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CHEMICAL COMPOSITION OF ASPHALT AS RELATED TO ASPHALT DURABILITY

Research, Development,
and Technology

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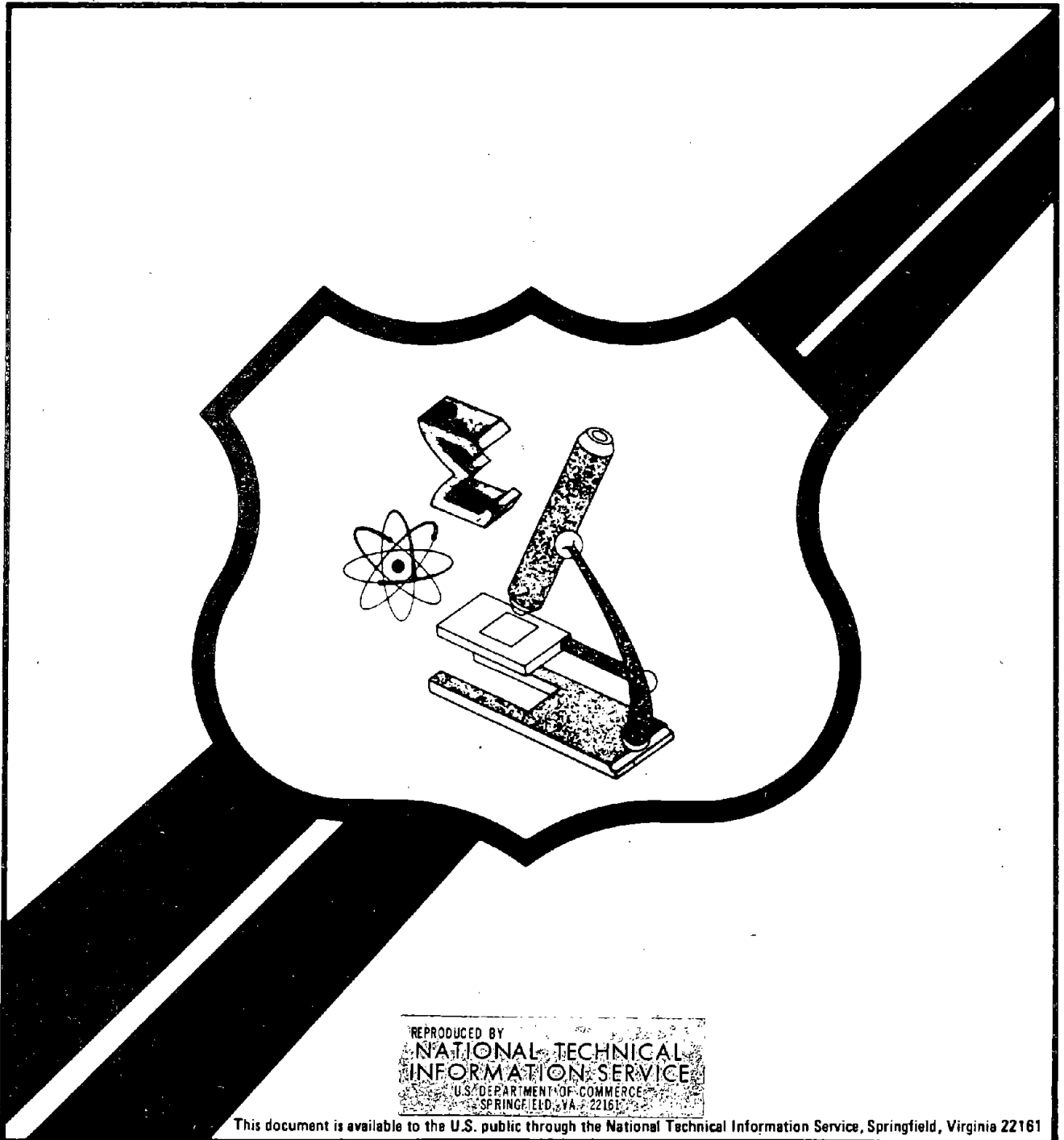
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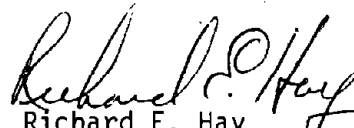
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FOREWORD

There has occurred a resurgence in interest in the properties of asphalt cements, and how these properties influence the performance and durability of asphalt pavements. This report presents a concise, critical review of the literature relating the chemical composition of asphalt to the durability of asphalt mixtures and pavements. It provides a full exposition of a presentation made by the author at the 63rd Annual Meeting of the Transportation Research Board in January 1984.

The report will be of interest to research and operations personnel concerned with solutions to problems of asphalt pavement distress. It will also provide a convenient reference for asphalt technologists concerned with the chemical properties of these materials.

This report is being distributed to materials and asphalt researchers and technologists who have requested copies or have previously indicated an interest in related reports. Additional copies for the public are available from the National Technical Information Service (NTIS), Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22161.



Richard E. Hay
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and Highway Operations
Research and Development

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16. Abstract The literature relating asphalt chemical composition and asphalt durability was reviewed and interpreted. Two major chemical factors affecting asphalt durability are 1) compatibility of the interacting asphalt components and 2) resistance to change from oxidative aging. Historically, studies of asphalt have been facilitated by separation of asphalt into component fractions; however, these fractions are complex mixtures whose composition varies significantly among different asphalts. Reaction of asphalt with atmospheric oxygen leads to its hardening and embrittlement. The hardening phenomenon results primarily from the formation of polar, oxygen-containing functional groups that increase asphalt consistency through strong molecular interaction forces. The identification and characterization of the interacting chemical functional types normally present in asphalt or formed on oxidative aging affords a fundamental approach to composition-property-performance relationships of both asphalts and asphalt-aggregate mixtures. In addition to chemical functionality formed on oxidation, asphalt properties are significantly altered by molecular structuring--sometimes called steric hardening. This phenomenon, although highly elusive and difficult to quantify, may also be a major factor contributing to pavement embrittlement.					
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CHEMICAL COMPOSITION OF ASPHALT AS RELATED TO ASPHALT DURABILITY--STATE OF THE ART

ABSTRACT

The literature relating asphalt chemical composition and asphalt durability was reviewed and interpreted by the author relative to the present state of the art. Two major chemical factors affecting asphalt durability are 1) the compatibility of the interacting components of asphalt and 2) the resistance of the asphalt to change from oxidative aging. Historically, studies of the chemical components of asphalt have been facilitated by separation of asphalt into component fractions, sometimes called generic fractions; however, these fractions are still complex mixtures whose composition can vary significantly among asphalts of different sources. The reaction of asphalt with atmospheric oxygen is a major factor leading to the hardening and embrittlement of asphalt. The hardening phenomenon is primarily a result of the formation in asphalt of polar, oxygen-containing functional groups that increase asphalt consistency through strong molecular interaction forces. The identification and characterization of the chemical functional types normally present in asphalt or formed on oxidative aging which influence molecular interactions affords a fundamental approach to relating asphalt composition with asphalt properties and thus the performance of both asphalts and asphalt-aggregate mixtures. In addition to the polar chemical functional groups formed on oxidation, asphalt properties can also be significantly altered by molecular structuring--sometimes called steric hardening. This potentially reversible phenomenon, although highly elusive and difficult to quantify in asphalt pavement mixtures, may also be a major factor contributing to pavement embrittlement.

INTRODUCTION

Differences in the quality of asphalts from different sources (different composition) and relationships between composition and performance properties have long been recognized as evidenced by the many publications on the subject, a few of which are cited (1-13). Asphalts meeting the same specifications often produce pavements with widely differing performance and serviceability. Admittedly, such factors as aggregate characteristics, design, construction variables, and environment play a major role in determining pavement performance and often overshadow the contribution to performance made by variabilities in asphalt cement quality. However, such studies as the well-known Zaca-Wigmore Experimental Road Test (4, 9), in which construction variables

were carefully controlled and asphalt source was intentionally varied, clearly demonstrate the importance of asphalt chemical composition on pavement durability.

For the purposes of this review, a durable asphalt is defined as one that: 1) possesses the physical properties necessary to produce the desired initial product performance properties; and 2) is resistant to change in physical properties during long-term, in-use environmental aging. Although design and construction variables are major factors in pavement durability, the use of more durable asphalts will produce more durable pavements.

The importance of chemical composition to asphalt durability, while not well understood, cannot be disputed. Durability is determined by the physical properties of the asphalt, which in turn are determined directly by chemical composition. An understanding of the chemical factors affecting physical properties is thus fundamental to an understanding of the factors that control asphalt durability.

The purpose of this paper is to examine the literature dealing with the chemical composition of asphalt and changes in composition during environmental aging that affect durability-related properties. Both past and recent research important to the state-of-the-art will be considered. Because of the extreme breadth of the subject and the voluminous literature related to durability, a complete bibliography will not be attempted, but sufficient references will be cited to allow the serious researcher to access additional literature. The author's approach to the fundamental chemical factors affecting asphalt properties and durability will also be presented.

PRELIMINARY CONSIDERATION OF FACTORS AFFECTING ASPHALT DURABILITY

To provide a background for the documented discussions which follow, the major composition-related factors that affect durability are briefly outlined. The most important aspect of a durable asphalt, assuming it meets initial performance requirements, is its resistance to change during in-use service. The dominant physical property change leading to reduced asphalt durability is a change in flow properties related to excessive stiffening or hardening of the asphalt. Three fundamental composition-related factors govern the changes that could cause hardening of asphalts in pavements: 1) loss of the oily components of asphalt by volatility or absorption by porous aggregates; 2) changes in the chemical composition of asphalt molecules from reaction with atmospheric oxygen; and 3) molecular structuring that produces thixotropic effects (steric hardening). With current specifications and construction practices, volatile loss is probably not a significant contributor to pavement hardening. Reaction with atmospheric oxygen is probably the major and best understood cause of asphalt hardening. Molecular structuring, although elusive and difficult to quantify, may also be a significant contributor.

Irreversible adsorption of polar asphalt components by mineral aggregate surfaces, although not a factor that might be expected to harden asphalt, will produce compositional changes in the asphalt that may also significantly affect asphalt properties and aging characteristics. Finally, it is recognized that environmental factors that affect the properties of the asphalt-aggregate bond, particularly water, can seriously affect the performance and durability of asphalt pavements; however, even though moisture-induced damage may be related to asphalt composition and adsorption of asphalt components on aggregate surfaces, it is primarily an interfacial phenomenon and beyond the scope of this paper.

CHEMICAL COMPOSITION OF ASPHALT

Elemental and Molecular Composition

Before attempting to discuss relationships between chemical composition and asphalt properties that affect durability, the chemical composition of asphalt will be reviewed. Asphalt is not composed of a single chemical species, but is rather a complex mixture of organic molecules that vary widely in composition from nonpolar, saturated hydrocarbons to highly polar, highly condensed aromatic ring systems. Elemental analyses of several representative petroleum asphalts are shown in Table 1. Although asphalt molecules are composed predominantly

Table 1. - Elemental analyses¹ of representative petroleum asphalts

Code ²	B-2959	B-3036	B-3051	B-3602
Source	Mexican blend	Arkansas-Louisiana	Boscan	California
Carbon, percent	83.77	85.78	82.90	86.77
Hydrogen, percent	9.91	10.19	10.45	10.94
Nitrogen, percent	0.28	0.26	0.78	1.10
Sulfur, percent	5.25	3.41	5.43	0.99
Oxygen, ³ percent	0.77	0.36	0.29	0.20
Vanadium, ppm	180	7	1380	4
Nickel, ppm	22	0.4	109	6

¹Data from (14)

²From (15)

³By difference

of carbon and hydrogen, most molecules contain one or more of the so-called heteroatoms nitrogen, sulfur, and oxygen together with trace amounts of metals, principally vanadium and nickel. As seen in the table, the heteroatoms, although a minor component compared to the hydrocarbon moiety, can vary in concentration over a wide range depending on the source of the asphalt. Because the heteroatoms often impart functionality and polarity to the molecules, their presence may make a disproportionately large contribution to the differences in physical properties among asphalts from different sources.

Elemental analyses are average values and reveal little information about how the atoms are incorporated in the molecules or what type of molecular structures are present. Molecular type and structure information are necessary for a fundamental understanding of how composition affects physical properties and chemical reactivity. The molecular structures in asphalt will be discussed in more detail in subsequent sections; however, an overview is important at this point.

Because asphalt was undoubtedly produced from living organic matter by maturation in the earth over millions of years, the molecular structures of the compounds present are highly diverse. Carbon in aromatic ring systems has been estimated by correlations based on carbon-hydrogen analyses and densities (16, 17) and directly by nuclear magnetic resonance (NMR) (18). Concentrations of aromatic carbon determined by NMR typically run from 25 to 35 percent for petroleum asphalts. The aromatic carbon is incorporated in condensed aromatic ring systems containing from one to possibly ten rings per aromatic moiety (18). These ring systems may be associated with saturated naphthenic (cycloalkyl) ring systems, and both the aromatic and naphthenic ring systems may have attachments composed of a variety of types of normal or branched hydrocarbon side chains. By NMR, carbon associated with naphthenic ring systems typically ranges (18) from 15 to 30 percent. Normal and branched chain hydrocarbons are present either as individual molecules or as the previously mentioned moieties associated with naphthenic or aromatic rings. The nonaromatic and non-naphthenic carbon content of asphalt would typically range from 35 to 60 percent. It should be emphasized that examples outside these ranges may be found and the variety of possible combinations of molecular structures in an asphalt is astronomically large and may vary widely from one crude source to another. The hydrocarbon molecular structures are further complicated by the heteroatoms sulfur, nitrogen, and oxygen which are often present in sufficient combined amounts so that, on the average, one or more heteroatoms per molecule may be present. These may be incorporated within the ring or nonring components, or in more discrete chemical functional groups attached to these components.

The heteroatoms, particularly nitrogen and oxygen, and the aromatic ring systems contribute considerable polarity or polarizability to the molecules which produce the major association forces that affect physical properties. This will be discussed in more detail in a later section.

