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RELATION OF ASPHALT CHEMISTRY TO PHYSICAL PROPERTIES AND SPECIFICATIONS

by

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PREFACE

This report is a synthesis of information concerning the chemical composition of asphalt and the relation of such composition to the physical properties of the asphalt and its performance as a binder in asphaltic pavements. Although an attempt has been made to avoid detailed discussions of complex chemical phenomena and the use of terminology unfamiliar to asphalt technologists and highway engineers, there appears to be no way that one can provide a meaningful picture of asphalt chemistry as it relates to highway engineering without some reference to terminology and phenomena unfamiliar to many highway engineers.

In recognition of this problem, the more complex discussions of chemical characteristics of components, analytical procedures, and molecular interactions have been placed in the appendices. The more general concepts concerning the origin of asphalt and its chemical composition are covered in Chapters 1 and 2, and Chapters 3 and 4 provide discussions of the generally recognized relationships of chemical composition to the physical properties of asphalts and how asphalt technology is applied in specifications for highway materials.

It is believed that the data presented and relationships discussed demonstrate that there is no simple "cook book" approach to specifying the characteristics of asphalt cements that will guarantee trouble-free mixtures with all types of aggregates. It thus becomes apparent that, even if possible, it would not be desirable from an economic or technological standpoint to write specifications for asphalt cements based on close control of their chemical composition. Success will come only from understanding the characteristics of the materials available and recognizing the unique parameters involved in specific combinations of materials.

As the reader will note, the report draws heavily from the work of Dr. Claine Petersen and his associates at Western Research Institute. In addition, Dr. Petersen reviewed a rough draft and provided corrections and clarification of a number of points. His assistance is greatly appreciated.

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

CHAPTER 1

ORIGIN OF ASPHALT

Asphalts come from crude petroleum, which in turn is a product formed by nature primarily from plant life. The process occurs over millions of years under varied conditions of temperature and pressure. Thus, even though all petroleums are basically hydrocarbons, that is, chemical combinations of carbon and hydrogen, crudes vary widely in the amount and nature of the hydrocarbons they contain. Similarly, asphalts, the residues left after the more volatile fractions of the petroleum have been distilled off, vary significantly from crude to crude, both in their characteristics and in the volume percentages present.

Corbett illustrates differences in crude sources from the standpoint of the amount of asphaltic residues as shown in Figure 1.(1) Typical volume percentages of various distillation fractions and the bitumen residue for three types of crude are shown. In this illustration, the residual component suitable for asphalt cement is shown to vary from 58% to 1%.

Straight reduction by distillation is a necessary first step in the processing of all crude petroleum. Figure 2, also taken from Corbett, illustrates the basic separation by distillation.(1) As shown, after distillation at atmospheric pressure, the residual is further distilled under vacuum. The residue from this treatment can be utilized in several ways, one of which is as a paving grade asphalt. As stated by Corbett, where the characteristics of the crude feed permit, asphalt cements are commonly prepared by straight reduction to grade. The higher the atmospheric equivalent vapor temperature used, the harder the residual asphalt.

When the residue from vacuum distillation is not completely suitable for asphalt, some additional treatments are possible. As indicated by Corbett, one of these may be treatment of the residue with a solvent such as propane or butane. This treatment precipitates asphaltic constituents from the residue and is used in some refineries when it is desired to eliminate such constituents from the residue for the manufacture of lubricating oils, or where catalytic cracking is to be employed to increase the yield of gasoline or other petroleum distillate fuels. In this case, the precipitated asphalt is generally a high softening point by-product that can be blended with other residuals to produce paving grade asphalt cements. Another technique employed to a limited extent is "blowing", in which air is bubbled through the residual to cause oxidation of some of the constituents and increase its consistency.

	BOSCAN VENEZUELA	ARABIAN HEAVY	NIGERIA LIGHT
API Degrees	10.1	28.2	38.1
SP. Gravity	.999	.886	.834
% Sulfur	6.4	2.8	0.2

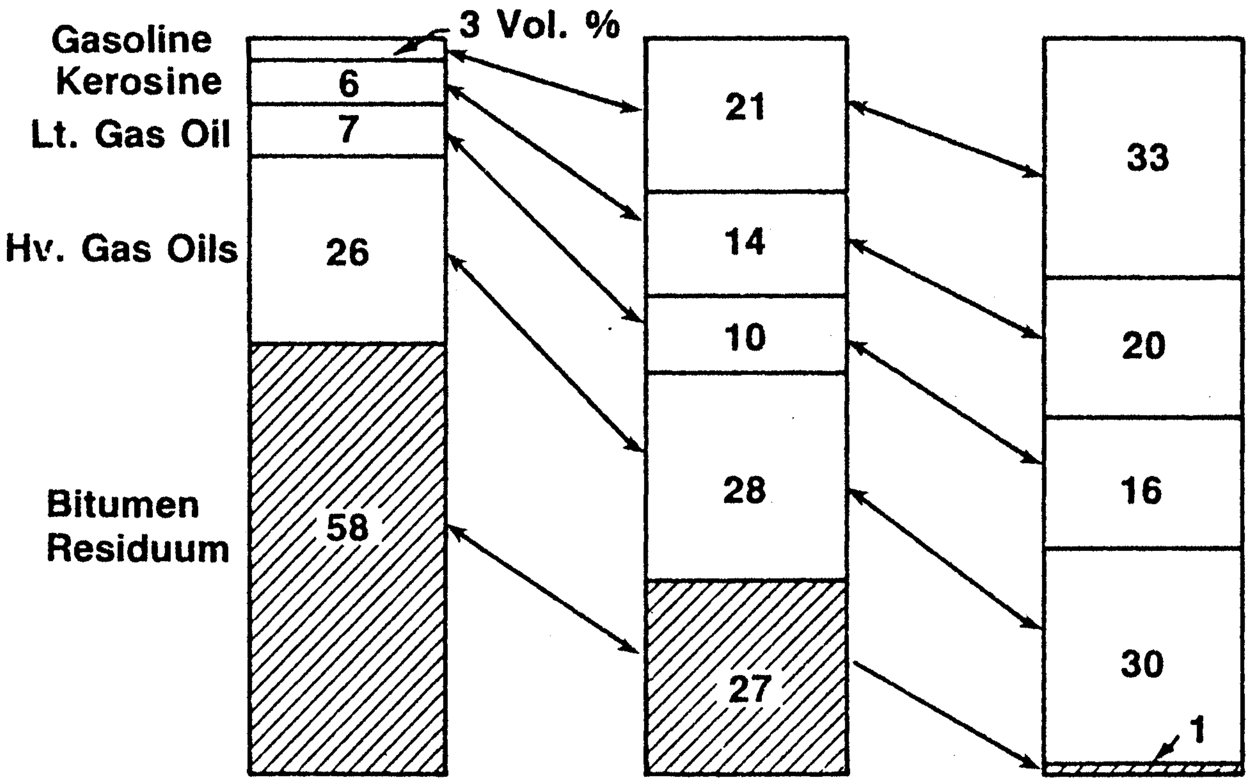


Figure 1. Makeup of crude petroleum. (Source: Reference 1)

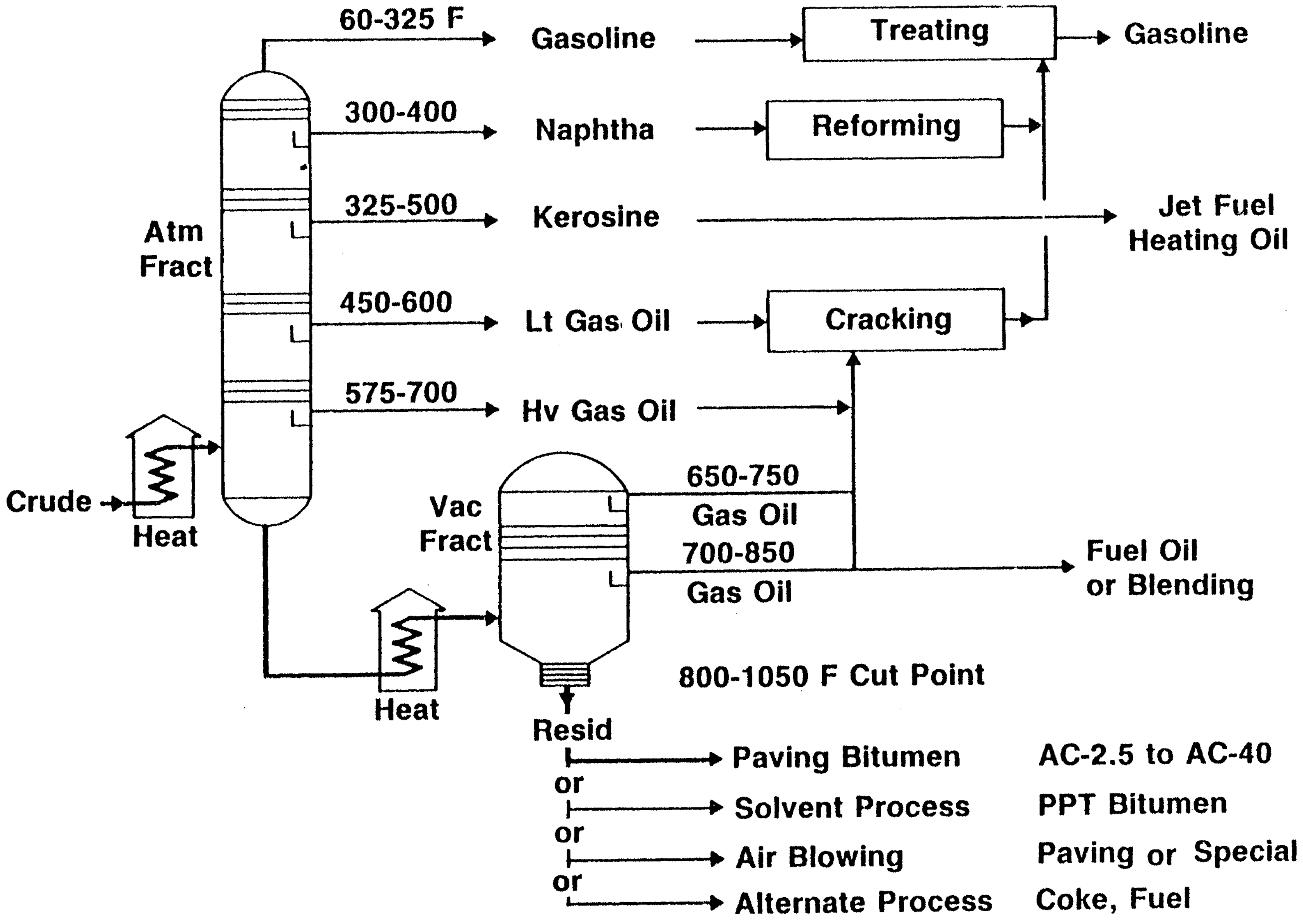


Figure 2. Crudes initially separated by distillation.
(Source: Reference 1)

CHAPTER 2

CHEMICAL COMPOSITION OF ASPHALT

Elements Present

The principal elements in asphalt are carbon and hydrogen. Sulfur is the next most abundant element, with small amounts of nitrogen and oxygen being next in order. Heavy metals such as vanadium and nickel may also be present in trace amounts. Table 1, taken from a report by Petersen, shows the elemental analyses of representative petroleum asphalts.(2)

Although the asphalt molecule is composed predominantly of carbon and hydrogen, most molecules contain one or more of the so-called heteroatoms -- nitrogen, sulfur, and oxygen -- together with trace amounts of metals, principally vanadium and nickel. The significance of the additional elements is discussed in the following section.

