SHRP ASPHALT RESEARCH PROGRAM TECHNICAL MEMORANDUM #4

AN ASPHALT PRIMER:

Understanding How the Origin and Composition of Paving-Grade Asphalt Cements Affect Their Performance

David R. Jones, IV, Ph.D.
Strategic Highway Research Program
The University of Texas
Austin, Texas

THE ORIGINS OF ASPHALT

Naturally occurring seeps of asphalt have been known to man since prehistoric times. Deposits of petroleum, brought to the surface by water or geological forces, evaporated, leaving sticky asphalt quagmires such as the famous La Brea Tar Pits in what is now Los Angeles, California.

One can only wonder what early humans thought as they gazed upon these seeps and pondered the animals trapped in the sticky ooze. Evidence of prehistoric hunting activity has been found around these pits, indicating that the early hunter-gatherers were quite willing to take advantage of asphalt's unique adhesive properties.

Interestingly, there are biblical references to the use of asphalt in the book of Genesis. Both Noah's Ark and the Tower of Babel are said to have used asphalt as cement and waterproofing agents.

Archaeologists have documented the use of asphalt as an adhesive and waterproofing material in the Euphrates Valley four thousand years before the birth of Christ. Asphalt was found in seeps and springs in the present-day oil fields of Iraq, Saudi Arabia, and Kuwait, and was first used as a paving material by the Babylonians, who used asphalt-impregnated blocks as paving stones in the royal

roads and palaces. Babylonian King Nebuchadnezzar constructed the city of Babylon with "roads glistening with asphalt," according to an ancient inscription found within the city. This use of asphalt by the Babylonians is mentioned in the Old Testament book of Daniel.

The Egyptians were quite aware of the unique properties of asphalts, and early Greek historians chronicling the Egyptian practices referred many times to asphalts mined from the area surrounding the Dead Sea. The ancient Egyptian process for embalming used asphalt as a preservative. Historical descriptions of this process used the Arabic word for asphalt, *mûmîa,* which has evolved into our modern term *m u m m y*.

The Greeks and Romans spoke of the uses of asphalt in their descriptions of the arts and sciences of the time. Early explorers such as Marco Polo and Christopher Columbus documented the uses of local asphalt deposits during their travels, and writers such as Shakespeare and Milton have also mentioned asphalt in their works. Despite this long and varied record of asphalt's uses throughout history, its wide spread use as an ingredient in paving materials didn't really begin until modern petroleum-refining techniques were developed in the early twentieth century.

MODERN USES OF ASPHALT

Although the first "modern" paving jobs were carried out in the late 1800s in France and England, these early efforts were limited to the use of naturally occurring asphalt deposits mentioned earlier. It wasn't until 1902 that sufficient quantities of asphalt were available from petroleum refining in the United States to allow an asphalt-based paving industry to develop. Early production data show the rapid growth in availability of asphalt as the United States developed its refineries:

YEAR	ASPHALT USAGE (TONS)
1902	20,000
1926	3,000,000
1950	11,000,000
1990	30,000,000

Because of asphalt's long history it should come as no surprise that it is used today in hundreds of products, many of which are not connected to traditional construction and transportation industries. But even though asphaltic materials

have many unique and interesting applications, asphalt still remains a critically important paving material in roadways throughout the world.

As the figures above demonstrate, large amounts of asphalt are currently being used. Today approximately 75 oil companies in the United States and Canada produce and market asphalt refined from petroleum crude oil. Of those, only a handful produce asphalt intentionally as their principal product. When trying to understand uses of asphalt, it is well to remember that the product we pave our roads with is not actually produced for that purpose. It is literally the "bottom of the barrel," and refiners exert very few controls in its production because gasoline, jet fuel, and fuel oil are more profitable, and drive the refinery business. Only after all these fuels are extracted from the crude oil is the remaining residue turned into asphalt.

In the past it has been difficult to learn about the crude sources from which asphalts are produced. If highway and street departments were to specify the crude sources from which asphalt was to be produced, the "tail would be wagging the dog," because that would require the least profitable material to drive the refinery process.

In addition, modern integrated refineries now can switch crude feedstock blends in a few days, enabling them to respond quickly to changes in the marketplace. Historically, refinery "turnarounds" (changing crude-oil feedstocks) were very involved operations. Prior to the 1973 Arab oil embargo, refiners tried to change their crude-oil feedstock as little as possible. This practice led to asphalts that were consistent over long periods of time, and may partly explain the widely held perception that asphalts were "better before the embargo." It is reasonable to say that there was probably less chemical variation within an asphalt from a given refinery prior to the embargo, but today's refinery practices have changed all that.

As a result of both the oil embargo and the natural depletion of existing crude-oil fields, and aided by the spurt of exploration driven by the high oil prices of the late 1970s and early 1980s, a number of new crude-oil fields have achieved notable impact as sources of asphalt. Oil from the Alaska North Slope (ANS) and Maya crude from Mexico are different chemically than oil from older fields, and they yield a different asphalt. For instance, refiners have learned that while Maya crude is very heavy, the asphalt it produces is not suitable for paving uses due to a high aging index. Mayan crudes are therefore blended with other crude sources prior to refining to produce an acceptable paving asphalt. The refiners have learned by trial and error which blends can be used to utilize Mayan crude, but they cannot explain why it has a high aging index.

The dynamics of the petroleum crude-oil market assures us that a wide variation in the crude oils used to produce asphalt will continue, and that an understanding of their fundamental (chemical) behavior will be necessary to enable refiners and users to predict the performance properties of asphalt.

ASPHALT CHEMISTRY

This primer has been prepared to explain the basic chemistry and composition of asphalt cements for the nonchemist. Common terms used by chemists when describing asphalt will be defined and explained. This section does not seek to be exhaustive, and interested readers seeking further information should consult a college-level organic chemistry text, several of which are listed in the references.

The smallest distinct form of matter is an atom. An atom consists of a nucleus, containing protons and neutrons, that is surrounded by a "cloud" of electrons. The number of protons (positive charge) and electrons (negative charge) is equal, but the electrons can interact with other atoms to form molecules. There are several ways that the atoms can interact with each other and form "bonds," so chemists have given names to the different types of bonding. When the atoms actually share electrons we call them covalent bonds. These are very strong and require a lot of energy to be broken.The number of electrons that can be shared is unique to each type of atom. Since atoms of carbon can share up to four electrons, many different types of molecules can be formed, and long chains or rings of atoms are possible. For a single covalent bond, each atom contributes a single electron. In chemistry shorthand a single bond between hydrogen (H) and carbon (C) atoms is shown as: **C-H**. In some particular cases each atom can contribute two electrons, forming a covalent double bond, which is illustrated for carbon (C) and oxygen (O) as: **C=O.**

Chemists often refer to asphalt as a **hydrocarbon,** which simply means that it is composed primarily of atoms of carbon and hydrogen. In fact, asphalts used for paving contain between 90 and 95 weight percent hydrogen and carbon atoms. The remaining 5 to 10 percent of the atoms in the asphalt consist of two types:

<div align="center">

heteroatoms
metals

</div>

The **heteroatoms** are nitrogen, oxygen, and sulfur. Their chemical symbols are N, 0, and S, respectively. These atoms are called heteroatoms ("hetero" meaning different) because they can replace carbon atoms in the asphalt molecular structure. However, their chemistry is very different from carbon, and because heteroatoms are responsible for most of the **hydrogen bonding** mentioned below, they contribute to many of asphalt's unique chemical and physical properties by forming associations between molecules This bonding occurs because the presence of heteroatoms in a molecule can make the molecule **polar** and thus more likely to react with other molecules. Both the kind and amount of heteroatoms present in a given asphalt are a function of both the crude oil(s) from which the asphalt was produced and the state of aging of the asphalt.