Because the number of molecules in asphalt with different chemical structures and reactivities is extremely large, chemists have not seriously considered attempts to separate and identify the different molecules in asphalt. Considerable progress, however, has been made in the study of asphalt composition by separation or characterization of asphalt based on the reactivity and/or polarity of the various molecular types present. The molecules in asphalt can be conveniently separated or grouped into classes of molecular types or fractions based on their chemical functionality. This separation and classification of molecular types has been useful to provide simpler component fractions that permit further characterization and has aided in determining how different molecular types affect the physical and chemical properties of the whole asphalt.

Asphalt Composition as Defined by Fractionation

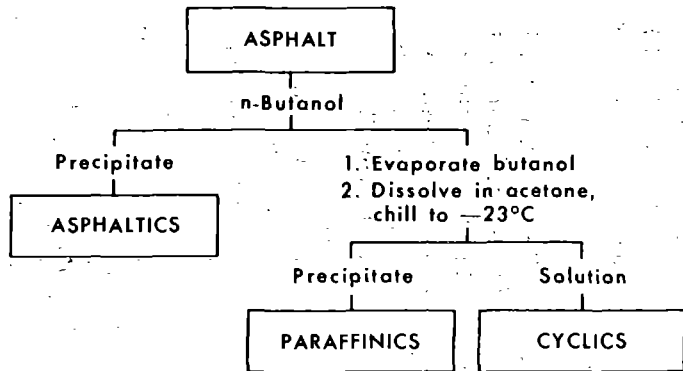
A variety of procedures has been employed in attempts to fractionate asphalt into less complex and more homogeneous fractions. Some are simple (19) and others are more complex (20, 21). Many are specialized and unique to a given research endeavor in which they were used to prepare fractions for further characterization. Several, however, have found more general use to characterize and classify asphalts. These separation schemes can be classified into three general types based on the procedure used: 1) partitioning with partial solvents (22-24); 2) selective adsorption-desorption (10, 19, 25); and 3) chemical precipitation (5,6). Gel permeation chromatography (GPC) is also an important separation method; however, because the method as normally used makes separations primarily on the basis of molecular size rather than type, its relationship to chemical composition is not well defined. Therefore, it will not be discussed further in this review. Relationships between GPC data and asphalt properties and performance characteristics, however, have been suggested and the reader is referred to the literature for more details on this separations technique (26-30).

Schematic diagrams illustrating the three types of component fractionation schemes are shown in Figure 1. Partitioning with selective solvents (Scheme 1-A), has not been widely used. Although it avoids contact with reactive adsorbants and chemicals that might irreversibly adsorb or alter asphalt components, the fractions obtained are usually not as distinctively different as with the other separation types. In general, one sequentially treats the asphalt with increasingly polar solvents precipitating a series of fractions with decreasing polarity.

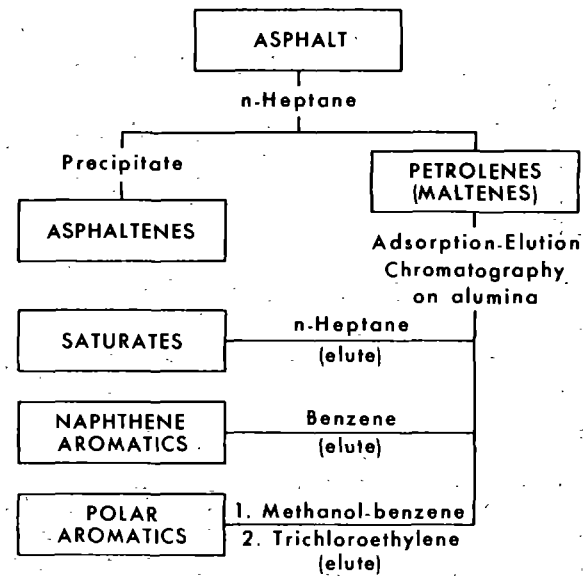
Selective adsorption-desorption chromatography has probably found the widest use as a research separation technique. This technique is typified by Scheme 1-B, Figure 1. The asphaltenes are first separated based on their insolubility in a nonpolar paraffinic solvent. This removes the most polar and least soluble asphalt components and generally facilitates further separation. The remaining petroleum (maltene) fraction, which is dissolved in the paraffinic solvent, is then adsorbed on a chromatographic column and sequentially desorbed with solvents of increasing polarity. By proper selection of the adsorbant and desorption solvents, a series of fractions with increasing polarity are obtained. The fractions obtained will be described in some detail to provide background for discussion in later sections of this paper.

The saturates fraction, because it lacks polar chemical functional groups, is not adsorbed on the column and is first to emerge. (It is important to note that although the names of component fractions were often intended to describe the predominant chemical types present, component fractions are still complex mixtures and do not represent clear-cut compound type separations.) The saturates fraction may contain saturated normal and branched chain hydrocarbons, saturated cyclic hydrocarbons (sometimes called naphthenic hydrocarbons) and possibly a small amount of mono-ring aromatic hydrocarbons; however, those molecules containing ring systems are dominated by attached saturated hydrocarbon sidechains. Sulfur is often found incorporated in molecules of the saturates fraction. Addition to the chromatographic column of a

SCHEME 1-A. Partitioning with Partial Solvents
(Schweyer and Traxler, Ref. 23)



SCHEME 1-B. Selective Adsorption-Desorption
(Corbett, Ref. 10)



SCHEME 1-C. Chemical Precipitation
(Rostler and Sternberg, Ref. 6)

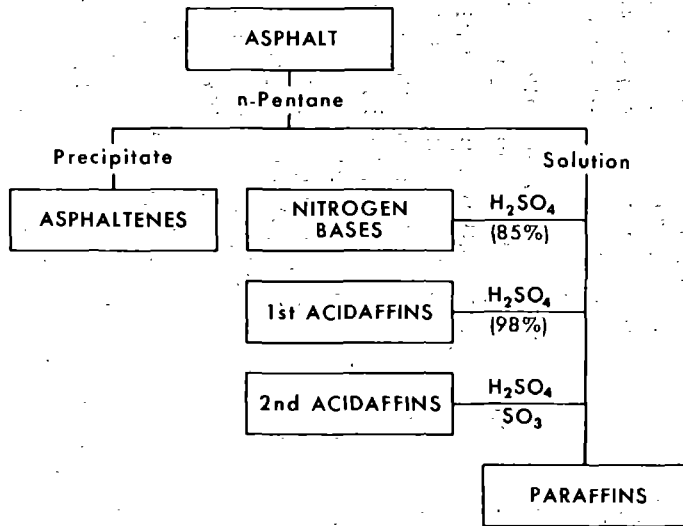


Figure 1. Schematic Diagrams Illustrating Three Types of Fractionation Schemes Used to Separate Asphalt into Component Fractions

more polar aromatic solvent such as benzene (now usually replaced by toluene), which competes for the polar sites on the adsorbants, displaces the more weakly adsorbed asphalt molecules. These molecules usually contain condensed nonaromatic and aromatic ring systems, and in addition to sulfur, the heteroatoms oxygen and nitrogen may also be part of the molecule. In Scheme 1-B, this fraction has been called the naphthene-aromatics fraction. Finally, a highly polar solvent such as an alcohol is added to the benzene to displace the most strongly adsorbed and most polar components of the petrolene fraction. The alcohol debonds these components which are held strongly to the adsorbant by highly polar functional groups and the benzene provides solubility for these components as they elute from the column. This fraction, called polar aromatics, contains more highly condensed aromatic ring systems and functional groups containing heteroatoms. It should be noted here, and will be important later on when discussing durability and oxidation susceptibility, that all fractions contain, to a greater or lesser degree, cyclic and noncyclic saturated hydrocarbon fragments either as individual molecules in the saturates fraction or as moieties attached to the aromatic ring fragments in the more polar fractions. Sulfur is usually found in a large percentage of the individual asphalt molecules, but in unoxidized asphalt it is rather nonpolar and thus is found distributed among all the component fractions. The so-called asphaltene fraction is chemically similar to the more resinous or polar components of the petrolene fraction (31). Although the asphaltene fraction may contain small amounts of occluded or insoluble "saturate-type" material, the significant differentiating feature of this fraction is the preponderance of molecules with highly condensed planar and polarizable aromatic ring systems together with a high concentration of polar, heteroatom-containing functional groups. Because of these features, molecules of this fraction are strongly attracted to each other, associate strongly, and are difficult to disperse even in polar solvents.

The last fractionation scheme to be considered is that of chemical precipitation (Scheme 1C, Figure 1). This scheme and its modifications are based on a fractionation procedure developed by Rostler and Sternberg (32) and later applied to asphalts (5, 6). It may not be exactly correct to call this fractionation procedure a separation scheme since it is really a method of analysis. Some of the steps are destructive and the method does not require the recovery of the altered fractions for further analysis. After separation of the asphaltenes, the remaining components are sequentially separated into fractions based on their reactivity with sulfuric acid of increasing acid strengths (decreasing degree of hydration). In practice, the sulfuric acid phase is added to a nonpolar hydrocarbon solution of the components to be separated, thus forming a second, polar acid phase containing those components reactive with the sulfuric acid together with other components sufficiently polar or polarizable to partition towards the sulfuric acid phase. In the first step, an 85 percent sulfuric acid solution is used to remove the most polar components, including most of the basic and nonbasic nitrogen compounds and many of the oxygenated molecules. This fraction is called nitrogen bases. Since the nitrogen in asphalt is usually associated with condensed aromatic ring systems, the so-called nitrogen base fraction is quite aromatic. Concentrated sulfuric acid (98 percent) is used next to precipitate the first acidaffin fraction which has been reported

as containing unsaturated hydrocarbons (5). The use of the term "unsaturated" is unfortunate because the term is usually reserved for the designation of double and triple carbon-carbon bonds in nonaromatic ring structures (olefinic and acetylenic types) which have not been found in significant amounts, if at all, in petroleum residues. The first acid-affin fraction is quite aromatic and low in nitrogen content. The most likely reaction leading to separation of this fraction is sulfonation or complex formation involving the aromatic ring systems. Sulfuric acid containing 30 percent SO_3 , which is a powerful sulfonating and complexing agent, is used to precipitate those components with less reactive or polarizable aromatic ring systems. Analysis (5) of this fraction, called second acidaffins, indicates that it is considerably less aromatic than the nitrogen bases or first acidaffins. The final fraction remaining is called paraffins. This fraction is the oily component of asphalt and is composed primarily of molecules embodying straight chain, branched and cyclic alkanes.

Although any of the fractionation schemes discussed separate asphalt into less complex and more homogeneous fractions, the "generic" fractions obtained are in themselves still complex mixtures and not well defined chemical species. In all the separation methods equilibria are involved. This may be solid-liquid equilibria in the chromatographic separation or liquid-liquid partitioning in the chemical precipitation method. The same "generic" fraction can vary considerably in composition and properties from one asphalt source to another; however, the separations are often sufficiently definitive to provide useful information in studies relating chemical composition with physical properties.

INTERACTIONS AMONG ASPHALT COMPONENT FRACTIONS AND RELATIONSHIPS WITH DURABILITY

As is evidenced from the results of component fractionation, a wide spectrum of molecular types is present in asphalt. The most nonpolar or oily fraction, in the absence of the resinous components, is so unlike the asphaltene 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 various components of asphalt interacting with each other to form a balanced or compatible system. It is this balance of components that gives asphalt its unique viscoelastic properties which are so important to its application as a pavement binder. Lack of compatibility or balance, as sometimes manifest by component phase separation, leads to undesirable properties. The role of the various component 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. The colloidal nature of asphalt was first recognized by Nellensteyn (33, 34) who considered asphalt as a dispersion of micelles in an oily medium. The asphaltene fraction was early associated with the dispersed or micelle phase (35). It was also recognized that the ability, or rather lack of ability, of the resinous components to keep these highly associated asphaltene components dis-

persed in the oily phase largely determined the "gel" or non-Newtonian flow characteristics of the asphalt (36, 37). Rostler (5) described the asphaltene fraction as the component of asphalt primarily responsible for asphalt viscosity and colloidal behavior due to its limited solubility in the remaining components. He concluded that the asphaltenes are kept dispersed by the peptizing ability of the nitrogen bases. The peptized asphaltenes are, in turn, solvated by the resinous acidaffin fractions and "gelled" by the paraffins. Corbett described (38) the effects on physical properties of the four fractions separated by his procedure: the asphaltenes function as solution thickeners; fluidity is imparted by the saturate and naphthene aromatic fractions which plasticize the solid polar aromatic and asphaltene fractions; the polar aromatic fraction imparts ductility to the asphalt; and the saturates and naphthene-aromatics in combination with asphaltenes produce complex flow properties in the asphalt. In summary, he concluded that "each fraction or combination of fractions perform separate functions in 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."

For purposes of comparison, one might consider the polar aromatic fraction from the Corbett separation (10, Scheme 1-B, Figure 1) to contain many of the components found in the Rostler nitrogen base fraction plus possibly part of the first acidaffin fraction. The Corbett naphthene aromatic fraction may be roughly compared to the Rostler second acidaffin fraction plus some components found also in the Rostler first acidaffin fraction. The saturates and paraffins fractions from the two schemes might also be somewhat comparable.

It has been widely recognized (6, 7, 12, 39-43) that a proper balance of chemical components is necessary in a durable asphalt. Not only may too much or too little of a given generic type as defined by the fractionation schemes be detrimental to the compatibility of the system, but variations in chemical composition within the same generic type classification may also be detrimental. For example, the presence of waxes in the oily fraction, which tend to crystallize and cause phase separation, can be detrimental (39). Asphaltenes that are not properly dispersed, either because of their inherent solubility properties or because of the solvent properties or dispersing power of the resinous components of the petrolenes, will have reduced compatibility with the oily fraction and thus reduce asphalt durability (5, 42). Exudation of oil may occur and undesirable gel characteristics be imparted.

