data reported in this document. Temperatures of near 100°C or higher have been routinely used in virtually all laboratory aging studies, and at these temperatures the microstructure containing the reactive components is broken up and no observable quenching occurs.

Next, consider the effects of voids content on the age hardening profile found through the depth of the pavement. Unfortunately, the void contents of the mixes used in the Coon and Wright study were not reported. It is intuitively obvious that with an increase in void content, or more fundamentally permeability, oxygen in the air can more readily permeate the pavement and increase the rate of age hardening. Fortunately, data in a study reported in 1970 by Vallerga et al. (112), the effects of void content on asphalt cement hardening were reported. This comprehensive and cooperative study was conducted by the Materials Research and Development group in Oakland, California, and was funded by the U.S. Bureau of Roads (now FHWA). In the study an attempt was made to relate measured asphalt chemical and physical properties with pavement performance. Extensive data were collected on 53 roads in the United States that had service lives between 11 and 13 years. The one variable out of the many evaluated that showed the best correlation with the age hardening of asphalt cements in pavement service was the void content. This writer has taken data from this report and developed a chart (Figure 30) showing the average aging indexes (viscosity of aged asphalt–original neat asphalt) of recovered asphalts as a function of void content. Also shown in Figure 30 are the viscosity–depth profiles suggested by this writer based on the model presented.

It is evident from the data shown, that at void contents of 4% or less, minimal amounts of average age hardening is evident in the recovered asphalts after 11 to 13 years of service. Note that average age hardening is emphasized because, as discussed earlier, recovered asphalt is a mixture of asphalt with varying degrees of hardening as a function of their location within the pavement. The general conclusion made in the Coons and Wright study was that increased viscosity with age was more apparent in the top ½ in. of the pavement than at lower depths; and that only relatively small changes in addition to the initial increase occurring before or during placing occurred at lower depths. Based on the Coon and Wright study, and the low viscosity of the asphalts recovered from whole cores with void contents in the range of 4% in the Vallerga study, this writer is lead to the conclusion that most of the oxidative hardening that occurs in asphalts with such low void contents occurs in the top layer of the pavement. This is illustrated by the suggested viscosity–depth profile shown for 4% voids in Figure 30. The assumption that
FIGURE 30 Average effect of void content on age hardening of asphalts from 53 11- to 13-year-old pavements. [Graphic produced from Vallerga et al. (112)].

many of the pavements sections examined in the Coons and Wright study had void contents near the 4% range seems justified based on practices in the mid-1900s when these pavements were built. At that time, pavement loads were not as heavy as today, and a major emphasis was placed on low void contents to prevent age hardening and improve the durability of the pavements.

Next, consider the data in Figure 30 at 7% voids. An increase in pavement void content from 4% to 7% increased the average oxidative aging hardening within the pavement over fourfold. Thus, based on conclusion from the Coons and Wright data that age hardening quenches near the surface, the significantly large increase in average recovered viscosity between 4% to 7% voids must come from increased aging within the deeper depths of the pavement. This suggests to the writer the viscosity–depth profile for 7% voids shown in the left center of Figure 30.

Finally, at 10% voids content, the viscosity increase of the recovered asphalt is estimated to be about 13 times greater than at 4% voids, suggesting considerable oxidation throughout the thickness of the pavement as suggested by the viscosity–depth profile shown in the upper left hand corner of Figure 30. In fact, in this void range, the viscosity–depth profile might be influenced as much or more by the decreasing maximum temperature as it is as a function of depth (discussed earlier) from restricted diffusion of air (oxygen) into the lower depths of the pavement.

It bears repeating that while the data correlated in this study used measured void contents, the fundamental parameters governing pavement oxidation are pavement permeability and
assessable voids. Permeability and assessable voids can vary significantly at the same measured void content. Also, it should be stated, that the scenarios proposed by this writer are based on top-down aging. Oxygen can also enter the pavement from the bottom when porous substructures are present and no vapor barriers exist.

The pragmatic importance of differential oxidative age hardening as a function of pavement depth to pavement service life, performance problems such as embrittlement and cracking, and the development of valid pavement performance modeling as discussed in this section, is self evident. More understanding is needed in this vital area.
References


43. Western Research Institute, Laramie, Wyoming, Private Communication.


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