The heteroatoms, especially sulfur, also play an important role in the aging of asphalt because they are more chemically reactive than hydrogen or carbon, and they can **oxidize,** or incorporate oxygen, more easily than the hydrocarbons. The reader is cautioned to note that the terms **aging** and **oxidation** do not mean the same thing. Aging is the overall process that occurs when asphalt is exposed to the environment. It can include loss of volatiles (low boiling point materials remaining in the asphalt after refining) through evaporation or other degradation, attack by water and light, as well as the process of oxidation. As mentioned previously, oxidation is the incorporation of oxygen into the molecular structure of the asphalt. When asphalts oxidize two main products are formed:

Sulfur atoms (S) are oxidized to sulfoxide (S=O)
Carbon (C) is oxidized to carbonyl (C=O)

The last group of atoms that asphalt contains, in addition to hydrocarbons and heteroatoms, are the **metals.** These are atoms such as vanadium, nickel, and iron (V, Ni, Fe) that are present in very small quantities in the asphalt, usually less than 1 percent. They, too, may play an important role in the aging process, and they also serve as a "fingerprint" for the asphalt because the amount of metals present in the asphalt is usually indicative of the crude source from which the asphalt was refined.

The hydrocarbons, heteroatoms, and metals are all combined in the asphalt in a wide range of different molecules. When describing these molecules we can group them in three broad groups:

aliphatics
cyclics
aromatics

Examples of these three types of molecules are shown in Figure 1. There are millions of different aliphatic, aromatic, and cyclic molecules in a given asphalt, and their sizes vary as well, ranging from those containing about 20 carbon atoms up to near 100. For ease of comparison each type of molecule in Figure 1 is shown consisting of 6 carbon atoms. These molecules are named hexane, cyclohexane, and benzene. Both larger and smaller molecules of all three types are possible, but in asphalt most molecules will be larger than the ones shown here. There is really no upper limit to the number of carbon or heteroatoms that can link together in these three types of structures, and many larger molecules are combinations of the types. For instance, Figure 2 contains a molecule that has both aliphatic and aromatic parts.
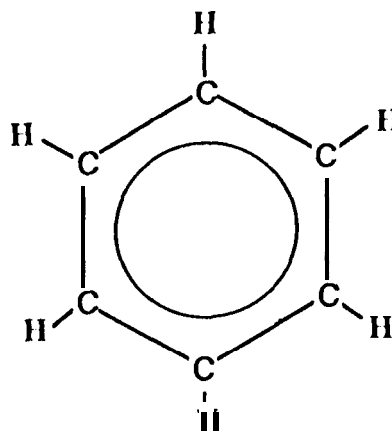
The term **aliphatic** (literally, "oily") can best be described as a linear or chain-like molecule in which the carbon atoms are linked end to end. As an example, the aliphatic molecule hexane contains six carbon atoms and fourteen hydrogen atoms (Figure 1).
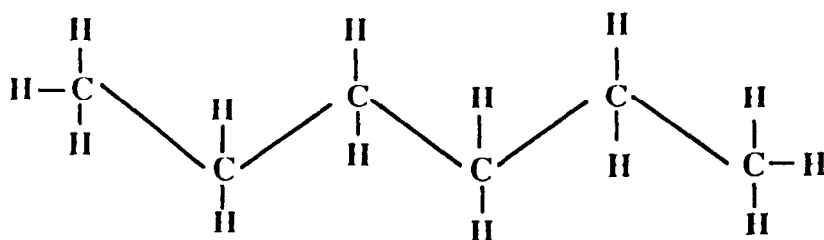
Aliphatic
(Hexane, C_6H_{14})
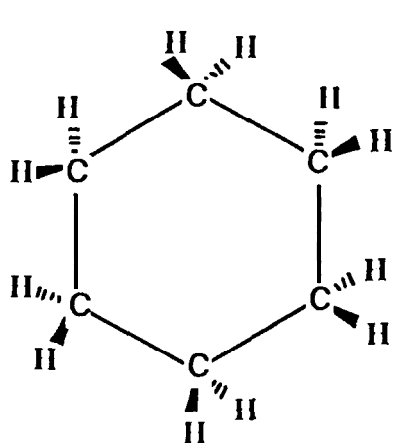
Cyclic
(Cyclohexane, C_6H_{12})

Aromatic
(Benzene, C_6H_6)

Figure 1
Types of Molecules in Asphalt

The **cyclic** molecule cyclohexane contains the same six carbons, but gives up two hydrogen atoms to form a cycle, or ring. As shown in Table 1, the loss of two hydrogen atoms has had a very large effect on the chemical properties of the molecule. This is due to both the change in shape of the molecule, as well as the interaction of the individual atoms in the molecule with each other.

The last class of molecules is the **aromatics** (so named for their strong odor). They are illustrated in Figure 1 by the six-carbon molecule benzene. This molecule has only six hydrogen atoms in its structure, and the electrons used to bond to hydrogen in hexane and cyclohexane have formed a "ring" of aromaticity, or shared electrons,

shown in our chemistry shorthand by the circle inside the structure. The unique property that aromatics bring to asphalt is their flat shape. Cyclics and aliphatic molecules are three-dimensional and form shapes that keep the molecules apart. On the other hand, aromatics are flat and can closely stack on top of one another. Comparison of the boiling and freezing points of these three very similar molecules will help demonstrate the large property changes brought about by minor chemical changes:

Molecule	Boiling Point,°C	Freezing Point,°C
Hexane	69°	-95°
Cyclohexane	81°	6°
Benzene	80°	5°

Table 1
Effect of Structure on Physical Properties

As stated above, atoms combine to form molecules, through the formation of strong covalent bonds. These molecules can then interact with one another through the formation of other, much weaker types of bonding. These types of interactions are important to chemists and asphalt technologists because they are responsible for determining many of asphalt's physical properties. Three types of "weak" bonds will be discussed here. All three require relatively little energy to break, being susceptible to both heat and mechanical forces. They are usually drawn as dotted lines to emphasize their weak, transitory nature, as opposed to the solid lines that are used to portray the much stronger covalent bonds. The three types of weak bonds are:

pi-pi bonding
hydrogen (or polar) bonding
Van der Waals forces

Pi-pi and hydrogen bonding are illustrated in Figure 2. The aromatic molecules form stacks of molecules due to their flat shape, and the electrons in the aromatic rings interact with one another to form **pi-pi bonds.** This pi-pi interaction is unique to aromatic molecules and leads to some interesting chemical properties. Graphite is commercially important because its aromatic rings form flat sheets of molecules that can easily slide around on top of one another, giving it the slippery properties that make it such an excellent dry lubricant.

