

SHRP-A-686

# **Guideline for Asphalt Refiners and Suppliers**

Suggestions for the Enhancement  
of Asphalt Binder Performance  
through Crude Oil Selection,  
Chemical Characterization, and Modification

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## **Abstract**

Key findings of the various researchers involved in the SHRP asphalt program are described. Emphasized are those fundamental chemical and physical properties of the binder which relate to its susceptibility to various distresses. Consideration and evaluation of the polar and non-polar molecules assists in understanding the performance of a given asphalt.

The polars largely dictate the ability of an asphalt to resist permanent deformation. Low temperature cracking and fatigue cracking are largely influenced by the non-polar fraction. The impact of aging and asphalt compatibility on these distress modes is also discussed.



## Executive Summary

The purpose of this report is to offer the asphalt producer a handbook of the more pertinent results of the Strategic Highway Research Program (SHRP) in two main areas: the relationships between the physical and chemical characteristics of asphalt binders and their performance in pavements; and the application of chemical characterization techniques to assist in the selection of crude oils and refining conditions.

Highlighted are the significant findings of the SHRP asphalt research program regarding the physical and chemical properties of asphalt. These include new methods for separating asphalt fractions and characterizing the chemical and physical characteristics of asphalts and asphalt fractions, a model and computer programs for investigating the phase behavior of asphalt and asphalt components, and new insight for predicting the performance of asphalt binders based on two models.

Modeling asphalt based on a microstructural model and on the thermodynamics of solutions explains many of the relationships between chemical composition and performance. Asphalt components were separated by solvent fractionation, size, and chemical functionality. Fractions with high glass transition temperatures ( $T_g$ ) and number average molecular weights ( $M_n$ ), namely, the asphaltenes, SEC I, and amphoteric fractions were found to be the viscosity builders (and largely responsible for the elastic behavior of asphalt). The results from blending studies with model compounds and SEC I fractions, and the evaluation of spin relaxation times of asphalts provide additional support for the latter model.

The chemical properties of asphalt which impact its viscoelastic properties are discussed. The low-temperature and fatigue properties of asphalt seem to be dominated by the  $T_g$  and  $\gamma$ -CH<sub>2</sub> content of the non-polar fraction.

A number of recommendations are made for quickly estimating the SHRP performance grade of an asphalt binder. These include use of gel permeation chromatography and the determination of the glass transition temperature of the asphalt binder.

## Scope

This report focusses specifically on the chemistry of the asphalt binder and its influence on permanent deformation, fatigue cracking, low temperature cracking, aging, adhesion, and moisture sensitivity. It draws principally upon research results from SHRP contracts A-002A (Western Research Institute (WRI), Laramie, WY), A-002C (Montana State University (MSU), Bozeman, MT), A-IIR-14 (MSU), ID-21 (Tri-Valley Research, Pleasanton, CA), ID-26 (National Institute of Standards and Technology (NIST), Gaithersburg, MD), and ID-32 (PSU).

This report is intended for an audience with some knowledge of asphalt chemistry and refinery operations. Some background information is provided for those lacking this specialized knowledge.

## Introduction

The SHRP research effort was a five-year, highly focused, product-oriented research effort. Of the \$150 million pledged for SHRP in 1987, approximately one-third (\$50 million) was designated for asphalt research. The goal of the asphalt portion of the program has been to develop and issue new performance-based binder and mixture specifications that aid federal, state, and local highway agencies in obtaining better performing hot-mix asphalt concrete (HMAC) pavements.

The asphalt research was specifically directed at ascertaining and developing predictive methods for measuring the following pavement distress mechanisms: permanent deformation, fatigue cracking, and low temperature cracking. In addition considerable emphasis was devoted to determining the mechanism and impact that oxidation has on these pavement failure modes.

At this time the Asphalt Research Program has concluded. The laboratory work has been completed; most of the final reports have been published, and an end-product specification and its associated test methods have been accepted as provisional standards by AASHTO. Not all of the questions have been answered, but there is now a much better understanding of the chemistry and processes that control pavement performance.

Early in the SHRP program, a refinery survey was conducted and reported (Puzinauskas, Harrigan, and Leahy 1991). Contained in the report were the results of an extensive survey of both the literature and approximately 72 U.S. and Canadian refineries producing paving

asphalts in 1988. Results of the survey accounted for 92% of paving-grade asphalt production during that year, making the survey a very accurate "snapshot" of the asphalt refining business.

The overwhelming majority of producers use atmospheric or vacuum distillation to refine the asphalt. While there is some solvent refining and air blowing utilized, they are clearly of secondary importance. The ROSE process is still little used, but gaining in popularity.

The refiners produce asphalt as a byproduct from the manufacture of gasoline and other fuels. Consequently, it is not surprising that asphalt production does not drive the refinery business. Over three-fourths of the refineries surveyed reported that asphalt accounted for 25% or less of their production. In only one refinery did asphalt represent more than 75% of production. Many refineries produce no asphalt whatsoever, consuming all residua through catalytic treatment or coking.

The shift to heavier crude oil feedstocks since the 1970's has also had an effect on refinery production of asphalt. Heavy crudes such as Maya crude from Mexico, and the Canadian heavy crudes, Bow River and Peace River, have also contributed to changing production dynamics at refineries producing asphalts. New crude oil sources that are yet to be developed will very likely consist of predominately heavy crudes with high resid fractions. This will assure that the asphalt supply continues to change and evolve in years to come.

Both refiners and terminal operators are faced with increasing problems in supplying conventional and modified asphalts to meet new construction requirements. Increasing demands on our pavements -- new axle configurations, higher tire pressures and increased traffic loads and volumes are pushing asphalt performance to its limits. One consequence of this has been the growth of polymer modification of asphalt binders as well as the development of other modification procedures. There is no opportunity to reverse the field and go back to the "good old days", because the crudes from which the old asphalts were made and conditions under which they were utilized are simply gone. The development of the SHRP binder specification, which is "blind" to asphalt modification, will challenge and assist both suppliers and users in meeting these new requirements.

This report will attempt to provide those seeking to benefit asphalt with a summary of the pertinent results of the SHRP Asphalt Research Program. As a starting point the physical properties used in the binder specification and their relationship to performance are briefly discussed. The remainder of this report is organized chronologically, starting with a review of historical knowledge and practices, and introduces the results of the SHRP research, and the changes that new knowledge has brought to the understanding of asphalt.

# Physical Properties and Their Relationship to Performance

## New Test Methods

As part of the SHRP investigation of asphalt and binder properties (Contract A-002A), researchers at The Pennsylvania State University (PSU) were charged with investigating the physical properties of asphalt, and developing a testing approach that allowed measurement of fundamental engineering properties of asphalt binders.

To achieve this the empirical physical tests such as penetration and softening point were evaluated, but found inadequate. In their place, a measurement system was developed which both recognized asphalt's viscoelastic behavior, and allowed fundamental engineering properties to be obtained. Building on the pioneering work of Van der Poel (1954), Jongepier and Kuilman (1969), Dobson (1969), and Dickinson and Witt (1974), DSR instruments were adapted which allow pavement technicians to fully characterize the rheological properties of asphalt over its entire service temperature range as well as its low temperature fracture properties.

While it is not within the scope of this paper to fully examine these new techniques, a brief review is provided since they are used to unlock the relationships between chemistry and performance. For a more extensive review of the fundamental and experimental aspects of these techniques, the reader is referred to Anderson et al. (1994), and Petersen et al. (1994b), respectively.

### *Dynamic Shear Rheometer (DSR)*

The DSR has been a standard fixture of rheology laboratories for years, and several of the researchers cited above have applied DSR measurements to the understanding of asphalt rheology. However, the results of the SHRP program will encourage the widespread use of DSRs is made for the routine characterization of asphaltic binders. A detailed review of the SHRP progress in rheology is cited for the interested reader (Anderson et al. 1994).

In the SHRP asphalt binder specification the DSR is used to determine the shear stress-strain relationships of the binder, and to predict the fatigue and rutting potential of the binder. This is accomplished by measuring the complex modulus,  $G^*$ , and the phase angle,  $\delta$ , at several temperatures, for both aged and unaged binders. The SHRP binder specification (see appendix) requires the binder to meet three conditions using the DSR.

To assure adequate performance at the hot-mix plant and during laydown, the value for  $G^*/\sin \delta$  of the original unaged binder must be greater than 1.0 kPa at an assigned temperature which depends on the high temperature service environment of the binder. This reduces the potential of having a tender mix should plant conditions not be as severe as those simulated by the RTFOT.

To evaluate an asphalt's ability to resist rutting, the binder is aged using the rolling thin film oven test (RTFOT, ASTM D 2872). The residue must have a value of  $G^*/\sin \delta$  which is greater than a 2.2 kPa at the service environment's highest temperature.

The third DSR measurement is carried out on the RTFOT-PAV aged residue to evaluate the fatigue cracking propensity of the binders. Binders are subjected to high pressure oxidative aging at a temperature fixed to simulate in-field service. The rheological measurement is carried out at the average temperature experienced by the pavement. To meet the specification  $G^*\sin \delta$  must be less than 5.0 MPa at this temperature.

### *Bending Beam Rheometer (BBR)*

To determine the low temperature properties of asphalt binders a new instrument was developed based on three point loading of a prismatic beam of asphalt at low temperatures. The test is based on the guidelines of ASTM D 790, and follows low temperature measurement techniques applied to polymeric materials. A more thorough discussion is available elsewhere (Anderson et al. 1994). Briefly, asphalts subjected to short loading times behave as stiff elastic bodies whereas at long loading times the asphalt can relax the stresses and exhibit a more viscous behavior.

In the BBR test the low temperature creep stiffness ( $S$ ) of a beam of RTFOT-PAV asphaltic binder is determined near the minimum service temperature of the pavement. At this specified temperature the stiffness of the binder and the slope of the log stiffness versus log loading time curve ( $m$ -value) must meet specified values ( $S(t) < 300$  MPa and  $m \geq 0.30$ ). Both of these parameters have been shown to relate to low temperature cracking.

### *Direct Tension Device (DT)*

The third test developed under SHRP characterizes the low temperature failure properties of asphalt binders by conducting a direct tension test (DT) on a dogbone specimen of neat or modified asphalt near the minimum service temperature of the pavement.

The tensile strain at failure is used as an indicator of the performance of mixes subjected to cold environments. In the DT test the binder must exhibit a minimum failure strain of 1.0% at the specified temperature.

In the following sections the ties between the chemistry of asphalt and its rheological behavior will be examined, and asphalt refiners and blenders will be provided with some guidance as to analytical techniques that can be applied to their processes to yield high performance asphaltic binders.

# Asphalt Chemistry

## Model Development

### *The Evolution of the Historical Asphalt Model*

Models relied on to explain the chemical structure and performance characteristics of asphalt have been historically defined and limited by the analytical tools applied to its study. The first separation of asphaltenes (Boussingault 1837) from asphalt (and the coining of the term asphaltene), set the tone for virtually all other investigations to-date. Without better definition of the constituents of asphalts, researchers were limited in determining the chemical relationships which govern performance.

For much of the 19th and 20th centuries, separations of asphalt components were made based on the solubility of various molecules in different solvents. As the analytical technique of chromatography blossomed after World War II, researchers applied the growing body of separation technology to asphalt. Affinity chromatography, by which the components are separated on an active surface such as alumina or silica gel, was applied to asphalts, and has evolved into the well known Corbett separation (ASTM D 4124).

Separation methods, such as those developed by Corbett and Rostler (Rostler and White 1962), were well founded on existing theory, but gave data that were difficult to correlate with asphalt performance or physical properties. There were always asphalts that were exceptions to the general trends noted. Each separation technique isolates various molecular classes, but they are cross-contaminated in ways that obscured the true chemistry-performance relationships of the binder. The failure of these analytical methods to separate discrete chemical fractions is demonstrated by the lack of correlation between the specific fractions and asphalt performance.

In a similar vein, surrogate physical measurements such as penetration and viscosity did not correlate with performance because they were insufficiently specific in defining a desired physical trait. With these limitations in mind, more fundamental and rigorous analytical chemical techniques were applied in the chemical investigation of asphalt in the SHRP program.

## *The Original SHRP Micellar Hypothesis*

A major tenet of the asphalt binder portion of the SHRP asphalt program was the use of an asphalt model as the basis for the experimental plan. The major asphalt research contract of SHRP was awarded to WRI. As a starting point for their experimental designs, WRI used the micellar model described by Nellensteyn (1924), and refined by Pfeiffer and Saal (1940), to describe the structure of asphalt.

When the SHRP asphalt program began, the micellar model was accepted as providing the best available explanation of how asphalts developed the structure that controlled their behavior. In this model aromatic asphaltenes exist as a discrete phase in the asphalt and are surrounded by the resins. The resins were intermediates in the asphalt, serving to peptize the otherwise insoluble asphaltenes. The resins and asphaltenes existed as "islands" floating in the final asphalt component -- the oils. In many ways the model at the beginning of the SHRP program was not very far from some of Boussingault's (1837) original discussions of the composition of asphalt. While there have been competing molecular structures proposed through the years to explain the viscoelastic behavior of asphalts (Ostwald 1921; Katz and Beu 1945; Ravey, Ducouret, and Espinat 1988), the micellar model had held forth for lack of a definitive proof to the contrary.

The original micellar model had been constructed from interpretations of historical data in which researchers looked for relationships between chemical parameters and pavement performance. Various separation techniques had been used to differentiate the various chemical groups that controlled or contributed to asphalt properties. Other surrogate measurements such as penetration and viscosity, and mathematical permutations of these constants such as penetration index (PI), penetration-viscosity number (PVN), and aging index (AI) have been used in attempts to discover or define the chemistry-property-performance relationship for asphalts. Often stirring impassioned debate by dedicated scientists and engineers, the arguments and discussion have gone on for many years.

## *The SHRP Microstructural Asphalt Model*

The research carried out at WRI and by others confirmed the judgement that the micellar model did not adequately explain the behavior and properties of asphalt. As a result of these investigations the micellar model was gradually replaced with new models which more fully address the chemical-physical property relationships of asphalt.

One of the models developed under SHRP has been named the "Microstructural" model, and as its name implies, states that asphalt is a single phase mixture of many different polar and non-polar molecules, all of which interact with one another (Petersen et al. 1994a). Localized concentrations of similar molecules can exist in this model. Both the polar and non-polar molecules form loose associations and networks that are dispersed throughout the asphalt. This structure is held together through weak intermolecular forces, which form and

break and reform in response to temperature changes and physical stresses. The polar molecules interact and primarily give asphalt its elastic characteristics. The non-polar molecules primarily contribute to the viscous behavior of the asphalt and control the low-temperature properties of the asphalt.

While virtually all of the data generated by SHRP can be reconciled by a microstructural model for performance, we will also address later in this report how the data also support a model derived from consideration of the thermodynamics of mixing.

These new fundamental explanations of how and why asphalts behave as viscoelastic materials will enable refiners and manufacturers to modify and benefit asphalts in a rational manner, which has never been possible before. It will also enable highway engineers to design pavement structures that take full advantage of asphalt's unique chemical and physical properties.

