

Development of a Performance Related Chemical Model of Petroleum Asphalt for SHRP

Raymond E. Robertson, Jan F. Branthaver, and J. Claine Petersen
Western Research Institute
P.O. Box 3395
Laramie, WY 82071

Keywords: Asphalt, Model, Aging

INTRODUCTION

In the three introductory papers for this symposium on petroleum asphalt used in roadway construction, the intent is to describe the current status of a comprehensive model of petroleum asphalt as developed during the Strategic Highway Research Program (SHRP). These papers are to lay out basic concepts which, in turn, are useful in describing the expected behavior of asphalt under various conditions in roadways. The primary purpose of this paper is to describe the current SHRP model in terms of the chemical composition of asphalt.

Any useful model must explain the observed behavioral characteristics as completely as possible for any given set of materials under any applicable set of conditions. In the case of petroleum asphalts, performance characteristics must include consideration of viscous and elastic properties at pavement service temperatures, nominally, -30 to $+170^{\circ}\text{F}$ (-34°C to $+77^{\circ}\text{C}$), over a wide range of shear conditions (high stress and rate under traffic to low rates associated with thermal stress) and must also describe the propensity to adhere to a wide variety of mineral aggregates under many conditions of temperature, stress, and moisture. Asphalts are chemically reactive with oxygen to the extent that their properties change upon oxidation, hence the model must also account for the effects of oxidation on their physical and performance properties.

The research that supports the model developed below has been conducted by numerous investigators and has been reported since the early part of this century. Much of the work during the Strategic Highway Research Program was refinement and validation to develop and report the current asphalt model. An extensive version of the research related to composition and physical properties of asphalt binders will appear within the next few months as the final report for SHRP Project A002A, "Binder Characterization and Evaluation." This report contains an extensive review and discussion of literature related to asphalt chemistry, physical behavior, and road performance as well as a review of the literature pertaining to petroleum. All of these areas were valuable in developing the current model, but too voluminous to cite here. Only selected publications of relevant SHRP studies are cited throughout the discussion of this paper.

RESULTS AND DISCUSSION

The function of petroleum asphalts in roadways is to serve as an adhesive to hold well compacted, graded aggregate together into what is commonly described as flexible asphalt concrete. Asphalt concretes should flex (rather than crack) under traffic load, yet be capable of viscous flow under stresses of day and night as well as summer and winter thermal cycling. Certain physical properties are unquestionably important for their behavior and their (perceived) performance in roadways. In order to understand and control physical properties, one must first understand what chemical structural units give rise to any given physical property, how the structure(s) change with various stresses, and finally what alterations in chemistry need to or can be made in order to adjust physical properties of asphalts to a desired performance.

The following discussion is devoted to a description of the chemistry of asphalts with reference to physical properties as necessary. The more detailed physical model of asphalts is presented in the following paper (1).

Current Model

The current SHRP version of a chemical description or model of petroleum asphalt can be stated rather simplistically as follows. Petroleum asphalts are roughly a half and half mixture of polar and nonpolar (neutral), relatively nonvolatile, organic compounds in which the polars are in such close proximity that a wide variety of interactions among polars occur. These interactions are presumed to be noncovalent bonds that range from a few to about 30 kilocalories per mole with a somewhat uniform distribution of bond energies. This is confirmed by rheological studies (1). Asphalts show rather uniform changes in viscoelastic properties with temperature suggesting again that a wide variety of low energy chemical bonds comprise some sort of microstructure.

The association appears to form a three dimensional network, or microstructure, that is intimately mixed with the neutral materials which behave somewhat as a plasticizer. Nuclear magnetic resonance (NMR) data have shown that intermolecular distances among polars are small, i.e. no major aggregations of polar species exist, but rather that polar species are relatively uniformly distributed within the neutral materials (2). A resulting whole asphalt is therefore somewhat elastic in nature but also has some viscous flow characteristics. The elastic nature is presumed to arise from the three dimensional network which behaves as if it is relatively high in molecular weight. However, under high shear and/or thermal stress, the molecular weight appears to decrease as viscous flow properties begin to appear. The viscous flow arises from the change in orientation of polars with respect to each other under thermal stress or stress of shear. The latter occurs without changes in any molecular structure; i.e., no chemical degradation occurs. Asphalts can also be described as metastable arrangements of polar molecules in a nonpolar medium, and the particular metastable state depends upon the thermal and shear history of each asphalt.