Pi-Pi Bonding

Sulfoxide

Carboxylic Acid

$CH_2CH_2CH_2S\text{-}CH_2CH_2\text{-}CH_3$

Polar-Polar or Hydrogen Bonding
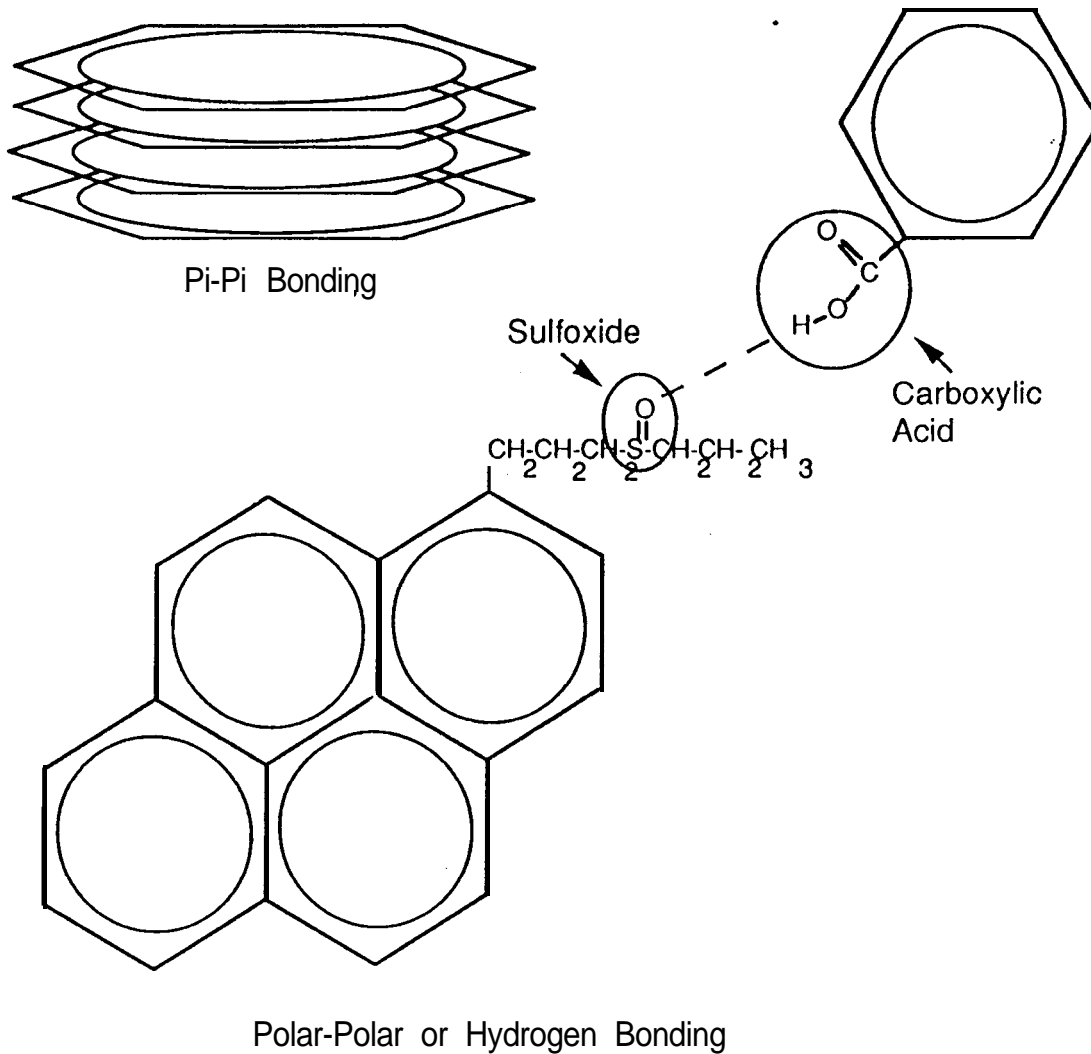
Figure 2
Types of Bonding in Asphalt

The molecules containing heteroatoms are generally **polar** (have unevenly distributed electrical charges) and play an important role in affecting asphalt's physical properties by interacting with other molecules through the formation of **hydrogen bonds.** This occurs when a heteroatom on one molecule interacts with a hydrogen atom next to a heteroatom on a different molecule. This is illustrated in Figure 2. In this illustration the carboxylic acid group is interacting with the sulfoxide group on the molecule below it. This interaction is shown as a dotted line to signify that the bond is relatively weak when compared with the covalent bonds holding the atoms of the two molecules together. In general, two heteroatoms are

required for the formation of hydrogen bonds. Research to date indicates that the heteroatoms play a crucial role in determining the physical properties of asphalt cements Thus, hydrogen bonding is probably the most important of the forms of weak molecular interactions.

Van der Waals forces are the last form of weak interactions between molecules that are important in asphalt chemistry. In this type of very weak bonding, long chains of aliphatic hydrocarbons (such as hexane in Figure 1, but with more carbon atoms) intertwine and are weakly held together. This type of bonding is dependent on the amount and type of aliphatic molecules in a given asphalt, just as pi-pi bonding will depend on the amount and type of aromatic molecules, and hydrogen bonding depends on the number of heteroatoms.

As mentioned above, all of these types of bonds are weak and are easily broken by heat or stress. They will form again when the molecules cool or the stress is removed. This property of formation and breaking of weak bonds between the asphalt molecules is the key to understanding the physical properties of asphalt. It explains why asphalt is a free-flowing liquid at temperatures above about 250° F, where virtually all the molecules exist as individual entities. It is also important to remember that the bonds between atoms that form the molecules such as those shown in Figure 1 are called **covalent bonds** and are not broken or reformed during the processes which normally take place in asphalt. The covalent bonds between atoms are 10 to 100 times stronger than the weak bonds between molecules.

All of the hydrocarbons, heteroatoms, and metals are combined into the millions of different molecules that make up asphalt. Each asphalt has a unique assortment of these molecules, and the molecules change as the asphalt ages. The heteroatoms are incorporated into the aliphatic, cyclic, and aromatic hydrocarbon molecules; they affect the chemical behavior of the individual molecules, as well as the associations which the molecules form.

As a result of the intensive chemical investigations carried out by the SHRP researchers, we have now achieved a much better picture of asphalt's chemical makeup. In simple terms we can now chemically characterize asphalt as follows:

1. Asphalt consists of two (and only two) *functional* families of molecules:

   Polar
   Non-polar

2. Polar molecules differ according to:

> Strength and number of polar group(s)
> Molecular weight
> Degree of aromaticity

3. Non-polar molecules differ according to:

> Molecular weight
> Degree of aromaticity

4. The "compatibility" of the polar and non-polar fractions, or the degree to which they can dissolve in each other, is controlled by the relative aromaticity (a measure of the amount of aromatic versus aliphatic and cyclic molecules) of the two fractions.

1. Polar vs. Non-polar Molecules. All of the molecules in asphalt behave in one of two ways. If they are polar at service temperatures they participate in the formation of a "network" through hydrogen and pi-pi bonding that gives the asphalt its elastic properties. The non-polar materials form the body of the material in which the network is formed and contribute to the viscous properties of the asphalt. If we consider the asphalt similar to spaghetti, the nonpolar materials serve as the sauce, while the polar molecules act as the pasta. The polar molecules interact to form the strands of spaghetti, which are surrounded and float in the nonpolar sauce. In asphalt, as in cooking, one wants the correct balance between the amount of sauce and amount of spaghetti.

Of course, there are a wide range of polarities in asphalt molecules, from very polar to completely non-polar. We draw the line between the two groups based on an analytical method of separating the molecules that will be discussed in a later section of this paper. Weakly polar molecules will actually be considered non-polar for the purpose of understanding their contribution to asphalt performance.

2. Polar molecules participate in the formation of the network of associated molecules and comprise a wide range of molecular types and sizes. They contribute to the performance of the asphalt through the network. Polar molecules that don't form part of the network are considered non-polar materials in this model.

The most important attribute of the polar molecules is the relative strength and number of polar sites per molecule because this directly affects network formation. The importance of these molecules to asphalt's performance will be discussed in more detail later. The amounts of polar materials present in asphalt are determined

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in practice by an analytical technique called "nonaqueous-acid-base titration." In this method the material is dissolved in a solvent other than water ("non-aqueous") and the amount of acids and/or bases present are determined by titration of either whole asphalts or selected fractions. To determine the amount of acid in a sample by titration, small amounts of base are added and allowed to react with the acids in the sample. Excess base in the solution signals when all the acids have reacted. The amount of base added is then proportional to the acids originally present in the sample. The process is simply reversed to determine the amount of bases present.

