INTRODUCTION -

Of the $150 million USD pledged for the Strategic Highway Research Program (SHRP), approximately one-third ($50 million USD) is designated for Asphalt Binder Research. The SHRP program is a five-year, highly focused, product-oriented research effort. The goal of the asphalt portion of the program is to issue a new binder and mixture specification that will help federal, state and local regulatory and specifying agencies obtain better performing hot-mix asphalt concrete (HMAC) pavements.

By the time this paper is presented, the SHRP Asphalt Research Program will have been underway for almost four years, and will be well on its way toward delivery of the end-product specifications. With just over a year left in the contract, many of the researchers will be in the midst of summarizing their research results, and draft binder and mixture specifications will have been issued for public comment and input from both users and producers of asphaltic paving products.

The SHRP Asphalt Research Program encompasses a wide variety of experimental approaches. All are focused on furthering understanding of how the chemistry of the binder affects the properties of the mix and the resultant performance of the flexible pavement. These research efforts are primarily aimed at the major areas of poor performance affecting roadways in the United States.

When the SHRP program was being organized in 1986 and the goals and objectives were being decided upon, the “Brown Book” (1) identified six areas of pavement distress that were to be the focus of SHRP’s Asphalt Research Program. They were:

- Low-Temperature Cracking
- Fatigue Cracking
- Permanent Deformation
- Aging
- Moisture Damage
- Adhesion
The program addresses these distress areas with a variety of fundamental and practical approaches. The unique part of the SHRP Asphalt Research Program is the practical, goal-oriented emphasis of the research and its focus on generating the required products, namely a binder and mixture specification.

The major tenant of the asphalt portion of the SHRP program was the use of an asphalt model as the basis for the experimental plan. The major asphalt research contract was awarded in 1987 to Western Research Institute (WRI) in Laramie, Wyoming. WRI used the micellar model (Figure 1), which has since been discredited, as a starting point for its experimental designs.

**Figure 1**
**The Micellar Model of Asphalt**

At the time the SHRP program began the micellar model was accepted as providing the best available explanation of how asphalts structured themselves. In the authors’ opinion the most significant result of the five-year asphalt portion of the SHRP program is the entirely new understanding of asphalt chemistry that has been achieved and the resultant asphalt model that has been developed to explain asphalt’s performance. This new fundamental explanation of how and why asphalts behave as viscoelastic materials will enable highway engineers to design pavement structures that take full advantage of asphalt’s chemical and physical properties. It will also enable refiners and manufacturers to modify and beneficiate asphalts in a rational manner, which has never been possible before.
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 permutations of these constants, such as penetration index (PI), penetration - viscosity number (PVN), and aging index (AI) were used to discover or define the chemistry-property-performance relationship for asphalts. Often stirring impassioned debate by dedicated scientists and engineers, the arguments and discussion have gone on for many years.

As a result of the many man-years of effort dedicated by the SHRP contractors, a clearer picture of the relationship between asphalt chemistry and pavement performance is evolving rapidly. Several very powerful analytical techniques have been applied to asphalts for the first time, and they are yielding startling results. These new chemical results, in combination with an exhaustive examination of the rheological properties of asphalts, lead us to the present understanding of the chemistry-property-performance relationships of asphalts, and the definition of a new asphalt model. This model will allow, for the first time, to predict pavement performance based on asphalt chemistry.

Having stated that the results of the SHRP program will give us the tools to predict pavement performance based on asphalt chemistry, it is prudent to add several qualifiers. Pavements are composites of multiple materials. Both the asphalt and aggregate will contribute to pavement performance, but construction practices, service environment, traffic loading and duration, and base characteristics all play an important role in the ultimate performance of the pavement. For the purposes of this paper the authors will assume that there are no confounding effects from these additional variables when considering the linkage between chemistry and performance.

3. ANALYTICAL METHODS AND THE MODEL

In reality, the historical model was defined and limited by the analytical tools applied to asphalt. Without better definition of the constituents of asphalts, researchers were limited in determining the chemical relationships that govern performance. Separation methods such as those developed by Corbett and Rossler gave data that were ambiguous, and there were always asphalts that were exceptions to the general trends indicated by these methods. In a similar vein, surrogate measurements such as penetration and viscosity didn’t correlate with
performance because they were not specific enough to define a desired physical trait. It was with these limitations in mind that analytical chemistry was applied to asphalts in the (then) new SHRP program.

3.1 Size-Exclusion Chromatography

One of the first methods to be brought to bear was size-exclusion chromatography (SEC). At both Montana State University and WRI new SEC techniques were applied to asphalts to follow up on earlier work by Jenmings and Pribanic (2). The method was refined by WRI to use toluene as the solvent, which caused less disruption to the asphalt structure than the original tetrahydrofuran. This was accomplished on a preparative scale, and for the first time allowed subsequent chemical analysis and characterization of separated SEC fractions.

