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Chemical Properties of Asphalts and Their Effects on Pavement Performance

TRANSPORTATION RESEARCH BOARD / NATIONAL RESEARCH COUNCIL

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Foreword

Asphalt has been and still is used to build and maintain most of the miles of American hard-surfaced roadways. All too often, those responsible for public purchase and use of enormous volumes of asphalt are taught to treat asphalt as a manufactured product, i.e., a product that is consistent within specification limits. Perhaps this is better said this way; the user is not taught how variable asphalt can be, even at the same specification grade level. This is quite understandable. The user typically has too many other concerns. Ideally, once asphalt meets specification, that should be the end of the user's concern.

The purpose of this Circular is to familiarize the asphalt user with the source of this "magical black glue," the variable chemistry of asphalt, why variable performance should be expected when asphalt is used in roadways and what is currently missing from the specification process. Several areas are identified where refinements in the specification process would improve the ability to classify asphalts by their expected performance.

This Circular summarizes more than 2,500 pages written during the past 20 years on the effects of fundamental chemistry on the rheological properties of asphalt. Clearly, it can not be comprehensive. It is designed as a document that can be read quickly to gain some familiarity with the events that led to the Strategic Highway Research Program (SHRP), the research during SHRP from 1987-93 and the research on asphalt composition that has been conducted up through 1998.

Finally, this Circular should be especially useful to civil engineering students who intend to work in some highway construction-related business. The more than 2,500 pages of original text would be overwhelming to read, somewhat like attempting to get a drink of water from the fire hose. This Circular is simply a small "drinking fountain" of this information.

Introduction: From Algae to Asphalt

Asphalt is the black adhesive that binds more than 90 percent of the 2 million miles of American, hard-surfaced roadways together. Around 30 million tons of asphalt are used to build and repair roadways in the United States every year. If 30 million tons is hard to imagine, think of it this way: 30 million tons per year is roughly equal to a rail tank carload per minute, every minute of the entire year.

SOURCE OF ASPHALT

Asphalt comes from the earth, where virtually all consumables are obtained. Asphalt is left over after refining crude oil. Crude oil is a naturally deposited organic material in the crust of the earth. It is formed principally from marine algae (a form of plant life) having been deposited underwater with silt (inorganic matter) anywhere from 1 million to 1 billion years ago. Deposits may be very deep (say 30,000 ft or more, approximately 9 km) or quite shallow (less than 5,000 ft, approximately 1.5 km). In a few cases, crude oil even seeps to the surface of the earth.

KEROGEN: THE FIRST STEP

The organic material first converts into what is commonly known as kerogen, a consolidated organic-mineral matrix that has little or no solubility in organic solvents. It must first be “pressure cooked” to be converted into petroleum. The deposit temperature will increase with depth of burial and it follows that millions of years of “pressure cooking” will produce different materials at different “pressure cooking” temperatures. Obviously the length of time the petroleum “pressure cooks” during its formation will also affect its final properties. The proper term for “pressure cook” is *diagenesis* of organic matter (dead algae) into petroleum.

During the process of forming petroleum, the organic liquid migrates through the rock from its original deposit, known as source rock, to another rock area that is porous and serves as a reservoir. This migration is somewhat equivalent to filtering the crude oil at the molecular level. That is, not all fractions of oil will move at the same speed, so what ends up in the reservoir is further altered compared to the organic liquid formed at the source rock. Again, the composition and hence the properties of the crude oil will vary with different conditions of migration.

As stated above algae is the principal source of organic carbon that forms petroleum, but it is not the only source. Some higher plant forms also are known to have been buried (usually in fresh water) and have undergone diagenesis to petroleum. Here the plant cuticle (water-resistant layer on leaves) is a waxy substance that often survives to become part of the crude oil. Hence, high-wax crudes are another common variation in the composition of crude oil. Tissot and Welte (1978) discuss petroleum formation in considerable detail for those further interested in this subject. Incidentally, not all kerogens have been converted to petroleum yet. The Green River shale formation in the three-corner area of Colorado, Wyoming, and Utah is a giant-sized deposit of kerogen.

The crust of the earth is known to fracture from time to time (San Francisco is a good example of earth fracturing), and if a fracture invades a petroleum deposit, any one or more of oxygen (air), surface water, and bacteria may invade the petroleum formation. Bacteria have a selective appetite for certain fractions of crude oil and will further alter the composition.

CRUDE OILS

Crude oils (petroleum stocks) are produced from many types of geological formations, as described above, and are shipped by various methods to refineries. Refining of petroleum is the next step. A crude oil refinery is designed to separate high value and common products from petroleum.

Petrochemicals, gasoline, diesel and jet fuels, and lubrication (lube) stocks are the high-value refining products. For each of these products, the properties are similar regardless of the crude oil or the refinery process used to produce each item. In a sense, the leftovers, i.e., the residua (resids), or asphalts, are concentrated versions of the differences among crude oils. The portions that are alike among crude oils have been removed as high-value refinery products. Gary and Handwerk (1975) discuss refining in significant detail and clarity for those further interested in this subject.

The purpose of the above elementary view of petroleum formation and refining is to teach or remind the reader that crude oil resids (asphalts) should be expected to be substantially different from each other. The mere fact that any two or more resids are refinery-processed to the same viscosity, or to any other physical property similarity, does not make them alike or interchangeable with one another in all circumstances. Their chemical compositions, regardless of similar physical properties, do vary from one asphalt source to the next, hence their reactions and interactions with their surroundings (service environment) also will vary. Surroundings for asphalt in asphalt concrete (pavement) include large amounts of mineral aggregate, atmospheric oxygen, water, ultraviolet light, bacteria, and extreme fluctuations in temperature and traffic load. The relative effects of these vary, but at a minimum, all of these impinge upon and may affect the performance of this black glue in asphalt concrete roadways. Hence, any method that classifies asphalts by expected performance must consider these real-world conditions.

ASPHALT INTERCHANGEABILITY

Asphalt concrete construction requires a large portion of the \$40 billion or so spent annually for highway and bridge construction (*AASHTO Journal*, 1998), so it behooves the buyer (public) to ensure that asphalt purchased performs well.

Few, if any, in the public purchasing process can specify a given source of asphalt. In this context source means the geological formation for the crude oil used to produce asphalt and does not mean the commercial supplier. In reality, this asphalt may be supplied from any crude oil source by any refining method provided the asphalt meets a given specification. In a sense, all asphalts that meet any given specification are considered to be interchangeable, i.e., any one of them can be used in place of another. This is an excellent way to purchase asphalts provided they are genuinely interchangeable with respect to the intended use. The burden of proof that asphalts are truly interchangeable lies with the correctness and completeness of the specification. So cost-

effective use of highway funds requires that the buyer's specification distinguish asphalts into true performance groups. Without exception though, a more rigorous specification will raise the price of any commodity. So the obvious question arises: How rigorous must the specification be in order to be satisfactory for highway use? Said another way, how interchangeable must one asphalt be with the next? The current level of interchangeability, as judged by specification, is examined in much of the remainder of this text. Before proceeding to attempt to answer the above questions, the next chapter presents an abbreviated history of the supply line and associated specifications for public purchase of asphalt. In other words, how did we get to the specifications we have today?

Asphalt Supply Line History

This chapter is a commentary on the history of the development of purchase specifications. It is presented in terms of major historical events experienced by suppliers (refiners). All too often, the importance of the effect of these events on roadway performance went unnoticed for a time by users. This discussion is intended to lead the reader through a series of steps to the current status in the development of a truly blind-to-source performance specification. Finally, it is intended to raise attention to performance measurables and related parameters that are not yet part of the binder purchase specification.

PRE-1970s

Historically, the asphalt user community enjoyed the luxury of relatively consistent supplies of cheap asphalt until the early 1970s. Prior to this time, the specifications imposed on asphalts were little more than quality control verifications of the refiners' products. In a majority of cases, the user became familiar with local or regional asphalt supplies and learned to build roadways with available asphalts that were supplied rather consistently from the same crude oil source(s). This amounted to asphalt of consistent composition, i.e., the same crude oils were used consistently by certain refiners to produce asphalt used in any given area. However, asphalts from some crudes were known to give good performance while others were poor. Some in the highway engineering community were aware that the specifications did not relate to performance. The literature of the time contains many technical papers dealing with variations in chemical and physical properties of asphalts of the same grade. This literature is also clear that variations in asphalt chemistry were known to have differential effects on performance.

However, it was largely ignored that asphalts graded as, for example, AC-20, or as 85/100 pen, were substantially different from each other in different regions of the United States where different crude oils were used for asphalt production. The viscosity grade specification of AC-20 or AC-10 or the penetration grade 85/100 pen, etc., did not mean that asphalt of any one of these grades was interchangeable with asphalt of the same grade from a different crude oil source with respect to performance in roadways. The penetration grading systems simply assured that any given asphalt met a few physical property requirements. The viscosity grading system that displaced penetration grading was a significant improvement. It was designed to classify the high and intermediate temperature properties of asphalt so that asphalts selected for any given application were more alike than those selected by penetration grading. At the time it was realized that low-service temperature properties should be evaluated, but the technology for meaningful determination of low-temperature properties was not developed. The effects of inevitable long-term oxidative age hardening of asphalt in pavement were ignored as were the differential effects of water on asphalts of different composition. Many of the properties of asphalt that affected its performance reflected the nature of the crude oil from which it was produced, and large variations in performance were observed. Anderson et al. (1983) and Plummer and Zimmerman (1984) clarified this

observation quite well. These authors also pointed out that the gradual change from penetration to viscosity grading further contributed to a lack of blind-to-source predictability. They probably meant that employment of two somewhat unrelated specification systems created confusion. The two systems measured properties that were somewhat unrelated to each other and neither was very well related to performance measurables. Again, both systems failed to measure critical performance characteristics such as stiffness at low road-service temperatures, long-term aging, and moisture sensitivity. Yet, many, such as Schweyer and Burns (1978), were concerned with low-temperature properties.