A second important parameter affecting the polar molecules is their degree of aromaticity, as shown in Figure 1. This can be determined by another measurement technique called nuclear magnetic resonance (NMR) analysis. In an NMR analysis the sample is subjected to an intense magnetic field and the response of the material is measured. Because of their pi-pi bonds, aromatic molecules have a very distinct "signature" in NMR analyses. As discussed before, the molecules that are not *aromatic are aliphatic or cyclic.* This distinction allows us to characterize the polars as containing some percentage of aromaticity, the balance being aliphatic and cyclic.

The molecular weight of the polar molecules is probably not as important a parameter in controlling the performance of asphalt as the other two factors of strength of polarity and aromaticity. It will play a minor role in the performance of the asphalt cement, as discussed below.

3.   Non-polar Molecules. An important feature of the non-polar molecules is their molecular weight because this directly affects the low-temperature cracking properties of the asphalt.   A preponderance of high molecular weight non-polar molecules will lead to asphalts that stiffen and perform poorly at low service temperatures due to brittleness.

The relative amount of aromatic character of the non-polar materials is also important. If the non-polars are waxy (a type of aliphatic molecule) in nature, they may precipitate or crystallize at low temperatures, contributing to poor performance. If the non-polars are cyclic or aromatic in nature, then they may resist the effects of low temperature better. There may well be an interaction with the molecular weight of the polar molecules as well, but evidence to date indicates the major effect is due to the molecular weight of the non-polars.

4.   Compatibility. The non-polar molecules are also important to asphalt's performance because they are the substance in which the polar molecules must interact. As such they combine with the polar network, and their compatibility with the polar molecules must be considered. If the molecules are similar in chemistry they will mix easily and be compatible. On the other hand, if they are quite different they will be incompatible, and the molecules may not want to stay in solution. The determination of aromaticity mentioned previously in item 2 will be important

here also because the compatibility of the two types of molecules will have an effect on the performance of the asphalt. A compatible asphalt will have both polar and non-polar molecules that are similar.

THE ASPHALT MODEL-HISTORICAL PERSPECTIVE

A major foundation of the SHRP Asphalt Research Program has been the use of an asphalt model as the basis for the experimental plan. As a starting point for experimental designs, researchers used the **micellar** model to describe the structure of asphalt. At the time the SHRP program began, the micellar model was accepted as providing the best available explanation of how asphalts were structured. In this model the aromatic **asphaltenes** existed as a discrete phase in the asphalt and were surrounded (and solubilized by) the **resins**. The asphaltenes were made up of highly aromatic groups of molecules that were quite large and insoluble in the remainder of the asphalt. The resins acted as intermediates in the asphalt, serving to homogenize and compatiblize the otherwise insoluble asphaltenes. The resins and asphaltenes existed as "islands" floating in the final asphalt component the **oils.**

The original micellar model had been constructed from interpretations of historical data in which researchers looked for relationships between chemical parameters and pavement performance. Other surrogate measurements, such as penetration and viscosity, and mathematical variations of these constants, such as penetration index (PI), penetration-viscosity number (PVN), and aging index (AI), were used to try to discover or define the chemistry-property-performance relationship for asphalts. Often causing impassioned debate by dedicated scientists and engineers, the arguments and discussion about the relationships have gone on for many years.

In the course of the research carried out by SHRP it became apparent that the micellar model could not adequately explain the behavior and properties of asphalt. As a result of these investigations, the SHRP research team postulated a new model to be tested by the experimental data.

If validated, this new fundamental explanation of how and why asphalts behave as viscoelastic materials will enable refiners and manufacturers to modify and improve asphalts in an orderly, informed manner, that has never been possible before. It will also enable highway engineers to design pavement structures that take full advantage of asphalt's unique chemical and physical properties.

CLASSICAL ANALYTICAL METHODS AND THE ASPHALT MODEL

Asphalt models are defined and limited by the analytical tools applied to them. Analytical methods control the researchers' ability to separate and characterize the critical chemical components that contribute to asphalt's performance properties. As the constituents of asphalt become better defined through the application of more effective analytical tools, the chemical relationships that govern its performance are more readily explored and understood.

Historically, the detailed chemistry of asphalt has been largely ignored by asphalt chemists, simply because it is so complex. The herculean task of trying to isolate and identify the hundreds of thousands of different molecules present in a particular asphalt was, and is, simply too difficult to undertake. In addition, the knowledge that the results were only valid for that particular asphalt led researchers to either ignore the chemistry entirely or attempt to only broadly characterize the molecules present in various types. While the latter approach is certainly valid, the analytical separation methods used at the time didn't have the necessary separation power to allow isolation of chemically meaningful fractions.

In the past, asphalt components were separated primarily by the solubility of the various molecules in different solvents. Separation methods such as Corbett (ASTM D-4124) and Rossler analyses gave ambiguous chemistry-performance relationships, and there were always asphalts that were exceptions to the general trends resulting from these methods. These sometimes confusing results were due to contamination or incomplete separation of the various fractions that were isolated using these methods. For instance, asphaltenes separated by the Corbett method *generally* contain polar molecules, but since the isolation technique depends on solubility in heptane, large nonpolar molecules insoluble in heptane will also be isolated, cross-contaminating the asphaltenes in ways that obscure their true chemistry-performance relationships. The failure of these analytical methods to separate discreet chemical fractions is demonstrated by the lack of correlation between single, separated fractions and asphalt performance.

In a similar vein, surrogate measurements such as penetration and viscosity didn't correlate with performance because they were not fundamental or specific enough in defining a desired physical trait directly related to performance. With these limitations in mind, new analytical approaches were applied to asphalts from the beginning of the SHRP program.

THE ASPHALT MODEL: ADVANCES IN ANALYTICAL TECHNOLOGY

Size Exclusion Chromatography

One of the first methods to be applied was size exclusion chromatography (SEC). In this method the asphalt is dissolved in solvent and passed through a column containing porous beads that have very uniform pore sizes. The smaller molecules flow into and out of these pores and are retained on the column due to the longer path they take in passing through it. Conversely, the larger molecules will not fit into the pores, and they pass through the column more quickly than the small molecules. This technique can be very effective in separating classes of molecules by size. Its weakness is that it separates only by size, and not by a more fundamental parameter such as molecular weight. Thus, long skinny molecules may behave differently in SEC separations than will short fat molecules of the same molecular weight. In addition, the ability of the solvent to affect the associations between asphalt molecules will also affect the separation.

During the SHRP program modified SEC techniques were applied to asphalts to follow up earlier work by Jennings (1). The SEC method was refined by using toluene as the solvent, which caused less disruption to the asphalt structure than the original solvent, tetrahydrofuran. The investigators wanted to take advantage of the fact that many of the molecules in asphalt formed loose associations. These relatively weak bonds could be broken by the use of a strong (polar) solvent like tetrahydrofuran. However, when the asphalt was dissolved in a less polar solvent such as toluene, many of these weak bonds were not broken, indicating that the dissolved sample had larger "groups" or "associations" of molecules, which the scientists wanted to investigate.

A major accomplishment of this SEC method is that the technique generates large amounts of separated fractions, for the first time allowing extensive chemical analysis and characterization of the separated SEC fractions.

The SEC technique results in isolating two fractions (called SEC I and SEC II) from the asphalts. SEC I contains the "associated molecules" and SEC II consists of "solvent" molecules. While in principle SEC separates the asphalt molecules based on their molecular size, additional analyses have demonstrated that the majority of the polar materials present in asphalt are found in SEC I, while the nonpolar materials are in the SEC II fraction. While many researchers have long felt that the polar materials in asphalts played a major role in pavement performance, they had been unable to demonstrate it conclusively. The adoption of SEC was a first step in proving that relationship.

