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Chemical Properties of Asphalts and Their Relationship to Pavement Performance

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EXECUTIVE SUMMARY

The chemistry of petroleum asphalt at the molecular and intermolecular levels is discussed herein and a combination of interpretation and speculation placed on how chemical data may explain performance characteristics in roadways. At the molecular level historical studies have shown that there are at least hundreds of thousands of unique molecular species that exist within any particular asphalt. Asphalts are known to be comprised of molecular species that vary widely in polarity and molecular weight. The major objective of this portion of the work is to explain behavioral characteristics of asphalts in terms of chemistry. Polarity is a very major contributor to the performance characteristics. Polar materials tend to associate strongly into a matrix which is dispersed in less polar and non-polar materials. In general, the mechanical or structural properties of asphalt are related to the intermolecular structuring among polar components. These polar interactions may arise by involvement of any of numerous different chemical species. The exact nature of the chemical specie is less important than the overall assemblage of a set of polar materials to form a matrix within the non-polar continuous medium. The matrix gives elastic character to the asphalt while the continuous non-polar phase gives a viscous component to asphalt. It is speculated that excessive structuring leads to brittle cements which tends to crack while too little structuring leads to materials which deform under stress. Oxidation adds to the age hardening and brittleness of asphalt cement by contributing additional polar materials to the structured zones within the binder. At very low temperature it appears that the

non-polar materials also tend to organize into a very rigid material, and that this rigid material shrinks at low temperature. It is speculated that this type of shrinkage is largely responsible for low temperature cracking.

A second major objective is to translate research methods into test methods. Numerous types of research methods have been employed to differentiate among asphalts with an emphasis on identifying methods which distinguish among asphalts in the same fashion that they are distinguished by their performance characteristics.

The expected advantages of this work, both technical and economic, are to develop methods for selection of asphalts that will perform in a predictable fashion thereby alleviating the current common problem of premature road failure. Throughout the program, both users and producers of petroleum asphalt have worked closely with SHRP contractor personnel both to give advice on program direction and to maintain a sense of what is practically implementable in each sector.

As with any new development questions arise as to how much specialization will be required for implementation of new test methods. Certainly new test methods could become extraordinarily complex, but it is still another objective to assure that there is no more complexity than is absolutely necessary. Problems of implementation, therefore, should be minimized and especially so when one considers that each new test method will enter a round robin test program in both state highway and user laboratories. The round robin effort, in fact, has already begun. Finally, this work is supported by public funding and the results that are implemented into new test methodology will be public domain.

1.0 INTRODUCTION

1.1 Objectives of the SHRP Asphalt Program

The SHRP asphalt research area is a highly focused endeavor which ultimately must develop specifications for binders and asphalt-aggregate mixtures that relate to the performance of both binders and mixtures in pavements. To accomplish this the fundamental material properties must be known first. Then fundamental properties are to be used to develop meaningful specifications. The current specifications for petroleum asphalt are little more than a quality control exercise for the refiner's vacuum crude tower operations, hence there is little or no distinction among asphalts other than a set of viscosities at two elevated temperatures and a mix plant oxidation susceptibility. That is, all of many asphalts may be classified as, for example, AC-20, and all will be applied as if they are a single material. Yet, their performance characteristics in pavements often vary quite significantly. The results of using poorly classified asphalts have been rude and costly surprises in the form of various types of early failures with increasing frequency. It behooves the user, therefore, to determine what properties of asphalt binders are reflected in pavement performance and then select binders which have desirable performance properties. From a practical viewpoint, no doubt many petroleum residua will require modification to prepare asphalts that have desirable performance characteristics.

1.2 Purpose of Report

The purpose of this report is to describe the current status of the SHRP chemical studies of petroleum asphalt. It is intended to be instructive to the non-chemist and further is a speculative effort to correlate some of the known chemical properties of asphalts with pavement performance characteristics. It is generally believed that performance-based specifications for binders will be mainly physical property tests. The objective of the composition studies is to develop correlations between the chemical and physical properties. Further, the composition studies are to define a set of practical analytical methods to describe composition. This then will allow definition of acceptable composition for a given performance which in turn is instructive to the producer in the manufacture of asphalt. If any given asphalt has a compositional deficiency, the producer can determine how to modify the asphalt and remedy the deficiency. It has become obvious that deficiencies vary from one asphalt to another. It is important to note that many chemical properties will not correlate with performance so it is a major goal to distinguish the chemical properties that do relate.

References are made to ongoing research which has been reported to SHRP, but in many cases has not been published. Many statements are based on current SHRP research and have no literature references.

2.0 CHEMISTRY

It is convenient to divide the chemistry of petroleum asphalt into two parts. The first part is the chemistry at the molecular level and the second part is the chemistry of interaction among all molecular species in asphalt. Much of the physical nature of asphalt can best be described, in terms of composition, as an assembly or matrix of molecular species (building blocks) into large multi-molecular units within the asphalt. Numerous techniques exist to examine asphalt at both the molecular and intermolecular levels. In the following subsection the chemistry of asphalt at the molecular level is reviewed without reference to experimental methods. This is to illustrate what types of "building blocks" are present. The chemistry of interaction among asphalt molecules is reviewed in the second subsection with reference to some of the techniques being used currently in the SHRP program.

2.1 Molecular Level

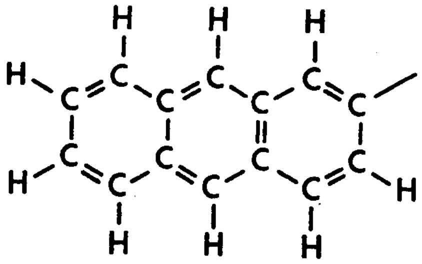
Extensive research on petroleum composition at the molecular level has been done by many workers for many years. At this point, much of it is essentially textbook material but worth reviewing here.