Elastic response, such as a rapid traffic loading, is the desirable characteristic in which the time of stress is too short for rearrangement of molecular orientation. Hence, an asphalt

responds elastically, flexing under traffic load, but returns to its original shape upon passage of the traffic. This property is important in avoiding a common failure mode known as rutting. Flow properties, or viscous flow commonly called "creep," are also desirable and occur under prolonged periods of stress in which asphalts experience day-night as well as summer-winter thermal cycling.

The evidence to support this model has been gathered from a variety of studies and experiments and is summarized as follows. Petroleum asphalts have been dissected into a series of compound types by ion exchange chromatography (IEC) (3, 4) and by size exclusion chromatography (SEC) (5). The component types are principally strong and weak acids, strong and weak bases, amphoteric (molecular species with acidic and basic sites), and neutral materials. Isolated neutrals may occur as waxlike (pseudocrystalline) materials or as oily materials which do not solidify. All fractions have aromatic and aliphatic carbon and hydrogen, but the carbon and hydrogen aromatic to aliphatic ratios vary among fractions and among asphalts (6). The polars, as defined by IEC, are generally a few percent bases, 10-20% acids, and 10-20% amphoteric. The specific percentage of each polar type varies with crude oil source.

Model compound studies using neutral (linear hydrocarbons) and their analogous mono and diamines, mono and dibasic carboxylic acids, and amphoteric (amino acids), show that addition of diacids and amphoteric had the most profound effect on physical properties. The viscosities of asphalts spiked with diacids and with amino acids rose sharply compared with all other model compounds. When naturally occurring amphoteric were isolated by IEC and then used to enrich tank asphalts, viscosities typically skyrocket with small levels of enrichment. Acids and bases have a similar but less pronounced effect. Neutrals reduce viscosities.

Further evidence for the existence of a microstructure was found using SEC experiments. The SHRP asphalts were separated into two major fractions (I and II) by SEC. The SEC experiments were conducted in toluene as a solvent, but as concentrated solutions which were chromatographed rapidly so as to disturb any microstructure as little as practically possible. Both fractions, as shown by carbon-13 NMR (6), contain sufficient condensed aromatic hydrocarbons to be highly fluorescent. Fraction I is nonfluorescent despite the significant amounts of condensed aromatic hydrocarbons. This quenching of fluorescence suggests strong association among the SEC I components. Further, the vapor phase osmometry (VPO) molecular weight of Fraction-I is always higher in toluene, a nondissociating solvent, than in pyridine, a strongly dissociating solvent. Fraction-II, on the other hand, is always highly fluorescent, suggesting a lack of association. The ratio of Fraction-I to Fraction-II is indicative of the ratio of the viscous and elastic moduli (7).

The probable existence of a microstructure was further demonstrated by cross blending SEC Fractions I and II. These experiments also demonstrated the sensitivity of each fraction to the other. Numerous examples were studied and one is cited here as a typical example. Asphalts AAD-1 and AAM-1 were separated into their SEC Fractions I and II, cross blends were prepared, and the viscosities of the resulting products measured. A portion of this experiment is as follows. Asphalt AAD-1 contains 23.4 wt % SEC-I and 76.6 wt % SEC-II.

When AAD-1 was reformulated from its own SEC-I and -II, the viscosity was 3,000 poises at 60°C. When a mixture of 23.4 wt % AAD-1 SEC-I and 76.6 wt % AAM-1 SEC-II was formulated, the 60°C viscosity was 234,000 poises. Asphalt AAM-1 is 30.6 wt % SEC-I and 69.4 wt % SEC-II with a viscosity of 5,400 poises. The crossblend of 30.6 wt % AAM-1 SEC-I and 69.4 wt % AAD-1 SEC-II had a 60°C viscosity of 380 poises. It is apparent immediately that Fraction I of AAM-1 is more dissociated by Fraction II of AAK-1 than by its own Fraction II. The opposite effect is observed for Fraction I of AAK-1 blended with Fraction II of AAM-1. In general the dispersive character of SEC Fraction II increases with decreasing average molecular weight. Molecular weight distributions of SEC Fractions II were determined by supercritical fluid chromatography (8).