Ion Exchange Chromatography [1,1]

Ion Exchange Chromatography (IEC) is a second powerful analytical technique applied to asphalt to help understand the relationships between its chemistry, physical properties, and performance. The early work by Green, et al. (2) was modified to tailor the method to asphalts. In this method the asphalt is dissolved in a solvent and passed through a series of columns that separate the molecules based on their acidic or basic character. As discussed in an earlier paper (3), researchers now have an analytical method that allows the polar molecules in the asphalt to be separated based directly on their polarity. The use of IEC to separate asphalt fractions based entirely on their polar nature gives researchers a means of unraveling the chemistry-performance link and also strengthens the validity of the asphalt model.

The IEC method is a very powerful analytical technique that can be applied to asphalt to unlock its molecular interactions. The asphalt is dissolved in a solvent and then passed through a series of ion-exchange resins, where the polar molecules attach to the resin bed according to their acidic or basic character. Just as importantly, the nonpolar molecules are not retained on the resins and are collected as a separate fraction. The significant and unique point of the IEC method is that, for the first time, it allows us to separate molecules based on the very characteristic (polarity) through which they contribute to the performance of asphalt. Earlier analytical methods, including the SHRP SEC separation, utilize a surrogate property to separate the asphalt molecules. By this we mean that the separation method doesn't use the same property it seeks to isolate for the separation. In the case of SEC, for instance, we separate based on molecular size, but seek to isolate materials according to their polarity. Some asphalts cannot be successfully separated into the fundamental building blocks using these surrogate methods. IEC allows us to finally describe the asphalt in its fundamental building blocks and to generate a new asphalt model based on its chemistry.
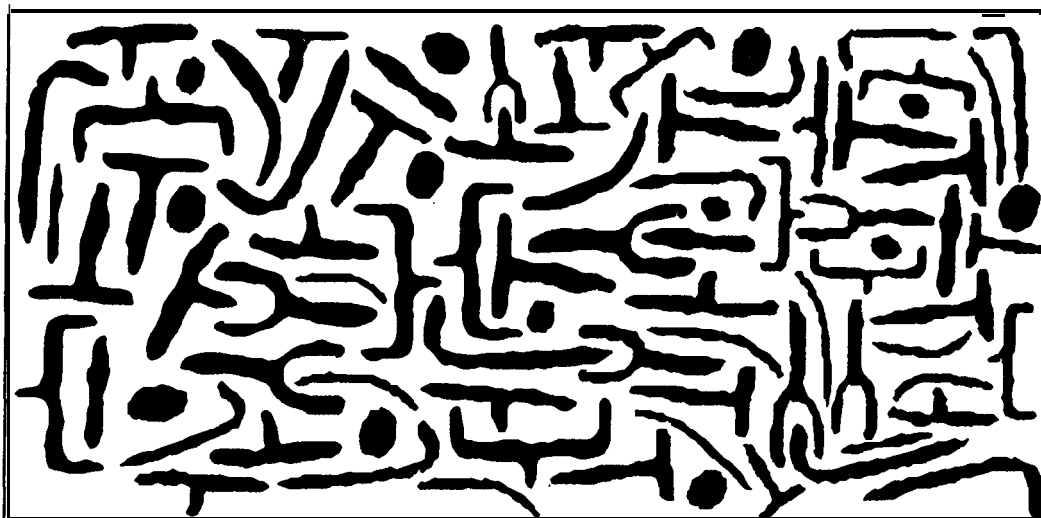

THE SHRP ASPHALT MODEL

As a result of using IEC, SEC, and other characterization techniques, a new, concise picture of the relationship between asphalt chemistry and pavement performance has rapidly evolved. The very powerful analytical techniques described above have been applied to asphalts, and they are yielding startling results.

These new chemical results, in combination with an examination of the response of asphalt to the application of both stress and strain, lead us to our present under-standing of the relationships of chemistry, physical properties, and performance of asphalts. This understanding has resulted in a new asphalt model that will allow us to explain the effects of asphalt chemistry on pavement performance.

However, even though the tools are now available to relate pavement performance and asphalt chemistry, several qualifiers must be added.. Pavements are composites of multiple materials. The asphalt and aggregate contribute to pavement performance, but construction practices, service environment, traffic loading and duration, and base characteristics also play an important role in the ultimate performance of the pavement. For our purposes, when considering the linkage between asphalt chemistry and pavement performance, it is our assumption that these additional variables produce no confounding effects.

As we have seen in the description of the IEC method, asphalt is divided into two broad classes. The polar molecules interact with each other through polar-polar or hydrogen-bonding interactions, forming associations, that create a network within the nonpolar "solvent" molecules. Both the polar and nonpolar molecules make significant contributions to the physical properties of the asphalt and, consequently, the pavement. Figure 3 illustrates how the polar molecules interact in the nonpolar "solvent."

Figure 3
The SHRP Asphalt Model

This figure illustrates the author's concept of the asphalt structure as it is now understood. The different shapes in the figure represent the associations of polar molecules in the asphalt. They are different sizes and shapes, and are surrounded by the nonpolar molecules (which are not shown in this illustration). The polar sites on the associations of molecules interact with one another by forming weak bonds. The associations of the polar molecules take place at polar sites on the asphalt

molecules through hydrogen bonding (polar-polar interactions), while other interactions take place through pi-pi bonding of aromatic rings and Van der Waals interactions of long-chain hydrocarbons. While these varied forms of interaction take place simultaneously, it is believed that the majority of asphalt's viscoelastic properties result from the polar-polar interactions of its associated molecules. It is important to note that there are no actual phases in asphalt, *per se*. The polar and nonpolar molecules exist as a homogeneous mixture, with no floating "islands" or colloidal structures. Since the bonds between polar molecules are weak, they are constantly being broken and reformed as the asphalt is subjected to heat and/or stress.

It is important to remember that all these interactions between asphalt molecules are weak, and the bonds may be broken through the action of heat or shear forces. This concept of weak interactions between the molecules explains why asphalt behaves as a Newtonian fluid (its viscosity change is proportional to the amount the temperature is changed) at elevated temperatures, and why asphalt exhibits a behavior that is so dependent on temperature and loading. Due to the weak nature of the polar-polar and pi-pi bonding forces, bonds are constantly being broken and reformed, each time in a unique way that never yields the same material again.

The most persuasive demonstration of this is shown when the asphalt is dissolved in solvent. Even if oxygen is rigorously excluded and the loss of volatile materials is carefully controlled, the physical properties of the reconstituted asphalt are not the same as the original starting material. This is because the solvent breaks the weak polar-polar and pi-pi bonds, and when the solvent is removed, the bonds reform in a unique new pattern, yielding a "new" asphalt with a new set of physical properties. It may be possible to gently heat, or anneal, the asphalt so that it returns to nearly its original properties, but it will still be a different material.

It is critical to be aware of this unique property of asphalt when examining its physical properties. This effect will be substantial in the case of field samples recovered from pavements in which the asphalt has been subjected to oxidative attack, loss of volatile molecules, and the effects of residual solvents.

As a result of the new understanding of how asphalt's physical properties should respond to the chemical differences in its molecules, the IEC analytical technique has been used to isolate a unique new fraction which is believed to be asphalt's "key" building block. This material has unique physical properties that explain the tendency of polar rnaterials in asphalt to aggregate and form associations. These materials are termed "amphoterics."

THE AMPHOTERICS

The <u>Webster's New Collegiate Dictionary</u> defines an amphoteric material as one that can exhibit either acid or basic character. When applied to asphalt, the term means that an asphalt molecule has *both* an acid and a base group (one or more of each) on the same molecule. Data have provided strong evidence that amphoterics play an important role in building the polar-polar bonds that give asphalt its unique properties. The data show that two or more functional groups on the asphalt molecule make it capable of forming "chains" of weak polar-polar interactions; these chains are the foundation of the network mentioned above. Single molecules containing two acid and/or two base groups also exhibit this property, but the amphoteric molecules show by far the largest effect.