As the SHRP program progressed our understanding of the chemical structure of asphalt and its relation to pavement performance has advanced. As mentioned above, the original hypothesis was rendered untenable and new models had to be devised and tested. This process continues to the present, and the models developed under SHRP will undoubtedly evolve as subsequent researchers delve into the complex chemistry of asphalt.

## **Analytical Techniques**

A Materials Reference Library (MRL) was established by the University of Texas. (Presently it is housed by Nichols Consultants, Reno, NV.) It contains over 40 different asphalts; eight were used by all of the SHRP researchers and are designated as core asphalts. These asphalts were selected as illustrative of the considerable diversity in the chemical and physical properties of asphalts currently used in the U.S. Physical and chemical characteristics of the MRL asphalts are provided elsewhere (Jones 1993; Branthaver et al. 1993).

Table 1 presents physical and chemical characteristics for four of the SHRP core asphalts. The first three asphalts were obtained from vacuum distillation of single parent crude oils; the fourth asphalt, AAM, is a solvent deasphalted asphalt (SDA) and has a considerably higher apparent number average molecular weight ( $M_n$ ) as determined by vapor phase osmometry (VPO). AAD and AAK are high sulfur asphalts and contain appreciable amounts of asphaltenes. AAG is a "sol type" asphalt and is quite viscous despite its low heteroatom content, low  $M_n$  and intermediate aromaticity. These four asphalts represent three different grades. Asphalts AAD and AAG are AR-4000 asphalts; AAM is an AC-20, and AAK is an AC-30.



Table 1. Selected Characteristics of Several of the Core Asphalts

Asphalt	C	H	O	N	S	C <sup>ar</sup>	M <sub>n</sub>	$\eta^{25}$	$\eta^{60}$	$\alpha_g$
AAD	81.6	10.8	0.9	0.77	6.9	23.7	700	40.6	1055	6.10
AAG	85.6	10.5	1.1	1.1	1.3	28.3	710	354.0	1862	5.97
AAK	83.7	10.2	0.8	0.70	6.4	31.9	860	107.7	3256	6.30
AAM	86.8	11.2	0.5	0.55	1.2	24.7	1300	112.3	1992	6.85

Key: CHONS expressed on wt% basis; C<sup>ar</sup>, % aromatic C; M<sub>n</sub> determined by VPO measurement in toluene;  $\eta^{25}$  expressed in kPa\*s at 25°C and 1.0 rad/s;  $\eta^{60}$  expressed in poise;  $\alpha_g$  is the coefficient of thermal volumetric expansion, 10<sup>-4</sup>/°C.

## Separation Techniques

Identification of the myriad compounds which comprise an asphalt would provide little insight into the relationship between chemical composition and physical properties. Instead, advances in the characterization of asphalt have been made through the analysis of chemically or physically similar components of asphalt. Asphaltene precipitation, size exclusion chromatography (SEC), and ion exchange chromatography (IEC) were three fractionation schemes used by researchers at WRI (Branthaver et al. 1993). Supercritical Fluid Chromatography (SFC) was used to further fractionate the "non-polar" fractions.

The SHRP research on asphalt chemistry centered on developing and utilizing analytical techniques which promised to permit isolation of chemical entities on a fundamental basis. Most earlier work had focused on using solubility as the basis for separation, but with a material as chemically diverse as asphalt, concern existed that this would inevitably render the methods incapable of providing chemically meaningful isolates. New techniques were called for and developed.

### *Asphaltene Precipitation*

This is one of the classical characterization methods of asphalt. It is the crudest and simplest technique for fractionating asphalts. Asphaltenes were precipitated from the asphalt using either n-heptane or iso-octane. These test procedures and the results are described elsewhere (Petersen et al. 1994b and Branthaver et al. 1993, respectively). The procedure is very empirical and quite operator dependent.

### *Size Exclusion Chromatography (SEC)*

SEC was used to separate asphalts based on apparent molecular size. In this method the asphalt is dissolved in a solvent and passed through a bed of porous beads having a very uniform pore size. The molecules flow through or around these pores depending on their size relative to that of the pore opening. The smaller molecules are retained on the column due to the more tortuous path they take in passing through the pores. Conversely, the larger

molecules will not fit the pores, and pass through the column more quickly than the small molecules. The weakness of SEC is that it separates only by "size", and not by a more fundamental parameter such as molecular weight. For example, aliphatic molecules may behave differently in SEC separations than will condensed aromatic molecules of comparable molecular weight. The separation of an asphalt is further convoluted by the ability of the solvent to cause or reduce aggregation of asphalt molecules, as this will influence the separation.

At both MSU (Jennings et al. 1993b) and WRI (Branthaver et al. 1993), new SEC techniques were applied to the SHRP MRL asphalts in order to follow up on earlier work by Such and Brule (1979), Jennings and Pribanic (1985), Donaldson et al. (1988), and others noted in a review by Finn et al. (1990). The approach of Jennings et al. (1993b) uses tetrahydrofuran (THF). This solvent is better suited to breaking up intermolecular associations (although it may leave some assemblies intact) and one obtains a truer distribution of molecular sizes. Characterizing asphalt binders in this manner lead Jennings to describe four distinct types or classes of patterns for the MRL asphalts they examined. Examples of these four classifications are shown in figure 1.

Type 1 asphalts (e.g., AAG) are typified by a narrow molecular size distribution which is composed of smaller molecules than the other three representative asphalts. An example of this type of GPC profile is shown in figure 1a. Eight of the 27 asphalts characterized fall into this category. These asphalts contain few asphaltenes (average of 10.3%) and SEC I (average 15.2%) and have low oxygen and sulfur contents. The average  $M_n$  for this class of asphalts is 870 daltons.

Type 2 asphalts exhibit a bimodal distribution of molecular sizes. AAK exemplifies this, and its profile is shown in figure 1b. This is the common behavior; 14 of the asphalt binders exhibit this bimodal profile. The asphaltene content is much higher for these asphalts (average of 17.6%) as is the SEC I content (mean of 23.2%) relative to those of type 1. However the molecular weight (mean of 870 daltons) of this class of asphalts is similar to the type 1 asphalts.

Only one asphalt fell into the type 3 classification, namely the California coastal asphalt, AAD. The GPC profile (figure 1c) indicates the presence of three distributions of molecules. Essentially this mirrors the type 2 profiles with the addition of a small component of very high molecular weight species. This asphalt is quite similar to the type 2 asphalts since its asphaltene and SEC I contents are comparable, 23.4 % and 20.5 %, respectively. The key differences are the smaller  $M_n$  for this asphalt (700 daltons) and the considerable amount of heteroatoms as noted in table 1.

Type 4 asphalts (e.g., AAM) consist of higher molecular weight species. This is evident in the shift of the profile to shorter retention times (figure 1d). The average  $M_n$  of these asphalts is 1100 daltons. There are few asphaltenes (similar contents to type 1 asphalts, average of 10.7%), but considerable amounts of SEC I (similar to type 2 asphalts, average of 24.4%).

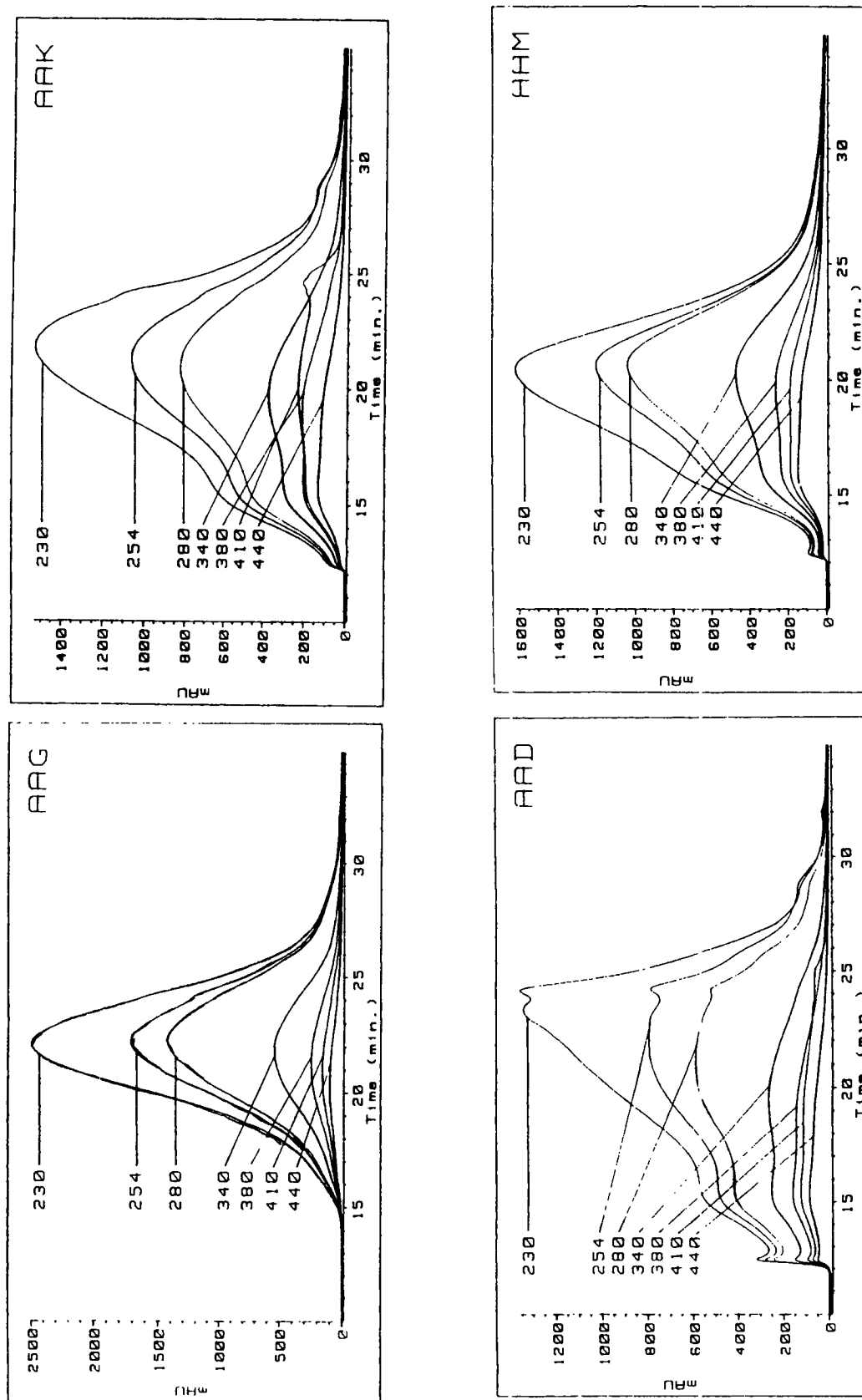


Figure 1. Representative HPLC Chromatograms of the 4 Groups of Asphalts: a) AAG; b) AAK; c) AAD; d) AAM

The investigators at WRI wanted to take advantage of the fact that many of the polar molecules in asphalt form intermolecular associations through Pi-Pi interactions or hydrogen bonding. These are relatively weak bonds (generally less than 10 kcal/mole) and are readily disrupted by the use of a polar solvent such as THF. Toluene was their solvent of choice since its solubility parameter is comparable to that of the solvent phase in asphalt and was deemed to be less disruptive to the asphalt structure leaving some of the weak bonds intact. This enables the investigation of both large and effectively large "groups" of molecules.

A preparative technique was developed for collecting appreciable quantities of the different fractions (Duvall et al. 1993). This allowed further chemical and physical characterization of the separated SEC fractions. They noted that the large molecular size material which eluted first was nonfluorescent. Consequently the cutoff established for the first fraction, designated as SEC I, is the onset of fluorescence under 350 nm light. Subsequent fractions were collected at set intervals. These were later grouped together and are referred to as the SEC II fraction. All fractions were determined gravimetrically.

SEC I contains the "associated molecules", and SEC II consists of "non-associated" molecules. While in principle SEC separates the asphalt molecules based on their hydrodynamic volume or molecular size, additional analyses have indicated that the majority of the polar materials present in asphalt are found in SEC I and most of the non-polar materials are in the SEC II fraction. Many researchers have long felt that the polar materials in asphalts played a major role in pavement performance, but they had been unable to demonstrate it conclusively. The use of SEC to obtain large quantities of these two fractions was a first step in proving that relationship. Subsequent chemical and rheological analyses were carried out on the isolated fractions to delineate their interactions and contributions to asphalt performance. These details are discussed elsewhere in this report.

### *Ion Exchange Chromatography (IEC)*

This is the second powerful analytical technique that has been developed and applied to asphalt to help understand its chemistry-physical property-performance relationships. Expanding on the seminal work by McKay et al. (1975), Boduszynski, Chadha and Pochopien (1977) and Green et al. (1984), researchers at WRI tailored the method to separating asphalts (Branthaver et al. 1992b; Duvall et al. 1993).

As discussed in an earlier paper (Jones and Youtcheff 1991), SHRP researchers now have an analytical method that separates the molecules into chemically distinct fractions. The earlier separations such as the Corbett and Rossler techniques, while resulting in the fractionation of asphalt into different classes of increasing polarity, averaged the impact of polar and non-polar functionalities on a given molecule. IEC captures the impact of specific polar functionalities (both acidic and basic) and provides researchers the wherewithal to help unravel the chemistry-performance link.

The WRI IEC separation method uses anion and cation exchange resins as the chromatographic medium. The process taking place is not a standard acid-base separation since nonaqueous solvents are employed. However, subsequent nonaqueous titrations of IEC separated fractions gives ample evidence that the acidic, basic, and amphoteric moieties have indeed been separated by IEC.

The methodology of the IEC separation is quite complex and time consuming. The original methodology required about 2.5 weeks to condition the resins prior to any separations, and complete the separation (Duvall et al. 1993). Great care had to be taken in order to achieve reproducible results and minimize irreversible adsorption of the asphalt on the resins. Currently researchers at WRI are modifying this procedure such that the actual IEC separation can be conducted within 1 day.

Asphalt is dissolved in a non-polar solvent and partitioned and desorbed on cation and anion resins into strong acids (SA), strong bases (SB), weak acids (WA), weak bases (WB), and neutrals. Amphoterics (defined as molecules containing both acid and base functional groups) were separated from select asphalts. The non-polar molecules are not retained on any of the resins, and are collected as a separate fraction.

The significant and unique point of the IEC separation is that for the first time polar molecules are separated based on the very characteristic which makes them contribute to the performance of asphalt. Earlier analytical methods, including the SHRP SEC separation, utilize a surrogate property to separate the asphalt molecules. Asphalts cannot be successfully separated into their fundamental molecular units using these surrogate methods. The use of IEC provides more definition to the understanding of asphalt and allows us to describe the asphalt in fundamental chemical units, and subsequently advance an asphalt model based on its chemistry.

### *Supercritical Fluid Chromatography*

This technique provides information on hydrocarbons having carbon numbers greater than 40 which are not readily analyzed by gas chromatography. SFC entails the separation of components with a gas in the supercritical fluid state. The supercritical fluid has nearly the solvation strength of a liquid while exhibiting the mobility of a gas. (Polar materials are generally not eluted from the columns and consequently were not examined.)