Rostler and coworkers (6, 43, 44) showed that the balance of the component fractions, as indicated by the ratio of most reactive fractions (nitrogen bases plus first acidaffins) to least reactive fractions (paraffins plus second acidaffins), was important to the resistance of asphalt-Ottawa sand pellets to abrasion loss in laboratory testing. Although the Rostler fractionation scheme has been used by many materials laboratories, and correlations with field performance attempted (45, 46), it has generally not been accepted as an accurate predictor of field performance. Lack of consideration of the asphaltene fraction, which contributes so significantly to flow properties, in the Rostler durability parameter may be unfortunate and a serious omission. In

field tests conducted in California (46), the Heithaus parameter, P, (state of peptization), which is an attempt to measure the internal compatibility of an asphalt by evaluating the peptizability of the asphaltenes and the dispersing power of the petrolenes (42) was found to correlate better with pavement field hardening than the Rostler durability parameter. Using six asphalts of widely differing composition, Traxler (47) 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. Better dispersed asphalts hardened more slowly. He further suggested that the degree of dispersion of the asphalt components is inversely related to the complex (non-Newtonian) flow properties of the asphalt and is indicative of the asphalt's colloidal characteristics.

CHANGES IN CHEMICAL COMPOSITION ON AGING

The discussion thus far has addressed chemical compositional factors that determine the physical properties of asphalts. Without question, a durable asphalt must possess acceptable physical properties to produce a pavement with initially acceptable performance properties. The companion requirement of a durable asphalt is that these initial properties be resistant to change during environmental aging in field service. However, asphalt composition changes with time when the asphalt is exposed as a thin film to atmospheric oxygen in the pavement. That asphalt reacts with atmospheric oxygen which stiffens or hardens the asphalt has been recognized for over 50 years and the literature in this area is voluminous. Atmospheric oxidation is the major factor responsible for the irreversible hardening of asphalts (2) and is the reason why pavement void content (which allows access to atmospheric oxygen) correlates so strongly with asphalt pavement hardening (48, 49). Hardening from loss of volatile components, the physical factor that might affect the hardening-void content correlation, is not considered a significant factor when using asphalts meeting current specifications. The potentially volatile components would be part of the saturate fraction; Corbett and Merz showed that the amount of this fraction remained virtually constant during 18 years of service in the well-known Michigan Road test (50). Thus, in dealing with asphalt durability a major factor that must be addressed is change that takes place in asphalt composition from oxidative aging.

The change in the amounts of fractional components of asphalt generally seen on oxidative aging is a movement of components from the more nonpolar to the more polar fractions. The saturates in the Corbett analysis (50) and the paraffins in the Rostler analysis (6) show least change on oxidation. There is usually some loss of the Rostler second acidaffins and a greater loss of the more reactive first acidaffins with these losses being offset by a significant increase in the asphaltene fraction. Similarly, the Corbett naphthene-aromatics and the polar aromatics decrease as asphaltenes increase.

King and Corbett (51) using thin films at 150°C and Knotnerus (11) using dilute toluene solutions showed that the saturates fraction is relatively inert to reaction with oxygen as measured by oxygen uptake.

The naphthene-aromatic (King and Corbett) and aromatic (Knotnerus) fraction 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 asphaltene fraction showed intermediate reactivity. Direct measurement of the formation of oxygen-containing functional groups by Petersen and co-workers (52) rank the relative reactivity with atmospheric oxygen of the saturates, aromatics, polar aromatics and asphaltenes fractions as 1:7:32:40, respectively, for a Wilmington (California) asphalt when the fractions were oxidized separately at 130°C. However, evidence was found that in neat asphalt, components of the more polar fractions may promote more oxidation of components of the less polar fractions than when they are oxidized separately.

The asphaltene fraction has been considered by some (5) to be "chemically almost inert"; however, the above data indicate that asphaltenes are quite reactive with oxygen. This supports the present author's criticism made earlier that it may not have been justified to eliminate the asphaltene fraction from the Rostler durability ratio. The apparent contradiction regarding the chemical reactivity of asphaltenes might be explained by the following observations made by the author. Isolated asphaltenes are brittle solids and in this state at ambient temperatures are indeed quite unreactive with atmospheric oxygen, probably because their solid, highly-structured state reduces molecular mobility, which in turn reduces reactivity with oxygen. However, when the asphaltenes are melted (as in the 130°C and 150°C oxidations) or in solution in solvents, their mobility is increased and thus so is their apparent reactivity. One might assume that if asphaltene components are well dispersed in neat asphalt, that they might also be chemically quite active. Their chemical structure, highly condensed ring systems with alkyl attachments, also suggests a system sensitive to hydrocarbon type oxidation.

More recent studies (14, 52-57) have yielded considerable information on the specific chemical changes that take place in asphalt on oxidative aging by reaction with atmospheric oxygen. The major oxygen-containing functional groups formed on aging are listed in Table 2 for

Table 2. - Chemical functional groups formed in asphalts during oxidative aging¹

Asphalt	Concentration, mol·L ⁻¹				Average hardening index ³
	Ketones	Anhydrides	Carboxylic acids ²	Sulf-oxides	
B-2959	0.50	0.014	0.008	0.30	38.0
B-3036	0.55	0.015	0.005	0.29	27.0
B-3051	0.58	0.020	0.009	0.29	132.0
B-3602	0.77	0.043	0.005	0.18	30.0

¹Column oxidation (59), 130°C, 24 hrs., 15 micron film; data from (14)

²Naturally occurring acids have been subtracted from reported value

³Ratio of viscosity after oxidative aging to viscosity before oxidative aging

four asphalts of different crude sources and aged under identical conditions (air, 130°C, thin film). Data (14) are averages for the four asphalts aged on four different aggregates and are for the same asphalts shown in Table 1. The level of oxidation has been judged to be equivalent to that typically found in asphalts after five years or more of pavement service (9). That the chemical functionality developed during laboratory oxidation at 130°C is similar to that developed during normal pavement aging at ambient temperatures is supported by data in Table 3 (58). Reasons for the lower levels of oxidation in some pavement samples compared with laboratory oxidation is discussed elsewhere (58), but they relate to the inaccessibility of some of the asphalt in the pavement to atmospheric oxygen.

Table 3. - Comparison of oxidation products in column-oxidized and pavement-aged samples

Asphalt	Concentration, mol·L ⁻¹			
	Column oxidized ¹		Pavement aged ²	
	Ketones	Anhydrides	Ketones	Anhydrides
60	0.76	0.024	0.53	0.018
25	.70	.025	.53	.022
30	.64	.027	.64	.038
61	.67	.022	.44	.020
67	.43	.013	.32	.010
71	.76	.026	.51	.022
72	.82	.033	.68	.029
73	.49	.013	.35	.011
74	.72	.027	.43	.017

¹Thin film oxidation, 130 C, 24 hr (59)

²Recovered from 11- to 13-year old pavements (15)

Data in Table 2 show that ketones and sulfoxides are the major oxidation products formed during oxidative aging with anhydrides and carboxylic acids being formed in smaller amounts. In some asphalts, the summed concentrations approach one mole per liter. If a molecular weight of 1000 is assumed for an asphalt molecule, then on the average, one functional group is formed for each asphalt molecule. Of course, not all molecules of asphalt have the same reactivity. Data in Table 4 show that ketones are formed in highest concentrations in the asphaltenes and polar aromatics fractions with lesser amounts in the aromatics fraction and considerably less in the saturates. These data are consistent with the earlier cited oxygen uptake experiments (11, 51).

The oxidation products formed are consistent and in good agreement with what is known about the hydrocarbon types in asphalt and the general chemistry of hydrocarbon oxidation. The major reaction pathway of hydrocarbon air oxidation is the formation of carbonyl compounds via the hydroperoxide intermediate (53, 54). The most sensitive hydrocarbon

Table 4. - Carbonyl functional groups formed in Wilmington asphalt fractions during column oxidation¹

Fraction	Concentration, mol·L ⁻¹		
	Ketones	Anhydrides	Carboxylic Acids
Saturates	0.045	0.010	Trace
Aromatics	0.32	0.017	² —
Polar aromatics	1.48	0.088	² —
Asphaltenes	1.82	0.080	ND ³
Whole asphalt	1.02	0.052	0.007

¹Data from (52)

²Some acids lost on alumina column during component fractionation

³Not determined

moiety expected to be present in asphalt is that associated with the carbon atom adjacent to an aromatic ring system, commonly called a benzylic carbon. The hydrogen attached to the carbon in this position is relatively easy to displace, forming a free radical on the carbon. Branching in the attached hydrocarbon chains also increases the sensitivity of the asphalt to oxidation.

A simplified, generalized scheme proposed by the author for the oxidation of the hydrocarbon moieties in asphalt is proposed in Figure 2 which shows ketones as the major functional group formed, consistent with the data in Tables 2 and 3. In the reaction scheme presented, the symbol, R, may represent either a hydrogen atom or an alkyl group. The reaction is initiated by the abstraction of a hydrogen attached to a benzylic carbon of an asphalt molecule (I) to form a free radical (II). The free radical reacts with atmospheric oxygen to form a peroxy radical (III). This in turn rapidly decomposes to form a ketone (IV), or, more likely, abstracts a hydrogen atom from the benzylic carbon of another asphalt molecule (V) to form a hydroperoxide (VII). The asphalt free radical formed (VI) can react with atmospheric oxygen to repeat the process. The hydroperoxide is rather unstable and may decompose to form either a ketone (VIII) or an alkoxy radical (IX). The alkoxy radical may rapidly decompose to form a ketone (X). This mechanism is admittedly oversimplified and minor amounts of other oxidation products not shown are undoubtedly formed. However, it adequately accounts for the major hydrocarbon oxidation product, ketones. Ketones as the major oxidation product in oxidized asphalt have been positively verified (53). Smaller amounts of anhydrides are formed (54) through what is believed by the author to be an alternate hydroperoxide decomposition route in certain asphalt molecules having stereospecific ring systems associated with the oxidizable alkyl moieties. Under certain conditions the alkyl moiety may oxidize to the carboxylic acid, however, only small amounts of carboxylic acids (and no measurable esters (54)) have been found in laboratory or pavement-aged asphalts. It appears that the oxidation reaction almost always stops at the ketone stage.

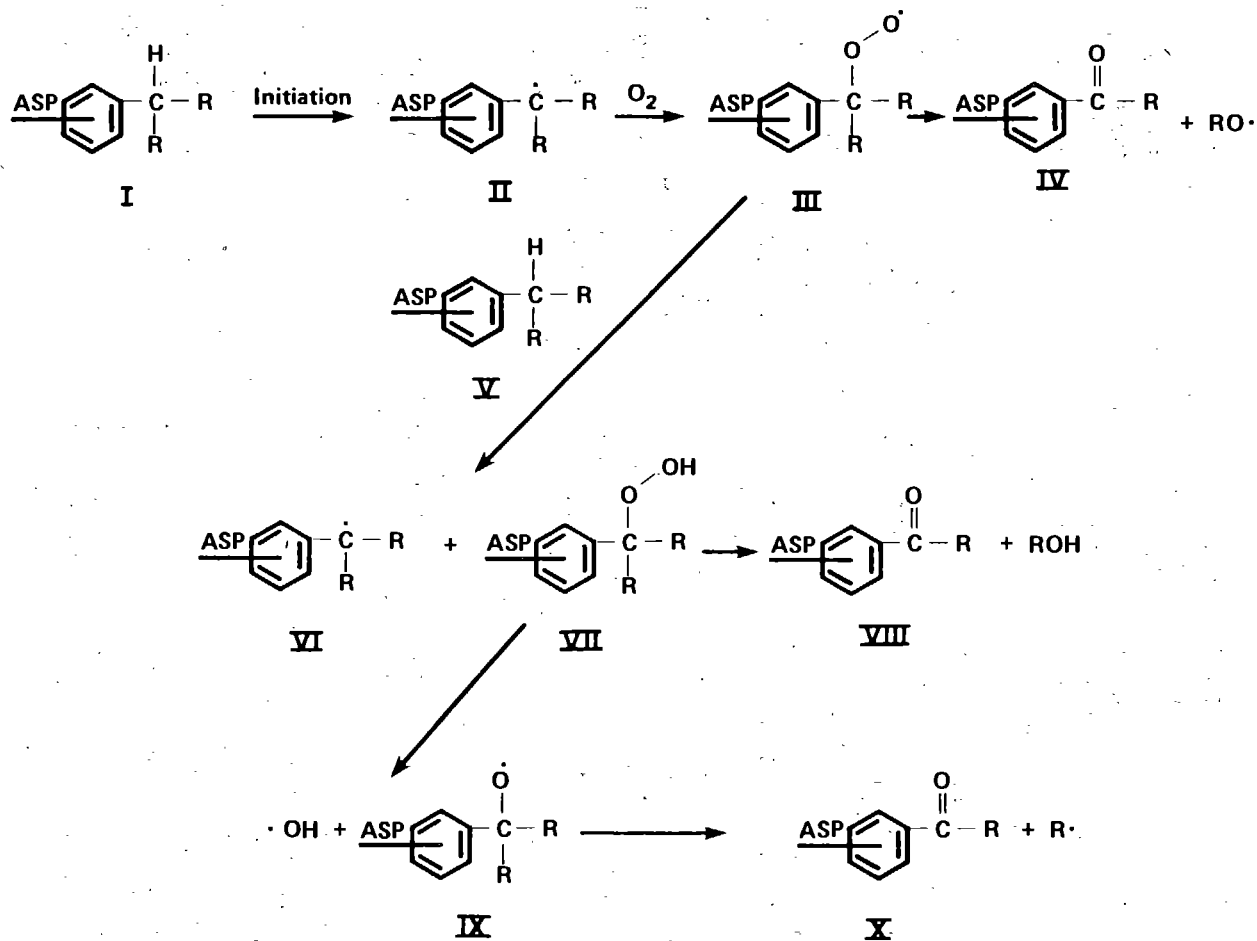


Figure 2. A Suggested Mechanism for the Free Radical Air Oxidation of Asphalt

Because the polar aromatics (or nitrogen bases and first acidaffins) and asphaltene fractions are known to contain the highest concentrations of aromatic ring systems, and thus benzylic carbons via the alkyl moieties attached, they have the highest content of hydrocarbon types sensitive to air oxidation. It is then not surprising that the polar aromatics and asphaltenes (Table 4) showed the highest ketone formation on oxidation.

The formation of sulfoxides, the second most dominant oxidation product, has been shown to result from oxidation of organic sulfides that are part of complex asphalt molecules (57). These sulfides are highly reactive. Sulfoxides are formed in asphalt at a much higher rate than ketones and their formation often precedes significant ketone formation. This is probably because sulfides are hydroperoxide scavengers and are converted to sulfoxides by the scavenger reaction.