The term *amphoterics* is used to mean an asphalt molecule that has both an acid and basic group in the molecule, *but not at the same site*. An example of this would be a carboxylic acid (COOH) and sulfoxide (S=O) on the same asphalt molecule.

Examination of viscosity and rheological data for combinations of IEC fractions, including the amphoteric materials, has unequivocally demonstrated the large contribution of this class of molecules to the viscoelastic properties of the asphalt. In experiments with both IEC fractions and model compounds, the strong viscoelastic effects of these molecules have been demonstrated. The two critical attributes in the formation of the polar "network" in asphalt are:

- Two or more functional groups per molecule
- Both an acidic and basic site per molecule

An illustration of amphoteric molecules that might exist in asphalt is shown in Figure 4. In this case two molecules are shown. The first is an aromatic molecule that has three heteroatoms in its structure, including a phenol group (O-H attached to the ring,) a sulfoxide group (S=O), and a ketone (C=O). The second is an aliphatic molecule that contains a carboxylic acid (COOH) and a mercaptan (SH) group.

AMPHOTERICS AND ASPHALT AGING

As asphalts age they incorporate oxygen into molecules where there are heteroatoms (N, O, S) or where there are chemically active carbon atoms such as benzylic carbon (carbon atoms that are located adjacent to an aromatic ring). These sites may well be nonpolar in the unaged asphalt when it is delivered from the refinery or terminal. For example, asphalt molecules containing aliphatic sulfur will be nonpolar, but following oxidation the resultant sulfoxide will be weakly

basic, and can participate in polar-polar associations. Similarly, carbon is nonpolar, but it can be oxidized to become carbonyl (C=O), and it will then behave as a polar site in the aged asphalt (Figure 4).
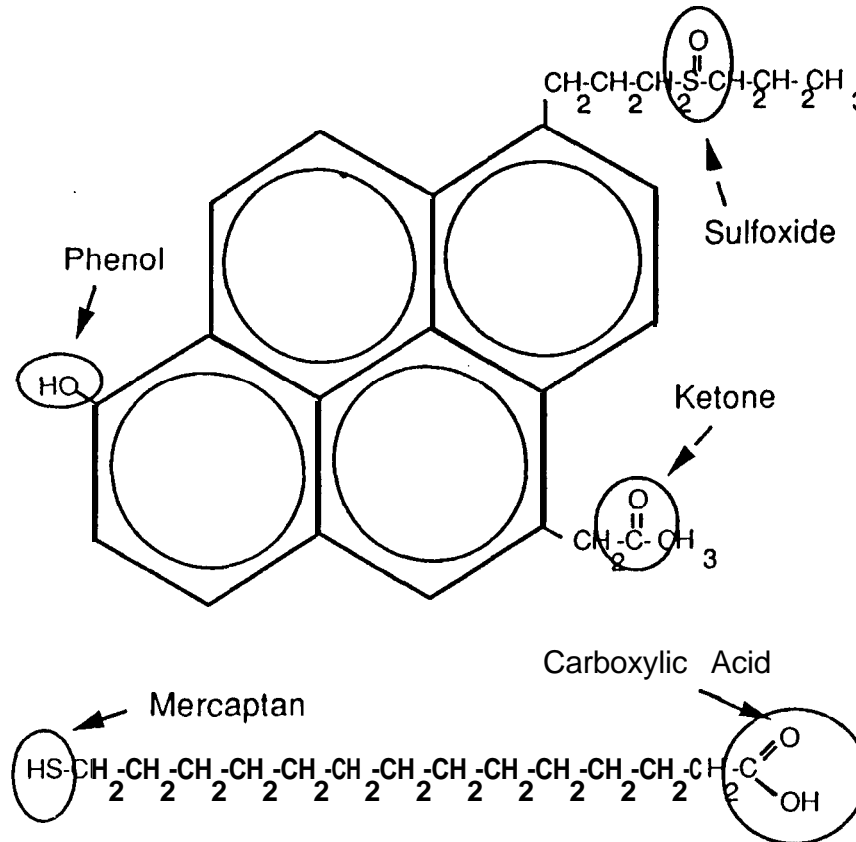
Figure 4
Types of Amphoteric Molecules

Previous research indicates that there is no correlation between asphalt properties such as aging index (AI) and sulfoxide and/or carbonyl content. For example, asphalts such as those from California Valley crudes produce large amounts of carbonyl, but they don't gain 140° F viscosity rapidly when oxidized. Conversely, asphalts such as those made from Boscan (Venezuelan) crudes do not form much carbonyl, but have large 140° F viscosity changes upon aging.

The SHRP asphalt model allows us to explain this previously anomalous behavior. The lower amounts of amphoterics found in California Valley asphalt mean that most of the molecules only have one oxidizable site and hence cannot form many

associations through the chain-building mentioned previously. Conversely, Boscan asphalt has higher levels of amphoterics and can build networks of associations (and viscosity) as it is oxidized. Thus the model explains the previously described lack of correlation between oxidation products and aging behavior.

The large contribution to physical properties brought about by amphoteric materials demonstrates an important point in understanding the effect of asphalt chemistry on the physical properties of the asphalt. The production of polar materials during aging is not in itself sufficient to cause major changes in the physical properties of the asphalt. The nonpolar molecules are also changed during aging; this process will be discussed later. As stated before, the production of polar materials must generate molecules that are amphoteric in nature to result in significant physical property changes. Some asphalts in the Material Reference Library (MRL) show large production of both carbonyl and sulfoxide functional groups when aged, but they do not show corresponding changes in physical properties, primarily because the aging products are not amphoteric in nature.

In the tank, or unaged state, the asphalt molecules aggregate together through their polar-polar interactions as well as their pi-pi interactions of aromatic rings and the Van der Waals interactions of the long-chain hydrocarbons. These bonds are weak and are easily broken by heating, resulting in asphalt's Newtonian behavior at elevated temperatures. As the asphalt is oxidized through the aging process, potential sites such as benzylic hydrogen and aliphatic sulphur are converted through reaction with oxygen to carbonyls and sulfoxides, respectively. These additional polar sites can now contribute to increased polar-polar interactions, leading to increased viscosity at service temperatures. However, since these are still weak bonds, the asphalt will continue to behave as a Newtonian fluid at mix temperatures. In asphalts where the average molecule only has one active site, the viscosity increases after aging will be modest, and the asphalt will have a low aging index. This case is shown in Figure 5. Asphalts with two or more active sites per molecule are illustrated in Figure 6.