SHRP activities used supercritical CO<sub>2</sub> as the fluid of choice for fractionating the C-40 through C-80+ hydrocarbons. SFC chromatograms were obtained for the maltene, neutral, and SEC II fractions. These profiles for fractions from a given asphalt are quite similar whereas the profiles for different asphalts over the C-30 to C-110 range varied greatly. Additional details regarding the methodology employed and results for the core asphalts are reported elsewhere (Petersen et al. (1994b), and Branthaver et al. (1993), respectively).

## Spectroscopic Techniques

### *Nuclear Magnetic Resonance*

Proton and carbon-13 NMR were used to help understand the chemical structure of asphalt and how changes in structure affect asphalt rheology. Jennings et al. (1993a) determined the amount of aromatic carbon in an average molecule of asphalt. These high resolution techniques were also used to provide information as to the average structural arrangement, size, and extent of substitution for the aromatic and aliphatic portions of different asphalts. That is, quantitative information is obtained regarding the degree of ring condensation (size) and extent of substitution on the aromatic rings; the number of alicyclic rings, and the length and degree of branching of the aliphatic chains.

### *Wide-line NMR*

Wide-line nuclear magnetic resonance (NMR) techniques were used to characterize asphalt binders and asphalt mixes. Free induction decay (FID) studies were developed to measure the relative amounts and relaxation times of three hydrogen populations that exist in most asphalt binders. The free induction decay signal for asphalt AAG is shown in figure 2. Essentially this is the measurement of the decay of the magnetization of the protons as a function of time. An off-resonance NMR signal was used to measure the molecular motion of asphalt mixes (Pearson 1994).

An automated curve-fitting routine was used to deconvolute the FIDs into three different hydrogen populations. These include a stiff phase, a flexible phase, and a fluid phase. Populations with steeper slopes have faster NMR relaxation times since the hydrogen atoms are more rigidly bound. Consequently, the overall stiffness of an asphalt can be determined by the relative relaxation times and concentrations of the different hydrogen populations.

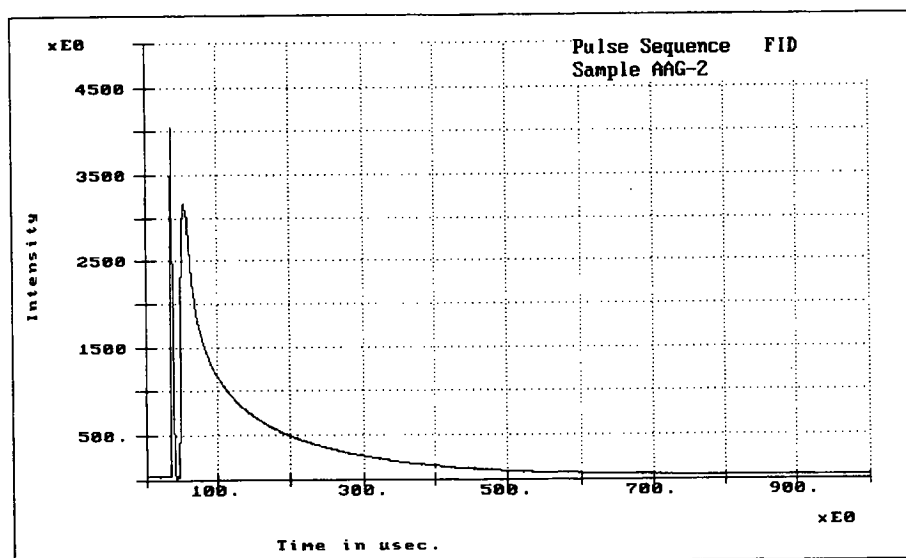


Figure 2. Free Induction Decay Plot of Asphalt AAG

# Chemistry and the Asphalt Model

## Examination of Fractions

By examining the attributes of the fractions that have been isolated from asphalt, SHRP researchers have been able to clarify the relationships between chemistry and performance.

Through a series of rheological measurements of the isolates, researchers have shown that the elastic properties of the asphalt come from its polar constituents. In the same way they also confirmed that the viscous portion of asphalt properties are due to the non-polar molecules. Representative data are shown in table 2.

Table 2. Viscosity of Base Asphalts and Mixtures of Their IEC Fractions at 25°C, 1 rad/s

Viscosity (Pa·s) @ 25°C, 1 rad/s

SHRP Asphalt	AAD-1	AAG-1	AAK-1	AAM-1
Whole Asphalt	57,280	354,000	251,700	364,400
IEC Neutrals	20	260	46	1,191
Neutrals + Acids	35	1,472	148	2,150
Neutrals + Bases	62	17,670	1,045	2,714
Neutrals + Acids + Bases	1,264	41,260	7,272	18,450

Tan  $\delta$  @ 25°C

SHRP Asphalt	AAD-1	AAG-1	AAK-1	AAM-1
Whole Asphalt	2.60	8.91	2.47	2.31
IEC Neutrals	9.4	92.1	33.2	4.7
Neutrals + Acids				
Neutrals + Bases				
Neutrals + Acids + Bases	17.09	97.85	14.01	12.48

The IEC neutral fractions consist of the non-polar molecules in the asphalt. As evident from the data in table 2, the neutrals are low viscosity liquids at room temperature. As the whole asphalt is reconstructed by recombining various IEC fractions, the viscosity of the mixtures increases as the polar fractions are combined with the neutral fraction. The last row in Table 2 shows the asphalt without its amphoteric fraction. The large differences between the viscosities of the whole asphalt (row 1) and the mixtures missing only the amphoteric fraction (row 5) demonstrate the major contribution of the amphoteric to asphalt properties.

While table 2 illustrates the effect of mixtures without the amphoteric fraction, table 3 shows the effect of adding the various IEC fractions to whole asphalts. In this case the IEC isolates were added back into the whole asphalt, and the viscosity was determined at 60°C. The level of addition was chosen to be equal to 50% of the natural abundance of amphoteric in the asphalt for all additions. For instance asphalt AAD-1 contains 25% amphoteric by IEC analysis, and so the various fractions were added to asphalt AAD-1 at the 12.5 wt% level. Similarly, asphalt AAG-1 contains 18% amphoteric, so the fractions were added to asphalt AAG-1 at the 9 wt% level.

In this table one can see there are two IEC fractions which make overwhelming contributions to the viscosity properties of the asphalts. One is the IEC neutral fraction which as a "solvent" can drastically reduce the viscosity of some asphalts. The other is the amphoteric fraction, which plays a key role as a viscosity builder.

Table 3. Viscosity of Asphalts and Asphalts Blended with IEC Fractions at 60°C, 1 rad/s

Viscosity (Pa·s) @ 60°C, 1 rad/s

SHRP Asphalt	AAD-1	AAG-1	AAK-1	AAM-1
Asphalt	131	240	413	258
Asphalt + Neutrals	40	131	117	137
Asphalt + Bases	327	346	656	399
Asphalt + Acids	174	285	517	292
Asphalt + Amphoterics	2,638	1,440	6,796	3,967

Based on this approach it is the amphoteric fraction and its combination with the asphalt which appears to hold the key to the modification of petroleum asphalts at the refinery level. The addition of non-polar material has the effect of increasing the viscous character of the asphalt, whereas the addition of amphoteric materials has a very large effect on the elastic character of the asphalt.



Of the five standard fractions separated by IEC, the SA and neutrals are most informative. Data regarding these fractions are provided in table 4. The neutrals compose over 50% of the asphalt and provide a stark contrast to the SA. They are considerably less polar, less aromatic, quite fluid, and have much lower solubility parameters ( $\delta$ ). In general, the  $M_n$  and  $\delta$  values for the neutrals reflect those of the parent asphalt. The SA are more aromatic and have higher average molecular weights than the parent asphalt.

Some pertinent characteristics of the SEC fractions are provided in table 5. SEC I is a friable solid at room temperature, whereas SEC II is a more fluid material than the parent asphalt. The percentage of SEC I present in asphalts typically ranges between 10% and 31%. The percent by weight (SA + SB) in asphalts roughly correlates with the SEC I concentration. The  $M_n$  determined for these fractions is considerably larger than the SEC II fractions. Similar trends generally hold for the aromaticity and heteroatom contents.

Table 4. Select Data Calculated and Measured for IEC Neutral and Strong Acid Fractions

	Strong Acids (SA)			Neutrals			
	$\delta$	$M_n$	$C_{ar}$	$\delta$	$M_n$	$C_{ar}$	$\eta$
AAD	11.32	2500	32.2	9.04	510	19.7	20
AAG	10.81	1080	37.0	9.67	590	16.6	261
AAK	11.42	2780	33.5	9.60	590	18.4	46
AAM	11.67	3040	35.1	8.99	1140	14.7	1191

Key:  $\delta$ , solubility parameter;  $M_n$  determined by VPO measurement in toluene;  $C_{ar}$ , % aromatic C;  $\eta$  (Pa\*s) at 25°C and 1.0 rad/s.

Table 5. Select Data Calculated and Measured for Asphalts and SEC Fractions

	Asphalt			SEC I		SEC II	
	$\delta$	$M_n$	$C_{ar}$	$M_n$	$C_{ar}$	$\eta$	$C_{ar}$
AAD	9.07	700	23.7	7000	30.9	336	24.0
AAG	9.34	710	28.3	7900	30.3	62380	28.3
AAK	9.35	860	31.9	10000	37.9	1124	26.9
AAM	9.03	1300	24.7	4600	23.0	26350	27.1

Key:  $\delta$ , solubility parameter;  $M_n$  determined by VPO measurement in toluene;  $C_{ar}$ , % aromatic C;  $\eta$  (Pa\*s) at 25°C and 1.0 rad/s.

The solid components separated by the three fractionation schemes are compared in table 6. The asphaltene, SEC I, and amphoteric all have a profound impact on the viscosity of the asphalt. (The viscosity of these components, by necessity, are calculated by difference.) Some fractions appear to be more effective enhancing the viscosity than others. For the high sulfur asphalts, AAD and AAK, both the SEC I and amphoteric fractions account for over 97% of the viscosity; whereas for AAG and AAM, the low sulfur asphalts, this falls off. All of these materials have  $M_n$ s on the order of several thousand daltons. As these are number averages, the possibility exists that a small percentage of this material is of sufficient size (i.e., greater than 600 carbon atoms) as to exhibit entanglement effects and thus be the actual viscosity enhancer. However, the size and molecular weight of these species remains the subject of debate. Green et al. (1991) point out that the use of VPO, the conventional method for determining molecular weights for petroleum and asphalt fractions, has a considerable number of limitations. Chiefly, VPO measurements on polar fractions yield  $M_n$  values for associated complexes. Consequently, caution must be used in interpreting these values.

A cross-check was performed to determine whether the most polar species (i.e., the amphoteric) are preferentially partitioned by SEC. Most of the amphoteric found in asphalt have high  $M_n$  values and should elute with the SEC I fraction. SEC I and SEC II samples were subjected to IEC fractionation, and amphoteric were run through the SEC separation. The results of this exercise are reported in table 7. The recoveries for the IEC separation of SEC I fractions from AAD and AAG averaged less than 80%.

Table 6. Indirect Evaluation of Impact of Asphalt Components on Viscosity

Asphalt Component	Asphaltene		SEC I		Amphoteric	
Asphalt	wt, %	% $\eta^*$	wt, %	% $\eta$	wt, %	% $\eta$
AAD	20.2	99.0	23.4	99.2	24.9	97.8
AAG	5.0	76.9	11.9	82.4	18.5	88.3
AAK	20.1	98.8	25.8	99.0	22.9	97.1
AAM	3.7	97.3	30.8	76.5	18.6	94.9

\* Defined as  $[1 - (\eta_{\text{asphalt - fraction}} / \eta_{\text{asphalt}})] \times 100$ , measured at 25°C and 1.0 rad/s

For asphalt AAD, the SEC I and amphoteric fractions are quite similar. Most of the AAD amphoteric elute in the SEC I fraction. On the other hand, much of the amphoteric material in AAG is of a smaller hydrodynamic volume as the bulk of this material is eluted with the SEC II fraction. One interpretation is that differences in size of these molecular species account for these results. The amphoteric obtained from AAD are found to be much larger than those obtained from AAG. VPO measurements made in toluene and pyridine yield average molecular weights for AAD amphoteric that are twice as large as those for AAG amphoteric (Branthaver et al. 1993). A second consideration is the nature of the functional groups defining the amphoteric molecules. The IEC procedure used to partition the amphoteric would include molecules containing the following functional group combinations: SA-SB, SA-WB, WA-SB, and WA-WB.

Table 7. Cross Check of SEC and IEC Separations

Material	SEC I	SEC II	Amphoteric	Base	Neutral + Acid
AAD	23.4	76.6	24.9	9.4	60.8
SEC I	100		70.0	6.4	2.7
SEC II		100	11.0	10.6	77.3
Amphoteric	71.0	29.2	100		
AAG	11.9	88.1	18.5	12.5	67.6
SEC I	100		57.4	4.5	16.8
SEC II		100	10.4	12.3	77.3
Amphoteric	39.0	62.3	100		

Averages of two runs, expressed as wt%.

It is interesting to note that the SEC II materials for the two asphalts are functionally quite similar as noted by the similarity in IEC fractional compositions. Much of the amphoteric present in these fractions is presumably the weakly polar WA-WB type.

The fact that a given asphalt has a greater relative abundance of amphoteric or SEC I needs to be placed in perspective. Clearly if an asphalt is doped with amphoteric, the viscosity will be enhanced. However, this in itself is of little predictive value in selecting an asphalt for a given climatic region. As shown in table 1, the viscosity of AAG is over 8 times that of AAD at 25 °C and nearly twice as great at 60 °C. This goes counter to the expectation that the greater the abundance of the SEC I or amphoteric, the more viscous the material. There are two reasons for this discrepancy. First, the whole system, particularly the impact of the neutrals, must be considered, and second, the polarity and molecular weight of the SEC I or amphoteric must be considered.

## Blending Studies

Researchers at WRI blended model compounds and SEC I fractions with the core asphalts in order to quantify the impact of chemical composition on asphalt properties (Branthaver et al. 1993).

### *Model Compound Study*

The effect of eleven different model compounds containing various functional groups and ranging in size from C-11 to C-16, as well as including the bulky model compound tetrastearoyl-pentaerythritol, was examined. These were evaluated at 1% and 2% levels of addition. Some of the model compounds (n-alkanes and monofunctional species) were found to behave as plasticizers in that the viscosity of the blend is greatly reduced. Others (some of the bi-functional species) had the effect of stiffening agents. Asphalts blended with 2% of the model compounds accentuated these effects relative to the 1% loadings. For polymeric systems, the glass transition temperature ( $T_g$ ) has been found to be related to the concentration of the components per Equation 1.

$$\frac{C_A}{T_{gA}} + \frac{C_B}{T_{gB}} = \frac{1}{T_g} \quad (1)$$

where:

$C_A$  is the concentration of component A in mixture;

$C_B$  is the concentration of component B in mixture;

$T_{gA}$  is the glass transition temperature for component A;

$T_{gB}$  is the glass transition temperature for component B; and

$T_g$  is the glass transition temperature for the mixture.