Ion exchange chromatography is a time consuming and expensive process, so it was decided to investigate the use of nonaqueous potentiometric titration (NAPT) to determine the quantities and strengths of acids and bases in petroleum asphalts. The development of a method for measurement of bases was rather straightforward (9). However, upon attempting to titrate petroleum asphalts in chlorobenzene for quantities and strengths of organic acids, it was observed that there were no endpoints. In fact pyridine had to be used to dissociate the acids before endpoints could be found. This is further evidence for the persistence of a microstructure, even into dilute solution.

Still another series of experiments was carried out to imply the metastable nature of asphalts. In this study, which is noted as steric hardening experiments, asphalts were stored for extensive periods of time in a well protected atmosphere. In this particular case no atmospheric oxygen was available so no chemical reaction could take place. Yet, upon examining the viscoelastic properties, it was observed that the viscosities as well as the elastic moduli of the asphalts continued to rise as the asphalts were examined periodically over a time of several months.

Oxidative Aging

Prediction of aging of asphalts, that process in which asphalts increase in stiffness, has been of primary interest during the program. Aging is an unavoidable conditioning step, and not necessarily a cause of failure. In extreme cases, increases in stiffness to the point of embrittlement leads to cracking in roadways which in turn leads to deterioration to an unusable structure. Oxidation takes place naturally in asphalts as they are exposed to the atmosphere and this is a major contributor to aging. But other phenomena under the collective name of compatibility have a major effect upon how oxidation products affect the age hardening in asphalts (10). For clarity, the terms oxidation and aging are distinguished as follows. Oxidation is used to describe increases in oxygen-containing products while aging (age hardening) is used to describe increases in the viscoelastic properties. The prediction of aging for all asphalts then becomes oxidation plus some measure of the ability of asphalts to accommodate oxidation products. Said differently, the prediction of aging from analytical information becomes a constitutive relationship that includes, but cannot be limited to, the level of chemical oxidation. We have shown (11), as have others (e.g., 12, 13), that aging of some asphalts has a rather sharp temperature dependence at higher pavement service temperatures (60-85°C [140-185°F]). Aging at any temperature is related to asphalt source.

Age hardening in asphalts has been shown to correlate well with the concentration of ketones formed upon oxidation for asphalts from any given crude oil regardless of grade, but aging differs sharply among asphalts from different crudes. The amount of ketone formed in asphalt from one crude oil cannot be used to predict viscosity changes in asphalt from another crude oil based solely on ketone concentration (10).

A substantial series of experiments was conducted during the program to oxidatively age harden asphalts artificially. These experiments were based on those reported earlier by D. Y. Lee (14) and are collectively referred to here as those conducted in a pressurized aging vessel (PAV). The PAV experiments demonstrated clearly that both an increase in temperature and/or an increase in time resulted in an increasingly stiffer (aged) products. However, asphalts are not used in roadways as petroleum asphalts alone, but rather in contact with mineral aggregate. Hence a series of PAV experiments was conducted with asphalts in contact with a variety of different mineral aggregates together with control experiments. Asphalts recovered from mineral aggregate after PAV treatment generally had aged less than neat asphalt controls. The chemistry of aging does not appear to change over limited temperature ranges whether neat or on aggregate, only the rate appears to be substantially affected. This is predictable from the model. Polar sites on aggregates should promote structuring of polars in asphalt. As asphalts age the oxidizable sites are consumed hence the oxidation rate diminishes. An increasingly polar environment evolves as oxidation products are formed. Polar aggregate surfaces should induce greater amounts of structuring and hence quench, or slow, the observed rates of reaction compared to aging of asphalts in neat form. Aggregate induced structuring is consistent with the thermodynamic data reported in project A003B (15).

The effects of oxidation on aging can be explained further in terms of amphoteric (16). It is clearly understood that the oxidation of carbon and sulfur species, those that oxidize in asphalts, do not produce strong bases. More typically, highly oxidized products of carbon and sulfur are acidic. However, oxidation of asphalts at pavement service temperatures produces principally ketones and sulfoxides, both of which are weak bases. It follows then that new amphoteric materials will be formed by the introduction of new, weakly basic sites. This should promote development of the microstructure with the accompanying increase in viscosity and elasticity as was also demonstrated by spiking asphalts with amphoteric isolated by IEC. Nonaqueous potentiometric titration was an invaluable tool in determining the increase in weakly basic materials produced during oxidative aging of asphalts.