The penetration and AC specifications were not at all blind-to-source. In most cases they did not need to be because refiners supplied asphalts rather consistently from specific oil fields. In reality, for the most part, a source specificity existed, but it was market driven. Asphalts were relatively consistent from batch to batch because of relatively consistent crude oil supplies or because of refiners' blending procedures. Reliability was *not* driven by the formal purchase specification.

There are notable exceptions to the above generalization. In some circumstances, the California Department of Transportation has blended resids from San Joaquin Valley, California, with coastal crudes. The coastal asphalts age-hardened too rapidly during service while the other hardened so slowly that its setting characteristics were poor. Fortunately, blends of these two materials had more desirable properties than either asphalt alone. However, this situation was experience-based and specific to two known crude sources. It definitely was not blind-to-source. Neither asphalt was interchangeable with a third, fourth, etc., asphalt with respect to performance.

In a somewhat different case, there is little doubt that J. J. Heithaus (1960) developed the Heithaus compatibility test at the Shell Wood River, Illinois, refinery to assure that blended asphalts produced at Wood River were somewhat consistent to the users. However, there was little choice since the Wood River refinery is fed by many supply lines (different crude oil sources). This is an early example of blinding the source, i.e., producing a consistent product regardless of the crude oil used, but it was self-imposed by the refiner and viewed by the refiner as necessary to produce a consistent asphalt supply. It was not part of the buyers' specification. In summary, to this point in history, there was essentially no requirement to purchase asphalts on a truly blind-to-source basis (unless the refiner chose to make it such) but neither was truly blind-to-source an important issue.

1970s

Then came 1973. Oil embargo! Scrambled supplies and rapidly rising crude oil prices were followed by sharp price differentials between light and heavy crude oils. Cokers that convert asphalt (resids) from cheaper heavy crudes into more valuable distillable fuel and solid coke (solid fuel) soon competed for large amounts of resids (asphalts). With that event, asphalt prices rose sharply. Further, cokers are very capital-intensive processing units, so once installed by a refinery (or separate company), the asphalt supply line dries up rather permanently. By the late 1970s, increased petroleum prices and cokers set the price of asphalt several times higher than any time before 1973. In addition, the historical crude oil source reliability was vanishing and rude surprises in performance became more and more commonplace in roadways. Still, the asphalts on the market at that time met the

specification requirements. The situation was bleak: prices were greatly increased and predictability greatly diminished. Something had to be done.

1980s AND NOW

Something was done. At first, in the early 1980s, it was called Strategic Transportation Research Study. Later came the Strategic Highway Research Program (SHRP). A principal mission was to develop a robust, somewhat forgiving, and blind-to-source performance-sensitive purchase specification for roadway asphalts. One of the selling points for SHRP was the notion that refiners must be removing the “stickies” and “goodies” from asphalt (Kennedy, 1989). Just what “stickies” and “goodies” are never was defined, nor was there any consideration of where they would otherwise have gone. Sticky materials certainly don’t go into petrochemicals, fuels, or lube stocks. Asphalt is the only refinery product that can tolerate sticky components. The simple fact is that some crude oils have resids (i.e., undistillable materials) that simply do not adhere satisfactorily to many aggregates, i.e., are not “sticky.” But then, why was this even a subject of concern? The historical binder purchase specifications never did include the word “sticky” or any other term to set a minimum requirement for adhesion of asphalt to aggregate. Neither does the current Superpave performance grading (PG) specification for asphalt cements call for any measure of adhesive quality. Almost certainly a properly designed mixture test would find differences of adhesion, but mixture tests are not part of any binder specification. In any event, the fear that refiners were somehow altering asphalt to the disadvantage of users did stimulate intensive research and development of specifications based on new criteria.

Clearly, some progress was made. A PG specification for public purchase of asphalts was developed and as of 1998 has provisional status. Tank car loads of asphalts (bulk liquids) which are graded alike no doubt are essentially interchangeable with respect to many physical properties over the entire roadway service temperature range. Further, this grading system includes an oxidative aging step so there is some assurance that asphalts graded alike will have similar aging sensitivities. This, the Superpave binder specification, represents a major advance in the purchasing system.

Asphalt used in roadways does not experience the same conditions as bulk (liquid) asphalt. Asphalt in asphalt concrete exists as very thin layers (variable thickness, but always very thin layers), exposed to atmospheric oxygen all the time and to water much of the time. Marek and Herrin (1968) showed that the stiffness of asphalt changes markedly in thin films. More recent works by Scholz and Brown (1996) and by Huang et al. (1998a and b) have shown that the change in stiffness from bulk to thin film is not predictable from any part of the PG specification. For prediction of physical properties, the composition of the asphalt must be considered once the asphalt film is less than 50 microns. At less than 50 microns, even with the same aggregate, some asphalts stiffen while others soften. It is obvious that the asphalt concrete mix properties may be different even though the same PG grade of asphalt was used. The compositional factors that cause this phenomenon are being studied at the present time.

Oxidation occurs and this changes both in-place stiffness and moisture sensitivity. Water goes in and out of pavement and alters the concrete properties unpredictably as shown, for example, by Peters and Lukens (1995) and Thomas et al. (1996). These authors report striking differences between conventional and shale oil-modified asphalt

with respect to moisture damage in field observations. Again, the chemical nature of the crude oil used to produce the asphalt strongly affects the in-service behavior, even for asphalts of the same specification grade.

Asphalts in pavements that exist as thin films exposed to aggregate, water, and oxygen are the real service conditions in which asphalt should have predictable performance. Yet, the assurance of interchangeability provided by the Superpave binder specification is only for bulk asphalt and not for asphalt in anything closely resembling roadway service conditions. There is no assurance that asphalts graded alike by the PG system will still have the same stiffness as each other as thin films. The PG system gives no assurance that asphalts graded alike will have the same stiffness or adhesive quality when water is present in pavement. There is no assurance that oxidation will not cause major differences in water sensitivity resulting in unpredictable stiffness after a few years. Oxidation very well may cause differential embrittlement (because of the influence of aggregate on oxidized asphalt) after a few years in service. The intent of developing a new specification was to classify asphalts by their expected roadway performance, but the above real-world environments are largely ignored in the PG system. Further, there is very little information on the effects of the above environments based on actual field trials where the asphalt source is the principal variable. The current Superpave binder PG system does not consider all common environmental factors and offers only some assistance in selecting appropriate asphalts to perform predictably in the above described real world roadway environments.

The Superpave PG system is a major improvement over any previous grading system, but modifications still are needed if true in-service performance predictability is to be achieved. This dependence of performance on composition has been shown clearly in older field studies such as the Zaca-Wigmore study by Hveem et al. (1959) and Zube and Skog (1969), and the Elk County study by Kandhal (1978). Variations in asphalt composition (i.e., variations in crude oil source) can cause major differences in performance.

There is a complicating factor. One asphalt (from a single source) may be used with three or four different aggregates, each of which affects the asphalt differently, hence the performances will vary. To be clear, this problem can not be solved by an “improved” binder specification. The important point to be realized here, with respect to specifications, is that two (or more) asphalts of the same PG may perform differently under “identical” conditions, hence they are not truly interchangeable. This sort of problem can be reduced in magnitude with an “improved” specification.

The effects of the above described roadway service situations, and how the chemistry of asphalt affects its physical properties (i.e., performance properties) in the roadway environment, can be better understood if the pertinent organic chemistry is understood first. For those not well versed in organic chemistry, the following chapter is a brief introduction of the widely variable chemistry of crude oil residua.

Chemistry of Petroleum Asphalts

It is convenient to divide the chemistry of petroleum asphalt into two parts. The first part is the chemistry at the molecular level. This part describes chemical structures that are thermally stable to temperatures that are well above asphalt concrete mixing and lay-down temperatures. The second part is the chemistry of interaction among the wide variety of molecular species in asphalt. Much of the physical nature of asphalt can best be described and explained in terms of an assembly, or matrix, of moderate-sized molecular species (building blocks) into large multimolecular units within the asphalt. These multimolecular assemblies behave somewhat like high molecular weight materials. Larger molecular assemblies behave as though they were entangled and do not pass each other readily, hence they exhibit viscous flow and impart some elastic nature.

Numerous techniques exist to examine asphalt at both the molecular and multimolecular levels. In the following subsection the chemistry of asphalt at the molecular level is presented without reference to experimental methods. This is to illustrate the types of "building blocks" (molecular pieces) that are present in asphalt. The chemistry of interaction among asphalt molecules to form multimolecular assemblies is presented in the second subsection with reference to some of the techniques that have been developed for or applied to asphalt in more recent years.

ASPHALT CHEMISTRY AT THE MOLECULAR LEVEL

Extensive research on petroleum composition at the molecular level has been done by researchers for many years. Much of this work was sponsored by the American Petroleum Institute and the research was especially intensive during the 20 years or so following World War II. At this point, the chemistry of molecular species in petroleum is textbook material and can be found, with primary references, in many introductory or intermediate organic chemistry textbooks. One example is the organic chemistry text by March (1968), but to be clear, there are numerous equally good texts.