The significance of the polar, oxygen-containing functional groups on physical properties will be discussed in detail in a later section of this paper. However, their influence on the hardening of the asphalt is apparent from the aging indexes (ratio of viscosity after oxidation over viscosity before oxidation) of the asphalts in Table 2 which range from 27 to 132. It is apparent that the relative amount of hardening is not directly related to the amount of oxidation when comparing one asphalt source to another. Note that the asphalts with the smallest and greatest aging indexes (Table 2) both showed about the same chemical reactivity with atmospheric oxygen. This is because all asphalts do not show the same sensitivity to the oxidation products formed. Asphalts from different sources have differing composition and thus their components interact differently with the oxidation products formed to increase viscosity. This varying sensitivity to oxidation products will be discussed later in more detail.

At this point, it is instructional to consider the Rostler durability parameter with regard to the chemical information just presented. As previously stated, this parameter is the ratio of the quantity of nitrogen bases plus first acidaffins divided by the quantity of second acidaffins plus paraffins. The polar aromatic fraction, which should include the Rostler nitrogen bases and a good part of the first acidaffins, was shown to be the fraction most chemically reactive with oxygen after asphaltene separation. Also, the saturates and aromatics, which should account for much of the Rostler paraffins and second acidaffins fractions, were shown to be least reactive. Thus, it is understandable that a correlation was found between the Rostler durability parameter (ratio of most reactive to least reactive components as recognized by Rostler) and abrasion loss in the pellet abrasion test (5, 6), which test is sensitive to asphalt hardening on oxidation. Although the ratio may indicate the relative amounts of components most reactive to oxygen (excluding the asphaltenes) to the amounts least reactive, it is not a precise measure of the compatibility of the sample, since the relative amounts of saturates and second acidaffins, and the relative amounts of first acidaffins and nitrogen bases, whose sums make up the denominator and numerator of the ratio, are not specified. Also, as previously mentioned, the asphaltenes, which have such a profound effect on asphalt compatibility and viscosity, are not considered in the ratio. These

problems are compounded by differences in composition that may occur among similar generic-type fractions from different asphalts. Consider again the large differences in the effects of similar amounts of oxidation products (from chemical reactivity) on the hardening rate of the two different asphalts shown in Table 2. Initial compatibility, rate of formation of oxidation products, and response of the system to the oxidation products produced are all interdependent variables and cannot be sufficiently defined by a single numerical value. The asphalt system is much too complex for this. It is the considered opinion of the author that while the Rostler parameter should show a general correlation with pavement performance, it is not sufficiently precise to be used as an accurate predictor and, if used, must be considered together with additional physiochemical data further defining the composition of the asphalt.

MOLECULAR INTERACTIONS--A FUNDAMENTAL APPROACH TO CHEMICAL FACTORS AFFECTING ASPHALT DURABILITY

This section of the paper will address a fundamental approach to asphalt chemical composition--physical property relationships. The approach draws heavily on past chemical data and information from component analyses, but is based on more recent research which recognizes the fundamental chemical factors that affect asphalt properties. Parts of this section have been previously summarized (60). Because the physical properties of asphalt are controlled by the interactions of the molecules from which it is composed, an understanding of these interactions should provide the basis for understanding its physical behavior, and thus, its durability. It is not necessary (and would be virtually impossible) to know the exact structure of each molecule for a workable understanding. It should be sufficient to identify or characterize the various types of chemical or structural features of the asphalt molecules and how these interact with each other and their environment.

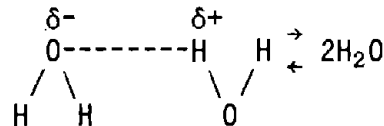
Many molecules of different composition will have similar features or "functionality" that will produce similar effects on physical properties. Functionality analysis has the advantage over component fractionation in that it can take into account the multiple functionality of asphalt molecules. Many asphalt molecules have several types of chemical functionality on the same molecule, often of diverse types, which frustrate chemical fractionation procedures since whole molecules must be moved into a given fraction. The molecular interaction approach taken here is primarily that of the author; however, many researchers both past and present have recognized the importance of chemical functionality on asphalt properties.

Fundamentals of Molecular Interactions and Effects of Molecular Interactions on Flow Properties

Because the chemical and physical properties of an asphalt are the sum total of the composition and interactions of its individual molecules, it is instructive, at this point, to briefly review some fundamentals of molecular interactions. Molecules attract one another and interact through a variety of secondary bonds or association forces. These association forces are generally one to two orders of magnitude

weaker than the covalent chemical bonding forces that hold the atoms together in the molecule. The association forces are significantly different from covalent bonding forces in that they form bonds that are generally reversible and are usually in dynamic equilibrium. That is, they "make" and "break" under forces induced by such factors as temperature and external stress, and thus they largely determine the physical properties of the composite material.

To illustrate the principles involved, the classic example of the hydrogen bonding of water molecules is considered. A simplified schematic of this bonding is as follows.



The electronegative oxygen atom reduces the electron density of the hydrogen atom by attracting its electron field, thus, creating a dipole-dipole interaction involving the oxygen and hydrogen of two different water molecules. Additional dipole interactions produce a three-dimensional network of associated species. 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 and are the major forces controlling the properties of water. The formation and breakdown of molecular structure via association forces is extremely rapid. In liquids, the average lifetime of a given arrangement of molecules, i.e. a structural unit, may be as short as 10^{-13} seconds and for water is estimated at 10^{-11} seconds.

To further illustrate the great influence of the electronegative oxygen atom on physical properties, consider replacing the oxygen in water with sulfur to yield hydrogen sulfide, H_2S . Because sulfur is less electronegative than oxygen, the strength of the hydrogen bond is greatly reduced. As a result, hydrogen sulfide, even though a heavier molecule than water, is not a liquid but rather a gas at room temperature. Its boiling point is 162°C (292°F) lower than that of water. The effects of intermolecular forces, as illustrated by the hydrogen bond, are basic to understanding the effects of chemical composition on asphalt properties because the intermolecular forces are the primary determinants of physical properties.

It should not be implied from the discussion above that the hydrogen bond is the most important interaction force in asphalt. Many other reversible interaction forces are important in a material so chemically complex. These include a variety of dipole and induced dipole interactions. For simplicity in discussing molecular interactions in this paper, 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.

Nonpolar hydrocarbon components in asphalt such as those dominant in the saturate fraction exhibit only weak interaction forces, which accounts for the rather fluid character of this fraction. On the other hand, asphalt components containing highly condensed ring systems and chemical functional groups containing oxygen and nitrogen atoms may be 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 may not be significantly different in molecular weight than the saturates (61), are high melting solids.

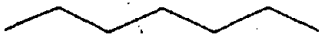
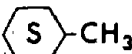
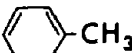
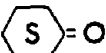
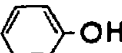
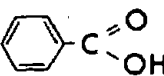


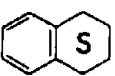
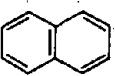
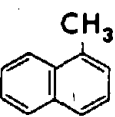
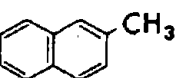
To illustrate the potential applicability of molecular interaction theory and molecular structuring to the physical properties of asphalt, it is helpful to examine the effects of the chemical functionality of a series of model compounds on the physical properties of these compounds. A list of selected model compounds together with their structure, boiling point, and melting point are shown in Table 5. These chemical functionalities also represent important types found in asphalt and thus, the reasoning developed may have direct application.

First, consider the series of compounds n-heptane through benzoic acid. All were chosen from the same molecular weight range to minimize the effects of this variable and are listed in their order of increasing polarity or increasing tendency of the molecules to interact. As previously mentioned, molecular interaction forces must be overcome to allow vaporization; thus, changes in boiling point reflect changes in the strength of the interaction forces between molecules. Note the continuously increasing boiling point with increasing polarity. The introduction of aromaticity in the molecule with toluene introduces mobile pi electrons which can be polarized, thus increasing its boiling point over methylcyclohexane. Introducing the ketone group with cyclohexanone adds a polar oxygen-containing functional group and significantly increases the boiling point over methylcyclohexane. Phenol has both aromaticity and a polar OH group which can form strong hydrogen bonds, thus it has an even higher boiling point. Finally, benzoic acid possesses a carboxylic acid functional group which forms very strong hydrogen-bonded dimers. Note its extremely high boiling point.

Next, consider the properties of the series hexahydronaphthalene through 2-methylnaphthalene in Table 5. As expected, the boiling point increases in a regular fashion with increasing aromaticity and the introduction of the methyl group; however, the melting point shows no such correspondence. Note also in Table 5 how introducing a methyl group on benzene to form the higher boiling toluene greatly reduced the melting point. The melting point, which reflects the interaction forces between molecules when in an ordered or structured configuration, is greatly influenced by the geometry of the molecule. Interfering appendages or structural arrangements of the molecules that do not allow them to fit together easily in the necessary geometric pattern for effective interaction greatly reduce the melting point. Thus, molecular shape dominates the low temperature structuring properties.

It is instructive to consider the molecular interaction effects just described with regard to the flow properties of asphalts. The rather predictable effect of polar functionality on boiling point can be

Table 5. Effects of molecular interactions and molecular structuring on the physical properties of model compounds

<u>Compound</u>	<u>Structure</u>	<u>Boiling Point, °C</u>	<u>Melting Point, °C</u>
n-Heptane		98.4	-90.5
Methylcyclohexane		100.3	-126.4
Toluene		110.6	-95
Cyclohexanone		156.7	-45 (frz.)
Phenol		182	41
Benzoic Acid		249	122
Benzene		80	5.5
Hexahydronaphthalene		205	liquid
Tetrahydronaphthalene		207.2	-30
Naphthalene		217.9	80.2
1-Methylnaphthalene		240	-22
2-Methylnaphthalene		245	35.1

related to the effects of polar functionality in asphalt on its flow properties at higher temperatures in the Newtonian flow region. The polar interactions between molecules dominate in influencing the flow behavior and the effects of molecular shape on geometry are minimized. This reasoning suggests why asphalts that have quite different flow properties at low temperatures "look more alike" at higher temperatures.

At lower temperatures, however, as the kinetic energy of the system is lowered, the asphalt molecules tend to associate or agglomerate into immobilized entities with a more or less ordered or structured spacial arrangement. Although this ordered arrangement is influenced by polar functionality, it is also greatly influenced (as was the melting point of pure compounds) by the geometry of the molecules. Thus, at low temperatures, the effects of differences in chemical composition of asphalt play a more significant role in determining the complex low temperature flow properties, e.g., viscosity shear and temperature susceptibility.

Data obtained on asphalt-based systems will now be considered. To illustrate the effect of different types of molecular interactions on viscosity, consider data taken from an early paper by Griffen and co-workers (12) and abstracted in Table 6. Griffen separated asphalt into component fractions and then determined molecular weight versus viscosity profiles on the fractions. Data in the table are taken for components of each fraction having the same molecular weight of 500.

Table 6. - Viscosity of molecular distillation cuts of asphalt fractions having similar molecular weights¹

Fraction	Apparent molecular wt.	Viscosity, Pa·s ² , 25°C
Saturates	500	10
Aromatics	500	1,000
Resins	500	100,000

¹Data from (12)

²To convert to viscosity in poise, multiply by 10

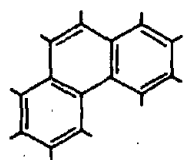
The saturates had a viscosity of only 10 Pa·s. They do not contain polar chemical functionality and molecular interactions are weak. Molecular interactions of increased intensity are exhibited by the aromatics fraction whose viscosity was 1,000 Pa·s. Finally, the resins which contain polarizable condensed-ring systems and heteroatom functionality, and thus exhibit even more intense molecular interactions, had a viscosity of 100,000 Pa·s. Because the molecular weights of each fraction were the same, the differences in viscosity resulted primarily from differences in the type and strength of molecular interactions. The association forces among asphalt molecules give asphalt many of the properties of high-molecular-weight polymers.

Major Chemical Functional Group Types Affecting Asphalt Properties

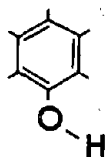
As previously stated, asphalt molecules contain hydrocarbon structural constituents varying from saturated, paraffin-like chains to highly condensed and polarizable aromatic ring systems. From the previous discussion of model compounds, it is apparent that the relative amounts of the different structural or functional moieties of each molecule determine how molecules interact with each other. Those molecules that are most alike are most compatible and vice versa. In fact, as stated earlier, some asphalt components such as the saturates and asphaltenes are not mutually soluble when separated from the whole asphalt. It is the wide spectrum of molecular types in asphalt, all interacting together, that gives asphalt its unique properties and makes it appear as a homogenous material. However, on a molecular level, asphalt is undoubtedly heterogeneous with a delicate balance existing among strongly associated or agglomerated components and dispersing or solubilizing components. It is this delicate balance, or the lack of it, that affects the performance properties of asphalts. Incompatibility and poor performance generally follow when one component type unduly dominates at the expense of others.

As previously discussed, although asphalt molecules are composed primarily of hydrocarbon constituents, heteroatoms such as nitrogen, sulfur, and oxygen may also be present as part of the molecule. Heteroatom concentrations vary widely among asphalts. In many asphalts, heteroatom concentrations are sufficient to average one or more heteroatoms for every asphalt molecule. Oxygen, nitrogen, and some forms of sulfur may introduce high polarity into the molecule; and although only a minor component, they can exhibit a controlling influence on the molecular interactions that control asphalt flow properties. Thus, chemical functionality containing these atoms becomes a major consideration in understanding asphalt properties.

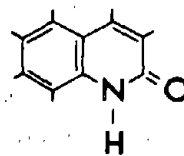
Much work has been done by the author and co-workers in identifying polar, strongly associating functional groups in asphalts, either naturally present or formed on oxidation, and in characterizing their association forces (9, 14, 52-56, 59, 62-69). Structural formulas of important chemical functionality in asphalts are shown in Figure 3. Nitrogen, which occurs in concentrations of 0.2 to 1 percent, is present in several forms from the slightly acidic pyrrole types to the more basic, and strongly interacting, pyridine types (69). The nitrogen types naturally occurring in asphalt are not known to be significantly altered by oxidation. Sulfur, in concentrations from about 1 to 5 percent, is present primarily as sulfides. Many of these sulfides are readily oxidized to polar sulfoxides by atmospheric oxygen during normal aging (57). Phenolics are also usually present. Naturally occurring carboxylic acids and 2-quinolone-type functionality, although occurring in relatively small amounts in asphalts, are highly polar and associate strongly (64). As previously discussed, asphalts are susceptible to oxidative aging by reaction with atmospheric oxygen which is a major factor contributing to age-hardening and embrittlement. The major oxygen-containing functional groups formed on oxidative aging are also included in Figure 3.