2.1.1 Typical Species in Virgin Asphalt. At the molecular level most of the total mass of neat (tank) asphalt is a mixture of a wide variety of high boiling hydrocarbons. Some are aliphatic (waxy materials), some are aromatic (more like air-blown asphalts) and some molecules have both aliphatic and aromatic carbon. Examples of such molecular fragments are shown in Structures 1 (aliphatic type) and 2 (aromatic type).

$-CH_2-(CH_2)_x-CH_3$

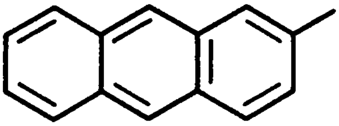
x Typically = 15 or More Carbons

Structure 1



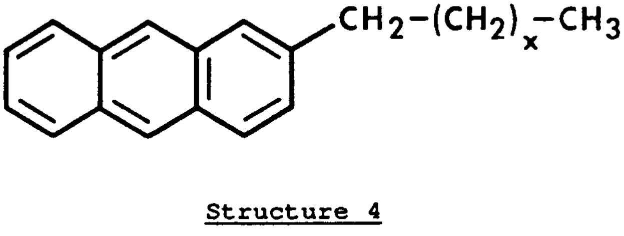
Structure 2

Structure 2 is more commonly represented by Structure 3. Both structures 1 and 3 are only representative molecular fragments of larger molecules that make up asphalts. Structure 1 is shown as a straight chain of carbon atoms, but typically in asphalt there are numerous combinations of aliphatic carbon chains which have one or more branches.



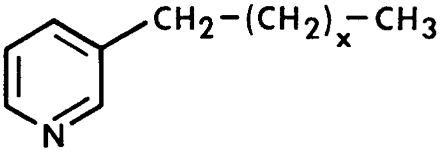
Structure 3

Structure 4 shows a molecule which is a mixture of aliphatic and aromatic carbon.



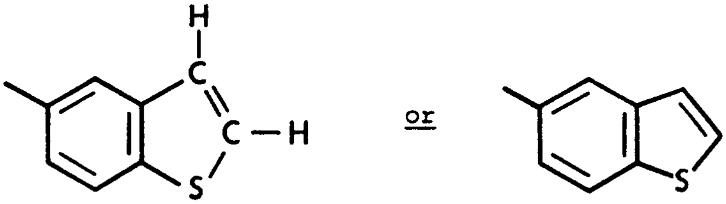
Structure 4

While the major mass of asphalt is hydrocarbon, a large proportion of molecules also contain one or more heteroatoms; nitrogen, sulfur, oxygen and metals. Nitrogen, in the form of a pyridine is shown in Structure 5.



Structure 5

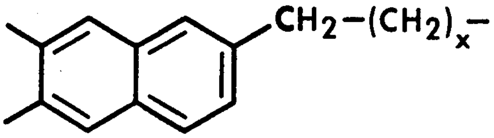
Sulfur, as a benzothiophene, is shown in Structure 6. Structure 6 on the right is a shorthand notation of the one to the left. These are identical molecular fragments.



Structure 6

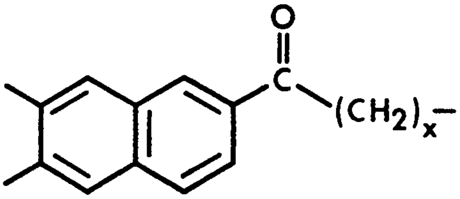
Both sulfur and nitrogen may appear in any of a variety of sites within molecules. Hence, it is easy to see that tens of thousands of different molecular species may be present in asphalt considering that every different arrangement of elements constitutes a different molecule. It also follows that any definition of properties based on specific molecular species would be a monumental task. It is much more effective to classify the chemistry in terms of the molecular types.

2.1.2 Oxidation to Form New Molecules. Certain types of carbon in asphalt are susceptible to oxidation. An aliphatic carbon next to an aromatic ring is known as a benzyl carbon and is an example of a readily oxidizable site. Structure 7 is an example of a molecular fragment showing a benzyl carbon in bold type (adjacent to the aromatic ring).



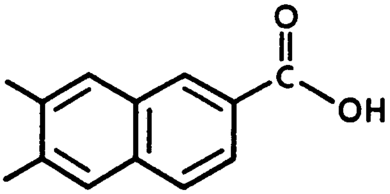
Structure 7

Sites such as these oxidize to form ketones as shown in Structure 8.

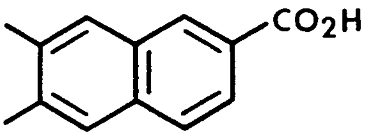


Structure 8

More severe oxidation may result in formation of carboxylic acids and loss of part of the molecule such as shown by both versions of Structure 9.

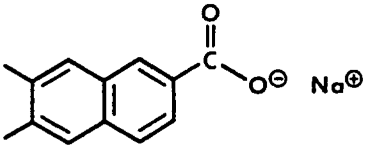


or

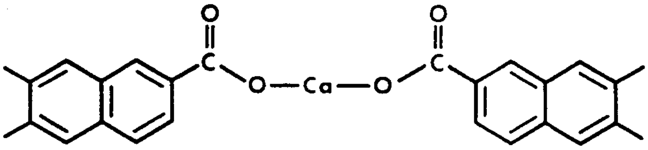


Structure 9

Carboxylic acids, whether present in the original crude or formed upon oxidation, may be converted to sodium (Na) salts (Structure 10) or calcium (Ca) salts (Structure 11) by appropriate reaction with sodium or calcium inorganic compounds.