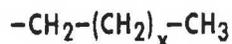
Numerous types of organic compounds are found in petroleum asphalt. The term organic compound means a molecular species made up of at least one carbon atom and at least one other atom except carbon dioxide and mineral carbonates. Examples of the most common types of organic molecules in asphalt, together with a few reactions and descriptions of the physical characteristics imparted by various molecular types, are the subject of this subsection. For those not versed in organic chemistry, each of the following partial molecular structures that are common in asphalt show specific arrangements of atoms represented by their respective chemical symbols. The chemical symbols are as follows. Carbon is represented by C; hydrogen is H; nitrogen is N; sulfur is S; oxygen is O; vanadium is V; nickel is Ni; and iron is Fe (the Latin name for iron is ferrium hence its symbol is Fe). Molecular weight is simply the sum of all atomic weights of all atoms in a molecule. Atomic weights in atomic mass units (amu), to the closest whole number, are: C = 12, H = 1, O = 16, N = 14, S = 32, V = 51, Ni = 59, and Fe = 56. So a molecule of composition $C_{10}H_{22}SO$ has a molecular weight of 190, i.e., 10 carbons at 12 amu each, etc. The single lines between atoms represent covalent, or thermally

stable, chemical bonds. Two lines represent a double bond. Each element is unique in the number of bonding sites. Hydrogen forms one bond, carbon four bonds, nitrogen three or five bonds, oxygen two bonds, sulfur forms two, four or six bonds (depending upon its contact with oxygen), and metals have variable numbers of bonding levels, again depending upon the oxidation state. Covalent bonds are typically formed by the contribution, or sharing, of one electron from each of the bonded atoms. In most of the following molecular structure illustrations, there is (are) one (or two) lines, or bond(s), shown at the end(s) of the partial molecular structure. This indicates that only a portion of the molecule (a molecular fragment) is shown, and that there is more of the molecule that continues beyond that bonding site.

Typical Molecular Pieces (Fragments) in Virgin Asphalt

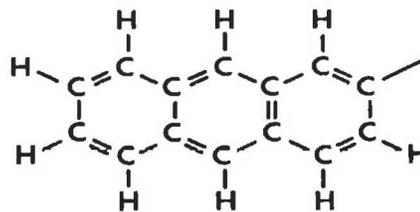
At the molecular level, much of the total mass of neat (tank) asphalt is a mixture of a wide variety of high-boiling hydrocarbons, i.e., compounds containing hydrogen and carbon. Some are aliphatic (oily or waxy materials), some are aromatic (more like air-blown asphalts), and some molecules have both aliphatic and aromatic carbon. It is emphasized here that only fragments of molecules are shown. The various fragments may be found assembled into thousands of combinations to make up actual whole molecules, i.e., any of the various fragments shown hereafter may each be part of larger molecules in asphalt.

Reactions and interactions of molecules take place at specific points (sites) in molecules, and it is these sites that are shown in the following structures. Examples of such molecular fragments are shown in Structures 1 (aliphatic type) and 2 (aromatic type). Aliphatics have no double bonds whereas aromatics are rigid, six carbon rings with alternating double bonds. Further, aromatic rings are planar (flat). This allows aromatic ring compounds to “stack” efficiently. Aliphatics have bond angles of approximately 109° (i.e., tetrahedral) so aliphatic chains are sort of a “zigzag” shape. Further, aliphatics are flexible, not rigid like aromatics, and do not “stack” as well as aromatics.



x Typically = 15 or More Carbons

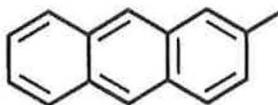
STRUCTURE 1 Aliphatic type hydrocarbon.



STRUCTURE 2 Aromatic type hydrocarbon.

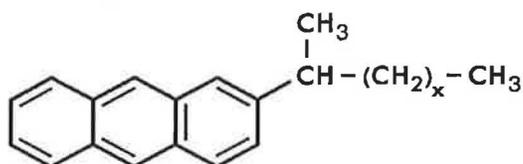
Structure 2 is more commonly represented by Structure 3. Both Structures 1 and 3 are only representative molecular fragments of larger molecules that make up asphalts. Each whole molecule would be much larger so as to have high enough molecular weight to relatively be nonvolatile. In general, boiling points increase with increases in molecular weight, i.e., volatility generally decreases as molecular weight increases.

Structure 1 is shown as a straight chain of carbon atoms, but typically in asphalt there are numerous combinations of aliphatic carbon chains that have one or more branches.



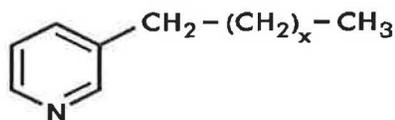
STRUCTURE 3 Equivalent to Structure 2.

Structure 4 shows a molecule that is a mixture of aliphatic and aromatic carbon, and has a branched aliphatic structure.



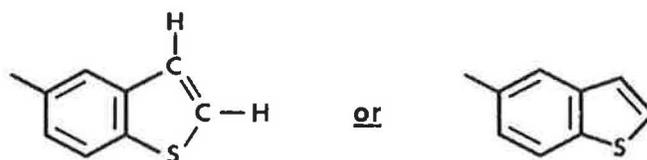
STRUCTURE 4 Molecule with aromatic and aliphatic portions.

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 substituted pyridine is shown in Structure 5.



STRUCTURE 5 Aliphatic substituted pyridine.

Sulfur in the form of an aromatic compound, 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 two representations of identical molecular fragments.



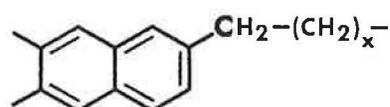
STRUCTURE 6 A benzothiophene.

Both sulfur and nitrogen may appear in any of a variety of sites within molecules typical of petroleum. Hence, it is easy to see that tens or even hundreds 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 practical to classify the chemistry of asphalt in terms of the molecular types shown above.

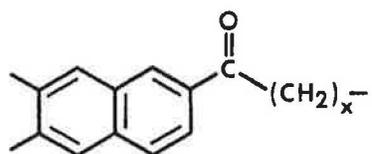
Oxidation to Form New Molecules

Certain types of carbon in asphalt are particularly susceptible to oxidation. An aliphatic carbon next to an aromatic ring is known as a benzyl carbon and is the molecular site where carbon in asphalt is most readily oxidized. Structure 7 is an example of a molecular fragment showing a benzyl carbon in bold type (adjacent to the aromatic ring).



STRUCTURE 7 Benzyl carbon highlighted.

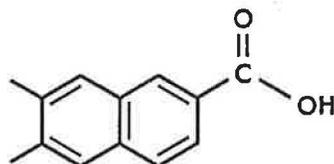
Sites such as these oxidize to form ketones as shown in Structure 8.



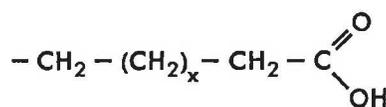
STRUCTURE 8 Ketone at the benzyl carbon.

Oxidation of asphalt requires reactions of gaseous oxygen (from air) with a viscous liquid (asphalt), so increases in surface area and temperature both promote oxidation. Thin films of asphalt (as found in asphalt concrete) oxidize much faster than the bulk liquid at any given temperature.

More severe oxidation may result in formation of carboxylic acids such as shown in Structures 9a and 9b. Aliphatic carboxylic acids are also naturally occurring materials in crude oils.



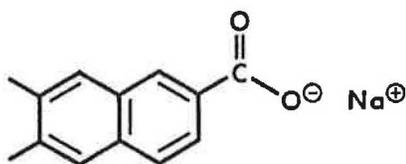
(a)



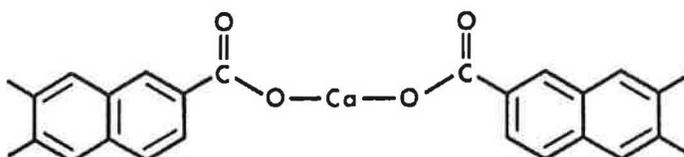
(b)

**STRUCTURE 9 (a) Aromatic carboxylic acid; and
(b) Aliphatic carboxylic acid.**

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 such as soda ash or lye to form sodium salts, or by using lime to form calcium salts. For the curious, the Latin name for sodium is natrium, hence the symbol Na.

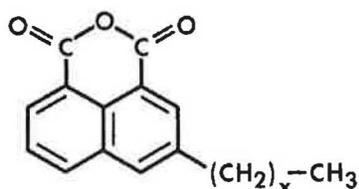


STRUCTURE 10 Sodium salt of aromatic, carboxylic acid.



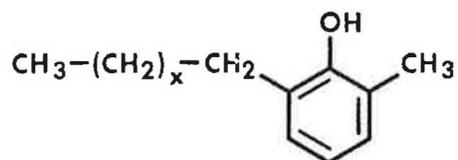
STRUCTURE 11 Calcium salt of aromatic carboxylic acid.

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. It is rare to find an anhydride in asphalt formed from carboxylic acid groups on two separate molecules, but it is not unusual to find cyclic anhydrides such as the type shown in Structure 12.



STRUCTURE 12 Cyclic carboxylic acid anhydride.

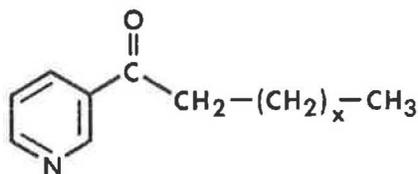
Another type of oxygen-containing molecule that may be present in asphalt is a class known as phenols where oxygen is attached directly to an aromatic ring. This class is illustrated by Structure 13.



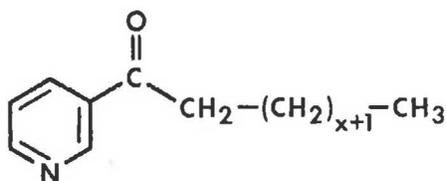
STRUCTURE 13 Aliphatic substituted phenol.

Again, numerous combinations of the same atoms (i.e., isomers) containing the fundamental phenol unit may exist.

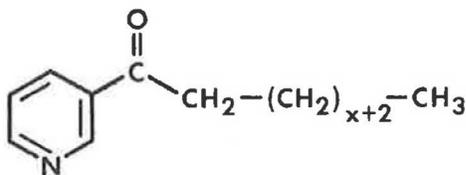
In addition to isomeric combinations of all molecular types shown above, homologs of each also typically exist. An example of a homologous series is shown by Structures 14, 15, and 16.



STRUCTURE 14 First of a homologous series (Structures 14, 15, and 16).



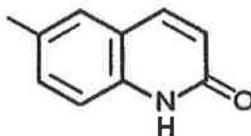
STRUCTURE 15 Second of a homologous series (Structures 14, 15, and 16).



STRUCTURE 16 Third of a homologous series (Structures 14, 15, and 16).
Each structure has one more aliphatic carbon than previous molecule.