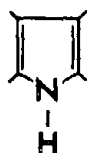
Polynuclear aromatic (1)



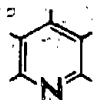
Phenolic (1)



2-Quinolone type (1)



Pyrrolic (1)



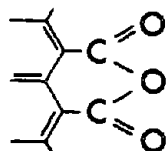
Pyridinic (1)



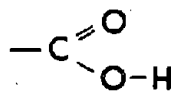
Sulfide (1)



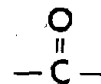
Sulfoxide (2)



Anhydride (2)



Carboxylic acid (1,2)



Ketone (2)

(1) Naturally occurring

(2) Formed on oxidative aging

Figure 3. Chemical Functionality in Asphalt Molecules Normally Present or Formed on Oxidative Aging

Effects of Polar Functional Groups Formed on Oxidation on Asphalt Performance

Asphalts vary considerably in their susceptibility to the effects of deteriorating oxidation. If during aging the concentration of polar functional groups becomes sufficiently high to cause molecular immobilization through increased intermolecular interaction forces, i.e., the asphalt molecules or micelles are not sufficiently mobile to flow past one another under the stress applied, fracturing or cracking of the asphalt will result.

Data in Figure 4 show a relationship between the amount of strongly interacting, polar groups formed in a series of asphalts during controlled laboratory oxidative aging and the resistance to failure from cracking in roads in which these asphalts were used. The asphalts were from the California Zaca-Wigmore test road previously mentioned (4, 9) in which construction variables were kept as constant as possible to evaluate the effect of asphalt composition (or source) on durability. In the laboratory studies (9), these asphalts were coated as thin films on inert fluorocarbon particles and were aged in a gas chromatographic (GC) column at 130°C (266°F) for 24 hours by passing air through the column (59). (This procedure oxidizes the asphalt an amount equal to approximately 5 years or more in a road.) Following oxidative aging, a polar test compound, phenol, was passed through the GC column using an inert gas carrier, and its interaction with the polar groups formed in the asphalt during oxidation was determined from the phenol retention time. As phenol passes through the column it is in equilibrium with the asphalt; those asphalts having a greater concentration of polar groups interact more strongly with the phenol functionality giving a larger phenol interaction coefficient.

As seen from Figure 4, an excellent correlation was found between the asphalt polarity as measured by the phenol interaction coefficient and the service performance rating after 51 months of road service. Those asphalts developing greater amounts of strongly interacting polar groups during aging failed sooner in the road. Figure 5 shows a similar correlation developed on 20 roofing asphalts whose weatherability was determined by resistance to cracking when aged in a carbon arc Weather-Ometer*. Thus, strong evidence exists relating the development of polar functional groups in asphalts on aging with asphalt failure from embrittlement and cracking.

Effects of Polar Asphalt Components on Viscosity and Aging Characteristics

Data plotted in Figure 6 illustrate the important influence of polar constituents (in this case, asphaltenes) on asphalt viscosity. In the cited study (14), four asphalts (all meeting the same specifications) were oxidatively aged in the laboratory both before and after a hydrated lime treatment (the lime with adsorbed asphalt components--

*Mention of specific brand names or models of equipment is for information only and does not imply endorsement by the sponsoring organization.

about 4 percent of the asphalt--was separated from the asphalt during the treatment). The asphalts were aged by different methods to achieve different levels of oxidation. Following aging, both asphaltene content and viscosity were determined at 25°C (77°F). Each data point in the figure represents a separate level of oxidation. Although each asphalt had its own unique relationship, a good correlation existed for each asphalt between asphalt viscosity and asphaltene content. Several important points can be inferred from the data in Figure 6. First, the asphaltene fractions of the different asphalts are quite different from each other in composition and/or the petrolene fractions have widely differing solubility power for the asphaltenes. This is a necessary condition in order for asphalts with widely varying asphaltene contents to have the same viscosity. Second, asphaltenes formed in asphalt on oxidative aging appear to have a predictable effect on viscosity increase.

Data in Table 7 show the effect of the lime treatment in reducing the hardening rate of the asphalts when subjected to a laboratory GC column oxidation procedure (59, 14) during which the asphalts were supported as thin films on the surface of four different aggregates. Note

Table 7. - Reduction of hardening rate of asphalt by treatment with hydrated lime¹

	Hardening index ²		Reduction, percent
	Untreated	Lime treated	
<u>Asphalt</u> (Averaged for aggregates)			
B-2959	37	17	54
B-3036	27	10	63
B-3051	132	35	73
B-3602	29	18	39

<u>Aggregate</u> (Averaged for asphalts)			
Quartzite	57	22	61
Hol limestone	58	22	61
Riverton limestone	36	13	63
Granite	75	22	70

¹Data from (14)

²Hardening index = $\frac{\text{Viscosity after oxidative aging}}{\text{Viscosity before oxidative aging}}$

that except for asphalt B-3602, lime treatment reduced the hardening index of the asphalts by more than 50 percent. Asphaltene formation on aging was also reduced by about 50 percent (14). Functional group analyses, however, showed that the oxidation reaction, as measured by

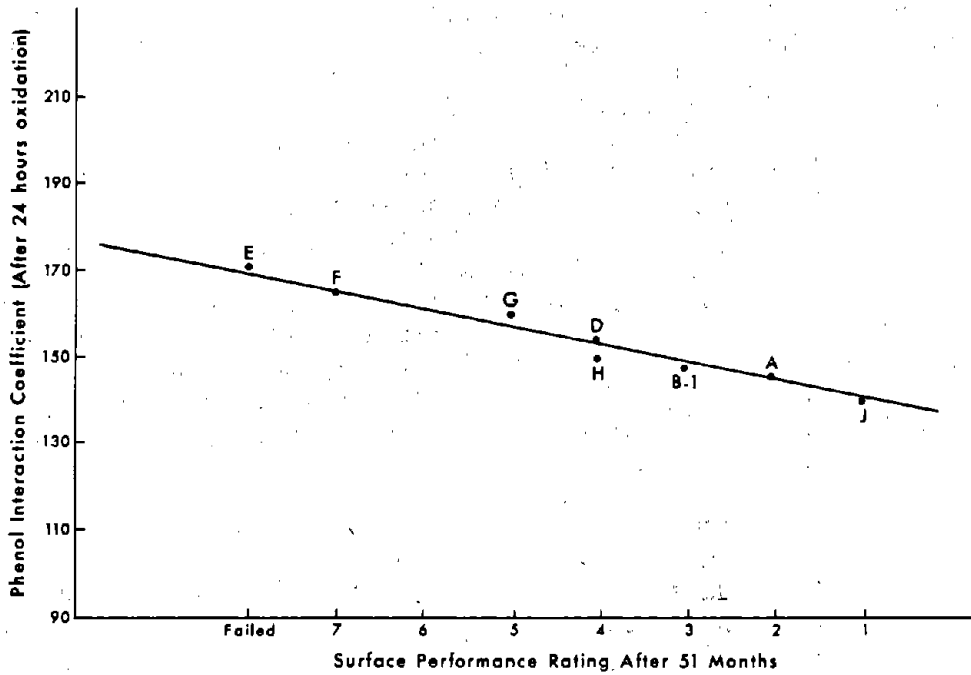


Figure 4. Relationship between Phenol Interaction Coefficient and Pavement Surface Performance Rating; Reproduced from (9).

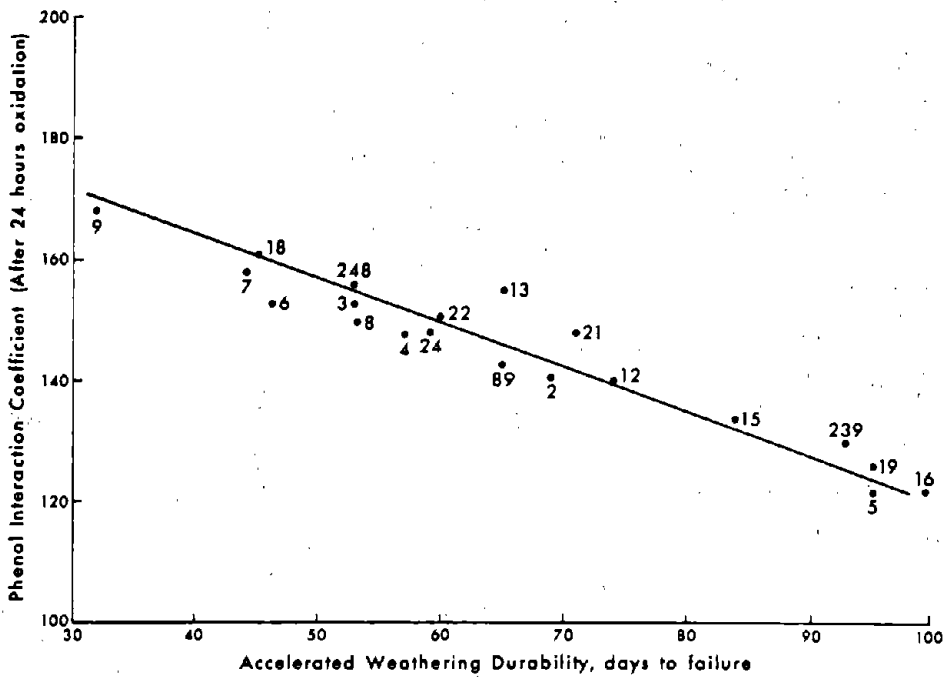


Figure 5. Relationship between Phenol Interaction Coefficient and Durability of Twenty Roofing Asphalts; Reproduced from (9).

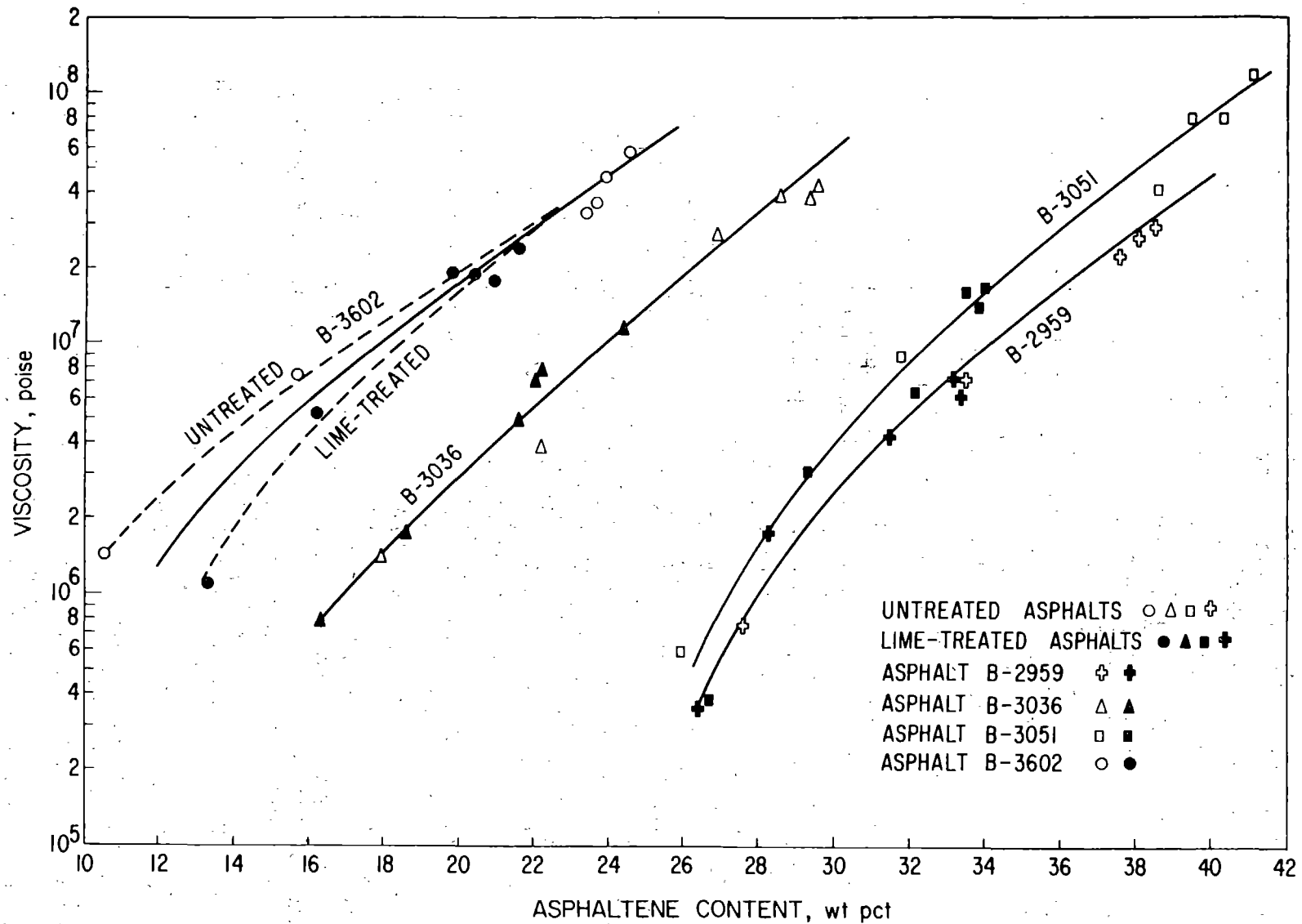


Figure 6. Relationships between Viscosity at 25°C (77°F) and Asphaltene Content of Untreated and Lime-Treated Asphalts Aged by Different Laboratory Methods; Reproduced from (14). To convert poise to $\text{Pa}\cdot\text{s}$; divide by 10.

the formation of ketones, was reduced by only about 10 percent by lime treatment. What was concluded was that lime removed carboxylic acids and other highly polar functionality that would have otherwise interacted with oxidation products to increase asphalt viscosity. Separate studies showed that the introduction of carboxylic acid functional groups into asphalt molecules greatly increased asphalt viscosity.