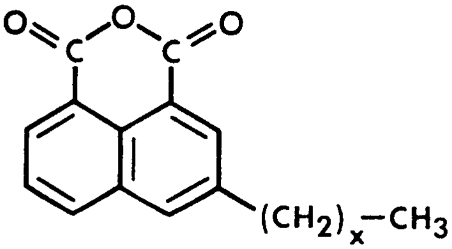


Structure 10



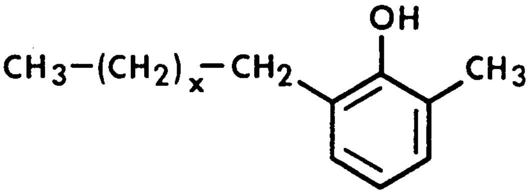
Structure 11

Carboxylic acid anhydrides (typically called anhydrides) may be formed upon oxidation when two benzyl carbons are present on adjacent aromatic rings. An example is Structure 12.



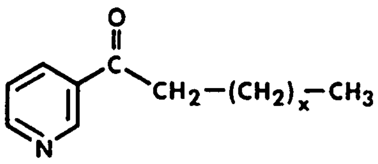
Structure 12

Another type of oxygen containing molecule which may be present in asphalt is a class known as phenols where oxygen is attached directly to an aromatic ring. This class is illustrated by Structure 13.

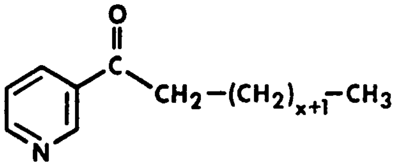


Structure 13

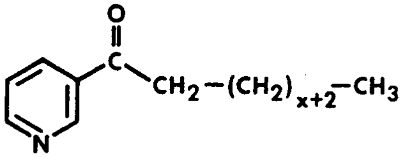
Again numerous variations, or isomers, containing the basic phenol unit may exist. In addition to isomeric combinations of all molecular types shown above, homologs of each also typically exist. An example of a homologous series is shown by Structures 14, 15, and 16.



Structure 14



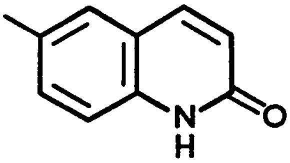
Structure 15



Structure 16

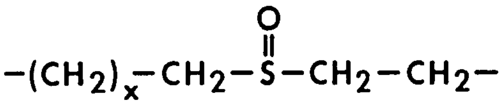
In the above case, each varies only by one aliphatic carbon. Each is a unique molecule, although the properties among all of these will be quite similar.

Another important class of compounds typically found in aged asphalts is quinolones as shown in Structure 17.



Structure 17

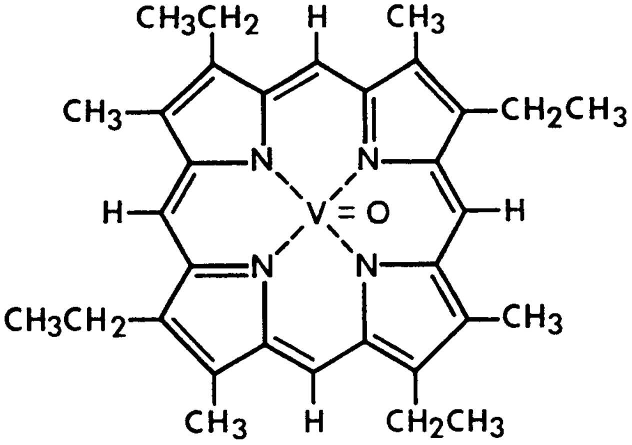
Many sulfur compounds are also susceptible to oxidation and typically form sulfoxides. A sulfoxide containing fragment is shown in Structure 18.



$$-(CH_2)_x-CH_2-\overset{\overset{O}{\|}}{S}-CH_2-CH_2-$$

Structure 18

2.1.3 Metals. There are also metals present in asphalts, again in varying amounts and distributions. The most common metals are vanadium, nickel, and iron although other metals may also be present. Typically metals are present as organo-metallic materials, specifically as porphyrins. An example is shown by Structure 19.



Structure 19

By now it is obvious that hundreds of thousands of unique molecules may be found in any given asphalt. Further, the second, third and so forth asphalts will contain hundreds of thousands of different molecules.

2.1.4 Polarity. All of the naturally occurring heteroatoms, nitrogen, sulfur, oxygen, and metals contribute to polarity within these molecules. Likewise, oxidation products formed upon aging are polar and further contribute to the polarity of the entire system. Polarity, which is the separation of charge within a molecule, can be seen by the following example. The dipole moment (separation of charge) of pyridine (C_5H_5N) is 2.19 debyes (in the gas phase) whereas the dipole moment of benzene (C_6H_6) is zero. Benzene is the all carbon analog of pyridine. Polarity also exists in all other heteroatom containing species. Polarity is important in asphalt because it tends to cause molecules to organize themselves into preferred orientations. Historically, these have been referred to as formations of micelles, colloids, etc., although these terms have been misused. A more current understanding of molecular orientation within asphalts is given in the following subsection.

2.2 Intermolecular Level

At the intermolecular level, polar molecules including those in asphalt, have another behavioral characteristic. This is attraction of one polar molecule for another as a result of their separated charges, or dipoles. Figure 1 illustrates this schematically.

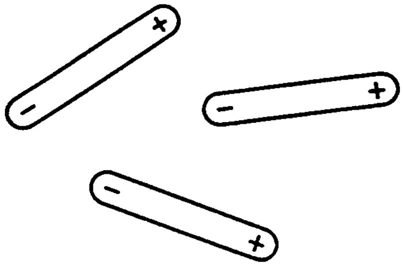


Figure 1A

Figure 1B

In part A the polar molecules are randomized, but in part B the molecules are well oriented with respect to each other. Part B represents a more stable thermodynamic state. It is important to note here that it makes little difference which of the many polar molecules shown earlier is involved. Any one of the many types of polar molecules may fill the molecular schematics shown in Figure 1A or B. The primary requirement is that some sort of charge separation is present in the molecules. It is obvious that a multi-molecular structure may form as illustrated schematically in Figure 2, although the individual molecular components will vary from one to the next so that no specific regularity exists within the organized zone (see note 1).