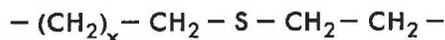
In the above case, each varies only by one aliphatic carbon. However, each is a unique molecular fragment, although the chemical and physical properties of these homologs will be quite similar.

Another important class of compounds typically found in aged asphalts is quinolones that contain both oxygen and nitrogen. An example is shown in Structure 17.

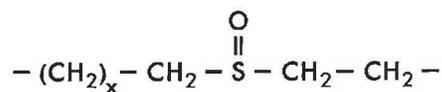


STRUCTURE 17 A quinolone.

Organic sulfides (sulfur compounds) are common in tank asphalt and are quite susceptible to oxidation. These typically oxidize to form sulfoxides. A sulfide, which is the sulfoxide-forming molecular site, is shown in Structure 18, and the sulfoxide that results from oxidation is shown in Structure 19.



STRUCTURE 18 Aliphatic sulfide.

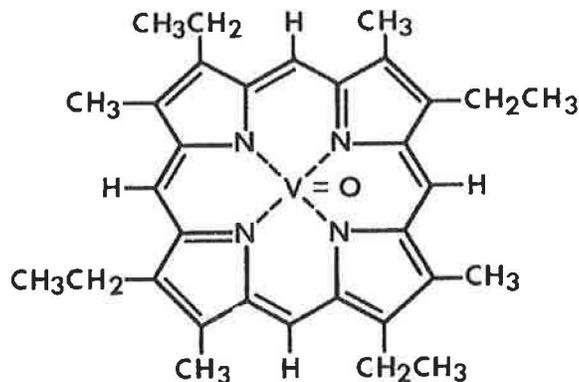


STRUCTURE 19 Aliphatic sulfoxide.

Metals

There are also metals present in asphalts, again in varying amounts and distributions. The most common metals are vanadium, nickel, and iron although trace amounts of other metals may also be present. Typically metals are present as organo-metallic materials, specifically as porphyrins, which are planar. Structure 20 is an example of a porphyrin found in asphalt. Porphyrins, the basic ring structure of chlorophyll, are extremely stable and survive millions of years of “pressure cooking” in the kerogen, petroleum source rock, and reservoir rock.

The distribution of metals in petroleum, usually present in parts-per-million quantities, is characteristic of each crude oil source. That is, each crude oil has specific amounts of specific metals, so an accurate metals analysis is essentially a “fingerprint” of a specific crude oil.



STRUCTURE 20 A porphyrin.

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

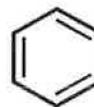
Polarity

Polarity most easily can be envisioned as an asymmetric distribution of charge within a molecule or molecular fragment. All of the naturally occurring heteroatoms, nitrogen, sulfur, oxygen, and metals contribute to polarity, or asymmetric charge distribution,

within these molecules. Likewise, oxidation products formed upon aging are polar and further contribute to the polarity of the whole asphalt. An example of polarity can be seen by examining benzene, a symmetrical hydrocarbon, and its nitrogen-containing analog, pyridine. The dipole moment, a measure of charge separation within a molecule, of pyridine (C_5H_5N) is 2.19 Debye units (in the gas phase) whereas the dipole moment of benzene (C_6H_6) is zero. These molecules are shown in Structures 21 and 22, respectively.



STRUCTURE 21 Pyridine.

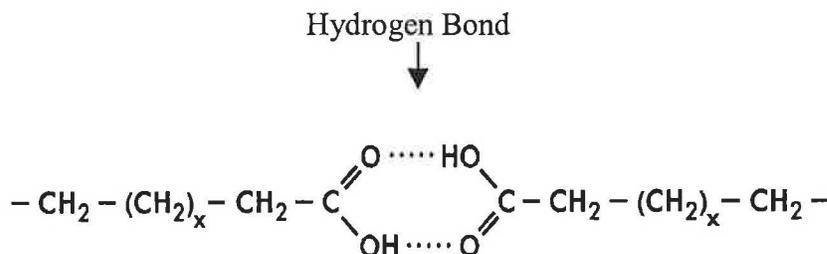


STRUCTURE 22 Benzene.

The effect of polarity can be seen easily using this example. The molecular weights of benzene and pyridine are very similar at 78 amu and 79 amu, respectively. Further, they are the same structural type, i.e., both are planar rings. Yet, the atmospheric boiling point of the polar pyridine is $115.5^{\circ}C$ whereas benzene has an atmospheric boiling point of $80.1^{\circ}C$. It simply takes more energy to separate polar molecules than to separate non-polar molecules of the same molecular size. The attraction of one pyridine molecule for another in the liquid state is greater than one benzene molecule for another. This type of attraction of polar molecules for each other is common in asphalt.

Polarity also exists in all other heteroatom-containing species. Polarity is important in asphalt because it tends to cause molecules to associate, or self-assemble, themselves into preferred orientations. While Structure 21 shows a partial separation of charge, it should be noted that this represents an asymmetric distribution of electron density. The nitrogen in pyridine is more electronegative (attracts electron density more than carbon) than the other end of the molecule. The overall molecule is neutral (not charged like ionic species), but behaves as if it has a partial negative (δ^-) on the nitrogen end and partial positive (δ^+) elsewhere.

Another example of the effect of polarity is shown in Structure 23 where hydrogen, which is relatively positive, of one acid molecule is attracted to oxygen of the other acid. This type of association is known as hydrogen bonding and has been shown to exist in asphalt (Petersen, 1967; Barbour and Petersen, 1974). This is known as a dimer and essentially doubles the molecular weight of the acid.



STRUCTURE 23 Aliphatic, carboxylic acid dimer formed by hydrogen bonds.

Historically, self-assembled groups of many molecules have been referred to as formations of micelles, colloids, gels, etc. These terms have been “borrowed” from other disciplines and each has a specific meaning. None of these terms is strictly correct for describing the internal structure of asphalt. A more current understanding of molecular orientation within asphalts is given in the following subsection.

ASPHALT CHEMISTRY AT THE INTERMOLECULAR (MULTIMOLECULAR) LEVEL

Asphalt chemistry at the intermolecular (multimolecular) level can be defined as the process that changes physical properties of a material when two or more polar molecules interact with each other. At the intermolecular level, polar molecules including those in asphalt, have a tendency to attract each other and form clusters of molecules. This attraction of one polar molecule for another is a result of their asymmetric charge distributions, or dipoles. Figures 1a and b illustrate this schematically.

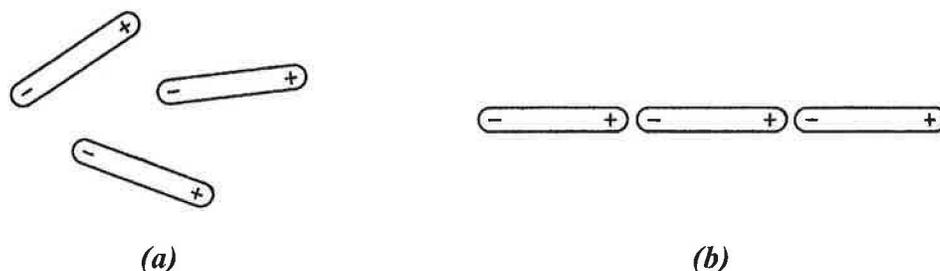


FIGURE 1 Schematic of polar molecule orientations: (a) Random polar molecules; and (b) Aligned polar molecules.

In Figure 1a the polar molecules are randomized, but in 1b the molecules are preferentially oriented, or self-assembled, with respect to each other. Figure 1b represents a more stable (lower energy) thermodynamic state. It is important to note here that it makes little difference which of the many polar molecular types shown earlier is involved. Any one of the many types of polar molecules may fill the molecular schematics shown in Figure 1a or b. Molecules with the greatest charge separation will be more driven to self-assemble than those that have a more symmetrical electron distribution. Molecules that have both acidic and basic sites present are referred to as amphoteric. These represent an extreme separation of charge, i.e., an electron poor acidic site and an electron rich basic site. As expected, amphoteric self-assemble very effectively and have a profound effect on viscosity enhancement. The amounts of amphoteric in asphalts have been shown to vary substantially [Branthaver et al., 1993 (SHRP-A-368)].

The primary requirement for self-assembly is that some amount 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 asphalt to the next so that no specific regularity exists

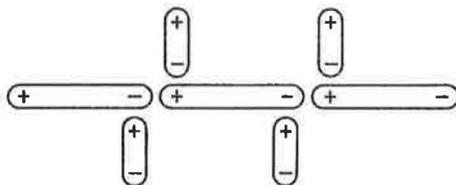


FIGURE 2 Schematic of 3-dimensionally assembled polar molecules.

within the organized zone.¹ During the organization (self-assembly) process, some amount of 3-dimensional intermolecular structure forms. The individual molecules have some preferred organizational structure, as indicated schematically in Figure 1b, compared to that shown in Figure 1a which represents 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, or bonds, range from about 3 to 20 Kcal/mole, while covalent bonds are much stronger. For comparison, carbon-carbon covalent bonds, those 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 (i.e., self-assembled) structure may be subject to rearrangement or may be scrambled either from physical stress or by raising its temperature. Both stress and increased temperature will disrupt (break) chemical bonds, but the electrostatic bonds are broken first because they are much weaker than covalent bonds. The low-energy bonds are quite easily broken and reformed compared to the covalent bonds. When covalent bonds are broken, totally new molecules are formed. At pavement service temperatures, virtually all covalent bonds survive intact except for those that experience oxidation. So if the self-assembled structure reorganizes, it does so without changing molecular composition. All of the molecular species remain unchanged as molecules, but simply rearranged with respect to each other. On the other hand, the physical properties will be different after reorganization of molecules. When the molecules are randomized, they can move about with respect to each other more easily than when they are in a more stable, organized arrangement. A simple example is crystals and liquids. Crystalline materials are more rigid than when they are in liquid form although melting a crystal into a liquid does not change the molecular composition. For example, water has the molecular formula H_2O , both as a liquid and as ice. The more highly organized crystalline structure has greater resistance to deformation. It follows then that 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. Kim and Branthaver (1996) have assigned numerical values to the intermolecular self-assembly tendency for all common organic compound types. Their method can predict the physical properties of an asphalt from ion-exchange chromatography composition data. This readily allows selection of additives to alter physical properties

¹ For simplicity, this schematic shows partial 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 schematic illustration.

predictably. Stiffening also depends upon external polar influences, in this case, those polar influences exerted by mineral aggregate. Aggregates all have polar surfaces and tend to promote self-assembly of asphalt polar molecules at their surfaces (Petersen et al., 1974; Petersen et al., 1976; Ensley, 1977).