Table 1

Elemental Analyses of Representative Petroleum Asphalts

Code	B-2959	B-3036	B-3051	B-3602
Source	Mexican blend	Arkansas-Louisiana	Boscan	California
Carbon, percent	83.77	85.78	82.90	86.77
Hydrogen, percent	9.91	10.19	10.45	10.93
Nitrogen, percent	0.28	0.26	0.78	1.10
Sulfur, percent	5.25	3.41	5.43	0.99
Oxygen, percent	0.77	0.36	0.29	0.20
Vanadium, ppm	180.	7.	1380	4
Nickel, ppm	22	0.4	109	6

Molecular Structure

As with the most organic materials, the way in which the atoms are incorporated in the molecules and the type of molecular structures present in asphalt are much more important than the total amounts of each element present. Since, as stated, asphalt is derived from living organic matter over a period of millions of years, the molecular structures of the compounds are highly diverse. While no effort will be made in this presentation to fully discuss the various types of organic compounds, reference needs to be made to three manners in which carbon atoms are linked to each other. This may be in straight or branched chains, in which case the materials are generally referred to as aliphatic or paraffinic types. A second type of combination is naphthenic, in which the carbon is linked in simple or complex (condensed) saturated rings, "saturated" meaning that the highest possible hydrogen to carbon ratio is present. The third type is aromatic. These materials are made up of one or more especially stable six-atom rings that form the basis of compounds such as benzene and toluene.

Asphalts are very complex combinations of all three of these type compounds. Petersen states that typically, 25% to 35% of the carbon in asphalt is combined in aromatic type molecules consisting of condensed aromatic ring systems containing from one to possibly 10 rings per group. (2) These ring systems may be associated with saturated naphthenic ring systems, and both the aromatic and naphthenic ring systems may have attachments composed of a variety of normal or branched hydrocarbon side chains. Fifteen to 30 percent of the carbon will be found in such naphthenic ring systems. The normal and branched chain hydrocarbons may either be present as individual molecules or be associated with naphthenic or aromatic rings and will comprise 35% to 60% of the carbon present.

Functionality -- Polar Groups

The elements other than carbon and hydrocarbon, referred to as heteroatoms by Petersen, enter the asphalt molecule in particular configurations referred to as functional or polar groups that are attached in some way to a carbon atom. These are the molecules that provide many of the "engineering" characteristics of asphalt. Generally, "functionality" (presence of functional groups) relates to how the asphalt molecules interact with each other or with surfaces and/or molecules from other materials such as aggregate. Polarity refers to an imbalance of electrochemical forces within the molecule, which produces a dipole. Thus each molecule that is polar has both electropositive and electronegative characteristics much like a magnet with north and south poles. As with a magnet, likes repel and unlikes attract, which induces molecular interactions that strongly influence physical properties. Because the heteroatoms impart functionality and polarity to the molecules, they have a much greater effect on the physical properties of asphalts and the differences in performance of asphalts from different sources than might be indicated from the small amounts present.

Conceptual Model of Composition

Because the number of molecules with different chemical structures is extremely large, chemists have not seriously attempted to separate and identify all the different molecules in asphalt. Attempts to determine asphalt composition generally consist of efforts to separate or characterize asphalt by determining different groupings or generic fractions based on the size and the reactivity and/or polarity of the various molecular types present.

In the most generally accepted concept of asphalt composition, asphalts are considered to be made up of asphaltenes, oils, and resins. Asphaltenes comprise the fraction that is the most complex and that generally contains the components with the highest polarity and tendency to interact and associate. This fraction is insoluble (or precipitated) when the asphalt is dissolved in a nonpolar solvent such as pentane, hexane, or heptane. The part of the asphalt that is dissolved and remains in solution is called "maltenes."

> Note: Maltenes is the term initially used by most asphalt technologists, but more recently the term "petrolenes" has been used. Rostler makes a distinction, defining petrolenes as the soluble portion with a relatively low boiling point and maltenes as the soluble portion with a relatively high boiling point.(3) He suggests that a boiling point of 300°C. be adopted to distinguish between petrolenes and maltenes. Under this concept, the term maltenes would apply to the pentane soluble portion of asphalt and, since most of the literature uses this designation, it is used in this report.

The maltenes contain both the oils and resins. The resins are said to be the agents that disperse the asphaltenes throughout the oils to provide a homogeneous liquid. Each of the three fractions are composed of many different chemical compounds, and the "mix" in each fraction will vary greatly with the source of the petroleum from which the asphalt has been extracted and with the method by which it has been obtained.

Although asphaltenes have often been considered as a relatively inactive component of the asphalt, they, in fact, play a major role in determining asphalt viscosity. A comprehensive study by Girdler in 1965 and more recent studies by others have shown that the amounts of asphaltenes present and their characteristics vary considerably from asphalt to asphalt.(4) These major studies are discussed in more detail in Appendix A.

Significant differences also exist in resins and oils from different sources of crude oil, and different procedures have been developed to characterize these components. Unfortunately, at the present time there is no universal agreement as to which of the various methods best defines the asphalt from an engineering viewpoint, or for that matter whether any method of separating the components provides the best information.

The details of the most frequently used procedures are discussed in Appendix B.

Colloidal Characteristics of Asphalt

The relative amounts and characteristics of asphaltenes, oils, and resins in a given asphalt have an important effect on its physical characteristics and its value as a paving material. It is known that asphalts exhibit properties that deviate from those of a true solution and thus may be considered colloidal systems.

This colloidal nature of asphalt was first recognized by Nellensteyn, who considered asphalt as a dispersion of micelles in an oily medium.(5,6) The asphaltene fraction is associated with the dispersed or micelle phase. The ability, or lack of ability, of the resinous components to keep these highly associated asphalt components dispersed in the oily phase is referred to as their "peptizing" ability, and this largely determines the "gel" or non-Newtonian flow characteristics of the asphalt. Rostler described the asphaltene fraction as the component of asphalt primarily responsible for asphalt viscosity and colloidal behavior due to its limited solubility in the remaining components.(3) He concluded that the asphaltenes are kept dispersed by the peptizing ability of the nitrogen bases. If this constituent is present in the proper amount, the asphaltenes are solubilized (made soluble) to an extent that the asphalt has flow properties close to those of a true liquid. On the other hand, the paraffins tend to reduce solubility, so that increasing amounts of this constituent in relation to the nitrogen bases would lead to increasing gel characteristics. The extent to which an asphalt acts as a "sol" or as a gel has a significant bearing on its rheological properties and its performance in an asphaltic pavement mixture. This will be discussed in more detail later.

Comparison of Analytical Procedures

Each of the procedures described in detail in Appendix B serves a useful purpose in various research studies and relative amounts of the various groups within each procedure have been shown to relate to certain physical aspects of asphalt. However, in all cases the "generic" fractions are still complex mixtures and not defined chemical species; thus the same generic fraction from different asphalts may have a quantitatively different effect on the physical properties.

The two most frequently used fractionation methods are the chromatographic method of Corbett (see Figure B-1, Appendix B) and the precipitation method of Rostler and Sternberg (see Figure B-2,

Appendix B). Unfortunately, controversy often arises between the proponents of the two methods, and different asphalt technologists favor one procedure over the other. Such controversy and choosing of one procedure over the other are completely unnecessary, if the difference in concepts of the two procedures are recognized and the limitations on the quantitative results by either method are properly recognized in their analysis.

The Rostler-Sternberg procedure is an analytical procedure intended to measure the amounts of several classes of molecules present in a mixture. Because sulfuric acid of different strengths is the basis of the analytical separation, asphalt technologists, particularly those with an engineering background, have difficulty relating the reactivity to sulfuric acid to asphalt performance. Since the component being determined is removed from the system, each fraction cannot be examined as in the chromatographic method. In the chromatographic method separation of components is attained by differential absorption and desorption forces. The quantitative amount of material absorbed and desorbed depends on an equilibrium between various forces, which is affected by the concentration and relative amounts of various groups present. The effects of changes in concentration can be demonstrated by repeating the procedure with a separated fraction instead of the original asphalt. It will be found that the rerun fraction will show a combination of fractions and not 100% of a single generic designation. However, the availability of the fractions for further study is an advantage in establishing relationships to physical characteristics. Another criticism of Corbett's method, principally cited by Rostler and his co-workers, is that the designations for the eluted fractions are in jargon that has no specific meaning in classical chemical terms.(7) Differences of opinion are expressed in the published discussion following reference 7. In particular, Schweyer points out that special terminology has been created even in the Rostler-Sternberg procedure. While such discussions may be of academic interest and asphalt technologists should be aware of these differences of opinion, they have little practical significance with respect to an understanding of the differences in asphalts that result in differences in performance in a highway mixture. If the procedures are examined for similarities rather than differences it is seen that asphaltenes are first separated in each case, even though the Rostler-Sternberg method employs n-pentane as the solvent and the Corbett method employs n-heptane. Pentane precipitates a greater amount of material than does heptane, but the characteristics of the total asphaltenes are similar. The Corbett polar aromatic fraction contains many of the components found in the Rostler nitrogen base fraction and, possibly, part of the first acidaffin fraction. The Corbett naphthene aromatic fraction may be roughly compared to the Rostler second acidaffin fraction plus some components found also in the Rostler first acidaffin fraction. The saturates in the Corbett procedure are very similar to the paraffinics in the Rostler-Sternberg procedure.

Although the LMS separated by the HPLC technique are found mostly in the asphaltenes, Jennings showed that asphaltenes also contained other size molecules.(8) Thus, a direct comparison of fractions obtained by this procedure and others is not feasible.

Characteristics of the Total Asphalt System

Component Compatibility

Petersen emphasizes the importance of component compatibility in an asphalt. He points out that it is not only the quantitative amount of any single component that controls its contribution to the overall behavior of asphalt, but also the relationships of the components.(2) The most nonpolar or oily fraction in the absence of the resinous components is so unlike the asphaltene fraction that the two fractions are not mutually soluble, yet these extremes in molecular types must coexist in asphalt as a microscopically homogeneous mixture. This is possible because the various components of asphalt interact to form a balanced or compatible system. It is this balance of components that gives asphalt its unique viscoelastic properties which are so important to its application as a pavement binder. A lack of compatibility or balance, as sometimes manifested by excessive component phase separation, leads to undesirable properties.

This compatibility, or lack of compatibility, of asphalt components has long been recognized as being directly or indirectly related to asphalt quality. Early work showing the solubility of asphalt in various solvents -- particularly the work of Oliensis relating to the development of the spot test(9) and the evaluation of asphalts by their reaction to partial solvents(10) -- recognized different responses to different conditions and solvents that were related to the "stability" of the asphalt constituents in solution, which in turn was thought by some to relate to the durability of the asphalt in service. This led many agencies to adopt the Oliensis spot test as a specification test for homogeneity of asphalts. As was shown by Heithaus and Fink, the Oliensis test did not precisely distinguish between good and bad asphalt.(11) However, the test served a good purpose when first introduced, in that it removed from the market as a highway material residues from the cracking of petroleum in certain refining processes that had been shown to be nondurable.

Reviewed from the standpoint of present understanding, indications obtained from tests such as the xylene-heptane equivalent may have offered better clues to potential problems with asphalts than most asphalt technologists recognized at the time. The problem was, and still is, an inability to relate the degree of incompatibility as shown by the characteristics measured in the laboratory test with the performance as a binder in an asphaltic pavement. A complete discussion of this aspect is beyond the scope of this report. However, those interested can review the Proceedings, Association of Asphalt Paving Technologists (AAPT), which contain not only numerous papers dealing with the subject but also discussions that show the extent of the agreement or disagreement with the data and ideas presented.

Asphalt Functionality -- Molecular Interactions

Petersen and his co-workers take a different approach in determining the chemical properties of an asphalt. Rather than attempt separation into fractions, they seek to identify and characterize the various types of chemical or structural features of the asphalt molecule and how these interact with each other and the environment.(2) They point out that many molecules of different composition will have similar features or "functionality" that will produce similar effects on physical properties. Such functionality analysis has the advantage over component fractionation in that it can take into account the fact that most asphalt molecules have several types of chemical functionality and such functionality may be significantly different. This frustrates chemical fractionation procedures, since whole molecules must be moved into a given fraction.