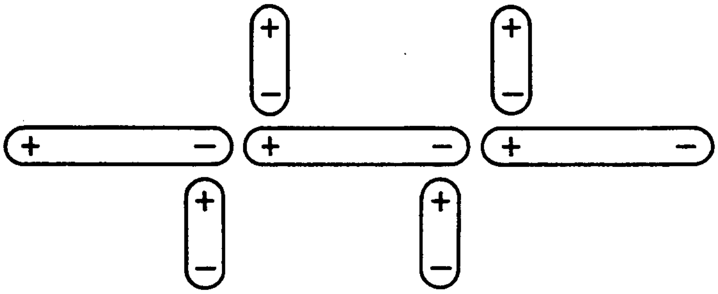


Figure 2

(Note 1) For simplicity, this schematic shows positive and negative charges at the ends of molecules. The associations among molecules are combinations of electrostatic and other short range forces. The actual charges are best defined in terms of asymmetric electron density and are not true plus and minus charges as would be the case with ions. Neither are charges necessarily distributed end to end. Figure 2 is only intended as a convenient illustration.

During the organization, some amount of three-dimensional, intermolecular structure forms. Historically, this has been called the micelle, or colloid. While it is not a true micelle, it is an organized set of molecules. The set does have some preferred organizational structure as compared to that shown in Figure 1A where it is only randomized molecules. The structure is held together by electrostatic and other short range forces which are weak compared to covalent chemical bonds. Short range (non-covalent) forces range from about 3 to 10 Kcal/mole, while covalent bonds are much stronger. For comparison, carbon-carbon covalent bonds, the bonds that hold organic molecules together, are 80 or greater Kcal/mole and carbon-hydrogen covalent bonds are typically 100 Kcal/mole. It follows then that the organized (intermolecular) structure may be subject to rearrangement or may be scrambled either from physical stress or by raising its temperature. However, this will occur without changing molecular composition. All of the molecular species remain the same. On the other hand, the physical properties <u>will</u> be different. When the molecules are randomized, they can move about with respect to each other more easily than when they are more organized. The more highly organized structure has more resistance to motion or deformation. Said differently, structured asphalt is more of a springlike material, more viscous, and is stiffer. The ability to form an organized, or self-assembled, structure depends upon the strengths of the attractions and upon the number of sites where intermolecular attractions occur.

Oxidation has a pronounced effect on the organized structure. As oxidation occurs, new sites that are greater polarity are formed and are formed in larger amounts than in the virgin asphalt. So the propensity to self-associate will increase. Also, the rate of association depends upon the number of sites and the magnitudes of the attractions. The stronger the attractions and the more there are, the greater the driving force to associate. But, association is inhibited by the high viscosity of asphalt. Hence, the overall process is slow. For example, in one experiment, virgin asphalt was observed to double in viscosity over a period of a few years. The sample was protected so that oxidation did not contribute anything. After this extended storage, the sample was heated to mix plant temperature while protecting it from oxidation. The viscosity returned to near its original value. The rates and magnitudes of stiffening of asphalt after oxidation, with and without aggregate present, and at various temperatures, are being studied at the present time in the SHRP asphalt program.

The degree of association varies from one asphalt to another and several methods can be used to determine type and magnitude of association. One method being used at the present time is size exclusion chromatography. It is illustrated in Figure 3 which shows three size exclusion chromatography (SEC) experiments, all plotted on the same axes. Asphalts AAG, AAK, and AAM (hereafter noted as G, K, and M) are all similarly classified petroleum asphalts. All three were separated by SEC in the same fashion. The SEC process separates materials (in this case, asphalts) into components according to size at the molecular or multi-molecular level. It matters not whether the size excluded entity is a single molecule or an associated group of molecules. In the current work, a system was chosen that causes the least possible disturbance to the association. The SEC separates asphalt by apparent molecular size so that if there are associated groups of molecules in the whole asphalt they will also exist and therefore be separated as an associated group by SEC. The SEC profiles shown in Figure 3 are plots of the fraction of the