Oxidation has a pronounced effect on the organized structure. As oxidation occurs, new polar sites are formed. The new polar sites are formed in addition to those in the virgin asphalt. So the propensity to self-associate, or "self-assemble" will increase and with this process, the stiffness increases. Also, the degree of association depends upon the number of sites and the magnitudes of the attractions. The stronger the attractions and the greater the number there are, the greater the driving force to self-assemble. However, because the propensity for polars to self-associate varies with asphalt source (i.e., asphalt chemistry), so does the rate of stiffening. Asphalts of the same grade, but from different crude oil sources, oxidize and embrittle at different rates. Clearly, a significant concern for any highway agency is to predict the length of time required for any given asphalt to oxidize to an unsatisfactory stiffness. While the limits of acceptable stiffness are experience-based, the cautious asphalt buyer still wants, or needs, to know how long to expect service from asphalt before it reaches some catastrophically high stiffness. A fast and accurate prediction of oxidative age hardening (preferably incorporated into a buyer's specifications) is the answer to this question, but the method to be used for this prediction must be based on realistic conditions of oxidation if any degree of in-service predictability is to be achieved.

The degree of association for tank and aged asphalt varies from one asphalt to another and several methods can be used to determine type and magnitude of association. One method developed during the Strategic Highway Research Program (SHRP) is size exclusion chromatography (SEC) [Branthaver et al., 1993 (SHRP-A-368)]. This is illustrated in Figure 3 which shows the results of three SEC experiments, all plotted on the same axes. Asphalts AAG-1, AAK-1, and AAM-1 (hereafter noted as G, K, and M) have very similar specification values. Asphalt G is classified as an AR-4000 and PG64-10, K is an AC-30 and PG64-22, and M is an AC-20 and PG64-16. 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 multimolecular size. It makes no difference whether the size-excluded entity is a very large single molecule or an associated group of smaller molecules. The experimental method employs a concentrated solution of each asphalt in toluene, a low boiling liquid with solvent properties similar to asphalt. Each asphalt was separated by SEC to cause the least possible disturbance to the naturally occurring self-assembled species.

The SEC separates asphalt by apparent molecular size so that if there are associated groups of molecules in the whole asphalt, they will persist in concentrated toluene solution and therefore be separated as associated materials by SEC. The SEC profiles shown in Figure 3 are plots of the concentration of asphalt in toluene on the y-axis versus time (which relates to the 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 (shortest elution time, i.e., time to come out of the SEC column), 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 molecular-size material in either G or K. Asphalt M, however, is more of a continuum. 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, a solvent that “breaks up” self-assembled molecules, it was discovered that the large species in K are comprised of assemblies of smaller molecules whereas in Asphalt M, the largest fraction (left of plot) is comprised of truly large molecules.

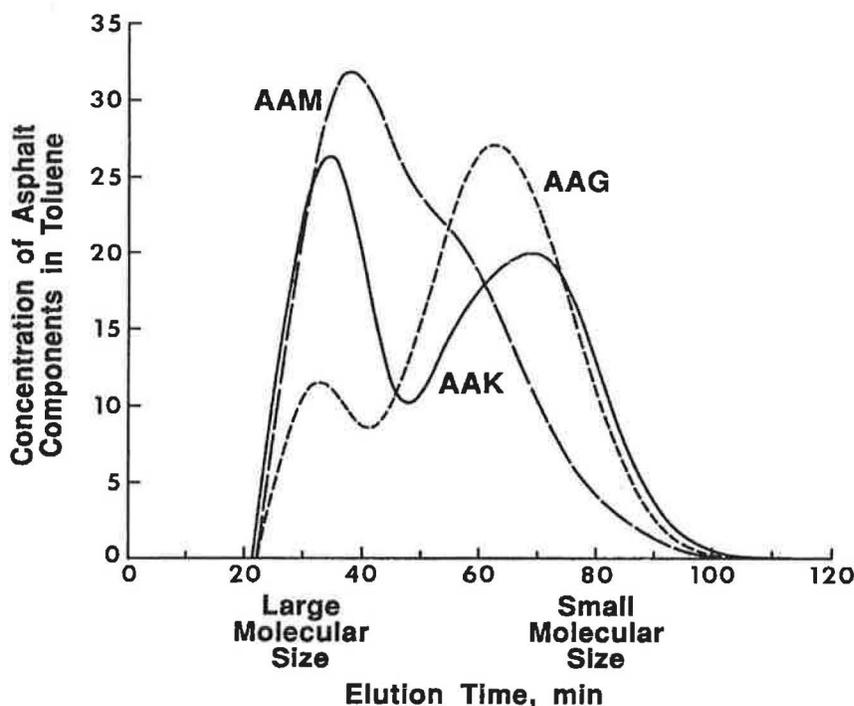


FIGURE 3 Size exclusion chromatogram of three asphalts.

The large molecules in M will not dissociate (break up) with shear or temperature increase whereas the large assemblages in K will dissociate. Hence, a change in temperature would be expected to affect K more than M (Branthaver et al., 1992; Branthaver et al., 1996). If nothing else is apparent, note that these three asphalts are very different from each other when examined by SEC. Superpave binder tests indicate that all three asphalts should have the same high-temperature properties (performance grade [PG] 64), but at 5 or 10°C above or below the grading temperature, the properties of G, K and M will be quite different, i.e., the “temperature susceptibilities”² near the PG upper limit are different. The compositional difference accounts for the difference in “temperature susceptibilities.” What is more important is that the buyer now has an analytical method to pick a desired “temperature susceptibility.” The information needed to pick the appropriate crude oil is available from SEC and molecular weight analyses, both of which are rapid methods.

² The term “temperature susceptibility” is used here for simplicity. Obviously an examination of any master curve shows there is a continuous change in viscosity (or stiffness) versus temperature. So in reality, one should define asphalt rheology in terms of a master curve which, in a sense, is a set of temperature susceptibilities. But the point should still be made clear that the effect of temperature on stiffness can be significantly different from one asphalt to another.

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 are less associated (to the right of the SEC plot). These are very small assemblies or are individual molecules, hence these smaller (and typically more neutral) materials are retained longer by the SEC column and elute (emerge from the SEC column) at longer times.

Ion exchange chromatography (IEC) and supercritical fluid chromatography (SFC) have both been used to show that the more neutral molecules vary substantially from one asphalt to another. In some cases, the IEC-separated neutrals solidify into crystalline-like material while other asphalts have neutrals that remain oily. Viscosities of the neutrals, while always much lower than the parent asphalt, do vary widely from one asphalt to the next [Branthaver et al., 1993 (SHRP-A-368)]. Asphalts having neutral materials that solidify (become very stiff) at ambient temperature can be expected to have poorer low-temperature performance properties than asphalts whose neutrals remain oily. The SFC, which fractionates neutral components by number of carbons, has shown that neutrals from asphalt vary widely in molecular weight and molecular weight distribution. To the extreme right of the SEC pattern are the smallest and most neutral materials, but SFC has shown clearly that these are not the same from one asphalt to the next. This less-associated material behaves as a "solvent," or dispersant, for the polar materials and will behave as an agent that disrupts assemblies of polar molecules. It will tend to reduce association of the polars.

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 relatively large fraction of small molecular species. This implies that the polar, strongly associated materials must be very tightly assembled in order to compensate for the large amount of "solvent-like" materials present in asphalt G. It would be expected that G would be able to accommodate additional amounts of polars with minor changes in its physical properties because the major part of G is solvent-like molecules. Hence, asphalt G should be able to tolerate significant oxidation before any major changes in physical properties occur, and this is what is observed for asphalt G. Asphalt K should be and is the reverse. Oxidation of K should increase the already predominant effect of the polars and, for example, raise its viscosity sharply with small amounts of oxidation. Experimental evidence from accelerated aging showed this to be the case. When oxidation of asphalts G and K was conducted in a 300 psi pressure-aging vessel (PAV) for 400 hours at 60°C (140°F), asphalt G had an aging index of 17 while K had an index of 23. Aging index is the ratio of asphalt viscosity after oxidation divided by original (unaged) viscosity.

When the oxidation temperature was raised to 113°C (235°F) and both were 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, more reactive, and both oxidized rapidly. Upon cooling both to 60°C to measure viscosity, asphalt G still has a large amount of "solvent-like" material which can accommodate its own oxidation products with little more change in viscosity than oxidation at the lower temperature. The newly formed polars in K strongly dominate its behavior. The newly formed polars in asphalt K associate very strongly and raise its 60°C viscosity quite substantially. Both asphalts are

oxidized to a greater extent at the higher temperature, but the effects of greater oxidation on physical properties are drastically different for G and K. The same trends have been observed with other asphalts [Branthaver et al., 1993 (SHRP-A-368)].

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 if predictability of aging is to be achieved. The present Superpave grading system oxidizes asphalts at 100°C or 110°C, well above known service temperatures. Hence, the Superpave binder oxidation may be too severe for some asphalts, but is still a good safeguard against asphalts that are excessively sensitive to oxidation. Said another way, an asphalt that passes a specific high temperature PG grade may actually oxidize and harden more slowly in a road than would be indicated by the Superpave specification, except that the Superpave test time is quite short (20 hours) which may reduce the amount of aging unrealistically. The down side of this “safeguard” is that the Superpave pressure-aging vessel (PAV) test could rule out asphalts that will perform quite well at actual pavement temperatures, although experience will be needed to show whether this is or is not likely. More on this in the next section.