Oxidized asphalts exhibit yet another interesting behavior. Consider steric hardening again. Steric hardening of tank asphalts results in rather minor increases in viscoelastic properties with prolonged periods of storage. However, asphalts aged under PAV conditions show rather substantial increases in viscosity upon storage for prolonged periods of time. In one example, viscosity of an asphalt rose 11 million poise (1.1 million Pa·s) over a period of seven months while stored at 25 °C (77 °F). Again, this suggests the metastable nature of asphalts and further suggests that the particular state is sharply sensitive to oxidation products.

SUMMARY AND CONCLUSIONS

In summary, petroleum asphalts can be defined as concentrated mixtures of polar materials dispersed in neutral materials so that the polars form continuous, rather homogeneous, three-dimensional networks. Some molecular species in petroleum asphalts are sensitive to oxidation. This increases the polar content and hence the size and strength of the three dimensional microstructure. In turn, the viscosity and elasticity increase as aging proceeds.

ACKNOWLEDGMENTS

The work reported herein has been conducted as a part of Project A002A of the Strategic Highway Research Program (SHRP). SHRP is a unit of the National Research Council that was authorized by Section 128 of the Surface Transportation and Uniform Relocation Assistance Act of 1987. This project is titled "Binder Characterization and Evaluation" and is being conducted by the Western Research Institute, Laramie, Wyoming, in cooperation with the Pennsylvania Transportation Institute, Texas Transportation Institute, and SRI International. Dr. Raymond E. Robertson is the principal investigator. Dawn Geldien is the project administrator. The support and encouragement of Dr. Edward Harrigan, SHRP Asphalt Program Manager, and Dr. Jack Youtcheff, SHRP Technical Contract Manager, are gratefully acknowledged.

LITERATURE CITED

- (1) Anderson, D.A., and Christensen, D.W., Presented at the Fall 1992 ACS Meeting, Div. Fuel Chem.
- (2) Vander Hart, D.L., Manders, W.F. and Campbell, G.C., Preprints, Div. Petrol. Chem., ACS, 35 (3) 445 (1990).
- (3) Branthaver, J.F., Catalfomo, M.W., and Petersen, J.C., Preprints, Div. Petrol. Chem., ACS, 35 (3) 376 (1990).
- (4) Branthaver, J.F., Catalfomo, M.W., and Petersen, J.C., Fuel Science and Technol. Int., 10 (4-6) 855 (1992).
- (5) Branthaver, J.F., Duvall, J.J., and Petersen, J.C., Preprints, Div. Petrol. Chem., ACS, 35 (3) 407 (1990).
- (6) Jennings, P.W., Desando, M.A., Raub, M.F., Moats, R., Mendez, T.M., Stewart, F.F., Hoberg, J.O., Pribanic, J.A.S., and Smith, J.A., Fuel Science and Technol. Int., 10 (4-6) 887 (1992).
- (7) Branthaver, J.F., Duvall, J.J., Petersen, J.C., Plancher, H., and Robertson, R.E., Fuel Science and Technol. Int., 10 (4-6) 1003 (1992).
- (8) Barbour, F.A., and Branthaver, J.F., Preprints, Div. Petrol. Chem., ACS, 35 (3) 421 (1990).
- (9) Robertson, R.E., Schabron, J.F., Gwin, A.A., and Branthaver, J.F., Preprints, Div. Petrol. Chem., ACS, 37 (3) 913 (1992).
- (10) Petersen, J.C., Transport, Res. Rec., 999, 13 (1984).
- (11) Harnsberger, P.M., Petersen, J.C., Ensley, E.K., and Branthaver, J.F., in press, Fuel Science and Technol. Int.

- (12) Oliver, J.W.H., Fuel Science and Technol. Int., 10 (4-6) 501 (1992).
- (13) Kemp, G.R. and Predoehl, N.H., Proc. Assoc. Asphalt Paving Technol. 50 492 (1981).
- (14) Lee, D.Y., Final Report, Project 717S and 828S. Iowa Highway Research Board HR-124, Engineering Research Institute, Iowa State University (1972).
- (15) Curtis, C.W., Final Report, Strategic Highway Research Program, Project A003B (1991).
- (16) Branthaver, J.F., Kim, S.S., Catalfomo, M.W., and Goray, D.C., Presented at the Fall 1992 ACS Meeting, Div. Fuel Chem. (1992).