In these illustrations the dot (**l**) indicates a site where oxidation can take place, and the asterisk (*) indicates an oxidized atom on the irregularly shaped molecular associations. After aging, the many new sites for polar-polar interactions allow the associations to form chains, leading to large gains in viscosity and physical properties, and high aging indices. It is critical to remember that the mere production of polar sites in asphalt is not sufficient by itself to cause the effects of aging. There must be multiple polar sites in the molecular associations for the asphalt to exhibit significant physical property responses to oxidation.
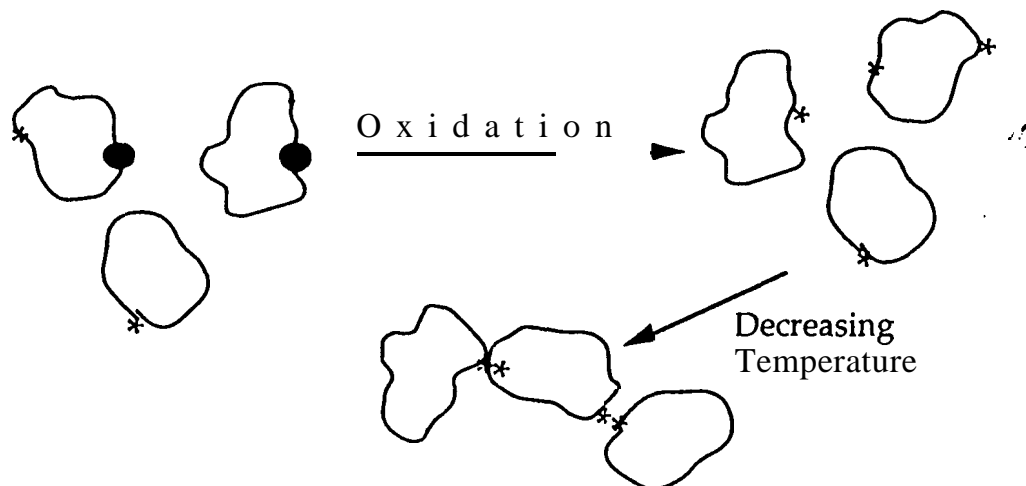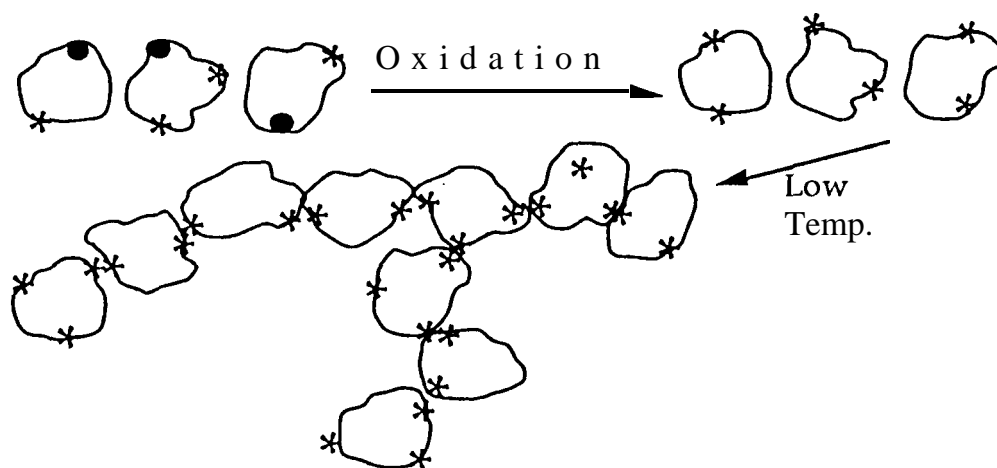
Figure 5
Asphalt with Simple Active Sites

Figure 6
Asphalt with Multiple Active Sites

This illustration also shows how molecules containing only one functional group would serve as chain terminators or "capping" agents, preventing the building of long networks of associated molecules. These two tendencies can be used to explain several of the behavioral traits of asphalts as they age.

The aging of asphalt binders is a complex process, involving several reactions that occur simultaneously. As oxidation of heteroatoms or carbon sites in the asphalt takes place, volatile materials of low molecular weight are lost at a rate that depends on both the temperature and environment.

When asphalts age, the molecular weight and quantity of the nonpolar "solvent" molecules are reduced. This reduction occurs due to both volatilization and the conversion of nonpolar atoms such as a benzylic hydrogen to a polar carbonyl group. These new polar sites will form associations with other polar materials, making the asphalt molecule to which it is attached (which had previously behaved as a nonpolar, non-associating molecule) act as a polar, associating molecule and be separated with the polar IEC fractions. The change in the IEC fractions upon oxidation of the asphalt is consistent with the model discussed above.

The role of volatilization in asphalt aging is also important, but until recently its effects on physical properties and the subsequent changes that relate to pavement performance had not been well understood. Experiments were carried out to explore and define the role that loss of volatile materials has upon physical properties. Thin Film Oven Testing (TFOT) was done in an inert (argon) atmosphere to differentiate volatilization from the oxidation process that is also simultaneously taking place in the conventional TFOT test. The researchers found that they could indeed separate the two effects, but that the variation in volatile loss among different asphalt sources was greater than the effects within a particular asphalt. The asphalts that underwent TFOT in an inert atmosphere stiffened slightly less than those samples tested by the standard TFOT method. Thus, it appears that when asphalts are aged in the TFOT procedure the majority of physical effects on the resultant samples are due to loss of volatiles, with only a small amount of oxidation taking place.

During the course of the SHRP program several different researchers also investigated the role of the aggregate in the oxidative aging of asphalts. Given the large variety of aggregate-asphalt combinations, an aggregate- and asphalt-specific oxidation process would have been very difficult to unravel. However, recent research results have now clarified the role of aggregate in the aging/oxidation process.

In pavement mixtures, the *oxidation* of asphalt is independent of aggregate type. That is, the oxidative products measured in asphalt (usually carbonyl and sulfoxide) do not vary when the same asphalt is aged on different aggregates. However, the asphalt aging, as measured by viscosity, is affected by aggregate. This apparent conflict can be explained as follows: The viscosity of a given asphalt at a given time

and temperature is a function of the molecular weight and the network that has been formed among the groups of polar molecules. How the polar networks form is a function of their environment, in this case the aggregate. As mentioned earlier, the millions of different molecules in a given asphalt can arrange themselves in millions and millions of different ways, and each arrangement is a "new" asphalt, with unique properties. If asphalts aged on different aggregates are heated to a liquid state and then slowly cooled and allowed to rearrange themselves into some preferred network, they will all approach the same "rest" condition because they are chemically the same. Since this effect is most pronounced on solvent-recovered asphalts, it is critical that future researchers consider this point when drawing conclusions from aged and recovered asphalts.

THE EFFECT OF NONPOLAR MOLECULES IN ASPHALT

Investigations have shown that the nonpolar molecules in asphalt have a large effect on the properties of both the asphalt and the pavement. Both the molecular weight and size distribution of these solvent materials play an important role. Speculation on the interplay of these "associated" and "solvent" materials and their likely effect on pavement performance is shown in Table 2.

SEC II		SEC I
Solvent Molecules		Associated Molecules
←	Amount	→
Rutting		Brittleness
Fatigue Cracking (Thick Pavement)		Low -Temperature Cracking
Moisture Sensitivity		Fatigue Cracking (Thin Pavement)

Table 2
Relationship of Molecule Type to Asphalt Performance

It is important to realize that a proper balance of these two types of molecules in asphalt is critical to good field performance. The pavement distresses that would

result from an imbalance of polar and nonpolar portions of the asphalt are illustrated in the bottom half of Table 2.

While both the SEC and IEC analytical methods can be used to obtain the nonpolar molecules from asphalt, the SEC procedure is much faster and yields a larger sample for subsequent study. Analysis of SEC II fractions of the SHRP asphalts shows that this fraction consists of nonpolar molecules that play two critical roles in asphalt:

The nonpolar "solvent" makes a critical contribution to the low-temperature properties of the pavement. The onset of low-temperature cracking in pavements is virtually independent of any other variable in the pavement system. At low temperatures the nonpolar asphalt molecules align themselves, resulting in shrinkage of the asphalt volume. This shrinkage takes place without crystallization, and will cause thermal cracking if it is too severe. It is primarily a function of the molecular weight of the SEC II fraction, but the shape of the molecules is also important, hindering collapse and retarding low-temperature cracking.