The asphalt blends presumably behave in similar fashion. Plots were constructed of the viscosity of the blend at 25 °C versus the melting temperature ( $T_m$ ) of the additive. Linear least-squares analyses of these relationships were examined. The coefficient of correlation ( $R^2$ ) ranged from 0.72 to 0.89 for the 2% systems. Data for blends made with asphalt AAD are shown in figure 3. The overall repeatability for each mix was on the order of 30%; much of the variability in the data may be attributed to a lack of temperature control within the rheometer and differences in storage time of the samples before running. Considering the poor reproducibility of these experiments, this is an exceptionally strong correlation. The correlation suggests that an overriding consideration (whether an asphalt is stiffened or softened) is the effect that the various functional groups have on the  $T_g$  of the blend, or more specifically the free volume of the system.

## SEC I Doping Experiments

In a second series of experiments, SEC I fractions were added at levels commensurate with their concentrations in different asphalts, and a number of rheological parameters were determined for these blends (Branthaver et al 1993). As shown in figure 4, an increase in the SEC I content increases the viscosity of the blend logarithmically. Excellent correlations were obtained in all cases ( $R^2 > 0.99$ ). Note that the slopes of the fitted lines for each temperature essentially parallel one another. If the viscosity building effect is attributable to secondary bonding, then a temperature effect should be evident, namely, at higher temperatures stronger hydrogen bonds should be disrupted. The effect of SEC I addition should diminish with increasing temperature. Evidence for this would be a decrease in these slopes with increasing temperature. In figure 5, the change in viscosity with SEC I content (slope in figure 4) is plotted as a function of temperature for asphalts AAD, AAG, AAK, and AAM. No temperature effect is evident for AAG, AAK, and AAM, and for AAD there is a slight increase in the stiffening effect of the SEC I at higher temperatures.

Based on this self-blended study (i.e., AAD SEC-I added to AAD), the stiffening propensity of SEC I is ordered  $D > K > G > M$ . In order to place this information in the perspective of performance, permanent deformation and fatigue values were determined and plotted against one another (figure 6). Asphalts having high values of  $(G^* \sin \delta)$  are susceptible to fatigue failure whereas increasing values of  $G^* / \sin \delta$  relate to improvement of the rut resistance of an asphalt. The asphalt blends having the steepest slopes, such as AAD and AAK, improve their performance with regard to permanent deformation with less deterioration of the fatigue properties than do AAM and AAG (not shown has the smallest slope).

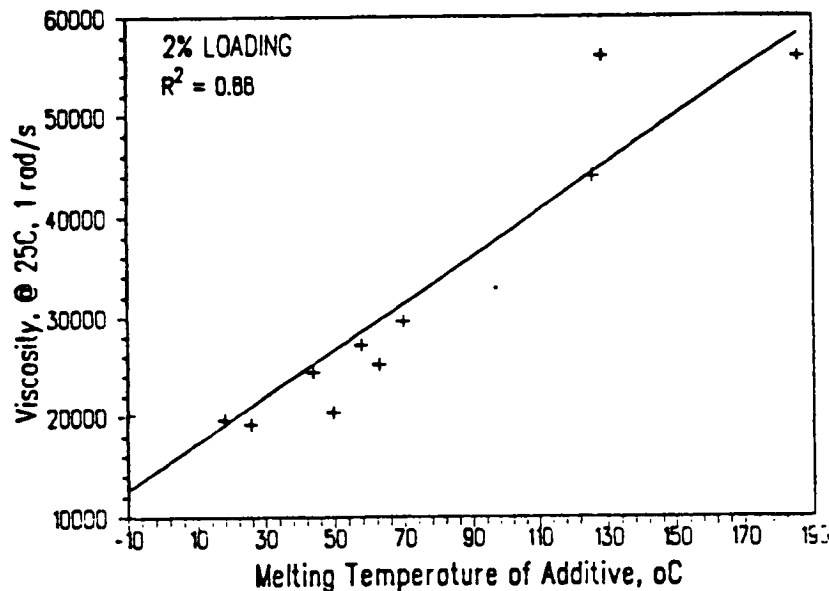


Figure 3. Relationship Between Melting Temperature of Additive and Viscosity of AAD Mixtures

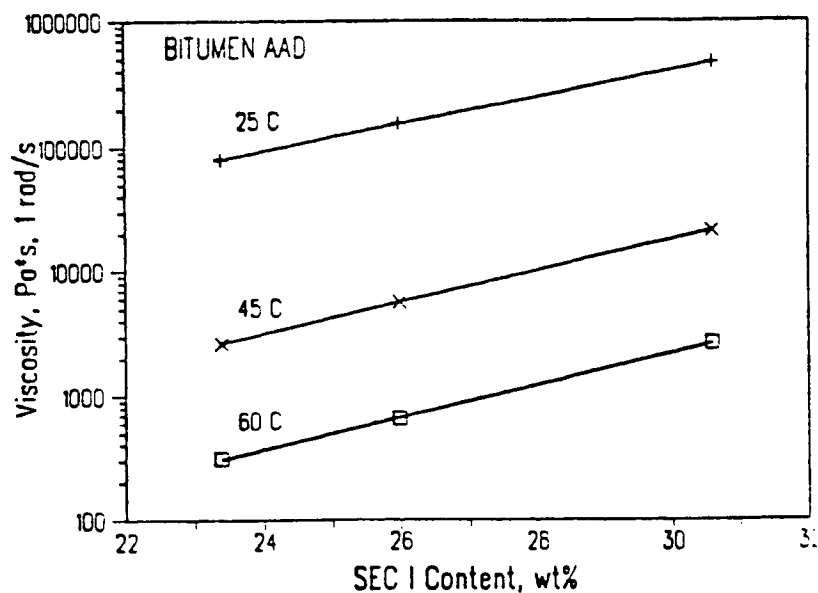


Figure 4. Effect of SEC I Content on Viscosity of Asphalt Blends Measured at Different Temperatures

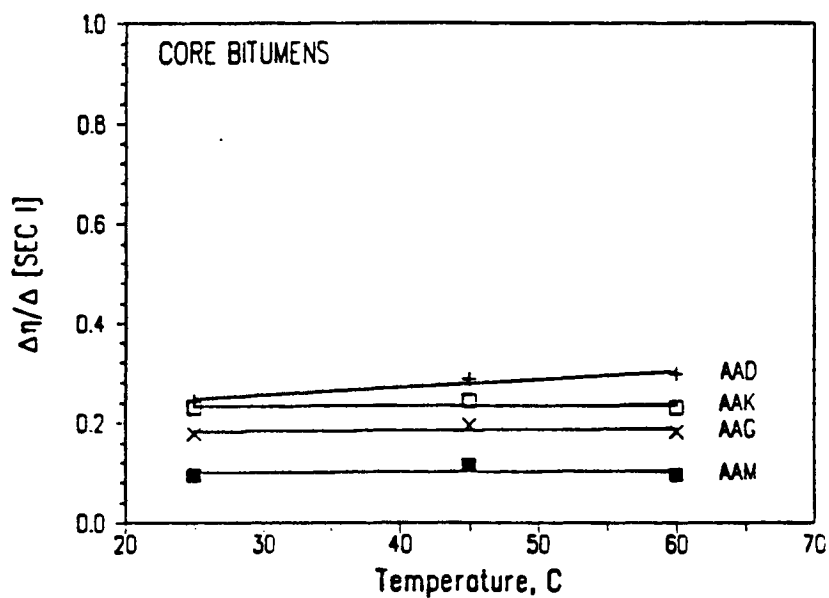


Figure 5. Effect of Temperature on the Change in Viscosity with SEC I Loading

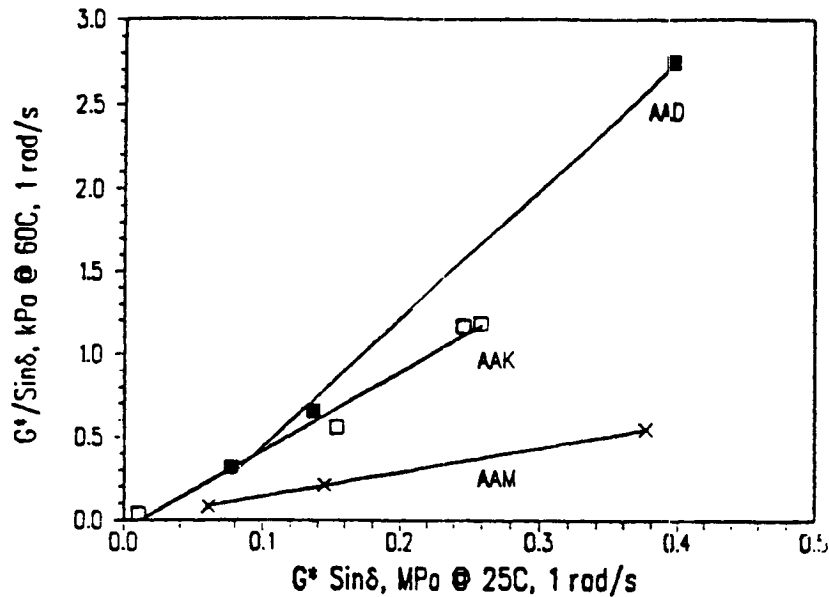


Figure 6. Effect of SEC I Loadings on Fatigue and Permanent Deformation Properties

## Wide-Line NMR

Pearson (1994) has been investigating the application of small NMR spectrometers as a means of controlling the quality of asphalts and asphalt mixtures. Spin-spin relaxation times ( $T_2$ ) from pulsed adaptations of standard wide-line NMR techniques were found to correlate with rheological properties of asphalts. For true relaxation decays, a plot of  $\ln$  intensity versus time gives a straight line for homogeneous hydrogen populations. Such plots of asphalts were found to divide into three distinct hydrogen populations (Pearson 1994). Listed in table 8 are the percentages of these populations, as well as their  $T_2$  values for asphalts AAD, AAG, AAK, and AAM. Note that the more tightly bound protons undergo faster decays and consequently have shorter  $T_2$  values. An excellent correlation coefficient ( $R^2 = 0.97$ ) was obtained for the relationship of computed  $\tan \delta$  (loss modulus/storage modulus), calculated from a regression equation using free induction decay (FID) data, versus experimentally determined  $\tan \delta$  (figure 7).

Table 8. Extrapolated Wide-Line NMR Data

Asphalt	Fast		Intermediate		Slow	
	%	T <sub>2</sub>	%	T <sub>2</sub>	%	T <sub>2</sub>
AAD	53.8	247	20.7	1013	25.5	1583
AAG	82.1	125	14.3	784	3.6	3729
AAK	61.3	198	27.2	748	11.5	1702
AAM	63.2	195	22.6	841	14.2	1704

Average of two runs measured at 35°C; T<sub>2</sub> expressed in  $\mu$ s.

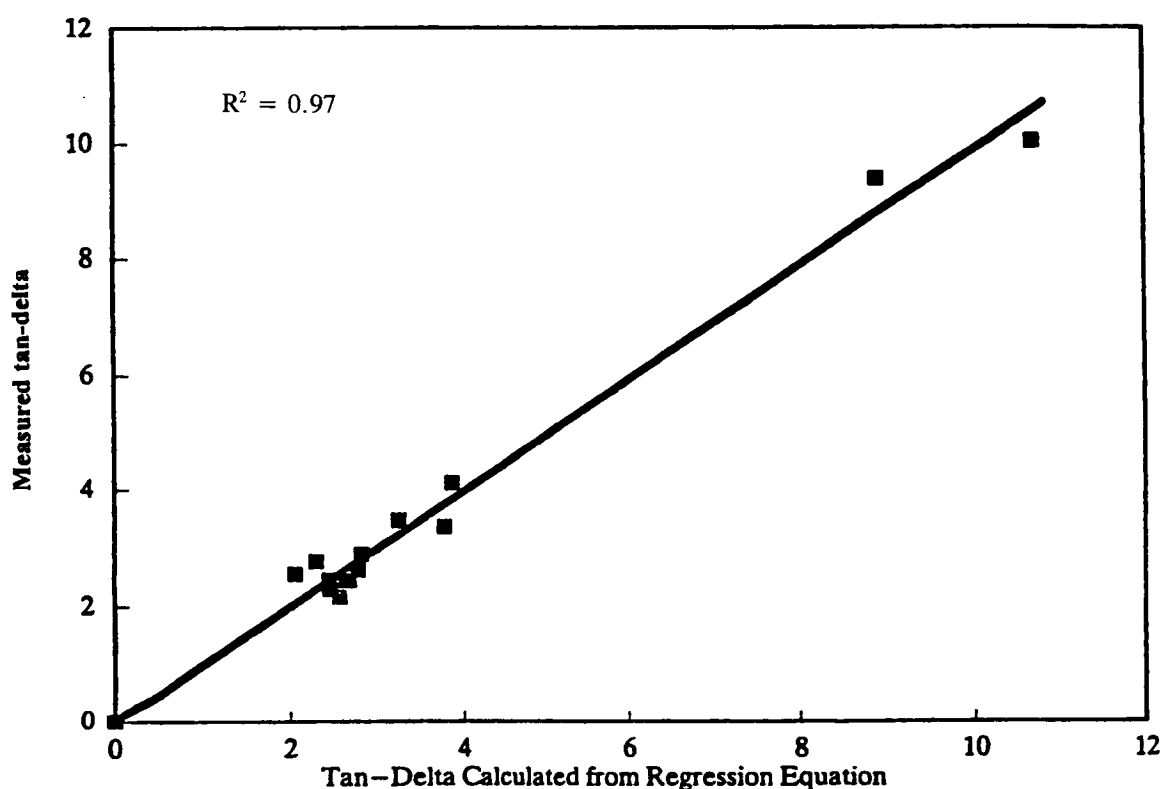


Figure 7. Regression of FID Components Versus Viscosity

The majority of the protons in asphalts measured at 35 °C have fast decays. AAG stands out since almost all (82.1%) of its protons are in this category and only a small population are of the slow type. Sol type asphalts such as AAG tend to have few asphaltenes and require higher cut points during the distillation in order to achieve a given viscosity. The outcome is that much more of the light-end materials are lost, and ultimately AAG appears to be lacking a plasticizer. Asphalts such as AAD and AAK have an abundance of viscosity building species and can be readily distilled to several grades at much lower temperatures or may even require cutting with a flux to limit their viscosity.



## Examination of Phase Behavior

Painter (1993) constructed a model and computer programs that provide a qualitative understanding of the phase behavior of asphalt and asphalt components. These programs were used to assess some of the models proposed for asphalt structure. Modeling as such is by no means unequivocal, but rather provides a sense of direction. In the course of this work the role and importance of hydrogen bonding was also re-examined.