Petersen illustrates how chemical bonds and secondary association forces affect the physical properties of asphalt.(2) A general discussion of the basic observations given by Petersen is included in Appendix C. He summarizes the importance of chemical composition in the following manner.

> Because asphalt chemical composition can vary widely with asphalt source, and a variety of combinations of asphalt components with varying chemical structures in individual asphalts may produce asphalts that will provide satisfactory service, it seems highly undesirable by the author to devise chemical composition specifications for asphalts. Such specifications would likely exclude from use many asphalts that would otherwise perform satisfactorily. Specifications should define the performance properties desired. Chemical information would be important in producing asphalts that meet the performance criteria.
>
> Composition information is useful in helping us understand asphalt -- what makes it behave as it does and what makes one asphalt behave differently from another. With given

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

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

CHAPTER 3

RELATION OF CHEMICAL COMPOSITION TO ASPHALT PROPERTIES AND PERFORMANCE AS A HIGHWAY MATERIAL

Even though most asphalt technologists recognize that chemical composition cannot be used as a direct requirement in specifications, in the final analysis it is the chemical composition that controls the physical characteristics of the asphalts. However, it must be recognized that it is possible for asphalts to have the same physical characteristics with different combinations of components. The generally recognized relationship between composition and performance characteristics is discussed in the following sections.

Asphalt Consistency

Different degrees of fluidity or hardness and softness for asphalt cements used in highway construction are specified either by limits on viscosity at 140°F. (60°C.) or penetration at 77°F. (25°C.). As previously stated, these grades may be attained by distilling off the lower boiling constituents of petroleum crudes or blends of crudes to obtain a residue of the desired consistency, using atmospheric and/or vacuum distillation, or by blending residues of different consistencies. For a given crude, the higher the equivalent atmospheric temperature, the harder the residue. However, different crudes or blends of crudes yield residues of different consistencies for equivalent distillation temperatures.

Chemically, the greater hardness is related to greater molecular forces causing greater association into larger molecular agglomerates leading to less mobility of the system. Thus, for a given crude or given blend of crudes, harder grades would be expected to have higher asphaltene contents and larger molecular agglomerates. However, as previously discussed, this generalization does not apply for all sources. The presence and position of polar groups can alter the general relationship so that higher asphaltene contents, per se, do not correlate with flow properties. These differences are of most concern to the asphalt manufacturer, and once the grade is established, the highway engineer generally accepts a given grade of asphalt for a given engineering application. This practice is acceptable in most situations but the highway engineer should recognize that it is possible and, in some areas of the country, normal to have asphalts of equal consistency (same grade) at the specified temperature that will be significantly different at other temperatures. This is the result of differences in viscosity-temperature susceptibility and/or shear susceptibility, which in turn relates to differences in the balance between various constituents in the asphalt and polar functional groups.

Another phenomenon of which the highway engineer should be aware is the possibility of incompatibility of chemical constituents of asphalts from different sources. This could affect either the grade of the blended material or its adhesive characteristics. Thus, two AC-20's blended in the same tank might, for example, have a lower viscosity than either has alone. Only a small amount of an asphalt having poor adhesive properties could adversely affect the properties of the blended material to a much greater extent than might be expected from the ratio of the two components.

Although these phenomena are exceptions rather than the rule, contractors should not blend materials from different sources of supply without predetermining that the sources are compatible. In most cases such information may not be available; thus, the blending of sources should always be avoided where possible.

Viscosity-Temperature Susceptibility and Complex Flow

Several chemical factors affect the viscosity-temperature susceptibility and degree of complex flow. Different combinations of asphaltenes, oils, and resins can result in the same viscosity of the asphalt at a given temperature, but because the changes in temperature affect each constituent differently, as well as the interaction between the constituents, the viscosity at different temperatures will be different. The presence of different polar or functional groups and their quantitative amounts and relative position to each other in the asphalt molecule also enter into the total picture concerning temperature and shear susceptibility. Some of these effects are discussed by Petersen.(2) The highway engineer needs to recognize the effects of these differences on the engineering properties of the asphalt. In particular, the phenomenon of shear susceptibility must be recognized. At high temperatures such as used for mixing, asphalts act as true liquids -- that is, they have Newtonian flow with the shearing stress being proportional to the shear rate. As the temperature is decreased, at some point complex flow is initiated. When this occurs, the "apparent" viscosity is no longer a constant and a higher "apparent" viscosity is indicated for lower rates of shear. These differences are not sufficiently large to affect compaction of bituminous mixtures but they may affect performance, particularly the tendency of pavements to crack in extremely cold weather. Differences that occur in viscosity and viscosity-temperature susceptibilities are illustrated in Figures 3 and 4 taken from the paper by Welborn and others.(12) As illustrated in Figure 3, above 140°F. (60°C.), there are relatively small differences in viscosity-temperature susceptibilities but significant differences occur in the range between 39°F. (4°C.) and 140°F. (60°C.). These changes are related to changes in associations of molecules or constituents in the asphalt and interactions among polar groups as discussed by Petersen.(2) Some of the differences depicted in Figure 3 are the results of non-Newtonian flow of the asphalt as indicated by Figure 4. This figure shows the limiting viscosity -- that is, the viscosity obtained at a sufficiently low shear rate so that Newtonian flow occurs -- plotted against temperature. In all cases the limiting viscosity is higher than the viscosity indicated at a shear rate at which non-Newtonian flow occurs. Differences in asphalts such as depicted in these figures are the basis of the controversy between those who advocate penetration grading of asphalt cements at 77°F. (25°C.) and those who advocate viscosity grading at 140°F. (60°C.).

The rationale for viscosity grading at 140°F. (60°C.) and the background of the development of the system are discussed by Halstead in reference 13 and will not be discussed here, except to emphasize that with proper mix design and asphalt grade selection, good results can be obtained with materials having either high or low viscosity-temperature susceptibility, but problems can arise if changes in asphalt sources significantly change the viscosity-temperature susceptibility and adjustments in mixing temperatures and possible other parameters are not made to compensate for them.(13)

Durability

The durability of an asphaltic pavement is a major concern of the highway engineer. It is well known that the amount of asphalt used, the type of aggregate, the degree of compaction, the amount of traffic, the weight of traffic, and weather conditions all have a significant influence on performance. Since the asphalt cement is the glue that holds the components of the pavement together it also plays a very important role in overall pavement durability. Thus, the durability of the asphalt cement is a major consideration. A durable asphalt is sometimes defined as one whose properties are resistant to change for the worse with time. However, a better definition is that used by Petersen.(2) He defines a durable asphalt as one that (1) possesses the physical properties necessary to produce the desired initial product performance properties, and (2) is resistant to change in physical properties during long-term, in-use environmental aging.

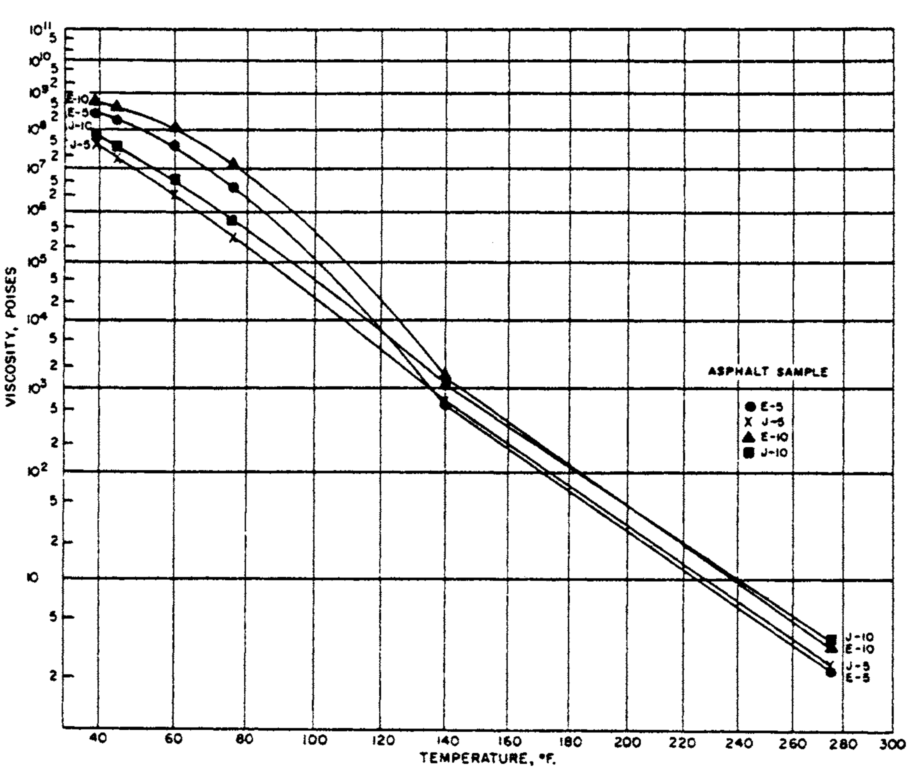


Figure 3. Viscosity (0.05 sec.$^{-1}$ shear rate) and temperature relation selected asphalt cements. (From reference 12).

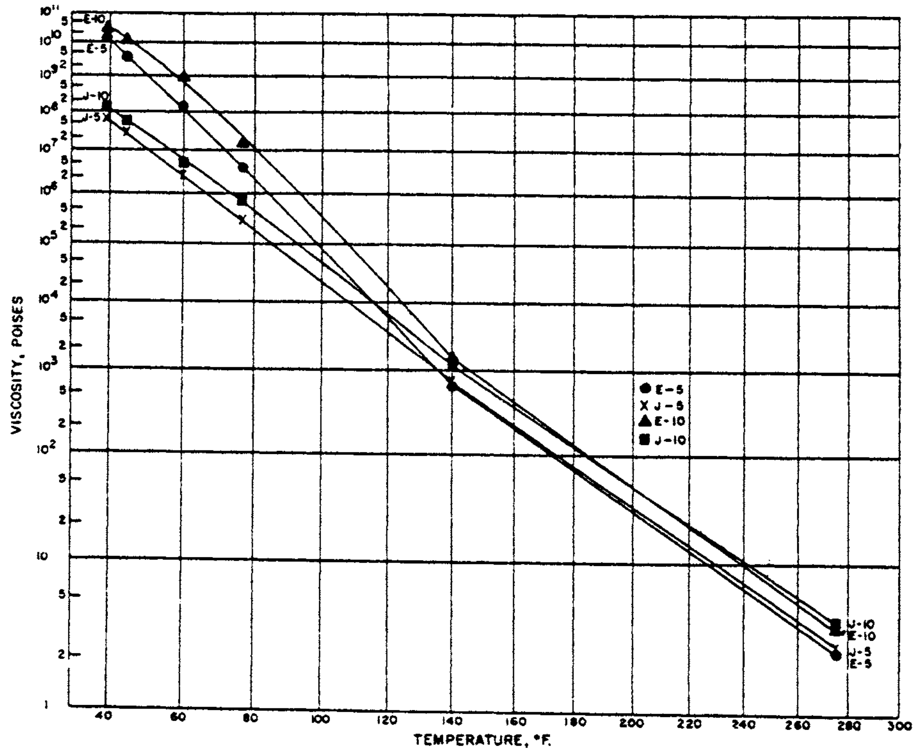


Figure 4. Limiting viscosity and temperature relation for selected asphalt cements. (From reference 12).

The asphalt cement often gets blamed unjustly for premature failures of asphalt pavement, but it is important to note that even though poor performance can result with good quality asphalt, with poor quality and nondurable asphalt early failure is inevitable, even with otherwise good design and construction. Poor durability of an asphalt cement is closely related to the chemical composition of the asphalt and the balance of components.