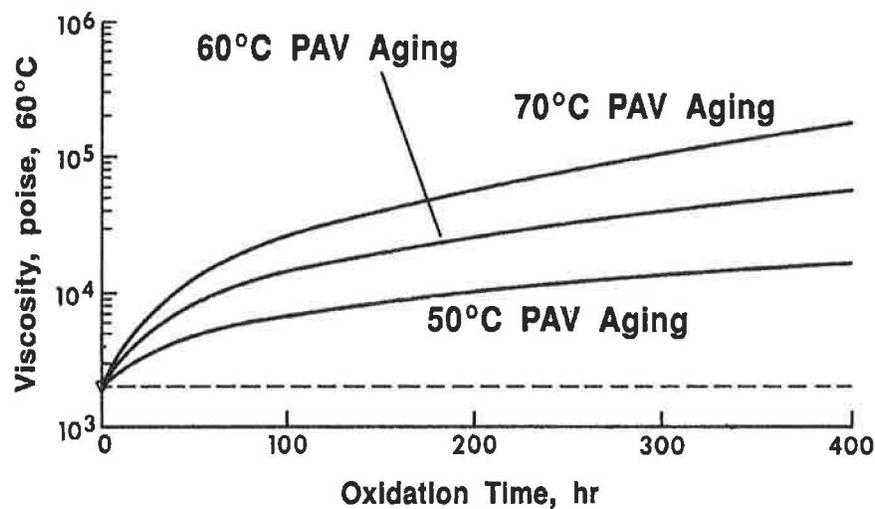


FIGURE 4 Effects of temperature on aging kinetics of an asphalt sensitive to molecular structuring.

OXIDATION

The subject of asphalt oxidation has received extensive attention for many years. Selected examples are Dorrence et al. (1974), Jennings et al. (1997), Kim et al. (1997), Petersen (1998), Petersen et al. (1975), Branthaver et al. (1993) (SHRP-A-368), Petersen et al. (1994) (SHRP-A-367), and Liu et al. (1998). The discussion that follows is only a cursory summary of asphalt oxidation together with the general effects that oxidation has on the physical properties of asphalt. As stated previously in the molecular chemistry

section, the principal species in asphalt that oxidize under road-service conditions are benzyl carbon and sulfidic sulfur, shown in Structures 7 and 18. Sulfidic sulfur, i.e., organic sulfide, oxidizes to sulfoxide and benzyl carbon oxidizes to benzyl ketone as shown in Structures 8 and 19. Organic sulfides generally oxidize faster than benzyl carbon, even at fairly high pavement temperatures (Petersen et al., 1993; Petersen, 1998). This means sulfides consume most of oxygen in the early stages of oxidation (until most of the sulfide is oxidized) and hence inhibit oxidation of benzyl carbon in the early life of a roadway. The differences in oxidation rates of sulfide versus benzyl carbon are important because sulfoxides generally cause minor increases in asphalt stiffness whereas ketones formed from oxidation of benzyl carbon typically cause major increases in stiffness (Petersen, 1998). This is more critical in asphalts that are close to saturation with polars, better known as low compatibility, or gel, asphalts. In a sense, if all else is equal, high levels of sulfidic sulfur in asphalt offer some protection against age hardening as oxidation proceeds.

Within roadway service temperatures, the oxidation rates of sulfide and benzyl carbon both increase with temperature, but the increase in oxidation rate of benzyl carbon, as temperature is increased, is typically larger than for sulfide. Hence, at 60°C pavement temperature, sulfides oxidize at a relatively higher rate than benzyl carbon. However, at 100°C or 110°C (the Superpave binder oxidation test temperatures) the oxidation rates of sulfide and benzyl carbon are much more similar, so relatively large amounts of ketones form during the test. Temperatures of 100-110° C are higher than road temperatures, hence the test is somewhat unrealistic. However, if oxidation were to be conducted at the preferred 60 or 70°C, the test would be so time-consuming it could not be used in commercial practice. Hence, there would be no measure of oxidation sensitivity. A more realistic simulation of oxidative aging that occurs in roadways is still needed and is still being sought. One promising new method of a more realistic test may come from the microwave aging studies first reported by Bishara and McReynolds (1996).

Clearly, access of oxygen to asphalt in a roadway should also control the oxidation rate. As seems obvious, the greater the compaction of asphalt concrete (i.e., lower voids), the poorer will be the access for oxygen. Hence, oxidation and the associated age hardening should decrease with greater compaction. Kemp and Predoehl (1981) showed this clearly in a systematic study in various California climates, but in the same study they also showed that the absolute high-service temperature is still the dominant factor in age-hardening.

CHEMICAL MODEL OF ASPHALT

The most current chemical model is built upon earlier models including that developed and refined during SHRP as well as improvements since SHRP [Petersen et al., 1994 (SHRP-A-367); Branthaver et al., 1993 (SHRP-A-368); Anderson et al., 1994 (SHRP-A-369); Anderson et al., 1996; Robertson et al., 1992]. In this case, model means a molecular and multimolecular structural description that leads to 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 revisit the production of asphalt. Petroleum

asphalt is typically a high boiling vacuum distillation residuum that is prepared from numerous different petroleum stocks. Some asphalts are produced by alternate methods but generally very similar portions of the crude oil end up as asphalt. The chemistry varies quite significantly from one asphalt to another and each reflects the nature of the crude oil used to prepare it at the refinery.

The most consistent model of petroleum asphalt is described 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 relatively non-polar portion of the asphalt. Calculations made from low-angle neutron scattering data by Sheu et al. (1992) and Storm et al. (1995), nuclear magnetic resonance data by Van der Hart (1989), and thermodynamic data by Ensley (1975) and Petersen et al. (1976) indicate that there are associations stable to temperatures above 90°C (194°F), but are consistently 40 or fewer molecules. Some have smaller assemblies and again it varies from one asphalt to another. Some show very little association at around 90°C (194°F). The non-polar phase, on the other hand, has the ability to dissociate the organized structure, but again its solvent power varies from one asphalt to another [Branthaver et al., 1993 (SHRP-A-368)]. As temperature is raised, associations of the least polar molecules decrease and the material becomes more dissociated and therefore less viscous. As temperature is raised further, dissociation of assemblages of the more polar molecules occurs. As temperature is reduced, the opposite occurs. Assemblages of molecules grow as temperature is reduced until the self-assembled pieces interact with each other and hence resist flow, i.e., the asphalt becomes stiffer. At still lower temperatures, ranging from high ambient to low road-service temperatures, the waxy neutrals solidify in some asphalts causing sharp increases in stiffness.

This model seems fuzzy compared to the rheological physical models developed during SHRP [Anderson et al., 1994 (SHRP-A-369)], and since refined by Bahia and Anderson (1995) and Anderson et al. (1996). But then, it should be fuzzy considering it is a single description intended to cover many variations in asphalt composition, which, in fact really means asphalts are many different materials. This model should be no better than, for example, attempting to describe the structural strengths of any number of other various types of glue. To help clarify this point, consider this analogy. Suppose you want to build a dining room table out of hardwood by gluing the parts together. Three bottles of glue are supplied which include carpenter's glue, rubber cement, and airplane glue. However, all three have been dyed the same color and adjusted to the same consistency. You must choose one of these blindly, but all three have the same physical properties. By chance, you choose rubber cement—don't put the good china on this table! Now you want to assemble a plastic model airplane. By chance you choose carpenter's glue. The glue "dries" and the model collapses. Your third job is to glue two pieces of paper together. Amazing, any one of the three works very well. While this analogy is somewhat extreme, by now it should be clear that the nature (composition) of the glue and the environment in which it is used profoundly affect performance. Physical properties alone never can distinguish expected performance of the above three types of glue. Likewise, only a generalized (fuzzy) model can describe these three very different materials. For asphalts, rheological properties can be measured very accurately in spite of the fact that each asphalt is a unique material. Good rheological models were developed during SHRP [Anderson et al., 1994 (SHRP-A-369)] and these have been refined since SHRP by

Anderson et al. (1996). However, rheological measurements alone cannot predict changes in asphalt behavior in roads as the asphalt itself changes due to oxidation and invasion of moisture. The chemical model does offer some useful information on alteration of properties by showing which components cause specific changes in physical properties. Further, composition is the only property that can be altered physically. One cannot add a bag of high-temperature stiffness or a bottle of low-temperature anti-cracking to asphalt. Alterations must be composition specific to cause predictable physical property changes. Physical and chemical models simply serve two different objectives.

It is important here to point out that the variations in behavioral characteristics of asphalts must be measurable. Again, one objective of the SHRP was to develop methods which can distinguish among asphalts and eventually adapt these methods to highway laboratory practice. The quantitation of all important aspects of the chemical model was only partially completed during SHRP and is still not completed. However, substantial amounts of progress have been made since SHRP (Western Research Institute, 1998). At this point, it is interesting to describe how the variations in chemical properties may be reflected in the pavement performance.

Speculation on Relationship of Chemistry to Pavement Performance

Throughout the highway community, the words “failure mode” are heard with great regularity in discussions of performance. While it is unusual to describe performance in terms of failure (for example, you buy a car for what it will do, not for how/when it will fail), it is instructive to do so here since it is generally understood that all pavements have a finite design life and will eventually experience distress and fail unless they are rebuilt periodically. Hence, acceptable performance might be defined best as sufficient time to failure, or to reconstruction (rehabilitation), to justify the use of any particular methodology and any given set of materials. Sufficient service life is defined by cost of construction and affected by traffic density, harshness of the environment, soil (support) conditions, and numerous other factors. While the determination of acceptable service life is not the subject here, clearly service lifetimes of a few months to a few years, which have been experienced all too frequently, are unacceptable, whereas 15 to 20 years of service gives more acceptable life-cycle costs. Neither is construction methodology the subject of this work, so it is assumed here that construction practice is both consistent and adequate, but in reality this varies from site to site. The reader is reminded that proper design, proper material selection and proper construction are all necessary in order to achieve a quality end product: roadway or any other manufactured item. The focus here is upon variations in the quality of construction materials, especially asphalts.