The starting place for Painter's approach is Flory-Huggins' simplified expression for the free energy of mixing. This assumes that only "weak" interactions are present; these would be London dispersion forces and weak polar forces. A lattice model was developed to account for strong interactions, such as hydrogen bonds (Coleman et al. 1991). A simplified expression for the free energy of mixing is

$$\frac{\Delta G'_M}{RT} = \frac{\phi_A \ln \phi_A}{x_A} + \frac{\phi_B \ln \phi_B}{x_B} + \phi_A \phi_B \chi + \frac{\Delta G'_H}{RT} \quad (2)$$

where  $\phi_A$  and  $\phi_B$  are the volume fractions of components A and B,

$\chi$  is the Flory-Huggins interaction parameter;

$x_A$  and  $x_B$  are the degrees of polymerization of components A and B, and

$\Delta G'_H/RT$  is the contribution to free energy of mixing from the change in number and type of hydrogen bonds.

The quantities  $x_A$  and  $x_B$  are equal to the molar volume of these molecules divided by a reference molar volume. If component A is a "solvent" and component B is a macromolecular species (e.g., asphaltene, SEC I, or amphoteric), it is convenient to use the "repeat" unit of the macromolecules to define a reference volume  $V_B$ . (If molecular weight data are lacking, a molar volume per oxygen group can be used.) Values for  $\chi$  are determined using;

$$\chi = \frac{V_B}{RT} (\delta_A - \delta_B)^2 + F \quad (3)$$

F is an empirically determined factor;  $\delta$ , the solubility parameters, and  $V_B$ , the molar volumes, are determined from atomic contributions (Coleman et al. 1990). This approach is less accurate than group contribution methods, but requires only a knowledge of the elemental composition and the aromaticity of the material. Errors are on the order of  $\pm 0.6$  (cal\*cm<sup>-3</sup>)<sup>0.5</sup>. Despite the potential for significant errors in calculating  $\delta$ , these values are useful in considering broad trends and the balance of forces that determine phase behavior. In modeling the phase behavior, an assumption is made that the hydrogen bonding functional groups of asphalt are randomly distributed, and an average unit or segment per group can be defined (Painter 1993).

Phase diagrams were generated for mixes of strong acid fractions and neutral fractions. Shown in figures 8 and 9 are phase diagrams for AAD and AAG, respectively. Modeling the phase behavior of AAD and the other core asphalts produces the type of phase diagram shown in figure 8. The region beneath the inverted U-shaped curve is predicted to be two phases. On the other hand, the phase diagram for asphalt AAG (shown in figure 9) is featureless, suggesting that the components are miscible over the entire range. This is not surprising since the solubility parameter,  $\delta$ , for the neutral and SA fractions are quite similar. (see table 4) Whether this is borne out in the pavement and what impact this has on performance remains to be established.

The laboratory findings of Nguyen et al. (1992) support these modeling results. In studying the impact of water on the asphalt-aggregate interface, films of the core asphalts were coated on aluminum plates and immersed in distilled water. Visual observation of asphalt films AAD and AAK following immersion for 50 hours indicated a color change and the formation of a highly-textured microstructure on the surface. In addition many large holes and craters were evident when the films were examined with a microscope. The surfaces of asphalts AAG and AAM on the other hand "became bumpy, with blunt peaks and flat valleys that resembled the skin of an orange." It appears that the asphaltenes (polars) in asphalts AAD and AAK undergo partitioning within the asphalt in the presence of water. Since this change was also found to correspond with faster water absorption rates, it suggests that asphalts composed of species of very diverse polarity (large spread in solubility parameters of the major components), may be moisture susceptible via water migration or when used with aggregates having a propensity to strip.

Based on differences in the solubility parameters of the neutral and strong acid fractions, one would expect asphalt AAM to be susceptible to phase separation. However, hydrogen bonding has a significant effect as to whether or not phase separation is exhibited, and the concentration and distribution of functional groups capable of hydrogen bonding need to be considered. Although the heteroatom content of AAM is considerably smaller than those of the other asphalts considered, the large spread in solubility parameters for AAM's fractions is attributed to differences in the size of the aromatic rings.

## **Chemical Parameters Which Significantly Impact the Viscoelastic Properties of Asphalt**

As we have discussed, asphalt is composed of a wide distribution of molecules ranging both in size and polarity. The molecular size is dictated by the nature of the parent crude oil and to some extent by the asphalt processing conditions. Lighter hydrocarbons are typically removed by refining whereas highly polar low molecular weight materials may be retained in the asphalt. With regard to the polarity of the asphalt, the molecules range from non-polar hydrocarbons to very polar molecules, functionally defined as asphaltenes, SEC I or amphoteric. The breadth of this variability is contingent on the parent crude and processing conditions employed by the refinery. For example, naphthenic type crudes (e.g., asphalt AAG) which do not contain appreciable amounts of heteroatoms or asphaltenes necessitate

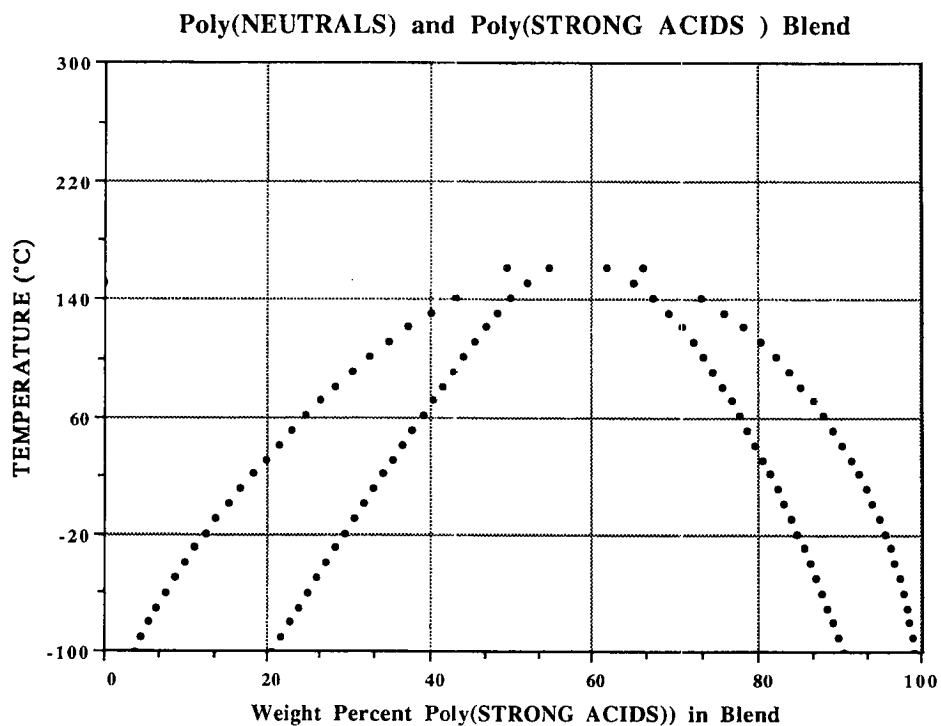


Figure 8. Phase Diagram for Mixes of Strong Acid and Neutral Fractions from AAD

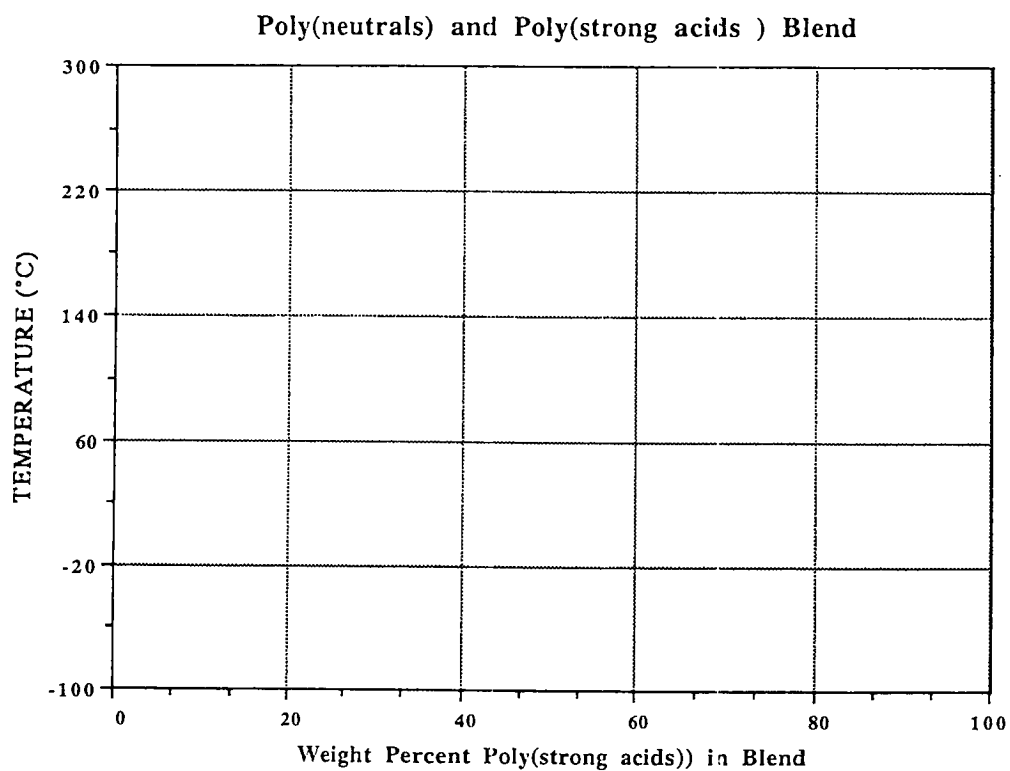


Figure 9. Phase Diagram for Mixes of Strong Acid and Neutral Fractions from AAG

the use of more severe processing conditions such as higher cut-off temperatures for the various asphalt grades. Heavy crudes contain appreciable amounts of polars and therefore achieve given asphalt grades at lower temperatures or necessitate the use of blending or cutting with other asphalts or oils to achieve the desired viscosity.

WRI researchers noted that SEC fractionation ratios, namely SEC-I/SEC-II, showed a strong correlation with viscoelastic properties (Branthaver et al. 1993). It was suggested that the non-fluorescent SEC-I component formed an elastic matrix at low temperatures, but the associations weakened at increasing temperature until the material became essentially viscous.

There are several methods for attempting to prove the validity of this scenario, though none are by any means conclusive. The results from doping studies using SEC I supports this theory. Increasing the SEC I content increases the viscosity of the system and decreases  $\tan \delta$ , much as the model would suggest. Addition of SEC I material would enable hydrogen bonding to be more prevalent (Petersen et al. 1994a). The physical response is an increase in viscosity and a decrease in  $\tan \delta$ . This response demonstrates that this component enhances the elastic properties of the asphalt. The fact that all SEC I materials are not equal was demonstrated (See figure 6.). Consequently, the quality of the polar and non-polar material also needs to be addressed.

All of the molecules in asphalt behave in one of two ways. If they are polar, at service temperatures they may participate in the formation of a "network" which reduces the free volume of the asphalt through hydrogen, VanderWaals, and pi-pi bonding. This gives the asphalt its elastic properties. The non-polar material contributes to the viscous properties of the asphalt through less extensive pi-pi and VanderWaals interactions. Of course, there are a wide range of polarities in asphalt molecules, from very polar to completely non-polar. Differentiation of these groups can be based on any of the three separation schemes noted. The weakly polar molecules are considered non-polar for the purpose of understanding their contribution to asphalt performance.

### *Role of Polars*

In the microstructural model, polar molecules are those considered responsible for the formation of the network. Based on this concept, the most important attributes of the polars are the relative strength and number of polar sites per molecule as well as their aromaticity, because these directly affect the network formation. The specific heteroatom and its location in the molecule will govern the polarity of the molecule and affect the planarity of the aromatic position of the molecule. In practice the amounts and strength of polar materials present in asphalt or asphalt fractions can be determined using nonaqueous acid-base titrations (Petersen et al. 1994b).

Hydrogen bonds are thought to play a key role in the association of asphalt molecules. Such associations have been used to account for various aspects of asphalt physical properties, as well as seriously influence such things as column separations and molecular weight measurements. In figure 10, plots are constructed that show the calculated fraction of two hydrogen-bonded groups for asphalt AAD/toluene mixtures at 25 °C. The concentration of carboxylic

acids and phenolic OH groups were determined by NMR following derivatization of the functional groups (Jennings et al. 1993a). Used in this modeling are a number of equilibrium constants that describe the self-association of these species (Coleman et al. 1991).

It can be seen from figure 10 that even though the overall concentration of hydrogen bonding functional groups is small, the fraction of such groups that are bonded is significant. This is particularly true for carboxylic acid groups, which strongly self-associate. More than 90% of such groups are calculated to be hydrogen bonded in pure asphalt at any particular instant of time. Even when diluted with a non-hydrogen bonding solvent, such as toluene, the fraction of hydrogen bonded COOH groups does not begin to significantly drop until the asphalt concentration falls below 5%.

The fraction of molecules that are hydrogen bonded to one another can be calculated from measurements of number average molecular weight and oxygen content. These results are shown in figure 11, where it can be seen that in the pure asphalt only 1% or 2% of the molecules are predicted to be hydrogen bonded to one another. It does not seem plausible that such a small number of molecules should produce any sort of network within the asphalt, and suggests that hydrogen bonds in themselves play only a secondary role in determining most bulk properties. Furthermore, oxidation of asphalt results in little if any increase in protonated hydrogen bonded species (though the viscosity of aged asphalts increases concomitant with a decrease in  $\tan \delta$ ), but rather generates additional receptor sites (e.g., C=O, S=O). Thus, the impact of aging is through alternative mechanisms. Increasing the amount of polars should result in a reduction in free volume of the system and be attributable for some of the stiffening the asphalt experiences upon aging. (Polymerization reactions which result in an increase in molecular size of the polars should also be considered.)

The aromaticity of the polars is a second important parameter. This can be readily determined by NMR analysis (Jennings et al. 1993a). Asphalt AAM has the lowest heteroatom content ( $O\% + S\% + N\% = 2.3\%$ ) of the four representative asphalts, yet as shown in table 4, its strong acid fraction has the highest solubility parameter. The aromaticity and in particular the degree of condensation of aromatic rings have a significant impact on the solubility parameter for the polar fractions.

One other factor to be considered is the molecular weight of the polar molecules. While the VPO measurements are the least dependable for this fraction, the existence of species of significant size to be involved in chain entanglement should not be readily dismissed.

### *Role of Non-Polars*

In the microstructural model, polar molecules that do not form part of the network are considered non-polar. For instance such species would be eluted with the SEC II fraction.