Petersen lists three fundamental compositional-related factors governing the changes that cause hardening of asphalts in pavements.(2) These are (1) loss of the oily components of asphalt by volatility or absorption by porous aggregate, (2) changes in the chemical composition of asphalt molecules from reaction with atmospheric oxygen, and (3) molecular structuring that produces thixotropic effects (steric hardening). He adds that with current specifications and construction practices, volatile loss is probably not a significant contributor to pavement hardening. Reaction with atmospheric oxygen is probably the major and best understood cause of asphalt hardening. Molecular structuring, although elusive and difficult to quantify, may also be a significant contributor.

When an asphalt hardens through oxidative aging, the oxygen forms polar oxygen containing functional groups that link molecules together to form larger molecular agglomerates. This induces a movement of components from the more nonpolar to the polar fractions. The saturates in the Corbett analysis and the paraffins in the Rostler analysis show least change on oxidation. There is usually some decrease in the amounts of the Rostler second acidaffins and a greater decrease in the more reactive first acidaffins. These decreases are offset by a significant increase in the asphaltene fraction, since molecules initially in the acidaffin fractions have combined and become parts of the asphaltenes. Similarly, the Corbett naphthene-aromatics and the polar aromatics decrease as asphaltenes increase. Petersen discusses the effects of strongly associating functional groups in asphalts either naturally present or formed on oxidation. He shows that the saturates fraction is relatively inert to reaction with oxygen. The naphthene aromatic and aromatic fractions have slight and no reactivity, respectively. The Corbett polar aromatics, resins, and asphaltenes are all highly reactive with oxygen.

In earlier work, Rostler and White generally considered the asphaltene fraction almost chemically inert; however, later work by others indicates the asphaltenes are quite reactive with oxygen. Work by Petersen and his co-workers has identified a number of polar groups formed during oxidation and offer a suggested mechanism for the free radical air oxidation of asphalt. It is hoped that their studies and similar ones by other researchers will lead to a better understanding of what occurs and provide clues as to how such reactions could be inhibited, or possibly lead to compositional adjustments to provide asphalt cements of greater durability. However, at present there is insufficient information to permit adoption of specification requirements based on chemical factors. Present specifications use the thin film oven test as a measure of the relative durability of asphalt cements. This test is considered to produce hardening similar to the hardening that occurs during pugmill mixing. There is also a relationship between the result of the test and the hardening that occurs in a pavement, although some believe that different reactions occur at lower temperatures and longer times than occur during the thin film oven test.

Special Problems with Drum Mixing

Another problem recently identified is the varying behavior of asphalts of the same grade in drum mixing plants. As Petersen concluded, and as is generally accepted based on experience with pugmill mixers, volatile components in an asphalt meeting present specifications are a minor factor in asphalt hardening. However, some asphalts have sufficient "light ends" (low boiling and low molecular weight constituents) to create problems of contamination of baghouses attached to drum mixers.(14) Such problems relate to the steam distillation of components when the asphalt has been produced by atmospheric distillation or by blending soft and hard residues for intermediate consistencies. Although Brock states that steam distillation test results are not compatible with thin film oven test losses, a correlation coefficient value of 0.83 from his data indicates that a reasonably good correlation does exist. The latter test was established to approximate the losses in a batch type pugmill.

There appears to be a need to further identify characteristics of asphalts affecting hardening during drum mixing, and particularly to give attention to the problem of distillation of components from the asphalt that contaminate baghouses and create potential hazards from fires. These considerations could possibly lead to the development of a test or tests suitable for use in specifications to limit light ends below a safe level when utilizing drum mixers. However, information now available is not sufficient to accomplish such an objective. The contractor's best course of action at present is to determine by trial and error which of several sources of asphalt that might be available to him would provide minimum baghouse contamination and the safest operation for his plant.

Asphalt-Aggregate Interactions

The asphalt technologist recognizes that certain combinations of asphalt and aggregate work together better than others. Often problems relating to tender mix, tearing behind the paver, and stripping can be solved by a change in the source of aggregate or asphalt, and it is very difficult to detect differences in the new and replaced components by the usual tests made on the material. The successful elimination of problems by a change in the source of one component is most likely attributable to differences in the asphalt composition or surface chemistry of the aggregate not normally measured. The excellent work of Petersen, Plancher, Ensley, and their associates at the Western Research Institute, formerly the Laramie Energy Research Center, at Laramie, Wyoming, has done a lot towards attaining an understanding of asphalt-aggregate interactions. Unfortunately, one of the more important findings of this group is that the problem is extremely complex. The many interrelations tend to rule out generalized solutions based on measurable engineering properties of the asphalt or simple physical attributes. But it is hoped that the work of this group and others in similar studies will continue and that an understanding of the underlying basic principles involved will eventually lead to means of detecting or avoiding improper combinations of factors.

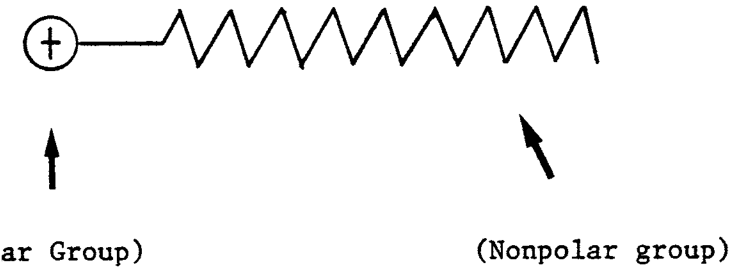
The complexity of the problems is typified by the symposium on Antistripping Additives in Paving Mixtures held during the 1982 meeting of the AAPT.(15) Although the stated objective of the symposium was to assess whether the antistripping additives measure up to expectations,(16) the papers and the published discussion generally emphasized that simple causes and effects could not always be isolated. The survey of states' practices reported by Tunnicliff and Root revealed that none of the tests used nor methods of evaluating the effectiveness of antistripping additives, by themselves, appeared capable of predicting moisture damage in asphalt concrete pavements.(17)

A complete review of all the various aspects of the problem is beyond the scope of this presentation; however, some generalized observations that may be helpful to engineers in understanding and possibly avoiding problems are summarized in the following sections.

Stripping

An early concept of stripping was that aggregates may be hydrophobic (water-hating) or hydrophillic (water-loving). Those that "hate water" were assumed to be preferentially wetted by asphalt while those that "love water" were preferentially wetted by water and under some circumstances the water would displace the asphaltic film. Under this concept, it was assumed that limestones would be hydrophobic and thus limestone-asphalt-mixtures would not have stripping problems. However, this assumption has been shown not to be true. In some states, long-term stripping with limestone has occurred.

Generally, commercial antistripping additives are cationic surfactants. These are often pictured as being composed of a polar group with a positive electric charge combined with a long chain nonpolar segment of the molecule. This is sometime depicted as follows:



This type of presentation has been referred to as the "tadpole" theory. The head of the tadpole, being positively charged, is attracted to the negatively charged aggregate surface and has the ability to displace water from the aggregate surface; the tail of the tadpole, being nonpolar, is compatible with asphalt so that a good adhesive bond is formed between the aggregate and the asphalt. Unfortunately, while this simplified picture essentially represents the ideal, many practicalities prevent its complete fulfillment. The additives are now known to react with different asphalts in different amounts. All of the tadpole molecules will not migrate to the surface, even if unreacted. It is also known that the strength of the attractive forces will vary for different combinations of aggregate and asphalt. Discussions of the fundamental chemistry and these difficulties are included in the presentation by Dybalski at the symposium.(18) Anderson, Dukatz, and Petersen also studied the effect of antistripping additives on the properties of asphalt cement and reported the following conclusions.(19)

1. Antistrip additives can affect the physical properties (consistency) of asphalt cement. In general, the addition of the additives tends to soften the asphalt. Aging characteristics and temperature susceptibility can also be affected; the limited results indicate a reduction in temperature susceptibility and an improvement in aging characteristics.

2. The effect of the antistrip additive is asphalt specific, that is, different asphalts are affected differently by different antistrip additives.

3. It appears that the additives affect properties of asphalts primarily by disrupting or altering the molecular interactions of polar species in the asphalts.

4. The addition of an antistrip additive to an asphalt that meets specifications may be sufficient to cause noncompliance. Agencies should make allowances for this effect if a specification asphalt is treated after the addition of an antistrip additive.

5. Each asphalt has a certain "demand" for the antistrip additive. This suggests that a minimum or threshold percentage of antistrip must be added to an asphalt before it is available to the aggregate surface, and explains why different asphalts require different minimum antistrip dosages.(19)

Fundamental Studies of Asphalt-Aggregate Adhesion

The fundamental approach to solving the problems relating to asphalt-aggregate adhesion taken by the group at Laramie has identified specific functional groups in the asphalts that are absorbed at the asphalt-aggregate interface. A number of papers have been published covering various phases of this work. These are generally summarized in reference 2. The practical significance of these efforts is best typified by the chemistry of the asphalt-aggregate interaction in relation to the pavement moisture damage prediction test, as noted in Transportation Research Record 843(20) and the discussions following the earlier paper presented to the AAPT identifying the chemical types in asphalt strongly absorbed at the asphalt-aggregate interface and their relative displacement by water.(21)

Plancher, Dorrence, and Petersen summarized their initial work as follows:

> This study showed that the strongly adsorbed asphaltic components found at asphalt-aggregate interfaces (less than 1 percent of the original asphalt sample in our nearly uniform samples containing no fines) formed a monomolecular layer that consisted primarily of five oxygen-containing functional group types and nitrogen compounds believed to contain basic pyridine-type nitrogen. The five oxygenated functional types were: ketones, carboxylic acids, dicarboxylic anhydrides, 2-quinolone types, and sulfoxides. Carboxylic acids were the compound type most selectively adsorbed from the asphalts on all aggregate surfaces. Adsorption studies involving model compounds gave results supporting those observed in the asphalt-aggregate adsorption study.

> The moisture-damage tests showed that carboxylic acids, the compound type most selectively adsorbed by all aggregate surfaces, was also the compound type most readily displaced by water. Anhydrides were displaced, but to a lesser extent than acids. Sulfoxides showed either selective retainment or displacement behavior, depending on the aggregate and asphalt system involved. Ketones and nitrogen compounds were selectively retained by aggregates during moisture-damage tests. Although sulfoxides and nitrogen compounds comprise a significant amount of the material displaced from the aggregate surface by water, their role in water stripping is not clear. It appears that both the relative amount and chemical type of the strongly adsorbed material displaced by water and the nature of the aggregate surface play an important role in moisture damage of asphalt pavements.(21)

In the follow-up work reported in Transportation Research Record 843, Petersen and his co-workers studied asphalt-aggregate combinations using the same materials as used in the National Cooperative Highway Research Program Field Evaluation Project on predicting pavement moisture damage conducted by Lottman. In summarizing their findings they stated:

> Relationships were found between fundamental chemical and physical properties of the asphalt-aggregate bond and moisture-induced damage in laboratory-prepared pavement mixtures that were subjected to accelerated conditioning by using the Lottman procedure. For most mixtures of the Lottman-NCHRP study, resistance or susceptibility to moisture-induced damage appeared to be controlled by a number of interrelated variables. These variables must be considered in concert to rationalize pavement moisture damage with fundamental bond properties. The moisture sensitivity of the pavement mixtures in the Lottman-NCHRP study, as predicted by the TSR ratios, was explained by considering fundamental properties of the asphalt-aggregate bond.(20)

The generalized picture that evolves from this work is that asphalts contain several types of functional groups that are adsorbed at the asphalt-aggregate interface. However, such adsorption occurs at specific sites or locations on the aggregate surface based on the aggregate chemistry. The chemistry of these sites may also be different. Thus, not only do different groups compete for the available sites, both the amount and types of groups present and the fluidity of the asphalt have a bearing on results. In addition, the surface area and type of aggregate involved affect the number of sites available. All of these interrelated factors affect the initial asphalt-aggregate adhesion and the relative strength of the bond. When water enters the system a whole new system of interrelated effects are triggered. The absorbed materials are subject to displacement by water in varying degrees. In some cases the most easily adsorbed compounds, for example, carboxylic acids, are also those most easily displaced by water. A further complication develops if sodium hydroxide is used in the asphalt refining process and the carboxylic acids are converted into organic salts that have an affinity for water and can act as emulsifiers of the asphalt under mechanical agitation, thus further destroying the strength of the asphalt-aggregate bond. A still further complication is that some of the reactive chemical groups can be formed with the passage of time and cause changes in the resistance to deterioration in the presence of water.