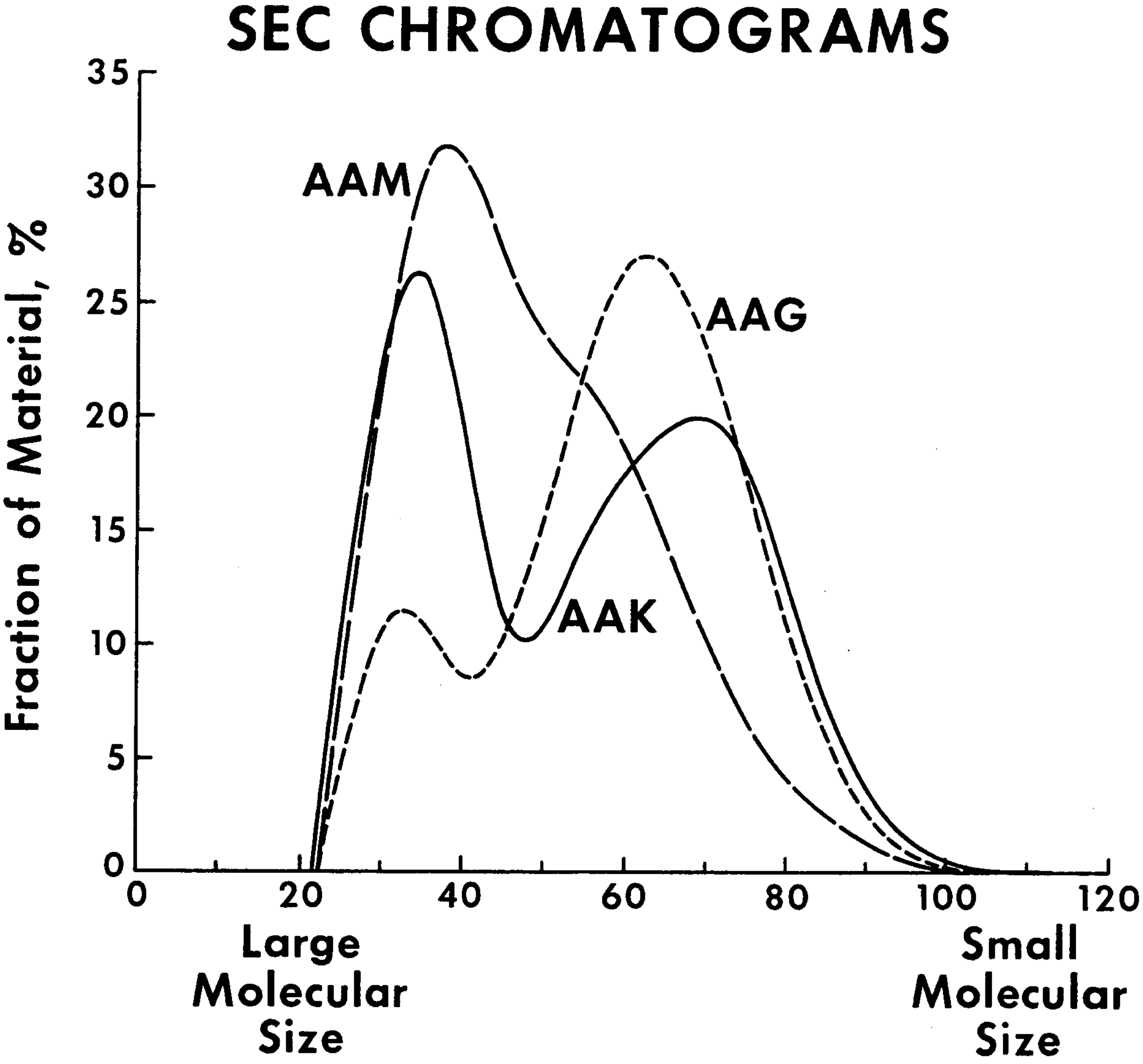

SEC CHROMATOGRAMS
Fraction of Material, %
35
30
25
20
15
10
5
0
0
20
40
60
80
100
120
AAM
AAG
AAK
Large Molecular Size
Small Molecular Size

Figure 3

whole asphalt on the y-axis and the molecular or multi-molecular size on the x-axis. The three materials illustrated are virgin asphalts. Note that asphalt G has a very small fraction that is in the large molecular size, and a significantly larger fraction that is smaller molecular size (the right side of the plot). Asphalt K is almost the reverse. Further, these two are bimodal indicating that there is a relatively small amount of intermediate size material in either. Asphalt M, however, is more of a continuum. That is, it is not bimodal. Asphalt M does have a significant amount of large molecular species present as does K. Upon further examinations of M and K by vapor-phase-osmometry molecular weight determination in pyridine, it was discovered that the large molecular species in K are comprised of many smaller molecules whereas in Asphalt M the largest fraction (left of plot) is comprised of truly large molecules. The large molecules in M will not dissociate, for example, with an increase in temperature, whereas the large ones in K will dissociate. If nothing else is apparent, note that these three asphalts appear to be very different from each other when examined by SEC. Yet conventional tests would indicate that all three are similar.

Another effect within asphalts is the behavior of the molecules which have very little association. These are not necessarily smaller molecules, but are the less polar and therefore less associated portions of the asphalt (to the right of the SEC plot). Ion exchange chromatography (IEC) and supercritical fluid chromatography (SFC) have both been used to show that these molecules also vary from one asphalt to another. Often called a maltene phase, this less-associated material behaves as a "solvent" for the polar materials and will behave as a dispersing agent. It will tend to reduce association of the polars.

At this point, it is worth considering a more integrated description of asphalt. It appears to be a material containing polar molecules that associate strongly into organized units that are dispersed in a less polar and continuous phase. The association of polars appears to depend upon composition of polars and upon thermal history. Some speculation can be made on the effects of the differing chemistry within the continuous neutral phase. First, it is apparent from the SEC curves that asphalt G has a large fraction of small molecular species which implies that the less polar and non-associated materials dominate its behavior. It would be expected that G would be able to accommodate additional amounts of polars with minor changes in its physical properties. For example, asphalt G should be able to tolerate significant oxidation before any major viscosity change occurs and this is what is observed. Asphalt K should be and is the reverse. Oxidation of K should increase the already predominant polar effect and raise viscosity rapidly with oxidation. This likewise is observed.

The propensity to oxidize has been observed by another method being used in the SHRP asphalt studies. Oxidation in a pressurized vessel is being studied as a method to simulate long-term aging of asphalt in pavement. After 400 hours of oxidation at 60°C (140°F) under pressure, asphalt G had an aging index of 17 while K had an index of 23. When the temperature was raised to 113°C (235°F) and both oxidized at atmospheric pressure for 72 hours, asphalt G had an aging index (measured at 60°C) of only 18 while K jumped to 530 under the same conditions. At the elevated temperature, both asphalts are more dissociated and oxidize rapidly. Upon cooling both to 60°C, G can accommodate its own oxidation products whereas the newly formed polars in K strongly dominate its behavior. The polars in asphalt K associate very strongly and raise the viscosity quite substantially. The same trends have been observed with other asphalts. While on the subject of differing rates of oxidation of any given asphalt at different temperatures, note in Figure 4 how the viscosity change increases with increasing oxidation temperature. This indicates that maximum road service temperatures must be taken into account in the selection process for asphalts.