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

- (a) Rutting (more correctly called permanent deformation);
- (b) Fatigue cracking;
- (c) Low-temperature (thermal) cracking; and
- (d) Moisture damage:
 - less than total stripping, and
 - total loss of adhesion.

Before discussing the relationships among the above failure modes and chemical properties of asphalts, it is important to discuss aging since there are mixed opinions on whether aging is also a failure mode.

AGING

Aging sometimes is included in the above list of detrimental effects, but the process of aging in pavement is actually a change in composition that may be beneficial or detrimental. Aging may be detrimental when excessive hardening or stiffening develops in an already adequate pavement. On the other hand, some amount of 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 low in stiffness, i.e., has insufficient shear strength (too soft) and therefore is prone to deform

and rut. On the other hand, it may be too stiff (brittle) and therefore subject to cracking, either under traffic load or with thermal stress. Figure 5 illustrates these points schematically and also includes the effects of temperature, time and oxidation.

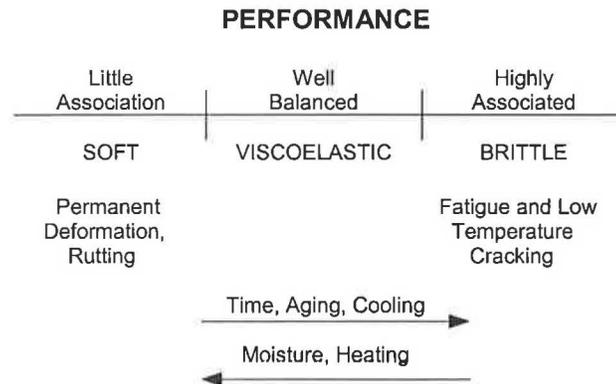


FIGURE 5 Schematic of performance characteristics.

Aging should be divided into two types: hardening that takes place upon prolonged standing (steric hardening) and hardening that results from chemical oxidation of asphalt from its exposure to air. Both proceed in pavement.

Steric Hardening at Ambient Temperature

Steric hardening (reversible hardening) is the process wherein polar molecules of asphalt slowly align themselves (self-assemble) into the most stable (lowest energy) arrangement. This results in the best intermolecular bonding, or association, as the asphalt acquires the greatest amount of internal structure (network) and hence the greatest stiffness. But since the intermolecular association is no more than low-energy bonds, either heat or shear is sufficient to disrupt the internal structure and disorient the molecules, hence returning them to a more random state that results in lowering the asphalt stiffness. Warming a sterically hardened asphalt in the absence of any other effects will soften it to its original stiffness and heating an asphalt to an elevated temperature such as a mix-plant temperature will reverse the effects of organizational hardening. In fact, it has been shown that temperatures of around 100°C (212°F) are sufficient to totally reverse steric hardening [Western Research Institute (WRI), 1998]. Short loading times with small strains disrupt the internal structure very little, hence asphalt shows an elastic behavior. With prolonged stress, such as a slow temperature increase that causes expansion, disruption of internal structure is greater and asphalt thus creeps. Elastic response at short loading times and creep at long loading times are both desirable in pavement.

Steric Hardening at Low Temperature

At low-service temperatures the more neutral materials, like waxes, also organize into a more crystalline-like material, imparting further stiffness to asphalt. Some refer to this as physical hardening. This is somewhat of a special case of what is classically called steric

hardening. Like steric hardening at ambient temperature, a rise in temperature reverses this hardening process very rapidly. Solid state nuclear magnetic resonance (SSNMR) spectroscopy has been employed to show that neutral materials in asphalt become rigid solids (some crystalline and some amorphous solids) at low temperature (Netzel et al., 1997; Daly et al., 1996; Netzel, 1998). In short, some portions of the aliphatic hydrocarbon material in asphalt have been shown to immobilize (i.e., become rigid) at low temperature. But, as one can guess by now, the temperature of “solidification” varies substantially from one asphalt source (i.e., crude oil source) to the next. Likewise the rate of “solidification” varies among asphalts, so the ill effects of low temperature appear in some asphalts more quickly than in others. Further, SSNMR and modulated differential scanning calorimetry (Turner and Branthaver, 1997) have been used to show that this process also reverses with heat. Essentially, the rigid hydrocarbon material “melts” as temperature is increased. Again, the composition drives the physical properties. The nature (composition) of the crystallizable fraction determines the temperature at which extreme stiffening (freezing if you like) occurs. Further, the composition also controls the time required to achieve maximum stiffness (Turner and Branthaver, 1997). This cautions the user to employ low-temperature test methods that allow sufficient time to capture the true low-temperature properties.

Oxidative Age Hardening

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 stays stiffer at any given set of conditions of storage time, temperature, and shear. Asphalt concrete suffers oxidative hardening continuously during its lifetime and this type of hardening is not removed by heat alone. The effects of steric hardening may be minor by comparison and intervention with another material (recycling agent) that dissociates (softens) the oxidized asphalt may be necessary.

The events that lead to aging in a pavement are very slow because the driving forces for orientation (dipole moment of each molecule) are small and the whole medium is quite viscous at road-service temperature. Nonetheless, the polar molecules will shuffle about slowly and eventually find the best orientation, known as the thermodynamic stable state (equilibrium), and in so orienting themselves become a system that is better packed and bound together, i.e., the whole asphalt becomes stiffer.

Aggregates, all of which have polar surfaces, have been shown to have a distinct effect on this orientation process, but also differ in their ability to cause orientation. The result is a change in the self-assembly of the asphalt toward a different thermodynamic equilibrium that involves the aggregate. This may cause an increase or decrease in the stiffness of the asphalt (Huang et al., 1998a and b).

In a roadway, achievement of thermodynamic equilibrium is a moving target. There are constant changes in composition that result from oxidation of asphalt. During oxidation polarity changes, 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 affects achievement of thermodynamic equilibrium.

The oxidative aging of asphalt experiences a “leveling off” phenomenon and this is somewhat of a saving feature. While some asphalts, such as asphalt G, may oxidize and accommodate their own oxidation products without major changes in viscosity, other asphalts show substantial increases in viscosity upon oxidation. As can be seen in Figure 4 virtually all asphalts eventually quench their own oxidation, and in so doing, quench the increase in viscosity that results from oxidation, i.e., the increase in viscosity levels off. However, the viscosity at which one asphalt self-quenches may be many times higher than another asphalt of the same PG grade. After an extended time of oxidation at some given temperature, asphalts of the same original grade, but from different crudes, can become very different in a roadway.

The actual high-service temperature becomes a critical factor in determining final physical properties when self-quenching occurs (Kemp and Predoehl, 1981). The following example cited earlier, demonstrates this clearly. Pressure-aging vessel (PAV) testing of asphalts G and K at 60°C (140°F) for 400 hours resulted in viscosity increases of 17 and 23 times, respectively. For the same two asphalts oxidized for 72 hours at atmospheric pressure and at 113°C (235°F), the viscosity of G increased 18 fold while K increased 530 times [Branthaver et al., 1993 (SHRP-A-368)]. The principal point here is that there may be a need for a specification for an upper limit of increase in viscosity, or stiffness, especially for asphalts used in hot climates. Those asphalts that age harden severely at high temperature may show substantially greater amounts of embrittlement in pavement that cools to intermediate temperatures compared to asphalts that age very slowly at high temperature. In thin pavements this likely will result in very different fatigue failure, yet the asphalts, by the current PG standards, are said to be interchangeable. Today there is no such upper limit of stiffness at high-service temperature in the PG grading system. Compositional variations among asphalts dictate the amount of viscosity increase that is observed as a result of oxidation at different temperatures. Again, refer to Figure 4. The chemistry of quenching is rather well understood and the rates and physical effects of oxidation are measurable (Petersen et al., 1993; Petersen and Harnsberger, 1998; Petersen, 1998). The chemical properties of asphalts can be used to predict the expected amounts of hardening in asphalts with age. Therefore, it behooves the user to consider using a test that differentiates asphalts by how much they will age harden at higher service temperatures, and hence be prone to fail by fatigue as the pavement cools.

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 imparted by the network formed by the polar molecules, but it is also a material with a viscous behavior that can flow or creep because much of the molecular network consists of low energy bonds that allow stable molecules to move with respect to each other under prolonged stress. The relative contributions of the elastic and viscous behavior vary with composition.

Rutting and Permanent Deformation

Again, consider asphalts G, K, and M. Their SEC plots are shown in Figure 3. Asphalt G contains largely the dispersing phase so it has little elasticity. One would expect it to be able to dissolve large amounts of its own oxidation products with little effect on its physical properties. This has been observed in oxidation and compatibility index studies. Asphalt G is somewhat insensitive to the effects of oxidation. It does not harden as much as other asphalts, which makes it a material more prone to rut or deform, especially at higher temperatures. It has little of the compositional feature of large molecular size or large amounts of self-assembled polars to give it elasticity. The mostly non-associated (waxy) material of asphalt G does tend to organize and harden at low temperature, somewhat like crystallization. Therefore G would be expected to be very stiff (susceptible to cracking) at 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 impart a greater elastic modulus at high temperature than is observed in asphalt G, and not have the propensity to rut. This is also observed for asphalt K. Asphalt M, with its truly high molecular weight, should and does behave somewhat like asphalt K at high temperature. Asphalt M, however, has a relatively high molecular weight and has a small amount of polars (about 4 percent asphaltenes). Therefore, self-assembly of M, as it cools, is less significant than in K. The increase in stiffness should be less temperature dependent than in asphalt K. This argument, of course, must be tempered with considerations of design and construction. Asphalt quality is only part of the whole phenomenon of rutting. Certainly poor design or construction practice can also lead to rutting and other failures.