Because of this complex picture, it is clear that a universally applicable solution to the asphalt stripping problem is not possible. Additives or admixtures effective with one combination of asphalt and aggregate may not work with another. Thus, highway engineers must use physical tests of the actual combinations of asphalt-aggregate in order to become aware of potential stripping problems and to evaluate remedial measures. At present, most available tests measure the adequacy of the asphalt-aggregate adhesion and resistance to moisture damage for a relatively short term. The cause of damage that occurs in the pavement after several years is not as yet well understood, nor is it clear what remedial measures might prevent such damage.

Tender Mixes

The term "tender mix" is often used to denote a condition noted during the construction of an asphalt pavement. It is applied to those mixes that "shove" under normal rolling procedures. It is also applied to mixtures that, after compaction and cooling, have a low resistance to being marred or scuffed by the turning action of vehicles, especially trucks.

While the asphalt often gets the blame for tender mixes, other causes may be predominant. Goode showed that the aggregate gradation was very often a contributing cause.(22) His study indicated that a hump in the aggregate gradation line above the maximum density line plotted on his gradation chart was inevitably found in the problem (tender) mixes he studied. (His maximum density line is a straight line plotted on the gradation chart where the percentage passing is plotted against the sieve sizes raised to the 0.45 power.)

Marker cited the presence of moisture as a major cause. He attributed the problem to an excess of fluid, the fluid being asphalt plus water. When this occurs, the aggregate particles are prevented from making good contact or interlocking because of the excess of fluid. Too much asphalt or too high temperatures are also possible causes unrelated to asphalt properties.(23)

In a number of cases tenderness in the mix is eliminated by changing the source of asphalt, which leads to the conclusion that the asphalt is at fault. However, it is probable that a combination of factors operate in any given instance and the asphalt is only one factor.

Skog considers "setting qualities" of the asphalt important.(24) Although he related the problem of different behavior of asphalts from different sources to the variation of changes in viscosity during mixing, asphalts set (harden) by molecular structuring. As Petersen states, this is probably one of the least understood physiocochemical phenomenon affecting physical properties.(2) It is a reversible phenomenon that can produce large changes in the flow properties of asphalt without altering the chemical composition of the asphalt molecules. Petersen further points out that without molecular structuring, pavement mixtures would not set to produce non-tender pavements with the desired structural integrity. However, too much structuring can produce pavements with poor low temperature properties and high shear susceptibility. Petersen also states that asphalt-aggregate interactions can affect the degree and rate of molecular structuring, which may be an explanation of why the same aggregate would work well with one asphalt and not another. On the basis of present knowledge, highway engineers faced with tender mixes after eliminating controllable causes such as improper amounts of asphalt, too high compaction temperatures, or poor aggregate gradation, can only resort to trial and error changes in asphalt sources. At this time there appears to be no direct test on asphalt that will predict the probability of such behavior.

CHAPTER 4

APPLICATION OF ASPHALT TECHNOLOGY TO SPECIFICATIONS FOR HIGHWAY ASPHALTS

The foregoing discussions of asphalt technology and composition, most of which were taken from the published Proceedings of the AAPT, show that despite the complexity of the many interrelated factors, considerable progress has been made in identifying significant relationships between chemical and physical properties. The question then becomes, How much of this increased knowledge has been utilized to improve specifications for asphalt cement? The answer to this question is, None to very little! This is not necessarily an indictment of asphalt technologists or those who prepare specifications for highway materials and highway construction procedures. It relates more to the facts of life regarding the manufacture, marketing, and use of asphalts in highway construction.

Asphalt is essentially a by-product of the manufacture, or separation, of liquid petroleum fuels from petroleum. Even though in a few cases the asphalt may be considered the major product from refining a crude petroleum, in a great majority of cases the liquid fuels -- gasoline, jet fuel, and diesel oils -- are the products of primary interest. Asphalt is the bottom of the barrel that must be disposed of either as a residual fuel, a paving material, or industrial products such as roofing shingles, etc.

In some cases use as a residual fuel is uneconomical because of antipollution regulations that limit the amount of sulfurous gases that can be discharged into the atmosphere. In such cases, disposal by sale as a highway binder is the most feasible option. In other cases, the relative demand for and price of residual fuel and asphalt will determine how the residual is to be marketed.

In general, the supply of asphalt is limited by the demand for fuels and not by the demand for a highway binder. This situation means that a refiner is not likely to process the residue to any greater extent than is necessary to comply with specifications -- if the product will meet specifications without processing, it most likely will be sold as is even if it is known that a better product could be provided by further processing. The specifications for asphalt, then, must control the quality of the product.

Requirements for Asphalt Quality

Efforts to determine asphalt quality by specification tests and requirements have been almost exclusively related to the physical characteristics of the asphalt, the exception being the Oliensis spot test for homogeneity that adequately identified cracked asphalts. However, as previously discussed, asphalts that gave only a slightly positive spot in the test (usually a ring difficult to see instead of a dense, centered spot) were shown to be good paving materials.

Krom and Dorman list the three main characteristics of asphalts that must be considered in relation to their quality as --

1. mechanical properties, i.e., properties governing behavior under stress;

2. adhesion; and

3. durability, i.e., changes in properties during storage, application, and service.(25)

Skog listed the desirable properties as consistency, rate of curing, or setting durability, and resistance to water action.(24) Although stated differently, those two lists are in essential agreement. Consistency is a part of the mechanical properties and resistance to water action relates to adhesion.

Mechanical Properties

Mechanical properties are a function of the consistency. The asphalt technologist has an independent choice of one of several degrees of hardness at a single temperature -- 77°F. (25°C.) for the system using penetration and 140°F. (60°C.) for the system using viscosity. However, since asphalts from different sources have different viscosity-temperature susceptibility, precise control is available for only the single temperature used for determining the asphalt grade. Under the viscosity grading system, the objective is to limit the viscosity-temperature susceptibility to a workable range by establishing a minimum viscosity at 275°F. (135°C.) and a maximum consistency, the equivalent of viscosity, measured by penetration at 77°F. (25°C.). It is noted that the minima and maxima established do not assure that all asphalts of the same grade will have the same mechanical or rheological properties over the total range of temperature to which the pavement is exposed. It is the intent of the viscosity grading system to equalize differences in asphalt at the compaction and mixing temperatures when they are the same grade but from different sources of petroleum. Mixing and rolling temperatures can easily be adjusted for optimum viscosity. However, adjustments for stiffness and other mechanical properties at low temperatures [32°F. (0° C.) or lower] can be made only by selecting a different initial grade of asphalt. In this case, the lowest asphalt grade consistent with the ability of the mixture to withstand rutting should be used.

It is known from studies of asphalt composition and functionality that changes in the ratios of generic classes of compounds in the asphalt could be used to improve (decrease) the viscosity-temperature susceptibility, but there is no strong evidence that such procedures would be effective from the viewpoint of overall asphalt quality. For example, oxidation by "blowing" will accomplish the purpose of lowering the viscosity-temperature susceptibility but it must be used with caution for highway asphalts, as the accompanying loss of ductility through the development of a gel asphalt with very high shear susceptibility will destroy the ability of the asphalt to perform well in the road.

The following discussion, essentially the same as previously presented in reference 13, evaluates the effects of the extreme differences in viscosity-temperature susceptibility when American Association of State Highway & Transportation Officials (AASHTO) specifications are used.(13)

Examination of data from the 1979 Asphalt Institute study of asphalt properties (26) shows the extremes of viscosity-temperature susceptibility being supplied by these specifications and permits an assessment of their significance. A good range for asphalt viscosity for mixing is considered to be from 150 to 300 centistokes. If the optimum is assumed to be 200 centistokes (equivalent to 2 poises), the Asphalt Institute data show that the most temperature-susceptible AC-20 has that viscosity at 292°F. (144°C.), and that the least temperature-susceptible AC-20 has this optimum viscosity at 307°F. (153°C.). In most specifications the allowable spread in mixing temperatures is the target value ± 20°F. (±11°C.). Consequently, the 15°F. (8°C.) spread indicated here for the extremes is hardly significant. Similarly, when the range of temperatures for the optimum compaction viscosity of 20,000 centistokes (equivalent to 200 poises) is examined, the most susceptible asphalt has this viscosity at a temperature of 173°F. (78°C.) and the least susceptible has it at 179°F. (82°C.). This 6°F. (4°C.) spread is certainly of no concern from the construction standpoint.

At low temperatures, the range of temperatures for equal apparent viscosities is relatively large. However, the concern is not with such differences, but with whether or not the hardest material forms a mixture that is not so stiff that excessive cracking occurs at the lowest temperatures encountered. A detailed discussion of what this critical stiffness should be is beyond the scope of this presentation, and more is involved than just the apparent asphalt viscosity.

The basic problem is to design a mixture that has adequate stability at the highest summer temperatures to avoid rutting and shoving and that at the same time is not so stiff or brittle at low temperatures that cracking occurs. A number of factors are involved in this problem, including aggregate type and gradation, percentage of asphalt used, and the range of ambient temperatures expected in service, as well as the characteristics of the asphalt. Differences in shear susceptibility of asphalts that significantly affect apparent viscosity-temperature susceptibility can have a significant effect on critical stiffness or the tendency of an asphalt mixture to crack at very low temperatures. This characteristic is not directly measured by present specifications.

Generally, most efforts to improve flexibility at low temperatures have involved the incorporation of rubber or some other elastomer in the mixture. More fundamental changes in the characteristics of the "natural" molecules found in asphalts might provide progress in this area, but more research is needed.

The Durability Aspect

In highway construction the durability of the pavement is of concern. That is, How long does it perform its intended purpose without excessive deterioration? It is known that many factors enter into such durability, including type and gradation of the aggregate and the amount and consistency of the asphalt used. Accordingly, the durability of the asphalt cement itself is difficult to define. However, as stated earlier, durability is considered to relate to how well the asphalt retains its original characteristics during the construction of the pavement and during its service, provided the initial characteristics were as desired. For specification purposes the resistance to change during the thin film oven test is considered related to asphalt durability. Such resistance to change should be considered from the standpoint of changes in ductility as well as changes in consistency.

Significance of the Thin Film Oven Test

The thin film oven test was developed as a means for measuring the relative hardening characteristics of asphalt cements during mixing.(27) When first introduced, there was opposition to this test primarily on the basis that the conditions of the test didn't "match" either performance conditions or conditions during service. However, the 1/8-inch (3.2 mm.) thickness and 5-hour time were established by trial and error from tests at a number of thicknesses and periods of time. The temperature of 325°F. (163°C.) was carried over from the initial test, since it represented a "normal" upper limit of mixing temperature in a pugmill. Hardening can occur during mixing of an asphalt in a pugmill from both oxidation and volatilization. The relative amount of hardening from each cause varies, depending on the source and method of refining of the asphalt. In the development of the test, it was found that the 1/8-inch (3.2 mm.) film and 5-hour time was the combination of conditions that most nearly matched the hardening that occurred during mixing of an 85-100 penetration asphalt at 300°F. (149°C.).

It is known that the amount of hardening during the test does not necessarily equal hardening in the pugmill when materials either harder or softer than 85-100 are tested. Changes in the temperature of the mixing would also affect the hardening. It would be expected that a material softer than an 85-100 or AC-10 that is mixed at a temperature appreciably lower than 300°F. (149°C.) would not harden as much during mixing as in the thin film oven test. Conversely, a material mixed at a temperature greater than 300°F. (149°C.) could harden more during mixing than in the thin film oven test. However, the relative amounts of hardening for different asphalts under different conditions are shown by the relative amount of hardening in the thin film oven test.