EFFECTS OF TEMPERATURE ON AGING
KINETICS OF AN ASPHALT SENSITIVE
TO MOLECULAR STRUCTURING

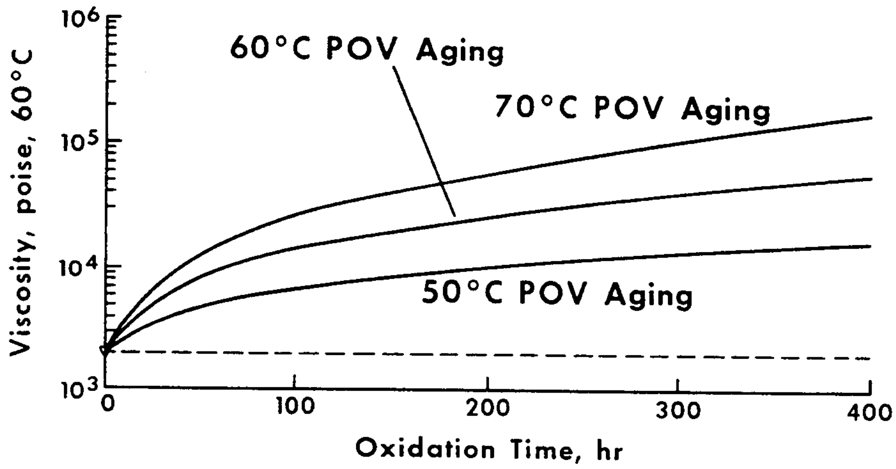


Figure 4

2.3 Chemical Model of Asphalt

The model that is emerging from this work is built upon earlier models and has been refined during the SHRP program. In this case model means nothing more than a clear understanding of the behavioral characteristics of asphalt. The model must be able to explain all of the observed behavioral characteristics as well as all of the variations in behavior from one asphalt to another. Here, it is worthwhile to review the manufacture of asphalt. Petroleum asphalt is typically a high boiling vacuum distillation residuum which is prepared from numerous petroleum stocks. Some asphalts are produced by alternate methods but generally very similar portions of the crude oil ends up as asphalt. The chemistry and physical properties, therefore, vary quite significantly from one asphalt to another and each reflects the nature of the crude oil used to prepare it. The most consistent description, or model, of petroleum asphalt is as follows. Asphalt is a collection of polar and non-polar molecules. The polar molecules tend to associate strongly to form organized structures throughout the continuous phase of the non-polar materials. Nuclear magnetic resonance data and thermodynamic data indicate that the associations are not more than about 40 molecules, but some have smaller assemblies and again it varies from one asphalt to another. Some show very little association. The non-polar phase, on the other hand, has the ability to dissociate the organized structure, but again it varies from one asphalt to another. As temperature is raised, the associations of polar molecules decreases and the material becomes more dissociated and therefore less viscous. As temperature is reduced, the opposite occurs. Recent observations indicate that the non-polar phase also organizes, but at very low temperature, temperatures below 0°C. Further, asphalt is susceptible to oxidation which increases both the amount of polarity and the number of polar sites present among asphalt molecules. This further contributes to the ability of an asphalt to organize, but again varies from one asphalt to another.

It is important here to point out that the variations in behavioral characteristics of asphalts must be measurable. And again the objective of the SHRP program is to elucidate methods which can distinguish among asphalts and eventually reduce these methods to highway laboratory practice. While the quantitation of all important aspects of the model has not been completed, it is interesting to speculate on how the variations in chemical properties may be reflected in the pavement performance.

3.0 SPECULATION ON RELATIONSHIP OF CHEMISTRY TO PAVEMENT PERFORMANCE

3.1 General Comments

While it is unusual to describe performance in terms of failure, nevertheless it is instructive to do so here since it is generally understood that all pavements will eventually fail unless they are rebuilt periodically. Performance must be defined as sufficient time to failure or to reconstruction to justify the use of any particular methodology and any given set of materials. Sufficient service life is determined by cost of construction, traffic density, harshness of the environment, soil (support) conditions, and numerous other factors. The determination of acceptable service life is not the subject of this work. However, service lifetimes of a few months to a few years, which are experienced all too frequently, are unacceptable, whereas 10 to 20 years of service gives more acceptable life cycle costs. Neither is methodology the subject of this work, so it will be assumed that construction methodology is both consistent and adequate. The focus will be upon variations in the quality of construction materials.

The significant failure modes in asphalt pavement that may be related to materials are generally agreed to be

1. Permanent deformation
2. Rutting
3. Fatigue cracking
4. Low temperature cracking
5. Moisture damage
6. Total loss of adhesion

Some speculations on the relationships of these failure modes to the chemical properties of asphalts are given in the sections following the section on aging.

3.2 Aging

Aging is often included in the above list, but aging is actually a conditioning step which may be beneficial or detrimental. It may be detrimental when excessive hardening or stiffening is observed in an already adequate pavement. On the other hand, aging may be beneficial when a soft mixture hardens into an adequate pavement. A simplified view of performance in terms of mechanical properties is that a pavement may be too soft and therefore rut and deform, or may be too stiff and brittle and therefore subject to cracking, either under traffic load or under thermal stress. Figure 5 illustrates these points schematically and also includes the effects of temperature, time, and oxidation.

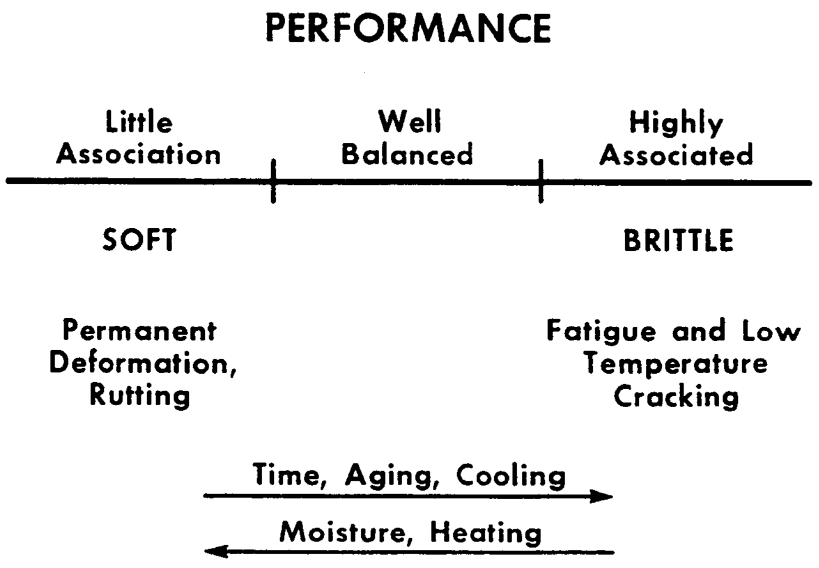


Figure 5

Oxidation, or oxidative hardening, imparts permanent hardening in asphalt while the hardening from reduced temperature and from molecular organization are reversible. That is, as an asphalt cement oxidizes, whether in bulk or in a mixture, the cement becomes and stays stiffer at any given set of conditions. However, warming a cold asphalt in the absence of any other effects will soften it to its original value and heating a cement to an elevated temperature such as a mix-plant temperature will reverse the effects of organizational hardening.