The reduction of asphalt viscosity by inactivating polar functionality was demonstrated (70) by adding 3 weight percent hydrated lime to an asphalt (B-3051), leaving the lime in the asphalt, and measuring its viscosity versus time at 25°C (77°F). During the initial 24-hour period after lime addition, asphalt viscosity steadily decreased in a regular fashion from about 5×10^4 to 1.5×10^4 Pa·s (5×10^5 to 1.5×10^5 poise). This decrease was interpreted to result from the adsorption of polar, strongly interacting groups on the lime surface, thus removing these viscosity-building components from the asphalt matrix. In some asphalt-aggregate systems, such phenomena might impart slow-setting or tenderness characteristics to a pavement mixture.

The flow properties and hardening rate of asphalt might also be significantly altered by manipulation of molecular interactions through chemical modification or the addition of modifiers that can interact with polar chemical functionality in the asphalt and alter its activity as suggested by the data on lime addition. The ability of surface-active materials such as antistripping agents (often amines) to alter asphalt viscosity, often to an extent not expected from simple additive effects, is familiar to many. Because antistripping agents have polar chemical functionality, they might be expected to affect the dispersibility of asphaltene-like components in asphalt by associating with polar functionality and thus alter association and micelle structure within the asphalt. The ability of high-molecular-weight amines to interfere with molecular structure buildup and subsequent viscosity increase in asphalt cutbacks during storage was reported as early as 1951 by Hoiberg (71).

The effects of antistripping additives on altering the flow properties and oxidative hardening rate of asphalts has been recently reported (72). It has been suggested (73) that cationic asphalt additives augment the peptization of the asphaltene constituent in many asphalts and thus reduce the asphalt hardening rate as reported in a trade newsletter (74). According to the report, of 82 asphalts tested, 81 percent were benefitted by the additives with a minimum of 15 percent and a maximum of 65 percent reduction in hardening rate during the rolling thin film oven test (ASTM D2872-77). The hardening rate of a recycled pavement mixture during laboratory aging was also reduced several fold by a high float emulsifying agent used to emulsify the recycling agent prior to recycling of the pavement mixture (75).

Composition and Component Compatibility

Previous reference was made to the need for a good balance among asphalt components of differing polarity. Compatibility in asphalt deals with the mutual solubility of a variety of components with widely differing solubility and solvent powers. Earlier workers in the field considered compatibility in terms of the "state of peptization" of

asphaltenes. Heithaus (42), stated that asphaltenes are the most polar and aromatic components in asphalt and are present in asphalts as rather concentrated solutions (10 to 40 percent). To obtain maximum solvency for the polar, strongly associating species in asphalts, the polarity of the solvent (maltenes, now preferably called petrolenes) must be matched to the materials to be dispersed (asphaltenes). For example, more polar asphaltenes require petrolenes with greater solvent power to effectively dissolve or disperse them.

A number of studies have addressed the dispersibility of asphaltenes and methods to measure dispersibility and compatibility (7, 42, 76-78). Altgelt and Harle (77) clearly demonstrated that selected asphaltenes from different sources had different effects on blend viscosity (different "thickening power") when added to the same petrolene fraction. They further showed that petrolene fractions derived from asphalts of different sources had different solubility power for asphaltenes. To illustrate the principles they developed, consider what happens when a highly polar asphaltene fraction having a strong tendency to self-associate is added to a petrolene fraction having relatively poor solvent power for the asphaltenes. Intermolecular agglomeration will result, producing large, interacting, viscosity-building networks. Conversely, when an asphaltene fraction is added to a petrolene fraction having relatively high solvent power for the asphaltenes, molecular agglomerates are broken up or dispersed to form smaller associated species with less interassociation; thus, the viscosity-building effect of the asphaltenes is reduced. One must conclude that chemical composition becomes an important factor to be considered when blending asphalts (or crudes) from different sources or when blending asphalt components. The principles described help explain why viscosities of asphalt mixtures or blends often show irregularities when compared with the viscosities of the original asphalts.

It follows that asphalt compatibility can be changed for better or for worse by blending and that the initial properties of blended asphalts are not necessarily additive in determining blend properties. Compatibility considerations are also important with regard to the aging characteristics of asphalt because, as already described in detail, oxidative aging greatly alters the polarity of asphalt molecules, and therefore, their interactions. The discussion thus far implies that a better knowledge of the chemical functionality responsible for the strong interaction forces in asphalt, and the ability to manipulate these forces, has great practical value in altering the flow and thus the performance properties of asphalt. Application of compatibility principles to pavement recycling in which a recycling agent is added to restore useful properties should also greatly benefit this rapidly emerging practice.

Importance of Molecular Structuring to the Flow Properties of Asphalt

Molecular structuring in asphalts is probably one of the least understood physiochemical phenomena affecting physical properties. Unlike oxidative aging which produces irreversible changes in asphalt composition, molecular structuring is a reversible phenomenon that can produce large changes in the flow properties of asphalt without altering the chemical composition of the asphalt molecules. Several factors

account for its elusive nature and resistance to quantification. First, in asphalts at ambient temperatures, structuring is a slow process which may go on for days and even years; second, it is promoted by mineral aggregate surfaces (as in pavement mixtures) in an environment where it is difficult to measure its effects; and third, most normal asphalt recovery methods using solvents and/or heat destroy or reverse the structuring process. Yet molecular structuring is largely responsible for asphalt's unique physical properties. Without it, pavement mixtures would not "set" to produce a non-tender pavement with the desired structural integrity, and too much structuring can produce pavements with poor low temperature properties and high shear susceptibility.

Although the phenomenon of structuring in asphalt is as yet little understood, it was recognized and received considerable study by early investigators (71, 79-85) and is often called "steric hardening" (83). It has been related to the thixotropic flow behavior commonly encountered in colloidal materials (80). The early literature is extremely revealing and might well be read carefully by present-day technologists, since little work has been done to build on or take advantage of the excellent past studies.

Traxler and coworkers characterized molecular structuring (also called by them age hardening, but not to be confused with age hardening caused by oxidation) in a number of asphalts from a variety of sources and related it to the degree of complex flow (sensitivity of measured viscosity to shear rate) (79-82). Their experiments were carried out on bulk asphalt in the absence of significant oxidation. Selected data in Figure 7 and in Tables 8 and 9 document this nonoxidative age hardening. In Figure 7, selected data on three paving asphalts show different hardening rates as a function of asphalt source. Air-blown asphalts showed a greater rate of structure hardening than unblown asphalts as illustrated by the air-blown Venezuelan asphalt in Figure 7. Note also that for the air-blown asphalt, the log viscosity versus log time plot was not linear as with the unblown asphalts but the rate of change increased with time. Traxler and coworkers (79) devised an expression called the asphalt aging index to quantitatively measure reversible hardening from molecular structuring. This index is the slope of the log viscosity versus log time plot. Asphalt aging indexes for eight unblown asphalts from different sources are shown in Table 8. The structuring phenomenon was found reversible and structured asphalt could be brought back to near its initial viscosity by heating to a temperature above its softening point or by continued mechanical working (81,85).

These early researchers found a correlation between the complex flow of asphalt (non-Newtonian behavior or viscosity lowering with increasing shear rates) and its tendency to exhibit molecular structuring. This is illustrated by data in Table 9, which compare the complex flow (a value of 1 indicates Newtonian flow) for a series of asphalts with the asphalt aging index resulting from structural hardening. Those asphalts which showed more rapid structuring possessed the greatest degree of non-Newtonian flow behavior.

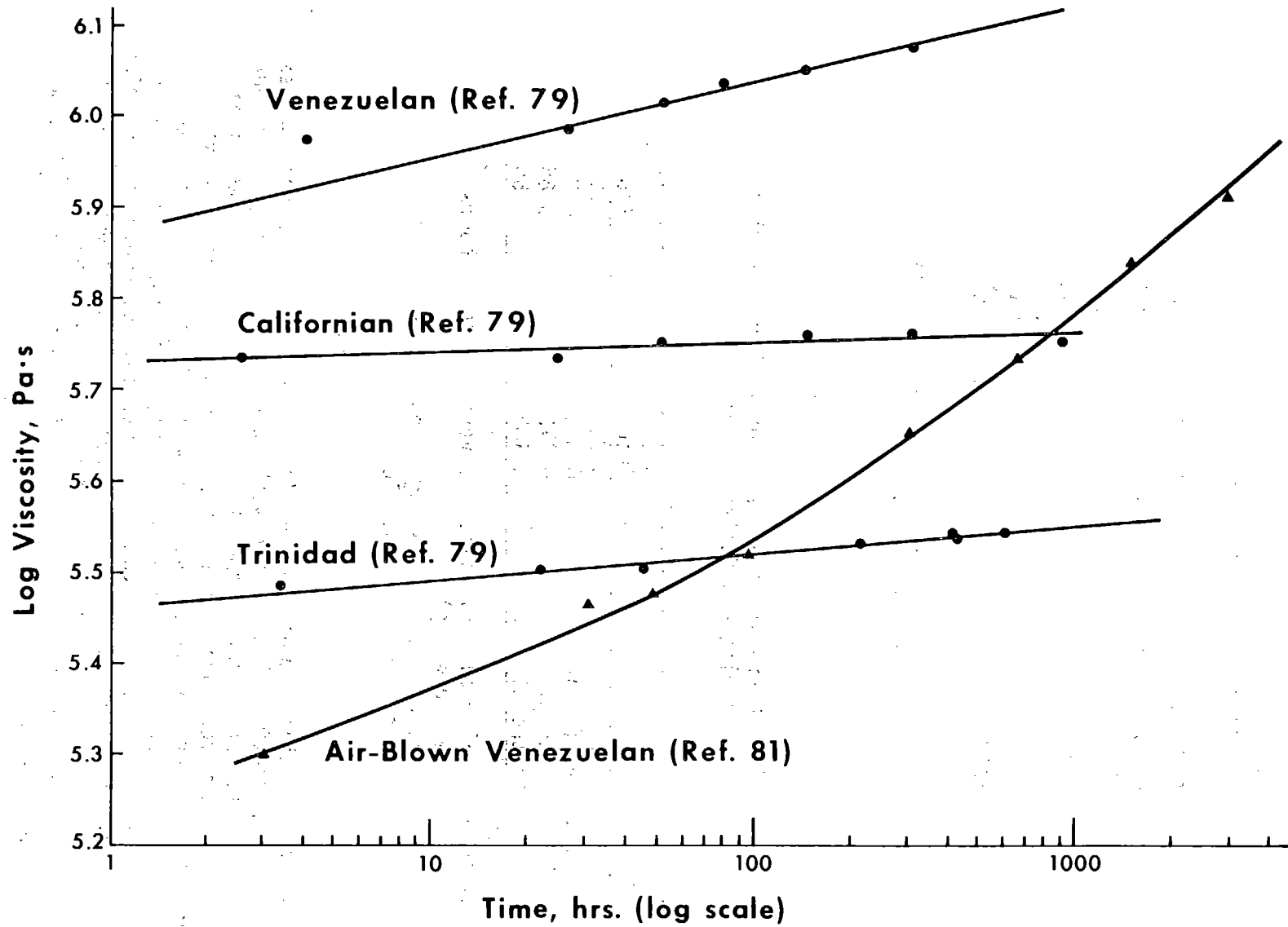


Figure 7. Hardening of Asphalts from Reversible Molecular Structuring at 25°C (77°F); data from (79, 81)

Table 8. - Reversible molecular structuring in
asphalts from various sources¹

Asphalt	Asphalt aging index ²
Californian	0.012
Californian	0.018
Trinidad	0.026
Venezuelan	0.037
Midcontinent	0.039
Mexican	0.051
Venezuelan	0.063
Venezuelan	0.071

¹Data from (79)

²Slope of log-log plot of viscosity versus
time in hours (non-oxidative hardening)

Table 9. - Correlation between reversible molecular
structuring and degree of complex flow¹

Asphalt	Asphalt aging index ²	Complex flow ³
Pressure-still	0.017	1.0
Air-blown Californian	0.023	0.95
Air-blown Midcontinent	0.073	0.85
Air-blown Northeast Texas	0.183	0.50

¹Data from (82)

²Slope of log-log plot of viscosity versus time in hours
(nonoxidative hardening)

³Slope of log-log plot of shearing stress versus shear
rate (measure of non-Newtonian flow)

The relationship between complex flow and structural hardening has considerable potential significance with regard to hardening of pavement mixtures. It is known that as asphalts undergo oxidative aging, their flow behavior becomes more complex or non-Newtonian. Recently, the author and coworkers, while studying oxidation (58), found that two asphalts that had been previously oxidatively aged, increased significantly in measured viscosity because of reversible molecular structuring after standing for two years from 2.5×10^4 to 1.2×10^5 and 1.1×10^5 to 3.0×10^6 Pa·s. The structural hardening was reversed upon heating the samples. The original unoxidized asphalt showed almost no increase from structural hardening (3.8×10^2 to 4.2×10^2 Pa·s) upon standing for the same length of time. This strongly suggests that the oxidation which takes place during the natural aging of asphalts in pavements

significantly increases the rate of structural hardening and that oxidative and structural hardening may be synergistic.

A problem in the determination and quantification of structural hardening is that the structuring is destroyed during the solvent recovery of asphalts from aged pavements and therefore escapes detection during measurement of recovered asphalt properties. Thus, the tendency for an asphalt to harden from structuring, which may be a major contributor to loss of durability and pavement failure, is being virtually ignored in pavement performance considerations by present day pavement technologists. A. B. Brown (83, 84), who studied reversible molecular structuring (called by him "steric hardening") in 1957 approximately two decades after the studies of Traxler and coworkers, noted that ". . . this is not a new discovery, but has had relatively little emphasis." In the last two decades, not much has changed in this regard but the need is still there.