Technologists on the West Coast use a rolling thin film oven test in lieu of the 1/8-inch (3.2 mm.) thin film. This test was developed by Hveem in California, because he believed that the reactions occurring during the service of an asphalt in the pavement were more nearly duplicated by the much thinner film of his test, which approximates the film thickness of the asphalt in the pavement. The 75-minute time was chosen to provide about the same amount of hardening that occurred in a pugmill. Later comparative studies have shown that the two tests give about the same results and are interchangeable. The rolling thin film oven test has an advantage in the time required to make the test, 75 minutes as opposed to 5 hours, but a disadvantage in that the amount of material tested, 20 ml as opposed to 50 ml, requires more individual determinations if sufficient residue is to be obtained for a ductility determination.

Both AASHTO M226 and ASTM D3381, the specifications for viscosity graded asphalts, have ductility requirements for the thin film test residues. The use of the thin film tests has eliminated from the market those materials having appreciable amounts of volatile constituents (2%-4%) that resulted in extreme hardening during mixing. It also prevents the use of materials that would lose ductility very rapidly during mixing or service in the pavement. The implications of a loss in ductility will be discussed in the following section. It is also noted that the grading of asphalt cement on the West Coast is based on the residue from the rolling thin film oven test. This is based on the concept that the residue consistency more nearly represents the consistency of the asphalt in the pavement immediately after laydown. Initial developmental work showed this to be generally true when based on pugmill mixing and temperatures then in general use. However, the introduction of drum mixing may require a reassessment of whether or not this condition still holds.

The problem of steam distillation of constituents from asphalt discussed by Brock and previously mentioned also requires further research to determine if a different test is needed for determining the suitability of asphalts for use in drum mixers.(14)

From the standpoint of chemical composition, the volatile materials removed in the thin film oven test are lower boiling constituents not removed in the preparation of the asphalt to meet specifications. If hard asphalts and soft asphalts have been blended to meet an intermediate grade, the volatile portion almost certainly is desired from the softer material. Hardening from loss of such volatile matter would not likely change the viscosity-temperature susceptibility or attributes of the asphalt other than viscosity. On the other hand, if hardening occurs from oxidation, the amount of asphaltenes in the asphalt system increases, the temperature susceptibility changes, and there are potential changes in ductility for the same consistency. Additives to retard the rate of hardening in asphalts have been proposed by various authors at different times but no general use has been made of these compounds.(28,29,30,31)

Significance of Asphalt Ductility

The ductility test, developed in 1903 by Dow, was part of the first "standard" specification for asphalt. It is without question the most controversial test in asphalt specifications. Some asphalt technologists believe that the test is an indication of a necessary property of asphalt related to its cohesive properties, or stickiness, but others consider the present laboratory test for ductility of no value for indicating the potential quality of an asphalt as a paving material. In a study reported in the 1963 *Proceedings* of the AAPT, it was shown that the consistency at which asphalt begins to lose ductility rapidly and the temperature at which such consistency occurs is a significant relationship affecting pavement performance.(32) An examination of data from a number of experimental projects indicated that there is a critical ductility-penetration (or viscosity) relationship. When ductility for a given penetration exceeds this critical value, problems resulting from insufficient ductility are not likely to occur. If ductility is inadequate at the indicated consistency, failures from insufficient ductility can occur. It is believed that this assessment of significance is applicable to asphalts containing "natural" constituents. Should adequate ductility be attained by the use of additives, there is a possibility that the resistance of the additive itself to heat and exposure in the pavement would affect results.

Most critics of ductility examine it at a given temperature and dismiss its importance. One reason given is that essentially all asphalts have ductilities greater than 150 cm -- the maximum length of most equipment for measuring ductility at 77°F. (25°C.); therefore, they conclude that the requirement is not needed. A second reason is that the precision of the test is not acceptable. Others show a lack of correlation of ductility (usually measured at low temperatures) with service behavior. All of these reasons have some validity, but the conclusion that a ductility requirement is not needed for highway asphalts on these bases is not warranted. First, the ductility requirement that now appears in essentially all asphalt cement specifications for highways effectively eliminates from the market materials that in the absence of such a requirement could be supplied. Field experiments using materials with very short ductility in pavements have almost universally showed poor performance. These are highly gelled asphalts that most likely lack sufficient internal cohesion to exhibit "self-healing" properties. Secondly, a linear type relationship between the amount of ductility and performance should not be expected. Ductility should be viewed on a go-no-go basis. If the ductility is adequate, failure from this cause is eliminated, and doubling ductility wouldn't double service life and probably would have little effect, because failure or distress then would develop from other causes. Because of the go-no-go approach, the poor precision of the test seldom creates problems in asphalt testing because once the use of materials unsuitable because of short ductility is eliminated, the suitable materials being supplied almost always exceed the acceptable limit by a wide margin. Support for the above conclusions is given and discussed in reference 13.

Adhesion of Asphalt to Aggregate

There is no requirement in present asphalt specifications that relates to how the asphalt adheres to aggregate or whether it is susceptible to stripping from the aggregate. Research is needed before test procedures and requirements to establish whether or not minimum functionality in this respect is feasible, or whether the use of additives in the asphalt might provide suitable properties. At present, some states have requirements for qualifying specific asphalt-aggregate combinations by means of tests such as the Lottman procedure or other physical tests for potential damage. Such requirements should be universal. The type of problem that can arise is typified by the experience of one eastern state which approved a source of asphalt based on the asphalt supplier. However, a change in the source of the asphalt furnished the supplier resulted in immediate failure of the asphalt mixture from stripping, even though the same aggregate had performed well with other asphalts over a long period of time. Later investigation revealed that the asphalt manufacturer had used sodium hydroxide in the course of refining, and even though the excess caustic may have been later neutralized, the presence of organic sodium salts in the asphalt made mixtures with a silicious type aggregate very highly susceptible to disruption of the asphalt-aggregate bond in the presence of water. In this case, the water used to wet the roller was sufficient to initiate stripping. Use of the same asphalt with a calcareous type aggregate in an adjoining state did not result in this difficulty.

This is an area of considerable concern to a number of state transportation departments since it reveals an unexpected inadequacy of the specification. As previously discussed, more needs to be known about the asphalt-aggregate interactions and the long-term effectiveness of additives in preventing water damage in pavements. While on the basis of present knowledge it is unlikely that revisions to the asphalt cement specification would solve the problem, it is believed that the addition of a requirement limiting the total or water soluble ash content would prevent the catastrophic failure mentioned.

Other Specification Requirements

Requirements for flash point and solubility are also usually found in specifications for asphalt cement. Flash point is required as an indication of how high the material may be heated before a potential fire hazard is created. It is useful from the standpoint of shipping regulations but has little significance from the standpoint of pavement quality. Solubility in trichlorethylene is a check for purity to avoid contamination with insoluble hydrocarbons.

Difficulties Created by Present Marketing Procedures

Present marketing procedures based on economic considerations create some potential problems for the asphalt contractor and the state. In Virginia, and a number of other states, asphalts are shipped to terminals owned either by the refining company or by an asphalt broker who may obtain asphalt from different refineries depending on costs. Similarly, a paving contractor may purchase asphalt from different suppliers. At times, different sources of supply are approved for the same job. In addition, the state is requested to establish a single grade it will use for all its work during a given season.

Although the use of a single grade for all work does not necessarily create problems, it has a potential to do so. Such problems could be extremely costly to the state and paving contractors. The potential danger lies in unexpected nonuniformity of asphalts meeting the same specification grade. Although the specifications are designed so as to minimize differences in viscosity-temperature susceptibility, changes from one permissible extreme to another could cause problems. Generally, these can be dealt with if it is known that the change has been made.

The "requirement" that a decision be made to use only one grade of asphalt for all construction during a single season takes one option away from the mix designer. Thus, characteristics of a pavement mix made with AC-20 may be optimum for one set of environmental conditions, but for another different weight and frequency of traffic or different environmental conditions may indicate that AC-10 would be a better grade. The option to change should be retained by the state.

The potential problems that might arise from changes in viscosity-temperature susceptibility are likely to be much less catastrophic than problems that would arise if the resistance to water damage of the asphalt-aggregate combination were to change drastically for the worse, as could happen. Thus, when either the asphalt source or aggregate is changed, the resistance of the mixture to water damage should be evaluated unless it is known from experience.

CHAPTER 5

RECOMMENDATIONS

1. Although present knowledge indicates that improvements in the physical properties of asphalt cements are possible by adjusting the ratios of generic fractions and possibly the functional groups by selective blending of asphalts from different sources, or through the use of additives, present knowledge is not sufficient for establishing specific requirements. Also, the effect of such adjustments on the cost of asphalt is not known, but is likely to be high. Accordingly, the insertion of composition related requirements in asphalt cement specifications is not recommended.

2. Asphalts resulting from refinery techniques in which sodium hydroxide has been used and which contain significant amounts of organic sodium salts have been shown to be highly sensitive to moisture damage when used with aggregates of known good performance records. Accordingly, such asphalts should be ruled unacceptable for highway construction. To accomplish this it is recommended that a requirement that the ash from burning a sample of asphalt not exceed 0.40% be adopted for asphalt cements as an interim measure. A study should be conducted to determine if a requirement for maximum amount of sodium and/or potassium in the ash is feasible or if a value other than 0.40% would be more realistic.

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APPENDIX A

CHARACTERISTICS OF ASPHALTENES

Asphaltenes make up the fraction of asphalt that is generally considered to have the highest boiling temperature and to be the most complex. A comprehensive study of asphaltene composition was reported by Girdler in 1965.(1)* He showed differences in properties of asphaltenes from different crudes. He also demonstrated that the amount of material precipitated as asphaltenes from the same asphalt varied depending on the solvent used. Lower amounts are precipitated as the number of carbon atoms in the nonpolar (or paraffinic) solvent increases. Thus, more asphaltenes are precipitated by n-pentane than by n-heptane.

One significant finding of Girdler's work is illustrated by Figures A-1 and A-2, taken from his report.(1) Figure A-1 shows that for values of carbon in the solvent chain above 7 the change in amounts precipitated is relatively small compared to changes for lower carbon chains. Figure A-2 shows that the carbon-to-hydrogen ratio of the precipitated asphaltenes is relatively constant for values of carbon numbers above 7 (n-heptane) in the solvent. Thus, Girdler concluded that using n-heptane as the solvent provides a measure of the "hard core" asphaltenes. The asphaltenes precipitated with pentane (carbon No. 5) apparently contains more resinous type molecules than those precipitated by n-heptane. Thus, to be precise, the solvent should be identified when referring to asphaltenes -- for example, pentane asphaltenes or heptane asphaltenes as the case may be.

Studies by Boduszynski and his associates emphasize that asphaltenes do not exist as an entity in asphalt cement but are made up of highly polar compounds that associate (combine) after the asphalt is dissolved and thus are precipitated from the solution.(2) Asphaltenes, therefore, are not chemically defined components but their composition is dependent on both the chemical composition of the asphalt and the type of solvent used for precipitation.

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*Numbers in parentheses indicate reference numbers found at the end of this Appendix. In some instances the reference duplicates a reference in the body of this report.