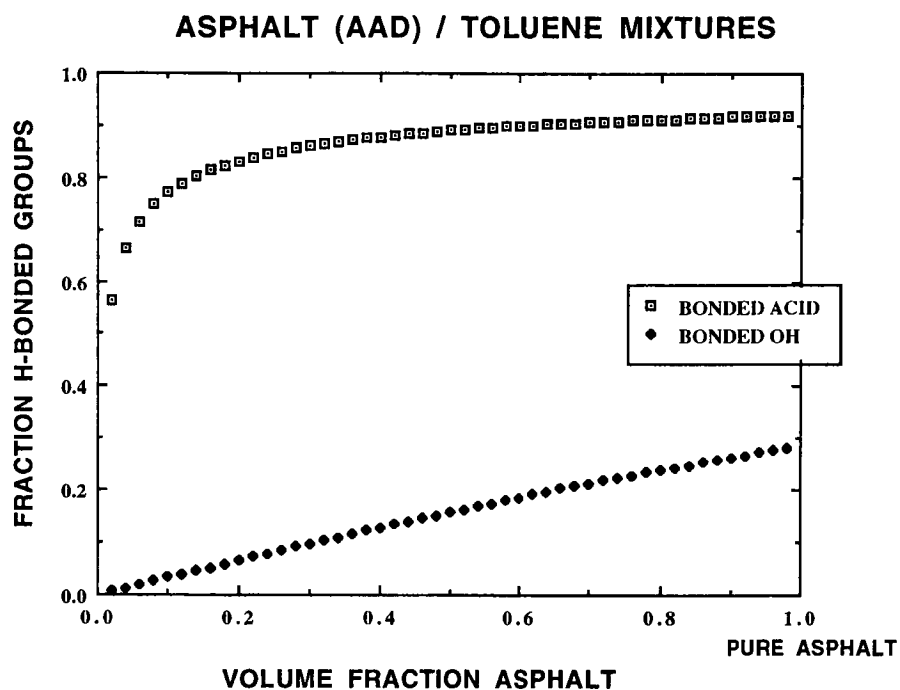


Figure 10. Calculated Fraction of Hydrogen Bonded Functional Groups in AAD as a Function of Dilution

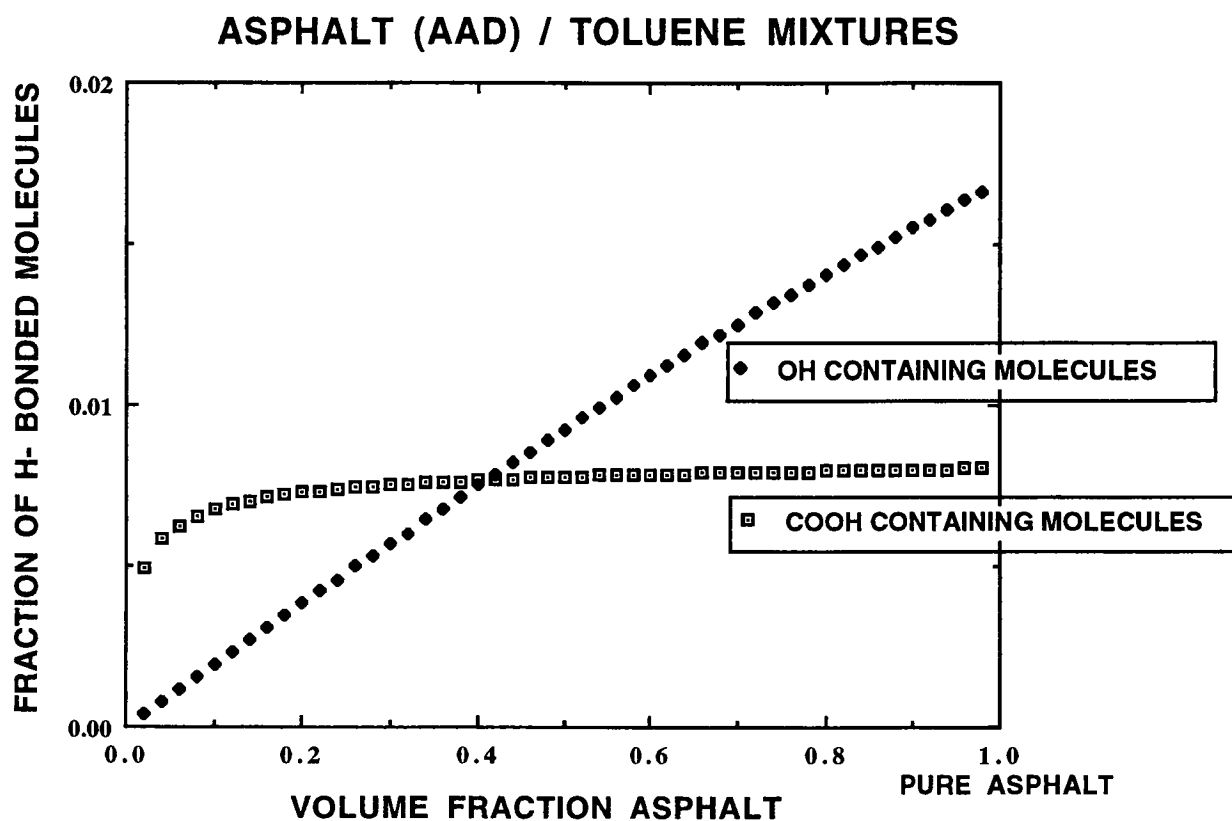


Figure 11. Calculated Fraction of Hydrogen Bonded Molecules in AAD as a Function of Dilution

The non-polars, as exemplified by the neutral fraction, are readily separated by IEC and constitute roughly 45 - 65% of asphalt. This portion of the asphalt behaves as a viscous fluid, as shown in table 2, and its rheological properties are controlled primarily by its molecular weight and size distribution. The viscosity of the neutrals were shown by Branthaver et al. (1993) to be linearly related to  $M_n$  ( $R^2 = 0.94$ ). In addition, the relative amount of aromatic character of the non-polar materials will affect its polarity and is also important from the standpoint of compatibility and interaction with the polar molecules.

From a global perspective components of the non-polars act as plasticizers. The results noted above as well as those from the blending study using model compounds confirm this. Ideally one would like to know the free volume of the material at the lowest temperature at which it is expected to perform. One parameter for estimating this is the glass transition temperature ( $T_g$ ). This is the temperature at which materials undergo a marked change in properties associated with the virtual cessation of local molecular motion. There are a number of procedures available to determine this parameter; these include DSC, NMR, volumetric and rheological methods.

Differential scanning calorimetry (DSC) measures the change in heat capacity of the material before and after going through a phase change. Dilatometry follows the change in volume in the asphalt as it is cooled. Above the  $T_g$  the coefficient of expansion is larger than that below this temperature. NMR can be used to measure the mobility (spin relaxation times) of the carbon or hydrogen molecules as a function of temperature. Below the  $T_g$  the proton line widths are broad and similar to a solid, whereas above this temperature, they narrow and reflect the properties of a liquid. Rheometry is used to measure the defining temperature,  $T_d$ . This is the temperature above which the WLF equation is used to determine the shift factors used in constructing a master curve of complex modulus versus frequency. Below this temperature an Arrhenius function is used to describe the shift factors. (Both cases assume newtonian behavior.)

The low temperature stiffness  $S(t)$  is related to the  $T_g$  no matter how it is determined. Data for this parameter obtained using four different approaches are presented in table 9. However, the ranking of the various asphalts remains essentially the same. The volumetric measurement of  $T_g$  yields values quite similar to the  $T_d$  values, and both tend to mirror the low temperature specification grading (PG -Y). The influence of the non-polars on asphalt's low temperature performance becomes apparent upon examining the relationship between the viscosity of the neutrals and  $T_d$  of the asphalt. Asphalts with lower  $T_g$ s or  $T_d$ s will generally meet lower low temperature grades. This is however not a steadfast rule since the  $m$ -values also needs to be considered, and  $T_g$ s are not necessarily related to this parameter.

Shown in figure 13 is the relationship between the coefficient of thermal expansion and  $\gamma$ -CH<sub>2</sub> content of the asphalt. The latter was determined from the peak at 30 ppm using NMR (Jennings et al. 1993a). The significance of this relationship is that asphalts composed of larger aliphatic molecules, though not necessarily linear molecules, will be affected to a greater extent upon cooling to low temperatures. This effect may lead to an increased amount of internal stresses being thermally induced.

The ability of linear molecules to form crystalline or micro-crystalline domains confounds this simplistic treatise. Crystallization will have an impact on the free volume but not to the same extent. Here domains of molecules are able to closely pack together which results in a loss in free volume. Long linear chains of methylene groups having lengths greater than C-20 are capable of forming close packed arrangements. Crystal growth stems from the molecules tending or reaching for lower free energies. The molecules undergo a decrease in entropy (become more ordered) and attain a lower enthalphy. The presence of side chains disrupts this tendency towards lower free energy, and prevents the stacking of aliphatic chains which would manifest itself as microcrystalline domains (waxes). In order for crystallization or microcrystallization to occur, the ordered segments must be linear or permit a regular arrangement of units. The wax content of most asphalts is quite small, generally less than 5%. In this case crystallites or domains of closely packed, ordered systems will be dispersed throughout the asphalt.

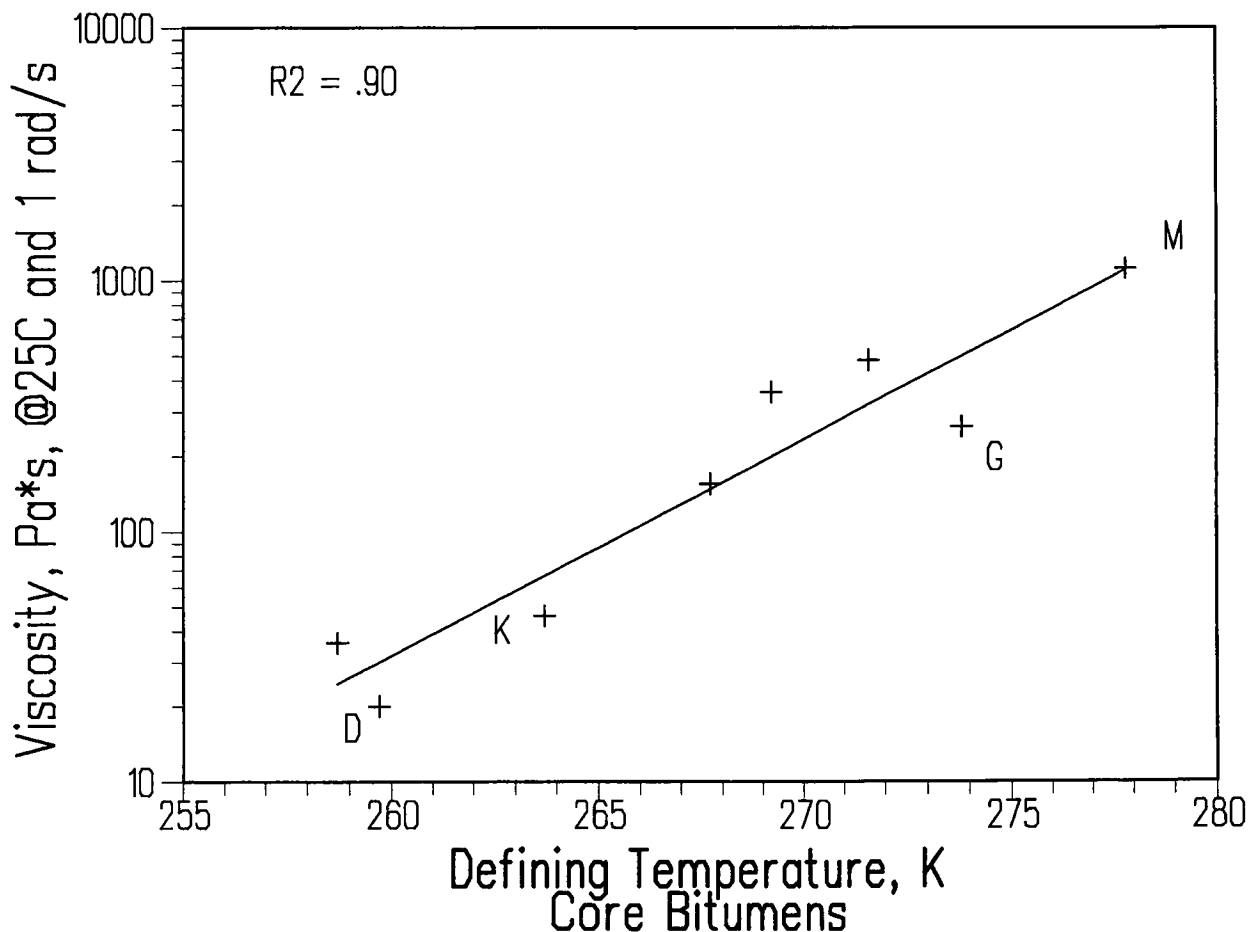


Figure 12. Relationship Between  $T_d$  and Viscosity of Neutrals



Table 9.  $T_g$  Measurements Determined for the Core Asphalts Using Various Experimental Procedures and PG -Y Grades

Asphalt	DSC	Volumetric	NMR	$T_d$	PG -Y Grade
AAA-1	-24.8	-28.2	-25	-19.3	-28
AAB-1	-27.3	-13.9	-23	-11.6	-22
AAC-1	-25.7	-9.9	-15	-5.5	-16
AAD-1	-28.8	-24.3	-23	-17.6	-28
AAF-1	-24.6	-6.1	-13	-7.0	-10
AAG-1	-5.2	-9.9	-2	-3.9	-10
AAK-1	-22.8	-16.5	-18	-14.7	-22
AAM-1	-24.8	-4.0	-20	1.0	-16

DSC  $T_g$ s determined by Buisine et al. (1993); volumetric  $T_g$ s and  $T_d$ s determined by Anderson et al. (1994); NMR  $T_g$ s estimated from data of Jennings et al. (1993a); PG -Y Grades reported by Jones (1993)

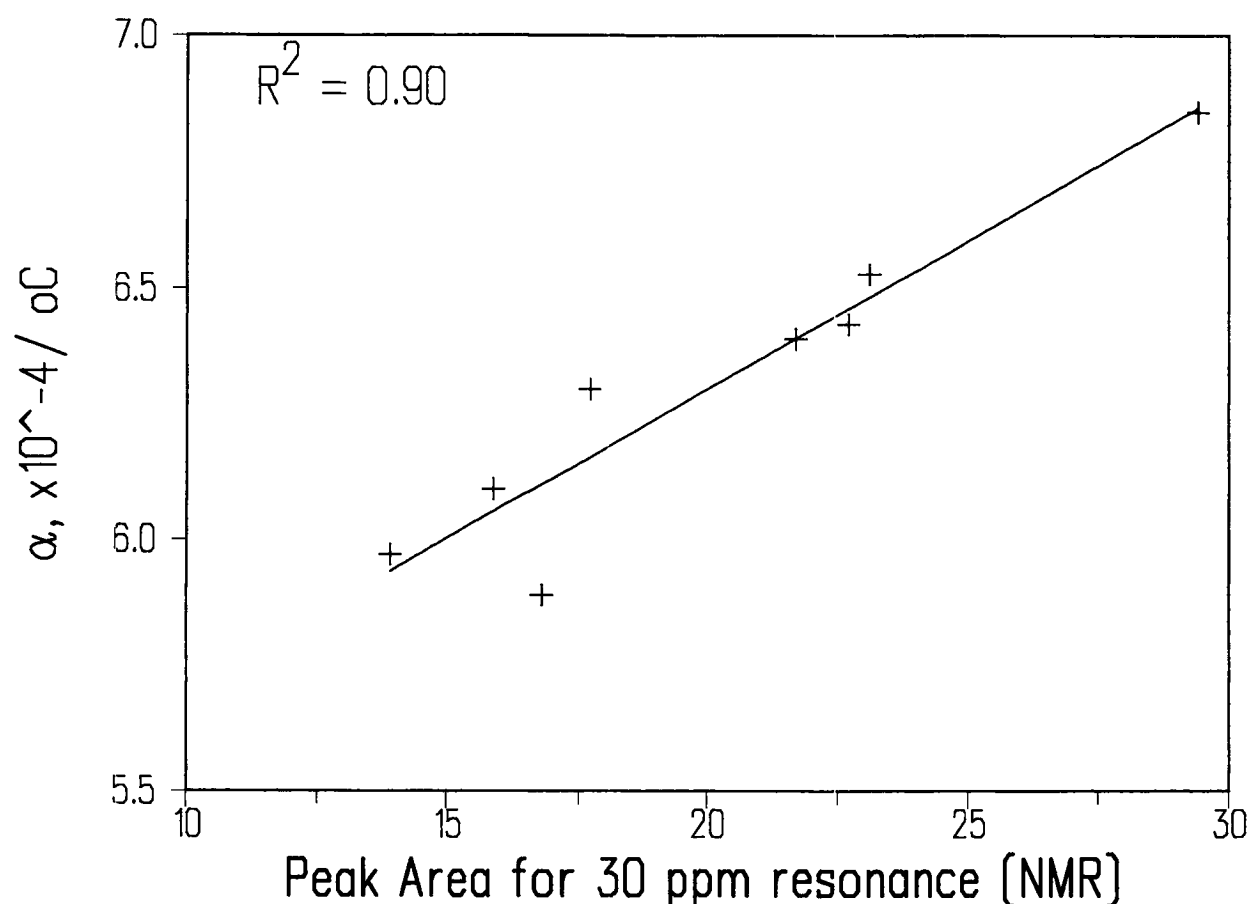


Figure 13. Plot of Thermal Coefficient of Expansion versus  $\gamma$ -CH<sub>2</sub> Content

## Summary

Asphalt can be considered to be composed of an infinite number of discrete molecules; these molecules differ as to shape, size and chemical composition. The combinations and interactions of these diverse molecules give rise to asphalt's behavioral characteristics through the impact on the free volume of the asphalt.