The SEC technique evolved as the SHRP program progressed, and it finally resulted in two fractions (SEC I and SEC II) being isolated from the asphalts. SEC I has been given the title “associated phase,” and SEC II is labeled the “solvent phase.” While in principle SEC separates the asphalt molecules based on their hydrodynamic volume or molecular size, additional analyses have conclusively demonstrated that the majority of the polar materials present in the native asphalts are found in SEC I, and the non-polar 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 key to proving that relationship. Examination of the SEC II “solvent phase” has also led to some interesting conclusions, and has allowed SHRP to establish the first chemistry-performance relationships, which are illustrated in Figure 2.
Analysis of SEC II fractions of many asphalts showed conclusively that this fraction consisted of non-polar molecules that played two critical roles in asphalt:

1. The non-polar “solvent” makes a critical contribution to the low-temperature properties of the pavement. In fact, low-temperature cracking in pavements is virtually independent of any other variable in the pavement system. At low temperatures the non-polar asphalt molecules align and order themselves, and there is a free-volume collapse in the pavement. This collapse takes place without crystallization and will cause thermal cracking if too severe. It is primarily a function of the molecular weight of SEC II, but chain branching in the molecules is also important, hindering collapse and retarding low-temperature cracking.

2. The second contribution of the 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, no networks, and no floating “islands” of materials. However, while there are no true phases in asphalts, there is a mixture of molecules of widely varying polarity and molecular weight, and the materials in this mixture interact with one
another to form what the authors will call associations. These associations form among the polar molecules in the asphalt, which create weak electrostatic bonds between polar sites on the molecules. These associations take place within the non-polar portion of the asphalt (SEC II fraction), and the molecular weight distribution and amount of non-polar materials affect the associations of the polar materials.

As a result of nearly four years of intensive research we now know that the polar molecules in the asphalt form weakly linked associations within the bitumen, and these associations are affected by the non-polar molecules surrounding them. Figure 3 attempts to display this new model of asphalt structure graphically.

**Figure 3**

**The Asphalt Model**

This figure illustrates the authors’ concept of the asphalt structure as it is now understood. The associations of the polar molecules (shown in this drawing as the different shapes) take place at the polar sites of the asphalt molecules through electrostatic forces or hydrogen bonding, and other interactions take place to a lesser extent through pi-pi bonding of aromatic rings and Van der Waals interactions of long-chain hydrocarbons. While these forms of interaction take place simultaneously, the majority of the viscoelastic properties of asphalts are a result of the polar-polar interactions of the molecules. The evidence which led to this conclusion is discussed below.
This new model has gone by several names during its development, and several SHRP researchers have independently come to the same conclusions when interpreting the data generated by the asphalt research portion of the SHRP program. The model has, at various times, been called the “spider,” “spaghetti and sauce,” “polar-dispersed fluid,” and “microstructural” model, among others. It is the authors’ opinion that the terminology of “microstructural model” perhaps is the most descriptive, and should be adopted by the industry.

It is important to remember that all of 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 at elevated temperatures, and also explains why asphalt exhibits constantly changing behavior. Due to the weak nature of the polar-polar bonds, the bonds are constantly being broken and reformed, each time in a unique way that never yields quite the same material.

Perhaps the most persuasive demonstration of this is shown when the asphalt is dissolved in solvent. Even if oxygen is rigidly excluded and loss of volatiles is carefully controlled, the physical properties of the reconstituted asphalt are never the same as the original material. This is because the solvent breaks the weak polar-polar bonds, and when the solvent is removed the bonds reform in a unique new pattern, yielding a “new” asphalt and a new set of physical properties. It is critical to be aware of this unique property of asphalt when examining its physical properties, especially in the case of solvent-recovered asphalts from pavements.

3.2 Ion Exchange Chromatography

Ion Exchange Chromatography (IEC) is the second powerful analytical technique that has been applied to asphalt to help understand its chemistry-physical property-performance relationships. The seminal work by Green, et al. (3) was modified by the researchers at WRI to tailor the method to asphalts. As discussed in an earlier paper (4), for the first time researchers have an analytical method that allows the polar molecules in the asphalt to be separated by polarity. Earlier methods such as Corbett and Rossler separations did not depend solely on polarity for the separation of molecular species. The authors believe 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. The use of IEC to separate asphalt into fractions based solely on their polar nature makes the technique unique in providing a means of unravelling the chemistry-performance link. It also strengthens the validity of the asphalt model.
IEC has been used to generate a unique new fraction of asphalt that is believed to be its “key” building block. These materials have unique physical properties that explain the tendency of polar materials in asphalt to agglomerate and form associations. They have been named “Amphotericis.”