It is important to note that hardening resulting from molecular organization can be reversed periodically by recycling pavement. However, the recycling process removes only the organizational hardening, but since pavement suffers oxidative hardening also, this portion is not removed during the recycled process.

The events that lead to aging in a pavement are very slow because the driving forces for orientation (dipole of each molecule) are small and the whole medium is quite viscous at road service temperature. Nonetheless, slowly the molecules will shuffle about and eventually find the best orientation, known as the thermodynamic stable state or equilibrium, and in so orienting themselves become a better packed and bound together system. Aggregates, no doubt, have a distinct effect on this orientation but also differ in their ability to cause orientation. The result is an increasingly stiffer (more rigid) material until thermodynamic equilibrium is achieved.

In a roadway, achievement of thermodynamic equilibrium is a moving target! There are constant changes in composition which result from oxidation of asphalt. During oxidation polarity changes, hence, the "best packing" changes. Further, temperature changes constantly in pavement and thermodynamic equilibrium varies with temperature. Also, traffic tends to disorient molecular species, especially under heavy traffic loads and this further effects achievement of thermodynamic equilibrium. It is not clear whether traffic loads speed up orientation by providing additional energy for molecules to move or if orientation is slowed by keeping the system "stirred."

Oxidative aging has one interesting and saving feature to it. While some asphalts, such as asphalt G, may oxidize and accommodate their own oxidation products without major changes in viscosity, other asphalts do show substantial increases in viscosity upon oxidation. As shown in Figure 4 earlier, virtually all asphalts eventually quench their own oxidation and in so doing quench their own increase in viscosity as a result of oxidation. Also, as was noted earlier in Figure 4, this phenomenon varies with the maximum temperature of oxidation. Compositional variations among asphalts dictate the amount of viscosity increase that is observed as a result of oxidation at different temperatures. While the chemistry of quenching is not fully understood, it is a measurable chemical property of an asphalt and does relate to the viscoelastic properties, and therefore relates to the performance characteristics of the asphalt.

3.3 Speculation on the Relationship of Composition to Various Failure Modes

The measurable chemical properties that are believed to relate to the mechanical or structural strength of a pavement are several. Again from the model, it is believed that asphalt is a set of "hardcore" agglomerates (structured units) that consist of polars dispersed in a less polar to nonpolar phase. The result is a material which has an elastic behavior as a result of the network formed by the polar molecules, but it is also a material with a viscous behavior that can flow or creep because various parts of the network can move with respect to each other under prolonged stress. The relative contributions of the elastic and viscous behavior vary with composition.

3.3.1 Rutting and Permanent Deformation. Again, consider asphalts G, K, and M. Their SEC plots are shown in Figure 3. Asphalt G is largely the dispersing phase, not much elastic in character. One would expect it to be very compatible as is observed in oxidation and compatibility index studies. Asphalt G is somewhat insensitive to oxidation. It does not harden well which makes it a material that will rut or deform, especially at higher temperatures. It has little of the compositional feature of large molecular size to give it elasticity. Asphalt G is mostly the non-associated material which does tend to organize and harden at low temperature. Therefore G would be expected to be very stiff (susceptible to cracking) at very low temperature. In fact, these are observed behaviors for G in roadways. Contrast this with the SEC plot for asphalt K. Asphalt K has a large amount of agglomerated material and would be expected to have a greater elastic modulus at high temperature than asphalt G and not have the propensity to rut; and this is also what is observed. Asphalt M, with its truly high molecular weight, should and does behave somewhat like asphalt K at high temperature. Asphalt M is also a more homogeneous material than K or G. This feature should impart a relatively low temperature susceptibility to M, and this likewise is observed.

If heretofore the relationship of composition to performance properties has not been obvious, consider some recent results from cross blending of dispersed and dispersing phases of asphalts. These separated phases were generated by SEC. Major changes in properties were observed in an asphalt prepared by blending fractions of different asphalts. In one case, the dispersed phase of one asphalt was mixed with the dispersing phase of a second asphalt. The resulting asphalt was more than 1000 times the viscosity of either original material! The dispersing phase of the second asphalt is not a good "solvent" for the dispersed phase of the first. By appropriate cross blending, one can, within reason, achieve a wide variety of properties. Viscosities can be pushed up or down at will. Tan deltas (a measure of the relative contribution of the elastic and viscous moduli) can be varied significantly. This area is not yet fully understood and is under intensive study at the present time. Obviously, a clear understanding of this phenomenon is needed for specification purposes, since many asphalts are sold as mixtures from different crude oils.