The second contribution of the nonpolar (SEC II) fraction to pavement properties is due to its role as a solvent for the polar materials. It is important to note that there is no solvent "phase" *per se* in asphalt. Asphalt is a single-phase, complex mixture of molecules. There are no micelles and no floating "islands" of materials. In the classical micellar model the resins acted as an emulsifier or solubilizer of the asphaltenes, and these asphaltene-resin micelles then floated in the oils. We have shown that this is not the case. However, while asphalts have no true phases, they do have a mixture of molecules of widely varying polarity and molecular weight, and these molecules interact with one another to form associations. These associations form between the polar molecules in the asphalt, which have weak bonds between polar sites on the molecules. These associations take place within the nonpolar portion of the asphalt (SEC II fraction); the molecular weight distribution and amount of nonpolar materials affects these associations of the polar materials.

THE RELATIONSHIP BETWEEN CHEMISTRY
AND PAVEMENT PERFORMANCE

Figure 7 illustrates the overall concept concerning the relationship between asphalt chemistry and pavement performance. Asphalt is divided into two broad classes of molecules: polar and nonpolar. In this model the thousands of polar molecules in the asphalt interact with each other to form "associations." These associations impart physical properties to the asphalt, which leads to its ultimate performance however it's used. This performance is also affected by the nonpolar "solvent" fraction, around and through which the associations of polar molecules form.
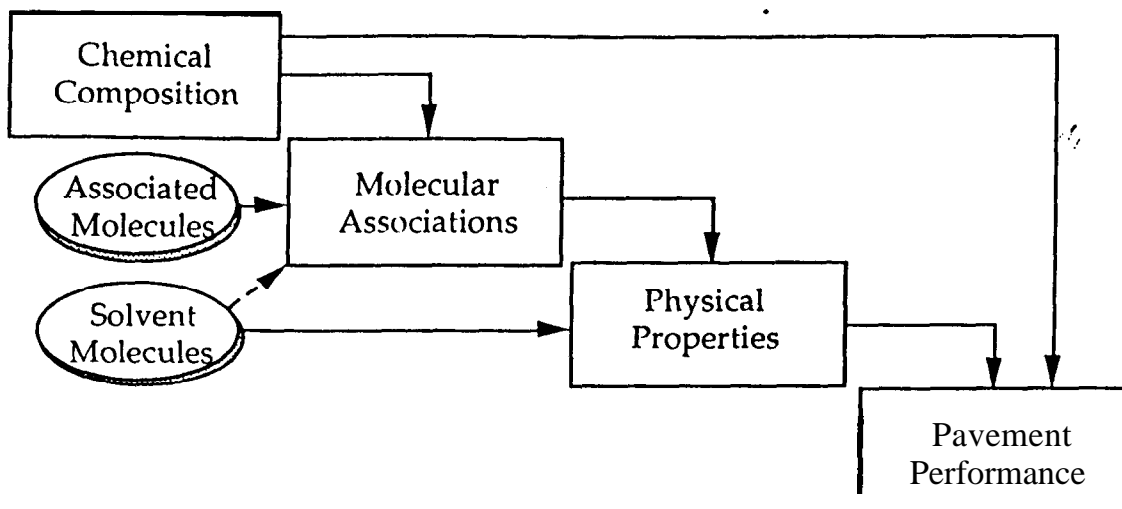
Figure 7
Relationship of Chemistry to Pavement Performance

CONCLUSIONS

This asphalt primer has attempted to explain some of the basic chemistry that concerns the SHRP asphalt research program. Its target audience is not asphalt chemists, and those desiring a more technical discussion of the chemical aspects of SHRP research are directed to the final reports of the A-003B and A-002A SHRP contractors, as well as the final SHRP report. The various researchers who have done so much to further our understanding of asphalt chemistry are also publishing these results in the technical literature.

Through the efforts of dozens of researchers at various institutions, a new model to explain asphalt's chemistry-physical property-performance relationships has been developed. This new "microstructural" model of asphalt has rendered the micellar model obsolete, and also explains many of the anomalies present in earlier asphalt models.

Asphalt is a single-phase, homogeneous dispersion of many different molecules that can be differentiated into two broad classes: polar and nonpolar. The nonpolar molecules serve as a matrix or solvent for the polar molecules, which form weak "networks" of polar-polar associations that give asphalt its elastic properties. There are no micelles or "cores" of asphaltenes in asphalt. The polar materials are distributed throughout the asphalt and when heated their weak interactions are broken, yielding a Newtonian fluid. When perturbed by stress or solvents these

interactions also break and reform to produce new combinations of interactions, which create a "new" asphalt.

As explained in the section entitled "The SHRP Asphalt Model," good asphalts will have a proper balance of polar and nonpolar molecules. With the millions of different molecules present in each asphalt, the performance and physical properties of the asphalt are the result of a combination of many different chemical variables, each type or class of molecules making its unique contribution, perhaps offsetting performance effects in some cases.

Within each class of molecules the chemical characteristics of the particular crude will also affect the performance of the asphalt. As an example, the nonpolar or neutral phase of the asphalt has been shown to be important in the low-temperature properties of the roadway, but competing chemical forces are at work. Generally the lower the molecular weight of the nonpolars, the better the low temperature performance. But if the nonpolar molecules are highly linear and unbranched (waxy), then they could embrittle or crystallize at low temperatures, and could be deleterious to the low-temperature performance of the roadway.

Similarly, both the amount and type of polar materials can also interact and balance one another. The strength and type of polar sites will interact, and, as stated earlier, the amphoteric or multifunctional molecules will have an important effect on physical properties. Data recently generated by SHRP researchers have conclusively demonstrated the contributions of the amphoteric molecules to the viscoelastic properties of the asphalt.

As mentioned above the molecular weight of the nonpolar molecules is important in asphalt performance, particularly in low-temperature environments. Asphalts that have too much polar material will be subject to thermal cracking, brittleness, and fatigue cracking in thin pavements. Asphalts that have too much nonpolar material or that have nonpolars too low in molecular weight, will suffer from rutting, moisture sensitivity, and fatigue cracking in thick pavements.

It is well to remember that the measurement of a physical property such as viscosity at 140° F only defines one point on a continuous viscoelastic profile, so we are not predicting performance. Some of the other empirical indices such as PI and PVN have been used at more than one temperature to try to anchor this curve. The final SHRP asphalt specification fully addresses this problem by defining the rheological master curve of asphalt stiffness for the aged and unaged asphalt over the full range of its service temperatures. Only in this way are we able to fully define asphalt's performance. With this knowledge base we can now deconvolute the interactions between the different chemical species affecting the rheological properties of asphalt.

Asphalts age through both chemical and physical processes. Heteroatoms, or sites near heteroatoms, react with and incorporate oxygen into the asphalt, and become more polar. This adds to the amount of polar molecules that can interact and strengthen the network in the asphalt. Additionally, volatilization of low molecular weight molecules takes place, further stiffening the asphalt by removal of the solvent phase. However, the process of volatilization appears to be fairly short-term in duration, taking place during the mixing and laydown phases of asphalt-concrete production. Oxidative aging is a longer process, extending over the life of the roadway, and is controlled by the service temperature of the pavement. Aggregate has little or no effect on the oxidative aging of asphalt, although it does affect the molecular structure, and thus, its stiffness.

Like all science, the progress in the SHRP program toward understanding the fundamental chemistry of asphalt has proceeded spasmodically, with many detours along the way. There has been, and continues to be, spirited debate between researchers who look at the same data and reach opposing conclusions. However, steady and gratifying progress continues toward understanding this simple, but extremely complex material with which we build so many roads. The long-term contribution of SHRP's Asphalt Research Program to the taxpayers who funded the work will ultimately be an ability to predict asphalt performance prior to building the road. What a simple, yet valuable contribution that will be!

ACKNOWLEDGMENTS

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