4. THE AMPHOTERICIS

The Webster’s New Collegiate Dictionary defines an amphoteric material as one that can exhibit either acidic or basic character. In the case of asphalt the term is used to mean that an asphalt molecule has both an acid and base group on the same molecule. Preliminary data from WRI (4) have provided strong circumstantial evidence for the importance of the role the amphoterics play in building the polar-polar bonds that give asphalt its unique properties. Additional experiments to verify and expand our understanding of the amphoteric molecules are underway as this paper is written. The preliminary data suggest that the presence of two or more functional groups on the asphalt molecule make it capable of forming “chains” of weak polar-polar interactions, as illustrated in figure 4.

![Chain Building in Asphalts](image)

It can also be seen in this illustration that molecules containing single functional groups would serve as chain terminators or “capping” agents, and would prevent 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.
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. These sites may well be non-polar in the unaged or tank asphalt. Aliphatic sulfur will be non-polar, but following oxidation the resultant sulfoxide will be weakly basic, and can participate in the polar-polar associations. Similarly, benzylic carbons, which are non-polar, can be oxidized to carbonyl, which can take part in hydrogen bonding and participate in the aged asphalt as a polar site.

But it has long been shown in the literature that there is no correlation between asphalt properties such as aging index (AI) and sulfoxide and/or carbonyl content. Asphalts such as SHRP asphalt AAG (California Valley) produce large amounts of carbonyl, but don’t gain 140 F viscosity rapidly when oxidized. Conversely, asphalts such as AAK (Boscan) don’t form much carbonyl, but have large 140 F viscosity changes upon aging.

The new asphalt model allows to explain this previously anomalous behavior. The lower amounts of amphoterics in AAG mean that most of the molecules in AAG only have one oxidizable site, and hence cannot form many associations. Conversely, AAK has a higher level of amphoterics, and thus can build networks of associations and viscosity as it is oxidized. This model explains the lack of correlation between oxidation products and aging behavior. It has also led us to look for the presence of additional oxidation products that may contribute to aging properties, but may have not been measured by classical analytical techniques applied to aged asphalts such as infra-red spectroscopy (IR).

A series of experiments to determine the oxygen balance of asphalts as they age is currently underway at SRI in Palo Alto, California. This research will assure that no unknown pathways play a role in the oxidative behavior of asphalts. Additional experiments are also underway at a number of institutions to determine the role of aggregate in the aging process.

The lack of agreement between the AI of asphalts and their chemical composition can also be interpreted in another important way. If we assume that analytical techniques such as IR have accounted for all the oxidation products that occur in asphalt, then we must conclude that the aging index is not measuring a property that has anything to do with pavement performance. This argument is made more compelling when one realizes that the AAK asphalt, which has a high AI, is historically seen as a good field performer and is not susceptible to the premature field aging effects its high AI would indicate.
The measurement of viscosity at 140 F only defines one point on a continuous curve. Therefore we are not defining performance. Some of the other empirical indices such as PI and PVN have used more than one temperature to try to anchor this curve. The final SHRP asphalt specification fully addresses this problem by measuring and defining the master rheological curve for the aged and unaged asphalt over the full range of its service temperatures. Only in this way can we fully define asphalt’s performance, and only with this knowledge base can we understand the interactions between the different chemical species affecting the rheological properties of asphalt.

6. CONCLUSIONS

Through the efforts of dozens of researchers at many different institutions we have developed a new model to explain asphalt’s chemistry-physical property-performance relationships. This new microstructural model of asphalt has made the micellar model obsolete and explains many of the anomalies present in earlier asphalt models.

Asphalt is a single-phase homogeneous mixture of many different molecules, which may be differentiated into two broad classes: polar and non-polar. The non-polar 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 uniformly distributed throughout the asphalt, and upon heating the weak interactions are broken to yield a Newtonian fluid. When perturbed these interactions break and reform to produce a new combination of interactions that gives a “new” asphalt.

“Good” asphalts have a proper balance of polar and non-polar molecules. The true molecular weight of the non-polar molecules is also important in asphalt performance, especially in low-temperature performance. Asphalts that have too much polar material will be subject to fatigue cracking in thin pavements, brittleness, and thermal cracking. Asphalts that have too much non-polar material, or asphalts in which the non-polars are too low in molecular weight, will suffer from fatigue cracking in thick pavements, moisture sensitivity, and rutting.

The objective of the SHRP Asphalt Research Program in its final months is to continue to determine and expand our understanding of the link between asphalt chemistry and pavement performance. Much has been accomplished; much remains to be done.
7. REFERENCES