More recently, studies of molecular interactions of asphalts and of asphalt-aggregate interactions have been conducted at higher temperatures (above 130°C) by microcalorimetry (66, 86, 89). Reversible molecular interactions were shown to be present at temperatures as high as 250°C. Interactions at these high temperatures undoubtedly reflect the disassociation-association of the more stable micellar bodies in asphalt (87). Aggregate surfaces have been shown to promote molecular structuring and immobilization of asphalt molecules in the vicinity of the aggregate surface which should have considerable effect on bond properties and thus properties of pavement mixtures (66, 88, 89). A relationship between molecular structuring and the "setting" characteristics of pavements was proposed by Hveem and coworkers (90) and a cohesiograph test was proposed to measure the setting property. A good correlation was found between the tendency for asphalts to form "tender-mix" pavements and their lack of molecular structuring when in contact with the surface of a standard Ottawa sand aggregate (89). Thus, the phenomenon of molecular structuring is not only important to the bulk properties of asphalt, but it is also important to the asphalt-aggregate interaction. Both types of structuring will affect the performance and durability of asphalts in pavements. The common practice of evaluating asphalt performance in the absence of the aggregate with which it is to be used leaves unevaluated important criteria for pavement performance.

SUMMARY AND CONCLUDING COMMENTS

Chemical composition is important in determining the physical properties and performance characteristics of asphalts. The interactions of polar or polarizable chemical functionality, either naturally present or formed on oxidative aging, play a major role in determining asphalt viscosity and related complex flow properties.

Two major factors affecting asphalt durability are: 1) the compatibility of the interacting components of asphalt; and 2) the resistance to changes resulting from oxidative aging. Both factors are a function of chemical composition, which can vary widely from one asphalt source to another because of inherent differences in crude sources or from processing and blending.

Historically, the study of asphalt chemical composition has been facilitated by the separation of asphalt into component fractions based on the polarity and/or adsorption characteristics of the molecular components present. The component fractions, sometimes called generic fractions, although useful in classifying and characterizing asphalts and to provide simplified mixtures for further study, are still complex mixtures whose composition is a function of asphalt source. The component fractions are, however, sufficiently unique to identify their particular contribution to the complex flow properties of asphalt. A proper balance of component types is necessary for a durable asphalt.

Because asphalt occurs as a film exposed to atmospheric oxygen in pavements, it rapidly oxidizes in service with the formation of polar, strongly interacting, oxygen-containing chemical functional groups which greatly increase viscosity and alter complex flow properties. This hardening often leads to asphalt embrittlement and ultimately asphalt pavement failure. Not only does the susceptibility to oxidation vary from one asphalt to the other, but the effect of the oxidation products formed on physical properties also varies widely with asphalt source. The sensitivity of the asphalt to the chemical functionality produced on oxidation can be significantly reduced by removing or altering the polar chemical functionality initially present that would otherwise interact with the oxidation products to increase viscosity.

The identification and characterization of the chemical functional types normally present in asphalt or formed on oxidative aging which influence molecular interactions affords a fundamental approach to the chemical compositional factors that determine physical properties which in turn governs the performance properties of both asphalts and asphalt-aggregate mixtures.

Not only are asphalt physical properties significantly altered by the oxidative formation of polar chemical functional groups, but they are also significantly altered by reversible molecular structuring (also called steric hardening). This latter phenomenon is a slow process that appears to proceed concurrently and synergistically with oxidative aging during the lifetime of the pavement and may be a major factor contributing to asphalt pavement embrittlement in the later stages of pavement service life. Limited data indicate that the complex flow properties of asphalt and the tendency of asphalt to structure are directly related. This suggests possibilities for ways to evaluate this elusive property.

Because asphalt chemical composition can vary widely with asphalt source, and a variety of combinations of asphalt components with varying chemical structures in individual asphalts may produce asphalts that will provide satisfactory service, it seems unlikely to the author that satisfactory chemical composition specifications can be devised for asphalts. Such specifications would likely exclude from use many asphalts that would otherwise perform satisfactorily. Ideally, specifications should define the performance properties desired. Chemical information would be important in producing asphalts that meet the performance criteria.

Composition information is useful in helping us understand asphalt-- what makes it behave as it does and what makes one asphalt behave dif-

ferently from another. With given asphalt sources available, composition information can be used to improve the product through modification with additives, by blending, etc., or to alter use design procedures to accommodate specific properties. Composition information can be used to match asphalt and aggregate, provide clues as to what modifications are necessary to make an asphalt-aggregate system more serviceable under a given environment, diagnose failures, and provide information needed in taking corrective measures.

As asphalts from new sources are utilized, and as processing and design procedures change, the use of more fundamental information, both chemical and physical, and particularly as related to long-term performance and durability, should provide for product improvement and reduce the number of early or unexpected failures of asphalt products.

It is hoped that this review will bring about a better understanding of the chemical compositional factors that control the properties of asphalt and will assist in providing direction to both research and application leading to improved asphalt products with better performance and durability.

RESEARCH NEEDS

In the opinion of the author, future research effort on chemical factors that affect asphalt durability should include, as some of the most important, the following interrelated areas.

1. Development of techniques to measure the effects of molecular structuring and evaluate the effects of molecular structuring (in both neat asphalt and on the presence of aggregates) on the physical properties of pavements.
2. Determine the relationships between molecular structuring and complex flow properties.
3. Identify and characterize the chemical factors that cause and control molecular structuring, including the effects of oxidation.
4. Develop and validate methods that will predict changes in physical properties of asphalts in aged pavements since the properties of aged asphalts, not initial properties, determine the properties affecting durability.
5. Relate the complex flow properties of asphalt (especially at low temperatures) with changes in chemical functionality resulting from oxidative aging and quantify relationships between chemical functionality and changes in physical and performance-related properties.
6. Develop relationships between asphalt compatibility, composition, and changes in physical properties on oxidative aging.

7. Examine ways to improve asphalt component compatibility and durability by altering molecular interactions by such means as chemical modification, additives, component blending, etc. This area should be highly rewarding in upgrading the performance of otherwise less durable asphalts.

REFERENCES

1. F. N. Hveem. Quality Tests for Asphalts--A Progress Report. Proceedings, Association of Asphalt Paving Technologists, Vol. 15, 1943, pp. 111-152.
2. W. P. Van Oort. Durability of Asphalt. Industrial and Engineering Chemistry, Vol. 48, 1956, pp. 1196-1201.
3. P. C. Blokker and H. van Hoorn. Durability of Bitumen in Theory and Practice. Fifth World Petroleum Congress, Section VI, 1959, pp. 417-432.
4. F. N. Hveem, E. Zube, and J. Skog. Progress Report on the Zaca-Wigmore Experimental Asphalt Test Project. ASTM Special Technical Publication No. 277, 1959, pp. 1-45.
5. F. S. Rostler and R. M. White. Influence of Chemical Composition of Asphalts on Performance, Particularly Durability. American Society for Testing Materials, ASTM Special Technical Publication No. 277, 1959, pp. 64-88.
6. F. S. Rostler and R. M. White. Composition and Changes in Composition of Highway Asphalts, 85-100 Penetration Grade. Proceedings, Association of Asphalt Paving Technologists, Vol. 31, 1962, pp. 35-89.
7. S. H. Greenfeld and J. R. Wright. Four Methods for Predicting the Durability of Roofing Asphalts. Materials and Research Standards, Vol. 2, 1962, pp. 738-745.
8. C. D. Smith, C. C. Scheutz, and R. S. Hodgson. Relationship Between Chemical Structures and Weatherability of Coating Asphalts as Shown by Infrared Adsorption Spectroscopy. Industrial and Engineering Chemistry, Product Research and Development, Vol. 5, 1966, pp. 153-161.
9. T. C. Davis and J. C. Petersen. An Inverse GLC Study of Asphalts Used in the Zaca-Wigmore Experimental Test Road. Proceedings, Association of Asphalt Paving Technologists, Vol. 36, 1967, pp. 1-15.
10. L. W. Corbett. Composition of Asphalt Based on Generic Fractionation Using Solvent Deasphaltene, Elution-Adsorption Chromatography, and Densimetric Characterization. Analytical Chemistry, Vol. 41, 1969, pp. 576-579.
11. J. Knotnerus. Bitumen Durability--Measurement by Oxygen Adsorption. Industrial and Engineering Chemistry, Product Research and Development, Vol. 11, 1972, pp. 411-422.
12. R. L. Griffin, W. C. Simpson, and T. K. Miles. Influence of Composition of Paving Asphalts on Viscosity, Viscosity-Temperature Susceptibility, and Durability. Journal of Chemical and Engineering Data, Vol. 4, 1959, pp. 349-354.

13. R. J. Peters. Compositional Considerations of Asphalt for Durability Improvement. Transportation Research Board Record No. 544, 1975, pp. 46-55.
14. H. Plancher, E. L. Green, and J. C. Petersen. Reduction of Oxidative Hardening of Asphalts by Treatment with Hydrated Lime--A Mechanistic Study. Proceedings, Association of Asphalt Paving Technologists, Vol. 45, 1976, pp. 1-24.
15. J. Y. Welborn, F. R. Oglio, and J. A. Zenewitz. A Study of Viscosity-Graded Asphalt Cements. Proceedings, Association of Asphalt Paving Technologists, Vol. 35, 1966, pp. 19-60.
16. H. E. Schweyer and E. L. Chipley. Composition Studies on Asphalt Cements: A Progress Report. Highway Research Record No. 178, 1967, pp. 30-59.
17. L. W. Corbett. Densimetric Method for Characterizing Asphalt. Analytical Chemistry, Vol. 36, 1967, pp. 1967-1971.
18. J. W. Ramsey, F. R. McDonald, and J. C. Petersen. Structural Study of Asphalts by Nuclear Magnetic Resonance. Industrial and Engineering Chemistry, Product Research and Development, Vol. 6, 1967, pp. 231-236.
19. R. L. Hubbard and K. E. Stanfield. Determination of Asphaltenes, Oils, and Resins in Asphalt. Analytical Chemistry, Vol. 20, 1948, pp. 460-465.
20. G. O'Donnell. Separating Asphalts into Its Chemical Constituents. Analytical Chemistry, Vol. 23, 1951, pp. 11-20.
21. M. Bestougeff. Isomerism of Petroleum Constituents. Proceedings, Third World Petroleum Congress, Section VI, 1951, pp. 11-20.
22. A. J. Hoiberg and W. E. Garris, Jr. Analytical Fractionation of Asphalts. Analytical Edition, Industrial Engineering Chemistry, Vol. 16, 1944, pp. 294-302.
23. H. E. Schweyer and R. N. Traxler. Separating Asphalt Materials--Butanol-Acetone Method. Oil Gas Journal, Vol. 52, 1953, p. 133.
24. M. Bestougeff. Constitution des Composés Soutres Cycliques du Pétrole. Proceedings, Fifth World Petroleum Congress, Section V, 1959, pp. 143-164.
25. L. R. Kleinschmidt. Chromatographic Method for the Fractionation of Asphalt into Distinctive Groups of Components. Journal of Research, National Bureau of Standards, Vol. 54, 1955, pp. 163-166.
26. K. H. Altgelt and E. Hirsh. GPC Separation and Integrated Structural Analysis of Petroleum Heavy Ends. Separation Science, Vol. 5, 1970, pp. 855-862.

27. D. Bynum, Jr. and R. N. Traxler. Gel Permeation Chromatography Data on Asphalts Before and After Service in Pavements. Proceeding, Association of Asphalt Paving Technologists, Vol. 39, 1970, pp. 683-702.
28. H. Reerink and J. Lijzenga. Gel-Permeation Chromatography Calibration Curve for Asphaltenes and Bituminous Resins. Analytical Chemistry, Vol. 47, 1975, pp. 2160-2167.
29. C. Such and B. Brule. Characterization of a Road Asphalt by Chromatographic Techniques (GPC and HPLC). Journal of Liquid Chromatography, Vol. 2, 1979, pp. 437-453.
30. P. W. Jennings, J. A. S. Pribanic, K. R. Dawson and C. E. Bricca. Use of HPLC and NMR Spectroscopy to Characterize Asphaltic Materials. Preprints, American Chemical Society, Division of Petroleum Chemistry, Vol. 26, No. 4, 1981, pp. 915-922.
31. T. C. Davis and J. C. Petersen. Inverse Gas-Liquid Chromatographic Studies of Asphalt--Comparison with Analyses by Fractionation. Analytical Chemistry, Vol. 39, 1967, pp. 1852-1857.
32. F. S. Rostler and H. W. Sternberg. Compounding Rubber with Petroleum Products. Industrial and Engineering Chemistry, Vol. 41, 1949, pp. 598-608.
33. F. J. Nellenstyn. The Constitution of Asphalt. Journal of the Institute of Petroleum Technology, Vol. 10, 1924, pp. 311-325.
34. F. J. Nellenstyn. Relation of the Micelle to the Medium in Asphalt. Journal, Institute of Petroleum Technologists, Vol. 14, 1928, pp. 134-138.
35. C. J. Mack. Colloid Chemistry of Asphalts. Journal of Physical Chemistry, Vol. 36, 1932, pp. 2901-2914.
36. J. Ph. Pfeiffer and R. N. J. Saal. Asphaltic Bitumen as Colloid System. Journal of Physical Chemistry, Vol. 44, 1940, pp. 139-149.
37. R. N. J. Saal, P. W. Bass, and W. Heukelom. The Colloidal Structure of Asphaltic Bitumens. Journal, Chim. Phys., Vol. 43, 1946, pp. 235-261.
38. L. C. Corbett. Relationship Between Composition and Physical Properties of Asphalt. Proceeding, Association of Asphalt Paving Technologists, Vol. 39, 1970, pp. 481-491.
39. J. Manheimer. The Effects of Paraffins on Asphalt. Proceedings, First World Petroleum Congress, Vol. 2, 1933, pp. 553-556.
40. G. L. Oliensis. Compatibility Between Bitumens--Exudation Versus Insudation. ASTM Materials Research Standards, Vol. 1, 1961, pp. 723-727.