3.3.2 Thermal and Fatigue Cracking. Cracking is another serious failure in roadways, and again can be related to binder composition. If the molecular network (agglomerate, micelle, colloid, or whatever term is preferred) becomes too rigid, the ability of an asphalt to deform elastically will be lost. Instead, the asphalt fractures and likely will be separated to a point that healing cannot occur. The constant working of very rigid matrix will eventually suffer fatigue and crack. The potential to crack is compounded by yet another organizational feature. At low temperature, the more neutral materials begin to organize into a more structured form as can be seen by differential scanning calorimetry (DSC). Now, the asphalt is quite brittle and subject to cracking under stress. To make matters worse, some cements shrink significantly at low temperature as a result of the organization of low polarity and nonpolar components. This aggravates cracking. Again, it varies with composition from one asphalt to another. All other things being equal, the more linear aliphatic materials show the most pronounced tendency to shrink with decreasing temperature. Hence, cracking at low temperature would be expected if shrinkage occurs, and is expected to be most closely related to the compositional feature of aliphatic/aromatic ratio when all other characteristics are equal. Aliphatic/aromatic ratios can be determined by NMR, but it is probably more practical to either measure shrinkage directly or predict it from very rapid DSC measurements.

3.3.3 Adhesion and Moisture Damage. Adhesion and moisture damage go together only to a point. While loss of adhesion certainly is a serious moisture damage problem, other forms of moisture damage may also occur. At this point, consider only adhesion. By definition, it must involve both asphalt and aggregate. While SHRP has commissioned studies to investigate the interaction of asphalts and aggregates, the examination of adhesion, per se, is not within the scope of the binder composition studies. Nevertheless, some interesting observations can be made considering only the binder.

Adhesion of components in asphalt to aggregate appears to be governed as much at the molecular level as at the inter-molecular level. Specific functional groups (molecular types) seem to be very important. Certainly overall polarity, that is, separation of charge within the organic molecules, promotes attraction of polar asphalt components to the also polar surface of aggregate. Several workers within the Strategic Highway Program have shown that aggregates vary quite substantially, and in some cases aggregate behavior varies with environment. Some aggregates have positive sites, some negative, and some show variation in polarity with moisture content, temperature, etc. For this discussion, aggregate will be considered to be simply a highly polar surface. Adhesion arises because of the interaction of the polars in asphalt with the polar surface of an aggregate. But polarity alone in asphalt may not be sufficient to achieve good adhesion in pavement because asphalt is affected by its environment. Asphalt has the capability of incorporating and transporting water. More on this in the moisture damage section. Absorption of water, like all other behavior, varies with asphalt composition including changes in composition as a result of oxidation. Incorporation of water is measurable as are the effects of the invasion of water into the asphalt aggregate mixtures. At the molecular level in asphalt it has been observed that basic nitrogen compounds (pyridines) tend to adhere to aggregate surfaces tenaciously. Carboxylic acid salts, while quite polar, tend to be removed from aggregate more easily, but this varies with the type of salt. Monovalent cation salts, such as sodium or potassium, of acids tend to be removed from aggregate quite easily. Calcium or other divalent salts of acids are much more resistant to the action of water. From a practical viewpoint, it would behoove the user to assure the acids in asphalts are not in the form of monovalent salts. The examples of pyridines and sodium salts are somewhat the extremes and it should be obvious that there is a spectrum of tenacity of adhesion among the organic molecules in asphalt. The evaluation of this spectrum is being done elsewhere within the program.

Moisture damage without apparent loss of adhesion is another common problem in pavement. Certainly, highway design is a major factor in reducing the availability of water, but to be clear, water is omnipresent in roadways, so the effects of moisture are unavoidable. For this discussion, consider that design is adequate to remove most water and also to resist its invasion in to pavement. Still, some water will come in contact with asphalt in pavement and will affect its performance when the water soaks into the concrete. Water, like aggregate, is a highly polar material and to some extent is transported into the asphalt by virtue of attraction of polar water molecules to polar asphalt components. Upon invasion into the asphalt, water will effect the mechanical properties, typically softening it. From a chemical viewpoint, the action of water is somewhat like the dilution of asphalt with a low molecular weight solvent. This typically results in reduced strength and further results in rutting or other deformation. Aged or oxidized asphalts, which have greater amounts of polars (oxidation products), tend to incorporate water to a greater extent than new asphalts. This would be expected from polarity considerations. The probability of moisture invasion, from a chemical viewpoint, increases with pavement age. But aged pavements are also harder than their counterpart new pavements, so the effects of moisture and oxidation are somewhat counter to each other. The combined effects are better measured in terms of the mechanical properties of the mix. As usual, the behavior varies with composition.

4.0 SUMMARY

The chemistry of petroleum asphalt at the molecular and intermolecular levels has been discussed. It is clear that hundreds of thousands of molecular species exist within any particular asphalt. The polarity among asphalt molecules varies widely and the physical properties are governed by the balance of polars and nonpolars components. Polars tend to associate while less polar and nonpolars cause dissociation. Several speculations on the effects of chemical composition on pavement performance have been offered. In general, the mechanical or structural properties of asphalt are related to the intermolecular structuring among the polars. These interactions may arise by involvement of any of numerous different chemical species. The exact nature of the chemical specie is less important than the distribution of charge within the specific molecule. Excessive structuring leads to brittle cements which tend to crack, while too little structuring leads to materials which deform under stress. Oxidation adds to age hardening and brittleness of asphalt cement by contributing to the structures zones within binder.

Finally, the word asphalt should be used in the same sense as the word glue. As much as there are significant differences among glues, e.g., carpenters glue, airplane glue and rubber cement perform very differently from each other, so are there tremendous differences among asphalts. The differences among asphalts are as great as the diversity of the crude oils used to manufacture them. The objective of developing new specifications to describe and achieve consistent behavior, and therefore consistent performance, is of high priority from the user's cost standpoint. But the user must also realize that the cost-effective supply line (crude oil) consists of a wide variety of materials, and there is little chance of significantly limiting the source of supply. That is, the selection of a very limited set of crude oils to manufacture asphalts is impossible. It is therefore obvious that achievement of consistent performance with asphalts frequently will require modification of materials that are produced today. A principal value of the composition studies is to develop an understanding of what compositional features are needed to produce material with the desired properties. Then this information can be used to select and/or modify asphalts to obtain binders that will perform in a cost-effective manner.

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