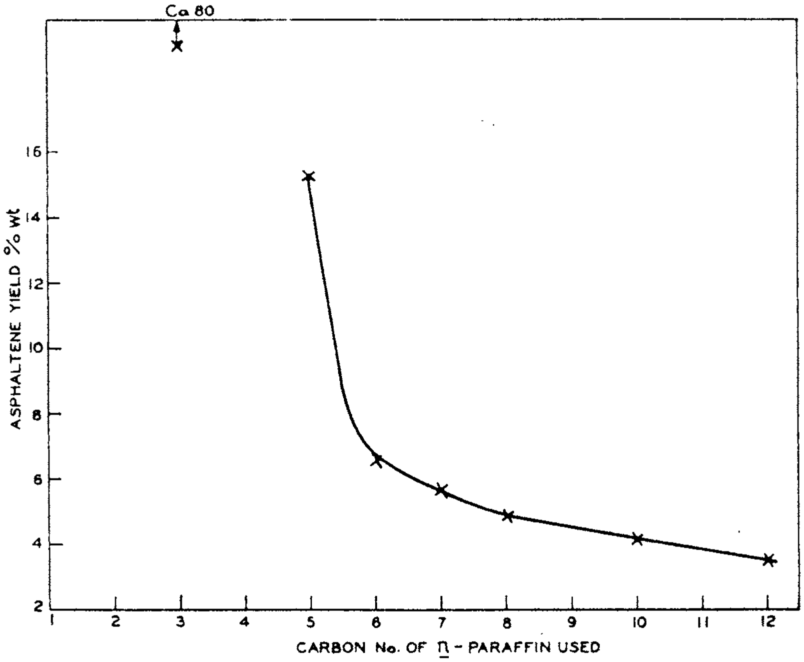

Figure A-1. Relation between Carbon No. of Precipitation n-Paraffin and Yield of Asphaltenes from Kuwait 120 Penetration Vacuum Residue. (From reference 1 of this Appendix.)

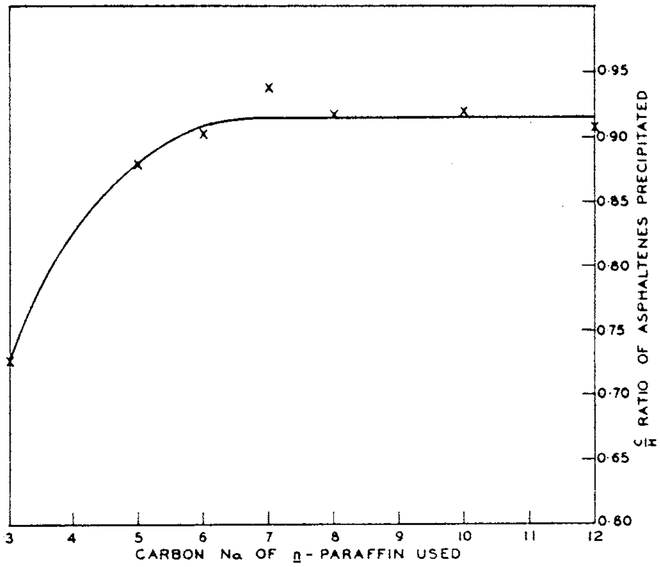

Figure A-2. Relation between Carbon No. of Precipitatin n-Paraffin and $\frac{C}{H}$ Ratio of Asphaltenes from Kuwait 120 Penetration Vacuum Residue. (From reference 1 of this Appendix.)

Asphaltenes generally have been considered to have the highest molecular weights of all components, a range of 5,000 to 50,000 having been reported. However, Boduszynski (reference 2) reports that the average mass value of asphaltenes is 873 -- the lowest of all fractions studied in his separation technique. The high degree of association and very high polarity account for the apparently very high molecular weights reported by others. The mechanism of asphaltene formation is explained by Boduszynski as follows:

> Treatment of the asphalt with normal alkane (heptane) upsets the solubility equilibrium of a very complex mixture of asphalt components. The excess of nonpolar solvent causes the most polar compound types present in the asphalt to become insoluble. These compound types are capable of strong intermolecular associations resulting in the formation of agglomerates which precipitate as asphaltenes. Both the formation and composition of the asphaltenes result from a solubility phenomenon of the physical separation procedure.

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APPENDIX B

ANALYTICAL PROCEDURES FOR CHARACTERIZING MALTENES

Four major procedures have been devised for characterizing the maltene fraction of asphalts. These are:

1. Selective adsorption-desorption
2. Chemical precipitation
3. Partitioning with partial solvents
4. Separation by molecular size, gel permeation chromatography, high pressure liquid chromatography also referred to as high performance liquid chromatography (HPLC).

Selective Adsorption-Desorption

Figure B-1 illustrates the method of analysis developed by Corbett, which was selective adsorption and desorption. This procedure, described in detail in reference 1(1)* is widely used as a separation technique in research. The asphaltenes are first separated on the basis of their insolubility in a nonpolar solvent composed of paraffinic hydrocarbons (n-heptane). This removes the most polar and least soluble asphalt components and generally facilitates further separation. The solution of the remaining fraction, the maltenes, is then introduced into a chromatographic column which absorbs most of the dissolved constituents. Different solvents of increasing polarity are then used to sequentially desorb (wash out) fractions of increasing polarity.

The first fraction to emerge from the column is termed the "saturates" fraction. This fraction lacks polar chemical functional groups and thus is not absorbed. As Petersen states, this fraction is named to indicate the major type of compounds present, but it is still a complex mixture and will usually be made up of saturated normal and branched chain hydrocarbons, saturated cyclic hydrocarbons (sometimes called naphthenic hydrocarbons), and possibly a small amount of mono-ring aromatic hydrocarbons.(2) Those molecules containing ring systems are dominated by attached saturated hydrocarbon sidechains. Sulfur is often found incorporated in molecules of the saturates fraction.

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*Numbers in parentheses indicate reference numbers found at the end of this Appendix. In some instances the reference duplicates a reference in the body of the report.

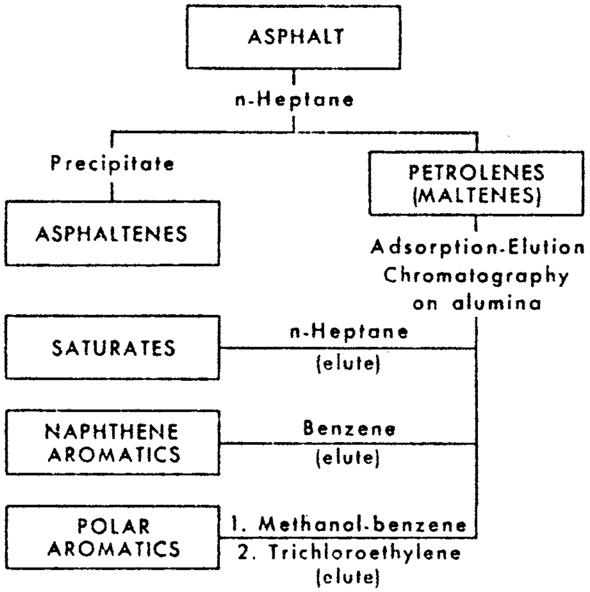

Figure B-1. Selective Adsorption-Desorption.
(From reference 1 of this Appendix.)

After the saturates are washed through the column, a more polar aromatic solvent such as benzene or toluene is added (toluene is now usually used because of a lesser health hazard). This solvent competes for the polar sites on the absorbents, and thus displaces the more weakly absorbed molecules. These molecules are condensed nonaromatic and aromatic ring systems, and, in addition to sulfur, the heteroatoms oxygen and nitrogen may be part of the molecule. In Figure B-1 this fraction is called the "napthene-aromatics" fraction. Finally, a highly polar solvent such as alcohol is added to the benzene or toluene to displace the most strongly absorbed and most polar components of the maltene fraction. The alcohol releases, or more correctly, debonds the components from the absorbent, and the benzene or toluene provides solubility as the components are eluted from the column. This fraction, called "polar-aromatics", contains a higher percentage of highly condensed aromatic ring systems and functional groups containing heteroatoms than other fractions.

All fractions obtained by this procedure contain, to a greater or lesser degree, cyclic and noncyclic saturated hydrocarbon fragments, either as individual molecules in the saturates fraction or attached to the aromatic ring fragments in the more polar fractions. Sulfur is usually found in a large percentage of the molecules, but in unoxidized asphalt it is rather nonpolar and thus is found distributed among all the component fractions. The asphaltene fraction is chemically similar to the more resinous or polar components of the maltene fraction. Although the asphaltene fraction may contain small amounts of occluded or insoluble "saturate-type"material, the significant differentiating feature of this fraction is the preponderance of molecules with highly condensed planar and polarizable aromatic ring systems, together with a high concentration of polar, heteroatom-containing functional groups. Because of these features, molecules of the asphaltene fraction are strongly attracted to each other, associate strongly, and are difficult to disperse, even in polar solvents.

Chemical Precipitation

The procedure depicted in Figure B-2 was developed by Rostler and Sternberg(3,4) and represents more of an analytical method than a method of separation. In this scheme the asphaltenes are separated by n-pentane and the solution of maltenes is sequentially treated with increasing strengths of sulfuric acid. In the first step, 85% sulfuric acid is used to remove the most polar components, including most of the basic and nonbasic nitrogen compounds and many of the oxygenated molecules. This fraction is called "nitrogen bases". Since the nitrogen in asphalt is usually associated with condensed ring systems, the so-called nitrogen base fraction is quite aromatic. Ninety-eight percent sulfuric acid is used next to separate (precipitate) the next fraction, named "first acidaffins" by Rostler. This fraction has been reported to contain unsaturated hydrocarbons.(5) However, Petersen considers this description as unfortunate because "unsaturated" usually refers to double or triple carbon-to-carbon bonds in nonaromatic ring structures (olefinic and acetylinic types) which have not been found in significant amounts in petroleum residues.(2) The first acidaffin fraction is quite aromatic and low in nitrogen content. The most likely reaction leading to the separation (precipitation) of this fraction is sulfonation or complex formation involving the aromatic ring systems. The next step utilizes sulfuric acid containing 30% SO_3 (fuming sulfuric acid). This is a powerful sulfonating-complexing agent, and it precipitates (or decomposes) those components with less reactive or polarizable aromatic ring systems than the components precipitated by the 98% sulfuric acid. Analysis of this fraction, called "second acidaffins", indicates that it is considerably less aromatic than the nitrogen bases or first acidaffins. The final fraction is those components nonreactive to the fuming acid. This is the oily constituent of asphalt and consists primarily of molecules embodying straight chain, branched, and cyclic alkanes.

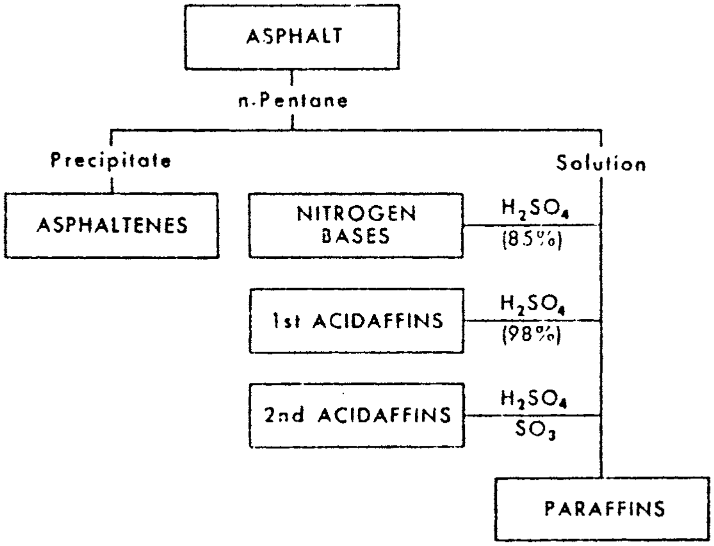

Figure B-2. Chemical Precipitation. (From reference 3 of this Appendix.)

Partitioning with Partial Solvents

Figure B-3 illustrates a procedure developed by Schweyer and Traxler whereby composition is determined by partitioning with partial solvents.(6) Petersen reports that this scheme has not been widely used. The fractions obtained are not as distinctly different as with the other separation methods. The basis of the method is to sequentially treat the asphalt with increasingly polar solvents precipitating a series of fractions with decreasing polarity. Details of the method are found in reference 6.