One of the key differences among asphalts is the diversity in polarity of these molecules. Consider the various types of secondary forces between molecules. These forces range from very weak van der Waal forces on the order of 0.3-1.0 kcal/mole on up to hydrogen bonds with strengths approaching weak covalent bonds (although typical OH-bonding strengths are on the order of 3-10 kcal/mole).

Hydrogen bonding does not play a seminal role. The number of oxygen functional groups per molecule is small. Hence, there are not many hydrogen bonds.

Asphalt behavior at upper pavement temperatures (60 °C or so) is dictated by the diversity of species (i.e., "spread" in  $\delta$  values) and hence the phase behavior of this mixture. Polar molecules most likely play a key role here, as they have a tendency to phase-separate from non-polar material. The extent to which this can occur depends upon chemical structure and, crucially, molecular weight.

Molecules composing the amphoteric fraction are highly polar. They are highly incompatible with the neutral molecules and have a strong proclivity towards phase separation in model systems.

The  $T_g$  of an asphalt should relate to its low-temperature properties. However, an increase in polarity of material (e.g., via aging or addition of an additive) should coincide with an increase in  $T_g$ . Low  $T_g$  values can be found in asphalts of similar grades that have been cut with a low molecular weight flux or have lower distillation cut points. In either case, the added or resulting low molecular species act as a plasticizer for the asphalt. Those asphalts lacking this "plasticizer" typically have high  $T_g$  values, and poor fatigue and low temperature properties.

The propensity for the aliphatic chains in asphalt to form microcrystalline regions will greatly impact the behavior at low temperatures. The non-polars or non-polar components on polar molecules are responsible for the susceptibility of an asphalt towards low-temperature age hardening and possibly contribute to steric hardening.

The length and distribution of these chains have a significant bearing on the coefficient of thermal volumetric expansion/contraction. The longer the chain (as determined by SFC), the greater the effect.

Oxidative aging is the reaction of labile groups (i.e., benzylic protons) in asphalt with oxygen through one or more pathways. Reactivity of an asphalt is dependent and somewhat controlled by the accessibility of oxygen to such groups. Once they are consumed, oxidation reactivity diminishes. An important aspect is not only the number of specific functional groups (i.e., C=O or S=O) formed, but their impact on the overall system. Values of  $\delta$  for the neutrals can be spread over a range that is largely dependent on its aromaticity.

Similarly, the  $\delta$ 's of the polars also exhibit a range of values. In systems where  $\delta_{\text{neutral}} - \delta_{\text{polar}}$  is small, perturbation of the latter by oxidation does not have a big affect. Conversely, when  $\delta_{\text{neutral}} - \delta_{\text{polar}}$  is large, a change in the latter as a result of oxidation can have a major affect and even lead to phase separation. Under such conditions, a partitioning of the polars may also be induced by the presence of water.

In conclusion, we can characterize the chemical composition of asphalt and its relationship to performance as follows:

1. Asphalt consists of two *functional* families of molecules, polars and non-polars.
2. Polar molecules differ according to: strength and number of polar groups, molecular weight, distribution of molecular weights, and degree of aromaticity (a measure of the amount of aromatic versus aliphatic and cyclic molecules).
3. Non-polar molecules differ according to molecular weight, distribution of molecular weights, and degree of aromaticity.
4. The "compatibility" of the polar and non-polar fractions, or the degree to which they can interact with each other, is controlled by the relative aromaticity of the two fractions.

## Guidelines

In this section, a number of recommendations are made for quickly estimating the SHRP performance grade of an asphalt binder. Essentially this is an assessment of a given asphalt's ability to resist permanent deformation, fatigue, and low temperature cracking based on a number of trends uncovered through SHRP research.

As discussed earlier, the MRL was the depository of over 40 different asphalts that are in production today. The asphalts reported in table 10 represent 12 different asphalt grades. These grades are compared with their PG grades determined from the SHRP binder specification. The conventional grades give rise to 5 different high temperature grades (46-, 52-, 58-, 64-, 70-) and 5 different low temperature grades (-34, -28, -22, -16, -10), generating a total of 12 different grades.

Table 10. Distribution of Conventionally Graded Asphalts in SHRP Material Reference Library

Binder Grade	Number	SHRP PG Grading	Temperature Spread (°C)
200/300	1	46-34	80
150/200	2	(1)*58-28	86
85/100	1	58-16	74
B 85	1	64-28	92
60/70	1	70-22	92
AR 2000	2	(2)52-28, 58-16	74-80
AR 4000	4	(3)58-10, 58-28, 64-16	68-86
AC-5	3	(1)52-22	74
AC-8	1	58-16	74
AC-10	8	(3)58-16, 58-22, 58-28	74-86
AC-20	16	(6)58-16, 58-22, 64-10, 64-16, 64-22, 64-28	74-92
AC-30	2	(1)64-22	86

\* Number of SHRP Grades

A better way to evaluate the SHRP PG grades is to consider the breadth or temperature range of utilization, that is, consider the spread in temperatures from the high temperature

(rut resistance) to the low temperature (crack resistance). It is widely recognized that lower boiling (less viscous) distillation products can be added to an asphalt to improve its low temperature properties, albeit its resistance to rutting deteriorates. Essentially the temperature spread or range of temperatures for useful performance remains constant and this range is merely shifted to lower temperatures.

Shown in figure 14 is the diverse temperature spread exhibited by the SHRP MRL asphalts. These ranged from 68 to 92°C and have a mean temperature range of 81°C. Specifying a wider spread of temperatures ( $> 92^{\circ}\text{C}$ ) may necessitate asphalt modification.

A bar plot of the temperature spread for the various AC-20 asphalt binders is shown in figure 15. Based on these asphalts, an AC-20 typically yields a performance temperature range of 80-86°C.

The HPLC approach of Jennings et al. (1993b) provides a quick way for predicting the temperature spread for an unknown asphalt. The 4 distinct types or classes of patterns provide some insight as to this range. The distribution of ranges for each type of asphalt is presented in table 11.

Table 11. Classification of SHRP Asphalts by HPLC Profile

HPLC Profile Type (number of asphalts)	Temperature Spread, °C				
	68	74	80	86	92
Group 1 (8)	2	4	2		
Group 2 (14)		1	6	6	1
Group 3 (1)				1	
Group 4 (4)			2	2	

Type 1 asphalts (figure 1a) generally exhibit poor fatigue performance characteristics as determined by their dissipated energy values and have narrow temperature spreads per the SHRP specification; the mean temperature spread is 74°C. Nearly all of the asphalts having narrow ( $< 80^{\circ}\text{C}$ ) spreads can be identified by their GPC profile.

The other three types of profiles correspond to asphalts having considerably higher temperature spreads. The mean spread for Type 2 and 3 asphalts is 83°C. Type 2 asphalts, shown in figure 1b, give rise to a wide range of spreads, and although there is only one type 3 asphalt, its behavior mirrors that of the type 2 asphalts. And as noted earlier, the Type 4 asphalts consist of higher molecular weight species and will tend to be more rut resistant.

While HPLC provides a useful indication of the range of useful temperatures for an asphalt, the approximate location of this range can be obtained from examination of the low temperature end via determination of the asphalt's  $T_g$  or  $T_d$ , or evaluation of the high temperature specification parameter ( $G^*/\sin \delta$ ). This simplistic approach can be useful for predicting potential blends rather than having to test each and every blend.

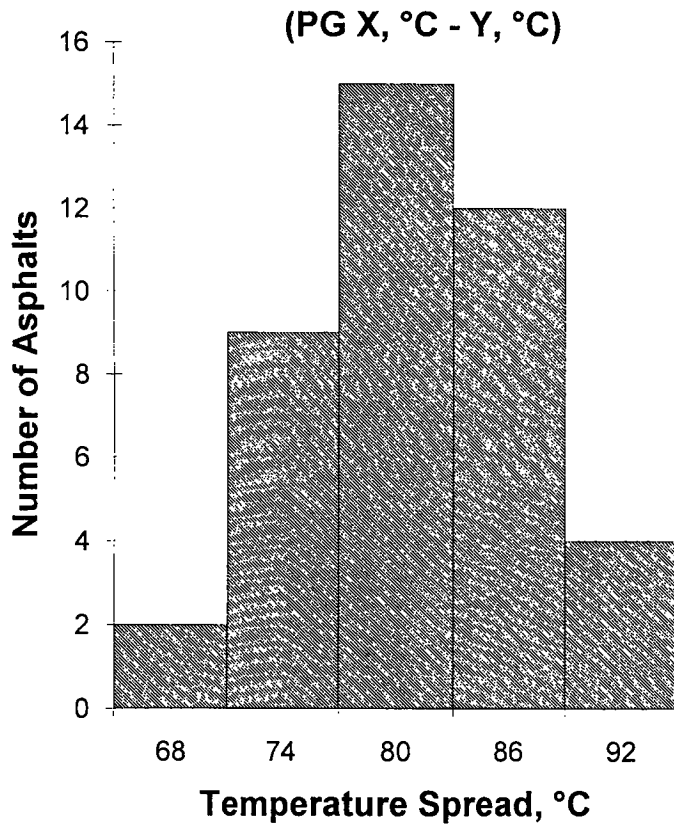


Figure 14. Temperature Spread for SHRP Asphalt Binders

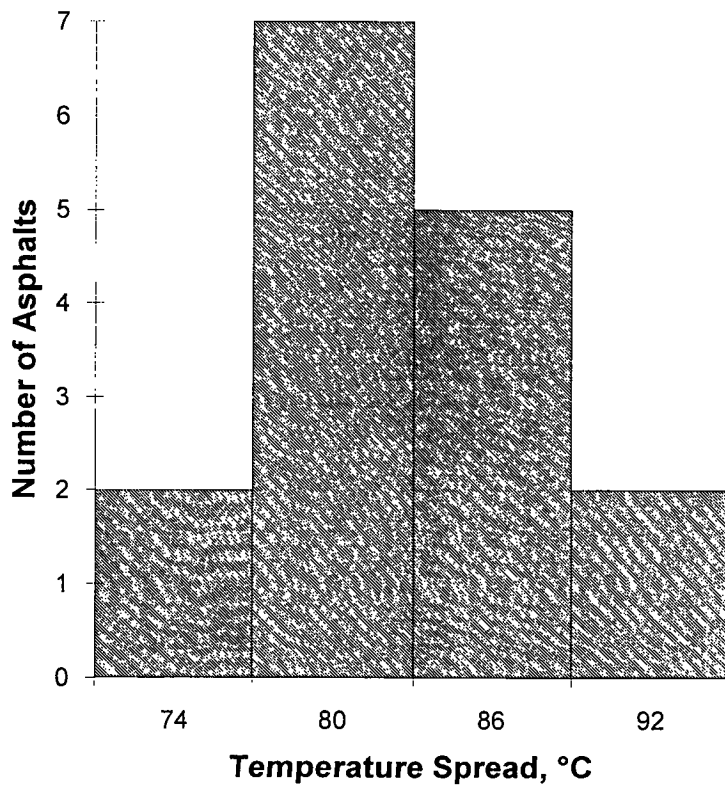


Figure 15. Temperature Spread for SHRP AC-20 Asphalt Binders

Support for this approach was demonstrated by the results from the SEC I blending study. Blending SEC I fractions with non-parent asphalts resulted in asphalts with properties between those of the parent materials.

Asphalt aging consists of two components--an oxidative aging component and a volatile loss component. The latter is associated with the loss of light ends of the asphalt through volatilization. This effectively changes the amount of "plasticizers" in the asphalt and results in an increase in the  $T_g$  as well as the overall viscosity of the asphalt. Since the neutral components are not as susceptible to oxidative attack as are the polar fractions (Petersen et al. 1974), oxidative aging will largely impact the high temperature properties of the asphalt.

The effects of aging on the physical and chemical properties of the 41 MRL asphalts were examined. Low aging indices (AI), determined from changes in the viscosity of the neat and aged binders, were found associated with asphalts having low asphaltene to resin ratios, relatively high nitrogen contents ( $>1\%$ ), and relatively low sulfur contents ( $<2\%$ ).

Low temperature cracking susceptibility is related to two parameters. One is the free volume of the asphalt under its expected pavement conditions; this, as noted earlier, is related to its  $T_g$ . The other is the thermal coefficient of expansion. The greater the propensity of a material to shrink at low temperatures, the greater the internal stresses induced. Thus these parameters are somewhat interrelated. The two binder specification parameters,  $m$  and  $S(t)$ , reflect this. The  $m$ -value is indicative of the ability of the asphalt to relieve these stresses. The low temperature stiffness of an asphalt is related to its  $T_g$ . AAG and AAM have relatively high  $T_g$ s and higher stiffness (than AAD and AAK) at any given temperature.