41. W. C. Simpson, R. L. Griffin, and T. K. Miles. Relationships of Asphalt Properties to Chemical Composition. American Chemical Society, Division of Petroleum Chemistry, Vol. 5, No. 4, 1960, pp. A79-A87.
42. J. J. Heithaus. Measurement of Significance of Asphaltene Peptization. Preprints, Division of Petroleum Chemistry, American Chemical Society, Vol. 5, No. 4, 1960, pp. A23-A37.
43. R. M. White, W. R. Mitten, and J. B. Skog. Fractional Components of Asphalt--Compatibility and Interchangeability of Fractions Produced from Different Asphalts. Proceedings, Association of Asphalt Paving Technologists, Vol. 39, 1970, pp. 498-531.
44. W. J. Halstead, F. S. Rostler, and R. M. White. Properties of Highway Asphalts--Part III, Influence of Chemical Composition. Proceedings, Association of Asphalt Paving Technologists, Vol. 35, 1966, pp. 91-138.
45. J. A. Zenewitz and J. Y. Welborn. Predicting Asphalt Performance. Report No. FHWA-RD-76-133, 1975.
46. G. R. Kemp. Asphalt Durability Tests and Their Relationships to Field Hardening. ASTM Special Technical Publication No. 532, 1973, pp. 100-122.
47. R. N. Traxler. Relation Between Hardening and Composition of Asphalt. Preprints, American Chemical Society, Division of Petroleum Chemistry, Vol. 5, No. 4, 1960, pp. A-71 to A-77.
48. J. F. Goode and E. P. Owings. A Laboratory-Field Study of Hot Asphalt Concrete Wearing Course Mixtures. Public Roads, Vol. 31, 1961, pp. 221-228.
49. B. A. Vallegra, R. M. White, and K. S. Rostler. Changes in Fundamental Properties of Asphalts During Service in Pavements. Final Report, Contract No. FH-11-6149 for Office of Research and Development, U.S. Bureau of Public Roads, January 1970.
50. L. W. Corbett and R. E. Merz. Asphalt Binder Hardening in the Michigan Test Road after 18 Years of Service. Transportation Research Board Record No. 544, 1975, pp. 27-34.
51. W. H. King and L. W. Corbett. Relative Oxygen Absorption and Volatility Properties of Submicron Films of Asphalt Using the Quartz Crystal Microbalance. Analytical Chemistry, Vol. 41, 1969, pp. 580-583.
52. J. C. Petersen, F. A. Barbour, and S. M. Dorrence. Catalysis of Asphalt Oxidation by Mineral Aggregate Surfaces and Asphalt Components. Proceedings, Association of Asphalt Paving Technologists, Vol. 43, 1974, pp. 162-177.

53. S. M. Dorrence, F. A. Barbour, and J. C. Petersen. Direct Evidence of Ketones in Oxidized Asphalts. *Analytical Chemistry*, Vol. 46, 1974, pp. 2242-2244.
54. J. C. Petersen, F. A. Barbour, and S. M. Dorrence. Identification of Dicarboxylic Anhydrides in Oxidized Asphalts. *Analytical Chemistry*, Vol. 47, 1975, pp. 107-111.
55. J. C. Petersen. Quantitative Method Using Differential Infrared Spectrometry for the Determination of Compound Types Absorbing in the Carbonyl Region in Asphalts. *Analytical Chemistry*, Vol. 47, 1975, pp. 112-117.
56. J. C. Petersen and H. Plancher. Quantitative Determination of Carboxylic Acids and Their Salts and Anhydrides in Asphalts by Selective Chemical Reactions and Differential Infrared Spectrometry. *Analytical Chemistry*, Vol. 53, 1981, pp. 786-789.
57. J. C. Petersen. Oxidation of Sulfur Compounds in Petroleum Residues: Reactivity-Structural Relationships. Preprints, Division of Petroleum Chemistry, Inc., American Chemical Society, Vol. 26, No. 4, 1981, pp. 898-906.
58. J. C. Petersen, H. Plancher, and G. Miyake. Chemical Reactivity and Flow Properties of Asphalts Modified by Metal Complex-Induced Reaction with Atmospheric Oxygen. *Proceedings, Association of Asphalt Paving Technologists*, Vol. 52, 1983, in press.
59. T. C. Davis and J. C. Petersen. An Adaptation of Inverse Gas-Liquid Chromatography to Asphalt Oxidation Studies. *Analytical Chemistry*, Vol. 38, 1966, pp. 1938-1940.
60. J. C. Petersen. Relationships Between Asphalt Chemical Composition and Performance Related Properties. *Proceedings, Ninth Annual Meeting of the Asphalt Emulsion Manufacturers Association, Las Vegas, Nevada, March 1982, and meeting of the International Slurry Seal Association, Phoenix, Arizona, January 1983.*
61. M. M. Boduszynski, J. F. McKay, and D. R. Latham. Asphaltenes, Where Are You? *Proceedings, Association of Asphalt Paving Technologists*, Vol. 49, 1980, pp. 123-143.
62. J. C. Petersen. An Infrared Study of Hydrogen Bonding in Asphalt. *Fuel*, Vol. 46, 1967, pp. 295-305.
63. T. C. Davis, J. C. Petersen, and W. E. Haines. Inverse Gas-Liquid Chromatography. A New Approach for Studying Petroleum Asphalts. *Analytical Chemistry*, Vol. 38, 1966, pp. 241-243.
64. J. C. Petersen, R. V. Barbour, S. M. Dorrence, F. A. Barbour, and R. V. Helm. Molecular Interactions of Asphalt: Tentative Identification of 2-Quinolones in Asphalt and Their Interaction with Carboxylic Acids Present. *Analytical Chemistry*, Vol. 43, 1971, pp. 1491-1496.

65. J. C. Petersen, E. K. Ensley, and F. A. Barbour. Molecular Interactions of Asphalt in the Asphalt-Aggregate Interface Region, Transportation Research Board Record No. 515, 1974, pp. 68-78.
66. E. K. Ensley. A Study of Asphalt-Aggregate Interactions and Asphalt Molecular Interactions by Microcalorimetric Methods: Postulated Interaction Mechanism. Journal of the Institute of Petroleum, Vol. 59, 1973, pp. 279-289.
67. R. V. Barbour and J. C. Petersen. Molecular Interactions of Asphalt: An Infrared Study of the Hydrogen-Bonding Basicity of Asphalt. Analytical Chemistry, Vol. 46, 1974, pp. 273-277.
68. J. C. Petersen, E. K. Ensley, H. Plancher, and W. E. Haines. Paving Asphalts: Asphalt-Aggregate Interactions and Asphalt Intermolecular Interactions. FHWA Report No. FHWA-RD-77-25, August 1976, available from the National Technical Information Service, Springfield, Va. 22161.
69. J. C. Petersen, H. Plancher, E. K. Ensley, and G. Miyake. Chemistry of the Asphalt-Aggregate Interaction: Relationship with Pavement Moisture Damage Prediction Tests. Transportation Research Board Record, No. 483, 1982, pp. 95-104.
70. Plancher, H., Chee-kin Chow, and J. C. Petersen. Viscoelastic Measurements and Their Relationship to Bitumen Properties. Proceedings International Symposium on Prograssi Nella Tecnologia Dei Bitumi, San Donato Milanese, Italy, pp. 248-262. Available from Stazione Sperimentale per i Combustibili, Viale A. de Gasperi 3, 20097, San Donato Milanese, Italy.
71. A. J. Hoiberg. Asphalt-Solvent Blends. Industrial and Engineering Chemistry, Vol. 43, 1951, pp. 1419-1423.
72. D. A. Anderson, E. L. Dukatz and J. C. Petersen. The Effect of Antistripping Additives on the Properties of Asphalt Cements. Proceedings, Association of Asphalt Paving Technologists, Vol. 51, 1982, pp. 298-317.
73. J. N. Dybalski, private communication.
74. Highway Chemicals Newsletter, Armak Highway Chemicals Department, Armak Company, Fall 1979.
75. N. P. Khosla. Effect of Emulsified Modifiers on the Characteristics of Recycled Mixtures. Proceedings, Association of Asphalt Paving Technologists, Vol. 51, 1982, pp. 522-539.
76. E. W. Mertens. Predicting Weatherability of Coating-Grade Asphalts from Asphaltene Characteristics. ASTM Bulletin, No. 250, 1960, pp. 40-44.
77. K. H. Altgelt and O. L. Harle. The Effect of Asphaltenes on Asphalt Viscosity. Industrial and Engineering Chemistry Product Research and Development, Vol. 14, 1975, pp. 240-256.

78. H. Plancher, A. J. Hoiberg, S. C. Suhaka, and J. C. Petersen. A Settling Test to Evaluate the Relative Degree of Dispersion of Asphaltenes. Proceedings, Association of Asphalt Paving Technologists, Vol. 48, 1979, pp. 351-374.
79. R. N. Traxler and H. W. Schweyer. Increase in Viscosity of Asphalts with Time. Proceedings, American Society of Testing Materials, Vol 36 (II), 1936, pp. 544-551.
80. R. N. Traxler and C. E. Coombs. The Colloidal Nature of Asphalt as Shown by Its Flow Properties. Journal of Physical Chemistry, Vol. 40, 1936, pp. 1133-1147.
81. R. N. Traxler and C. E. Coombs. Development of Internal Structure in Asphalts with Time. Proceedings, American Society of Testing Materials. Vol. 37 (II), 1937, pp. 549-557.
82. R. N. Traxler and H. E. Schweyer, and J. W. Romberg. Rheological Properties of Asphalts. Industrial and Engineering Chemistry, Vol. 36, 1944, pp. 823-829.
83. A. B. Brown, J. W. Sparks, and F. M. Smith. Steric Hardening of Asphalts. Proceedings, Association of Asphalt Paving Technologists, Vol. 26, 1957, pp. 486-494.
84. A. B. Brown and J. W. Sparks. Viscoelastic Properties of a Penetration Grade Asphalt at Winter Temperature. Proceedings, Association of Asphalt Paving Technologists, Vol. 27, 1958, pp. 35-51.
85. C. E. Coombs and R. N. Traxler. Rheological Properties of Asphalts IV. Observations Concerning the Anomalous Flow Characteristics of Airblown Asphalts. Journal of Applied Physics, Vol 8, 1937, pp. 291-296.
86. E. K. Ensley and H. A. Schulz. A Study of Asphalt-Aggregate Interactions by Heats of Immersion. Journal, Institute of Petroleum, Vol. 58, 1972, pp. 95-101.
87. E. K. Ensley. A Kinetic Investigation of Association in Asphalt. Journal of Colloid and Interface Science, Vol. 53, 1975, pp. 452-460.
88. E. K. Ensley. Multilayer Adsorption with Molecular Orientation of Asphalt on Mineral Aggregate and Other Substrates. Journal of Applied Chemistry and Biotechnology, Vol. 25, 1975, pp. 671-682.
89. R. E. Robertson, E. K. Ensley, and J. C. Petersen. Physiochemical Studies of Tender Mix and Nontender Mix Asphalts. Federal Highway Administration Report. No. FHWA/RD-80/130, December 1980. Available from National Technical Information Service, Springfield, Virginia 22161.
90. F. N. Hveem, E. Zube and J. Skog. Proposed New Tests and Specifications for Paving Crude Asphalts. Proceedings, Association of Asphalt Paving Technologists, Vol. 32, 1963, pp. 271-327.

FEDERALLY COORDINATED PROGRAM (FCP) OF HIGHWAY RESEARCH AND DEVELOPMENT

The Offices of Research and Development (R&D) of the Federal Highway Administration (FHWA) are responsible for a broad program of staff and contract research and development and a Federal-aid program, conducted by or through the State highway transportation agencies, that includes the Highway Planning and Research (HP&R) program and the National Cooperative Highway Research Program (NCHRP) managed by the Transportation Research Board. The FCP is a carefully selected group of projects that uses research and development resources to obtain timely solutions to urgent national highway engineering problems.*

The diagonal double stripe on the cover of this report represents a highway and is color-coded to identify the FCP category that the report falls under. A red stripe is used for category 1, dark blue for category 2, light blue for category 3, brown for category 4, gray for category 5, green for categories 6 and 7, and an orange stripe identifies category 0.

FCP Category Descriptions

1. Improved Highway Design and Operation for Safety

Safety R&D addresses problems associated with the responsibilities of the FHWA under the Highway Safety Act and includes investigation of appropriate design standards, roadside hardware, signing, and physical and scientific data for the formulation of improved safety regulations.

2. Reduction of Traffic Congestion, and Improved Operational Efficiency

Traffic R&D is concerned with increasing the operational efficiency of existing highways by advancing technology, by improving designs for existing as well as new facilities, and by balancing the demand-capacity relationship through traffic management techniques such as bus and carpool preferential treatment, motorist information, and rerouting of traffic.

3. Environmental Considerations in Highway Design, Location, Construction, and Operation

Environmental R&D is directed toward identifying and evaluating highway elements that affect

the quality of the human environment. The goals are reduction of adverse highway and traffic impacts, and protection and enhancement of the environment.

4. Improved Materials Utilization and Durability

Materials R&D is concerned with expanding the knowledge and technology of materials properties, using available natural materials, improving structural foundation materials, recycling highway materials, converting industrial wastes into useful highway products, developing extender or substitute materials for those in short supply, and developing more rapid and reliable testing procedures. The goals are lower highway construction costs and extended maintenance-free operation.

5. Improved Design to Reduce Costs, Extend Life Expectancy, and Insure Structural Safety

Structural R&D is concerned with furthering the latest technological advances in structural and hydraulic designs, fabrication processes, and construction techniques to provide safe, efficient highways at reasonable costs.

6. Improved Technology for Highway Construction

This category is concerned with the research, development, and implementation of highway construction technology to increase productivity, reduce energy consumption, conserve dwindling resources, and reduce costs while improving the quality and methods of construction.

7. Improved Technology for Highway Maintenance

This category addresses problems in preserving the Nation's highways and includes activities in physical maintenance, traffic services, management, and equipment. The goal is to maximize operational efficiency and safety to the traveling public while conserving resources.

0. Other New Studies

This category, not included in the seven-volume official statement of the FCP, is concerned with HP&R and NCHRP studies not specifically related to FCP projects. These studies involve R&D support of other FHWA program office research.

* The complete seven-volume official statement of the FCP is available from the National Technical Information Service, Springfield, Va. 22161. Single copies of the introductory volume are available without charge from Program Analysis (HRD-3), Offices of Research and Development, Federal Highway Administration, Washington, D.C. 20590.

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