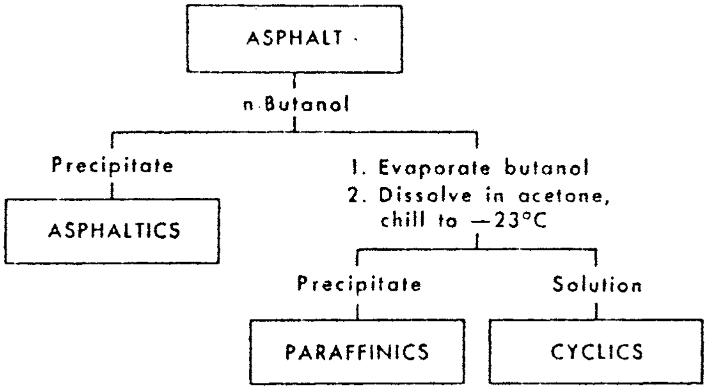

Figure B-3. Partitioning with Partial Solvents. (From reference 6 of this Appendix.)

Molecular Size Distribution by High Pressure Liquid Chromatography

This procedure obtains a chromatogram of the relative amounts of large, medium, and small molecules in an asphalt but it does not result in a physical separation by molecular size. The most recent work with this technique is that of Jennings at Montana State University.(7,8) The technique is most accurately described as high pressure liquid chromatography in the gel permeation mode. It generally is referred to as "HPLC" or "HP-GPC".(8) In the procedure, a solution of the asphalt is passed through gel permeation columns which separate components of a mixture by molecular size. The system permits the largest molecules to pass most quickly through the columns but successively retards the progress of the smaller molecules.

A detector and recorder within the system produces a chromatogram depicting the relative amount of molecules being eluted from the system at different times. Jennings classifies the molecules eluted during the first third of the elution period as large molecular size (LMS), those eluted during the second third of the period as medium molecular size (MMS), and those eluted in the final third as small molecular size (SMS).(7) To provide for comparisons of different runs, an internal standard, polystyrene, that contains molecules of known size, is added to each sample to form a marker on the chromatogram. Superimposing markers permits comparison between chromatograms. The solvent used by Jennings was tetrahydrofuran (THF). A 1% solution in THF of the polystyrene standard having a molecular weight of 35,000 was used to prepare 2% solutions of the asphalts used in the HPLC instrument. Figure B-4 illustrates the type of chromatograms obtained by this procedure and how the data are compared. From the two curves shown in Figure B-4 the differences in the molecular size distribution of the two asphalts can be seen. Generally comparisons of "unknown quality" asphalts are made with known quality materials. When the molecular size distributions are similar, similar field performances are expected. Significantly different molecular size distributions indicate that significantly different performances would be expected.

Significance of Components Obtained by Various Procedures

Corbett Chromatographic Separation

Corbett described the effects on physical properties of the four fractions separated by his procedure in the following manner: "The asphaltenes function as solution thickeners; fluidity is imparted by the saturate and naphthene-aromatic fractions; the polar aromatic fraction imparts ductility to the asphalt; and the saturates and naphthene-aromatic in combination with asphaltenes produce complex flow properties in the asphalt."(9) In summary, Corbett concluded that each fraction or combination of fractions performs separate functions with respect to physical properties, and it is logical to assume that the overall physical properties of one asphalt are thus dependent upon the combined effect of these fractions and the proportions in which they are present.

Rostler-Sternberg Procedure

The functions of the components determined in the Rostler-Sternberg procedure are given as follows: "The asphaltenes are bodying agents. The nitrogen bases (N) are peptizers for the asphaltenes. (A peptizer is a material capable of forming a colloidal solution of the peptized material.) The first acidaffins (A_1) are considered solvents for the peptized asphaltenes as are the second acidaffins (A_2). The paraffins (P) act as gelling agents."(4)

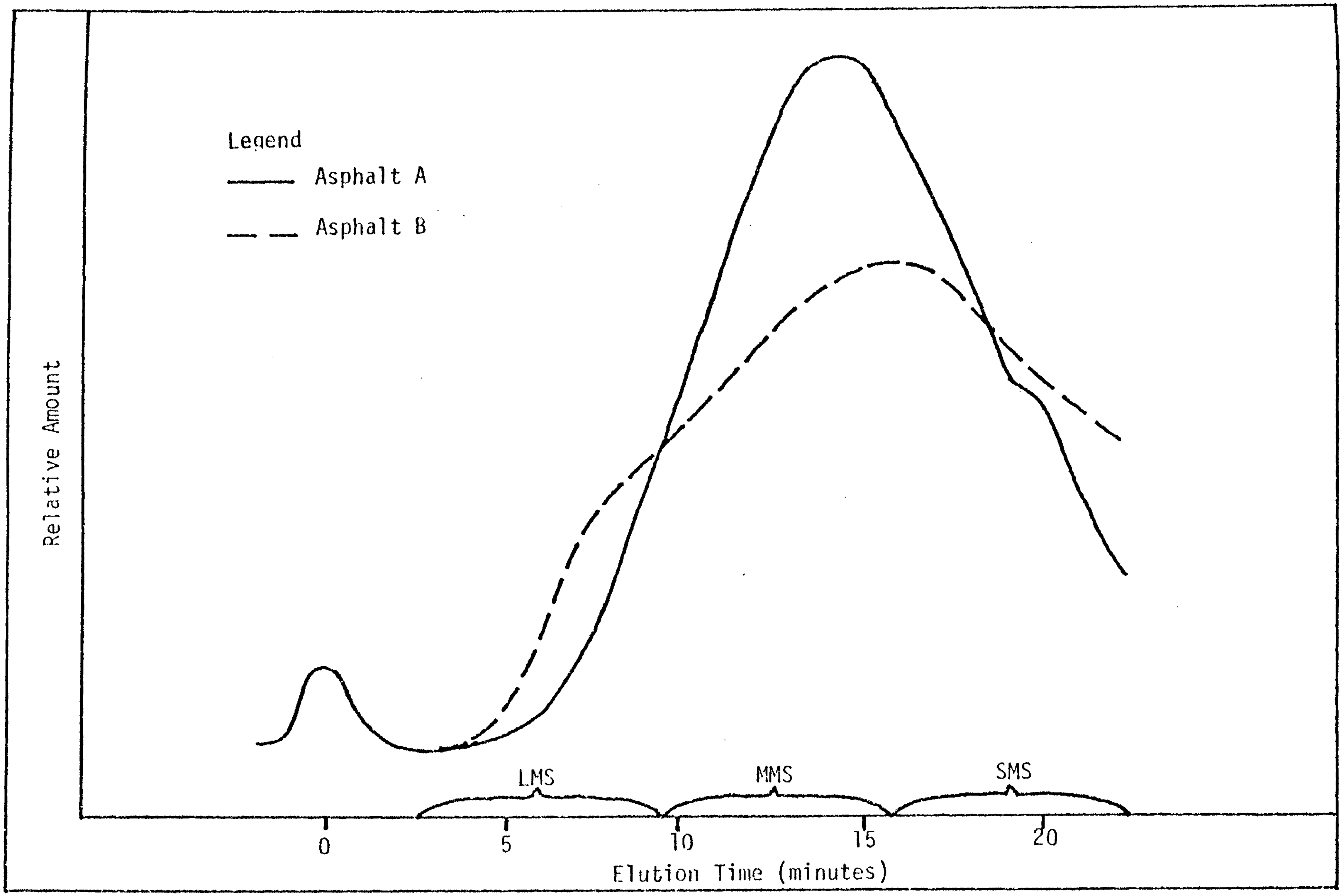

Figure B-4. Typical chromatograms of whole asphalts.
(From reference 7 of this Appendix.)

The most frequent application of the Rostler-Sternberg analysis is the consideration of the ratio of the more reactive components ($N + A_1$) to the less reactive components ($P + A_2$). This ratio is termed "durability factor" in the report by Rostler and White in 1962 (4), and the "compositional parameter" in the report by Halstead, Rostler, and White.(10) It is generally shown that the resistance of an asphalt to abrasion in the pellet abrasion test decreases as the value of the parameter increases from a minimum of 0.5 to the maximum of 2.24 measured in research testing. Because asphalts with values of the parameter less than 0.8 are likely to have inadequate cementing qualities and poor ductility, it has been concluded that materials with ratios within the range of 0.8 to 1.5 have good original and retained cementing quality and thus are "good" asphalts. The values of this ratio as an overall index of asphalt quality has been questioned since it does not take into account the amount and characteristics of the asphaltenes. However, some work in South Africa has shown reasonably good correlations of the parameter with performance in highways.(11) It should also be pointed out that there has never been a claim that the compositional parameter is the sole measure of asphalt quality. It is one indication, but other factors certainly must be considered in judging asphalt quality.

Molecular Size Distribution

In his work with HPLC, Jennings compared the relative amounts of large molecules (LMS), medium molecules (MMS) and small molecules (SMS) for asphalts providing good performance in the road to those providing poor performance.(7) Additional studies are under way, but reported results on materials from Montana highways show greater relative amounts of large molecules (LMS) associated with poor performance. It is probable that a balance between the relative amounts of LMS, MMS, and SMS in an asphalt is an important attribute relating to its durability and its ability to perform properly as an asphaltic binder.

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APPENDIX C

MOLECULAR INTERACTIONS IN ASPHALT

Petersen describes molecular interactions in asphalts as follows:

> Molecules are held together in a specific structural arrangement in space by covalent chemical bonds. Molecules also tend to attract and interact with each other through a variety of secondary or association forces. These association forces, which are one to two orders of magnitude weaker than the covalent chemical bonds, are significantly different from covalent bonding forces in that they form bonds that are generally reversible and are usually in dynamic equilibrium. That is, they make or break under induced forces created by temperature and external stress and thus they largely determine the physical properties of the composite material. Different atoms in the same configuration with carbon and hydrogen can produce significantly different intermolecular forces and consequently significantly different physical characteristics and behavior.
>
> Nonpolar hydrocarbon components in asphalt such as those dominant in the saturates fraction exhibit only weak interaction forces, which accounts for the rather fluid character of this fraction. On the other hand, asphalts containing highly condensed ring systems and chemical functional groups containing oxygen and nitrogen atoms may be highly polar or polarizable, and thus interact strongly with each other. These strong interactional forces largely account for the fact that asphaltenes, even though they may not be significantly different in molecular weights than the saturates, are solids at ambient temperatures and have high melting points. The polar interactions between molecules dominate in influencing flow behavior and the effects of molecular structuring are reduced. This explains why many asphalts whose flow properties may be quite different at low temperatures may tend to be similar at high temperatures.

> At low temperatures, factors related to molecular size and shape become increasingly important. The asphaltene fraction, which has the highest concentration of aromatic ring systems and heteroatom functionality, thus has a high melting point and a very large effect on the non-Newtonial flow properties of the asphalt.(1)*

Petersen, using data from Griffen and coworkers,(2) also demonstrates the large effect of molecular structure on viscosity.(1) He shows that fractions of saturates, aromatics and aromatic resins of the same molecular weight (approximately 500), have large differences in viscosity depending on the molecular structure and polarity. The saturates, with a viscosity of only 10 Pa.s, do not contain polar chemical functionality and the molecular interactions are weak. The aromatics have molecular interactions of increased intensity and a viscosity of 1,000 Pa.s. Finally, the resins, which contain polarizable condensed-ring systems and heteroatom functionality, exhibit even more intense molecular interactions and have a viscosity of 100,000 Pa.s. In summarizing overall effects he states:

> It is apparent that those molecules of an asphalt that are most alike are most compatible and vice versa. It is the wide spectrum of molecular types in asphalt, all interacting together, that gives asphalt its unique properties and make it appear as a homogeneous material. However, on a molecular level, asphalt is undoubtedly heterogeneous, and there is a delicate balance among strongly associated or agglomerated components and dispersing or solubility components. It is this delicate balance, or lack of it, that affects the performance of asphalts. Incompatibility and poor performance generally follow when one component type unduly dominates at the expense of others.(1)

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*Numbers in parentheses indicate reference numbers found at the end of this Appendix. In some instances, the reference duplicates a reference in the body of the report.

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