Fatigue susceptibility of asphalt has not been addressed in great detail. The relationship between structural parameters and fatigue is not readily identifiable due to the complexity of the mechanism. Dissipated energy ( $G^* \sin \delta$ ) was identified as a key parameter relating to this distress mechanism. Whether this relates to crack healing (excessively stiff material may not be able to experience healing) or a resistance to crack initiation and propagation is not completely known. The fact that AAG has both poor low temperature crack resistance and fatigue resistance suggests that a diversity of molecules is needed as well as a low  $T_g$ . Increasing the mobility of the molecules by addition of a plasticizer or low molecular weight component should assist the overall performance of an asphalt. Among the SHRP MRL asphalts were several series of asphalt consisting of two or more grades. These were produced from a common crude oil slate and with similar refining methods. The lower grades give rise to more favorable fatigue properties and exhibited lower  $T_g$ s.

The low temperature stiffness of asphalt,  $S(t)$  measured at  $-10^\circ\text{C}$ , was found to relate to its dissipated energy,  $G^* \sin \delta$  determined at  $25^\circ\text{C}$ . This relationship is shown in figure 16. Thus the DSR can be used to estimate the low-temperature properties determined by the BBR.

Finally, some mention should be made regarding asphalt compatibility. Asphalt compatibility is not in itself readily associated with any of the above distress mechanisms and has only been cursorily addressed, however it merits due consideration. Phase separation of an asphalt blend or modified asphalt at an inappropriate time may have a critical impact on performance. Knowledge as to whether a propensity for phase separation exists, or whether phase separation of the asphalt is induced by its moisture sensitivity, could lead to reductions in stripping, raveling or even rutting.

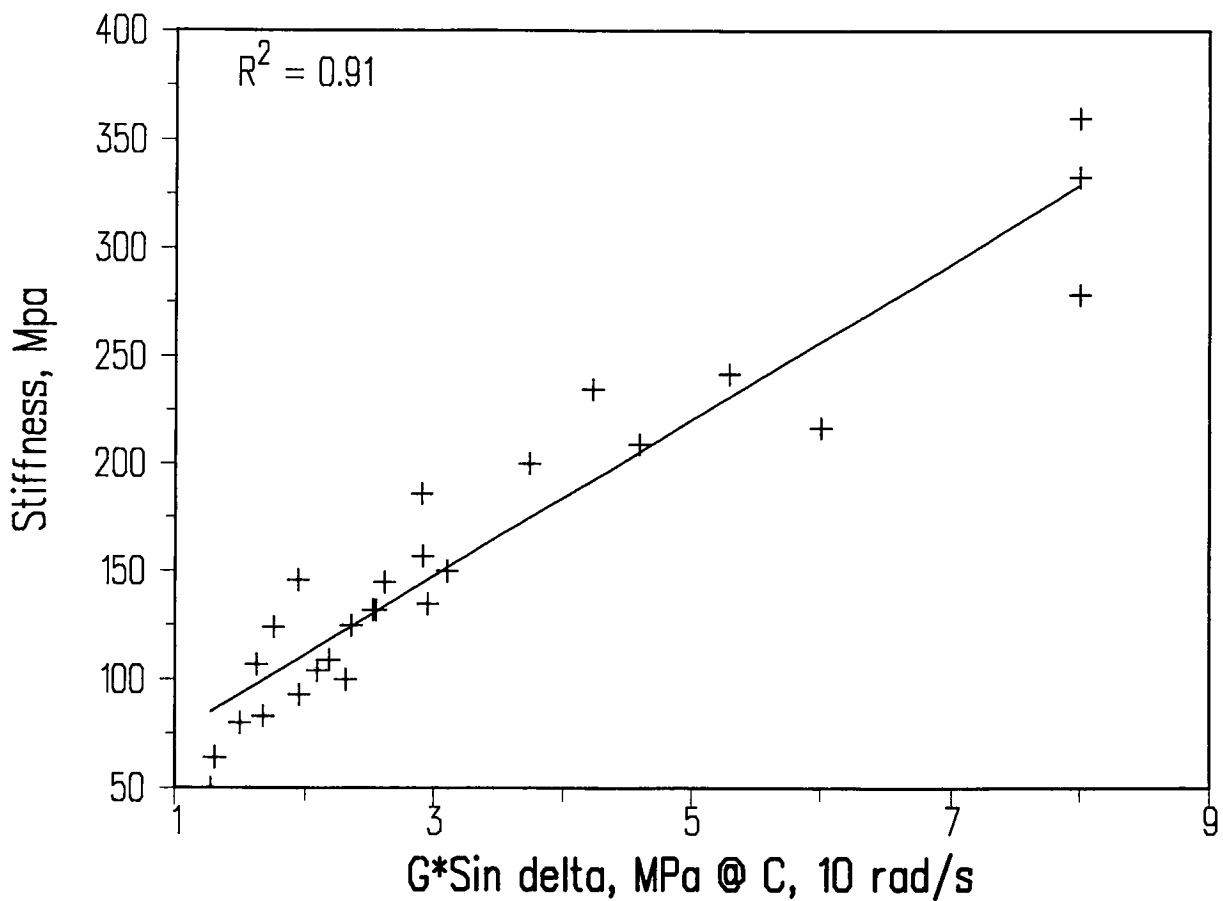


Figure 16. Plot of Fatigue Parameter Versus Low Temperature Parameter



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## Appendix

### Standard Specification for Performance-Graded Asphalt Binder

#### AASHTO Designation MP1

# **Standard Specification for Performance Graded Asphalt Binder**

AASHTO Designation: MP1<sup>1</sup>

**1. Scope** - This specification covers asphalt binders graded by performance. Grading designations are related to the average 7-day maximum pavement design and minimum pavement design temperatures.

Note 1 -- For asphalt cements graded by penetration at 25°C, see M20. For asphalt cements graded by viscosity at 60°C see M226.

Note 2 -- Guide PP5 provides information on the evaluation of modified asphalt binders.

Note 3 -- Guide PP6 provides information for determining the performance grade of an asphalt binder.

## **2. Reference Documents**

### **2.1 AASHTO Documents:**

- PP5 Guide for the Laboratory Evaluation of Modified Asphalt Systems
- PP6 Guide for Grading or Verifying the Performance Grade of an Asphalt Binder
- PPX Selection of Asphalt Binders (Being Developed)
- M20 Specification for Penetration Graded Asphalt Cement
- M226 Specification for Viscosity Graded Asphalt Cement
- PP1 Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel (PAV)
- T40 Practice for Sampling Bituminous Materials
- T44 Solubility of Bituminous Materials in Organic Solvents
- T48 Method for Flash and Fire Points by Cleveland Open Cup
- T55 Method for Water in Petroleum Products and Bituminous Materials
- T179 Test Method for Effect of Heat and Air on Asphalt Materials (Thin-Film Oven Test)
- T201 Kinematic Viscosity of Asphalts
- T202 Viscosity of Asphalts by Vacuum Capillary Viscometer
- T240 Test Method for Effect of Heat and Air on a Moving Film of Asphalt (Rolling Thin Film Oven Test)
- TP1 Test Method for Determining the Flexural Creep Stiffness of Asphalt Binder Using the Bending Beam Rheometer (BBR)
- TP3 Test Method for Determining the Fracture Properties of Asphalt Binder in Direct Tension (DT)
- TP5 Test Method for Determining Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer (DSR)

### **2.2 ASTM Documents:**

- D8 Standard Definitions of Terms Relating to Materials for Roads and Pavements
- D4402 Method for Viscosity Determinations of Unfilled Asphalt Using the Brookfield Thermosel Apparatus

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<sup>1</sup> This standard is based on SHRP Product 1001.

## **2.3 SHRP Documents:**

P00X Superpave Software (being developed)

## **3. Terminology**

### **3.1 Definitions**

**3.1.1** Definitions for many terms common to asphalt cement are found in ASTM D8.

**3.1.2** asphalt binder, n — an asphalt-based cement that is produced from petroleum residue either with or without the addition of non-particulate organic modifiers.

**4. Ordering Information** - When ordering under this specification, include in the purchase order the performance grade of asphalt binder required from Table 1 (e.g. PG 52-16 or PG 64-34).

**4.1** Asphalt binder grades may be selected by following the procedures described in provisional practice PPX, Selection of Asphalt Binders.

## **5. Materials and Manufacture**

**5.1** Asphalt cement shall be prepared by the refining of crude petroleum by suitable methods, with or without the addition of modifiers.

**5.2** Modifiers may be any organic material of suitable manufacture, used in virgin or recycled condition, and that is dissolved, dispersed or reacted in asphalt cement to enhance its performance.

**5.3** The base asphalt binder shall be homogeneous, free from water and deleterious materials, and shall not foam when heated to 175°C.

**5.4** The base asphalt binder shall be at least 99.0% soluble in trichloroethylene as determined by T44.

**5.5** This specification is not applicable for asphalt binders in which fibers or other discrete particles are larger than 250  $\mu\text{m}$  in size.

**5.6** The grades of asphalt binder shall conform to the requirements given in Table 1.

**6. Sampling** - The material shall be sampled in accordance with Method T 40.

**7. Test Methods** - The properties outlined in 5.3, 5.4 and 5.6 shall be determined in accordance with T44, T48, T55, T179, T240, PP1, TP1, TP3, TP5 and ASTM D4402.

**8. Inspection and Certification** - Inspection and certification of the material shall be agreed upon between the purchaser and the seller. Specific requirements shall be made part of the purchase contract.

**9. Rejection and Rehearing** - If the results of any test do not conform to the requirements of this specification, retesting to determine conformity is performed as indicated in the purchase order or as otherwise agreed upon between the purchaser and the seller.

**10. Key Words** - Asphalt binder, asphalt cement, modifier, performance specifications, rheology, direct tension, pressure aging, flash point.



Table 1. Performance Graded Asphalt Binder Specification

PERFORMANCE GRADE	PG 46-			PG 52-							PG 58-					PG 64-					
	34	40	46	10	16	22	28	34	40	46	16	22	28	34	40	10	16	22	28	34	40
Average 7-day Maximum Pavement Design Temperature, °C <sup>a</sup>	<46			<52							<58					<64					
Minimum Pavement Design Temperature, °C <sup>a</sup>	>-34	>-40	>-46	>-10	>-16	>-22	>-28	>-34	>-40	>-46	>-16	>-22	>-28	>-34	>-40	>-10	>-16	>-22	>-28	>-34	>-40
ORIGINAL BINDER																					
Flash Point Temp, T48: Minimum °C	230																				
Viscosity, ASTM D4402: <sup>b</sup> Maximum, 3 Pa*s, Test Temp, °C	135																				
Dynamic Shear, TP5: <sup>c</sup> G'/sinδ, Minimum, 1.00 kPa Test Temp @ 10 rad/s, °C	46			52							58					64					
ROLLING THIN FILM OVEN (T240) OR THIN FILM OVEN RESIDUE (T179)																					
Mass Loss, Maximum, percent	1.00																				
Dynamic Shear, TP5: G'/sinδ, Minimum, 2.20 kPa Test Temp @ 10 rad/s, °C	46			52							58					64					
PRESSURE AGING VESSEL RESIDUE (PP1)																					
PAV Aging Temperature, °C <sup>d</sup>	90			90							100					100					
Dynamic Shear, TP5: G'·sinδ, Maximum, 5000 kPa Test Temp @ 10 rad/s, °C	10	7	4	25	22	19	16	13	10	7	25	22	19	16	13	31	28	25	22	19	16
Physical Hardening <sup>e</sup>	Report																				
Creep Stiffness, TP1: <sup>f</sup> S, Maximum, 300 MPa, m - value, Minimum, 0.300 Test Temp @ 60s, °C	-24	-30	-36	0	-6	-12	-18	-24	-30	-36	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	-30
Direct Tension, TP3: <sup>g</sup> Failure Strain, Minimum, 1.0% Test Temp @ 1.0 mm/min, °C	-24	-30	-36	0	-6	-12	-18	-24	-30	-36	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	-30

<sup>a</sup> Pavement temperatures are estimated from air temperatures using an algorithm contained in the SUPERPAVE software program, may be provided by the specifying agency, or by following the procedures as outlined in PPX.

<sup>b</sup> This requirement may be waived at the discretion of the specifying agency if the supplier warrants that the asphalt binder can be adequately pumped and mixed at temperatures that meet all applicable safety standards.

<sup>c</sup> For quality control of unmodified asphalt cement production, measurement of the viscosity of the original asphalt cement may be substituted for dynamic shear measurements of G'/sinδ at test temperatures where the asphalt is a Newtonian fluid. Any suitable standard means of viscosity measurement may be used, including capillary or rotational viscometry (AASHTO T201 or T202).

<sup>d</sup> The PAV aging temperature is based on simulated climatic conditions and is one of three temperatures 90°C, 100°C or 110°C. The PAV aging temperature is 100°C for PG 58- and above, except in desert climates, where it is 110°C.

<sup>e</sup> Physical Hardening — TP1 is performed on a set of asphalt beams according to Section 13.1, except the conditioning time is extended to 24 hrs ± 10 minutes at 10°C above the minimum performance temperature. The 24-hour stiffness and m-value are reported for information purposes only.

<sup>f</sup> If the creep stiffness is below 300 MPa, the direct tension test is not required. If the creep stiffness is between 300 and 600 MPa the direct tension failure strain requirement can be used in lieu of the creep stiffness requirement. The m-value requirement must be satisfied in both cases.

**Table 1. Performance Graded Asphalt Binder Specification  
(Continued)**

PERFORMANCE GRADE	PG 70-						PG 76-					PG 82-				
	10	16	22	28	34	40	10	16	22	28	34	10	16	22	28	34
Average 7-day Maximum Pavement Design Temp, °C <sup>b</sup>	<70						<76					<82				
Minimum Pavement Design Temperature, °C <sup>b</sup>	>-10	>-16	>-22	>-28	>-34	>-40	>-10	>-16	>-22	>-28	>-34	>-10	>-16	>-22	>-28	>-34
ORIGINAL BINDER																
Flash Point Temp, T48: Minimum °C	230															
Viscosity, ASTM D4402: <sup>2</sup> Maximum, 3 Pa·s, Test Temp, °C	135															
Dynamic Shear, TP5: <sup>c</sup> G'/sinδ, Minimum, 1.00 kPa Test Temp @ 10 rad/s, °C	70						76					82				
ROLLING THIN FILM OVEN (T240) OR THIN FILM OVEN (T179) RESIDUE																
Mass Loss, Maximum, percent	1.00															
Dynamic Shear, TP5: G'/sinδ, Minimum, 2.20 kPa Test Temp @ 10 rad/s, °C	70						76					82				
PRESSURE AGING VESSEL RESIDUE (PP1)																
PAV Aging Temperature, °C <sup>d</sup>	100(110)						100(110)					100(110)				
Dynamic Shear, TP5: G'/sinδ, Maximum, 5000 kPa Test Temp @ 10 rad/s, °C	34	31	28	25	22	19	37	34	31	28	25	40	37	34	31	28
Physical Hardening <sup>e</sup>	Report															
Creep Stiffness, TP1: <sup>f</sup> S, Maximum, 300.0 MPa, m - value, Minimum, 0.300 Test Temp @ 60s, °C	0	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	0	-6	-12	-18	-24
Direct Tension, TP3: <sup>g</sup> Failure Strain, Minimum, 1.0% Test Temp @ 1.0 mm/min, °C	0	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	0	-6	-12	-18	-24

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