If heretofore the relationship of composition to performance properties has not been obvious, consider some results from cross blending of dispersed (SEC I) and dispersing (SEC II) phases of asphalts. These are the fractions shown by the left and right hand parts of the SEC plots (Figure 3), respectively. These two fractions were generated by SEC. Major changes in properties were observed in a laboratory-prepared asphalt prepared by blending fractions from different asphalts. In one case, the dispersed phase (SEC Fraction I, the left side) of one asphalt was mixed with the dispersing phase (SEC Fraction II) of a second asphalt. The resulting asphalt was more than 1,000 times the viscosity of either original material. The dispersing phase (SEC II) simply could not disperse the polars (SEC I) so the result was an extremely stiff asphalt. The opposite configuration of blending gave the expected result, a very low viscosity blend, much lower than either original asphalt. Here the dispersing phase was extraordinarily effective at dispersing the polars. In the first example above, the dispersing phase of the asphalt is not a good "solvent" for the dispersed phase mixed into it. The self-assembled polars remain tightly bound to each other. The variation of solvent power of SEC II is best described in terms of the fundamental thermodynamic property, solubility parameter, which is a measurable property. Generally, the closer the solubility parameters of solvent and solute (SEC I and SEC II for this discussion), the better the dispersion will be. Said more simply, like dissolves like.

By appropriate cross blending of various petroleum stocks, one can achieve a wide variety of properties. Viscosities or viscoelastic properties can be pushed up or down at will. Phase angles (a measure of the relative contribution of the storage and loss moduli) can be varied significantly.

Thermal and Fatigue Cracking

Cracking is another serious failure in roadways, and again can be related to binder composition. If the molecular network (agglomerate, self-assembled matrix, or whatever term is preferred) becomes too rigid (too stiff), the ability of an asphalt to deform elastically will be lost. Instead, the asphalt fractures and likely will be separated sufficiently so that healing cannot occur. Healing is the phenomenon in which asphalt concrete is observed to regain strength (i.e., a mixture regains strength) during a rest period after loss of strength during heavy traffic use. Little and co-workers (1994, 1997, 1998) have studied this phenomenon extensively in recent years. They envision a process wherein microcracks formed in asphalt concrete during heavy traffic loads fuse back together when allowed to rest. Clearly this would require the asphalt to flow to refill the microcracks and certainly would be accelerated by confining pressure. A critically important observation is that not all asphalt concretes heal at the same rate nor to the same extent. In well controlled experiments where only the source of the crude oil to make the asphalt was varied, some asphalt concretes healed fast while others were slow, and some healed nearly 100 percent while others healed very little. Variations in asphalt composition, even for asphalts of the same grade, cause major differences in healing propensity. Clearly, fast and complete healing are performance advantages, but currently there is no binder specification for healing rate or efficiency, so the advantages of fast or complete healing asphalt over slow or poor healing material go undetected. No advantage is made of this knowledge that asphalts can be distinguished with respect to performance.

Low-Temperature Cracking

A very rigid matrix subjected to constant loading 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), SSNMR, and forced sphere or cylinder methods (Ensley, 1977). Under these circumstances, the asphalt is quite brittle and subject to cracking (sudden failure) under stress. To make matters worse, some asphalt cements shrink significantly more than others 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. Think of it this way. Presumably everyone has seen sealing wax used on jelly jars. This sealing wax (or paraffin wax) is a high molecular weight aliphatic hydrocarbon. As it cools, it shrinks very noticeably, usually leaving a depression in the middle of the wax circle. If these types of materials are a significant part of a given asphalt, shrinkage with decreasing temperature can be quite severe. Now when the jelly jar is well cooled, try to bend the wax. You can't, it breaks. Cracking of asphalt at low temperature would be expected if large amounts of such paraffins are present. Shrinkage is a good indication of forming a brittle, somewhat crystalline material. The property of shrinkage and formation of a brittle asphalt 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 solution nuclear magnetic resonance, a

common and fast analytical technique, but it is probably more practical to either measure shrinkage directly or predict it from very rapid DSC measurements.

Adhesion and Moisture Damage

Prediction of moisture-induced damage has been the subject of many studies. Lottman's classic study (Lottman, 1971) and National Cooperative Highway Research Program Report 246 are examples. Adhesion and moisture damage go together only to a point. While loss of adhesion certainly is a serious moisture damage problem, other forms of damage also may occur when moisture is present. At this point, consider only adhesion. By definition, it must involve both asphalt and aggregate. While SHRP commissioned studies to investigate the interaction of asphalts and aggregates, the examination of adhesion to the point of developing a specification test, per se, was not within the scope of the SHRP binder composition studies. Nevertheless, some interesting observations can be made considering only the binder.

Adhesion

Adhesion of components in asphalt to aggregate appears to be governed largely by specific functional groups (molecular types) (Plancher et al., 1977). Certainly overall polarity, that is, separation of charge within the organic molecules, promotes attraction of polar asphalt components to the also polar surfaces of aggregates. To be clear, neither asphalt nor aggregate has a net charge, but components of both do have non-uniform charge distributions. Both behave as if they have charges that attract the opposite charge of the other material. To complicate matters further, several researchers have shown that aggregates vary quite substantially, and in some cases aggregate behavior varies with environment (Curtis et al., 1993). Some aggregates show major changes in polarity with changes in moisture content, temperature, etc. For this discussion, aggregate will simply be considered to be 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. Absorption of water, like all other behavior, varies with asphalt composition. The behavior of asphalt with water changes further as the asphalt becomes oxidized. 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 acids in asphalts, while quite polar and adhere tightly when dry, tend to be removed from aggregate easily when water is present, but this varies with the type of acid. Monovalent (singly charged) cation salts, such as sodium or potassium salts of carboxylic acids in asphalt, tend to be removed from aggregate quite easily (Plancher et al., 1977). Why? These are surfactants (soaps), and with water and traffic action, should be expected to scrub the asphalt away from aggregate as observed in some roadways. On the other hand, calcium (from lime) or other divalent (doubly charged) salts of acids are much more resistant to the action of water (Scott, 1978; Plancher et al., 1977; Petersen et al., 1987). One very recent observation (WRI, 1998) indicates that some aged asphalts may be much more prone to moisture damage than others, even for asphalts of the same

grade. In some, but not all asphalts, a very strongly acidic material appears with oxidation. This was first detected with non-aqueous potentiometric titration (NAPT). This is likely to be a highly oxidized sulfur species, but its structure has not yet been determined. There is no doubt though, using NAPT and acidity measurements of water-washed samples of oxidized asphalts, that some (not all) asphalts show this phenomenon. In short, if these materials are converted to sodium salts (as could happen with some aggregates), a detergent would be formed. These are even more effective scrubbing agents than soaps. Also, like soaps, the calcium salts of detergents are far less moisture sensitive, i.e., detergents are “inactivated” with lime. From a practical viewpoint, it would behoove the user to assure the acids in asphalts are neither free nor in the form of monovalent salts. The examples of pyridines and sodium salts are somewhat extreme. It should be obvious that there is a spectrum of tenacity of adhesion among the organic molecules in asphalt. The evaluation of this spectrum of adhesion is still being studied in several laboratories.

Moisture Damage

Moisture damage without apparent loss of adhesion is a common problem in asphalt pavement. Moisture (water) may invade pavement from rain, subgrade water from poor drainage, humidity, the “solar still” effect, or any combination of these. 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 into pavement. Still, some water will come in contact with the 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 of water into the asphalt concrete, the mechanical properties will be affected, but again, current studies in this area are showing that variations in chemical properties of asphalt (crude oil source) cause variations in physical properties of wet asphalt (Thomas et al., 1998). From a chemical viewpoint, the action of water is somewhat like the dilution of asphalt with a low molecular weight solvent. This should be expected to result in reduced strength and an increase in the propensity of rutting or other deformation. However, these studies are too preliminary to predict performance. 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 also are harder than their precursor new pavements, so the effects of moisture and oxidation are somewhat counter to each other. Poor adhesion of very stiff asphalt can appear to be a fatigue failure (which it is), but it is caused more by oxidation and moisture than by traffic.

Summary

From the discussion of the chemistry of petroleum asphalt at the molecular and intermolecular levels, it is clear that many 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 polar and nonpolar components. Polars tend to associate and cause stiffening while nonpolars cause dissociation of polars and softening of the whole asphalt. Several speculations on the effects of chemical composition on pavement performance have been offered. In general, the mechanical (structural) properties of asphalt are related to the intermolecular structuring among the polars. These interactions may arise by involvement of any number of different chemical species. The exact nature of the chemical species is less important than the distribution of charge within the specific set of molecules. Excessive structuring leads to brittle cements that tend to crack, while too little structuring leads to materials that remain soft and deform under stress. Oxidation adds to age hardening and brittleness of asphalt cement by increasing the 3-dimensional network (self-assembly) within the binder.

Asphalts are graded today by the Superpave binder specification, or performance grade system. While this is a major improvement over all previous specifications, it has been shown that asphalts of the same performance grade (i.e., asphalts that are interchangeable as bulk materials) may behave differently in pavement, and hence may give different performance in actual roadway environments. That is, asphalts that are considered to be interchangeable by specification may still vary in performance as composition (source) is varied.

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, which perform very differently from each other—so are there tremendous differences among asphalts. The differences between asphalts are as great as the diversity of the crude oils used to produce them. The objective of developing new specifications during the Strategic Highway Research Program was to describe and achieve consistent behavior, and therefore consistent performance. This 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 petroleum stocks that, of necessity, are produced from many crude oil sources. The selection of a very limited set of crude oils to produce asphalts is essentially impossible. Achievement of consistent performance with asphalts requires accurate classification and, in many cases, modification of materials that are produced today. The principal values of the chemical composition studies are 1) to improve the performance classification system (specification), and 2) 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 or modify asphalts to obtain binders that will perform in a predictable and cost-effective manner.

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