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Binder Characterization and Evaluation
Volume 4: Test Methods

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At the outset of the A-002A contract, Dr. J. Claine Petersen was the Principal Investigator. Upon Dr. Petersen's retirement in 1990, Dr. Raymond E. Robertson assumed the role of Principal Investigator. Dr. David A. Anderson of The Pennsylvania State University served a Co-Principal Investigator for the contract and was responsible for managing the technical direction of the work reported in this volume.

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A number of lead researchers at Penn State played very important roles and were responsible for conducting the research, interpreting data, and writing this report. Areas of responsibility were as follows: Dr. Donald W. Christensen, development of rheological models, dynamic mechanical analysis, microstructural modeling, and physical-chemical relationships; Dr. Hussain Bahia, physical hardening and oxidative aging; Dr. M. G. Sharma, fatigue and fracture, direct tension, indentation and permanent deformation; Raj Dongre, direct tension test development and fracture; and Dr. Charles Antle, statistical experiment design and analysis.

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Abstract

Binder Characterization and Evaluation Volume 4: Test Methods describes the development of test methods for the characterization of asphalt cement. These test methods may be used in specifications and for developing correlations between physical and chemical properties. To understand how the properties of asphalt cement and asphalt concrete mixtures relate to one another, fundamental material properties expressed in engineering units were required. This information was used to develop models that relate the properties of asphalt cement to mixture properties and, in turn, to pavement performance. A method for the extraction and recovery of asphalt binder from asphalt mixes is also included.

Executive Summary

Binder Characterization and Evaluation Volume 4: Test Methods contains detailed descriptions of test methods and research tools utilized to obtain the results reported in volumes 1, 2, and 3. The physical test methods developed at The Pennsylvania State University under SHRP contract A-002 are products that fulfill SHRP objectives. Early in the research, it became apparent that new test methods would be needed to characterize asphalt cement, both for use in the specifications and for developing correlations between physical and chemical properties. In order to facilitate the development of relationships between the properties of the asphalt cement and asphalt concrete mixtures, fundamental material properties expressed in engineering units are required. Sound, fundamentally based relationships between the properties of asphalt cement and the mixtures are needed in order to develop models that relate the properties of asphalt cement to mixture properties and, in turn, to pavement performance.

Initially, a large number of physical property tests were considered; however, many of these tests were considered either too time-consuming or too sophisticated for specification purposes, or they required extensive analysis to interpret the data and develop engineering properties. Both rheological (stress, strain, time, and temperature) and test procedures as well as failure (strength, fatigue, and fracture mechanics) models and test procedures were considered; however, many were rejected for the reasons cited above. Of the test procedures that were reviewed during the original evaluation in the first 1 to 2 years of the project, the following physical test methods were selected:

- Dynamic shear rheometry (DSR) at 10 radians/second in the temperature region where the complex modulus is in the range of 1 kPa to 5 mPa. Measurements are obtained at strain levels within the linear response region and at frequencies (10 radians/second or 10 Hz) that represent traffic loading.

- Bending Beam Rheometer (BBR) measurements in the temperature region where the stiffness is greater than 10 mPa after 60 seconds loading time.

- Direct Tension (DT) measurements at a single rate of elongation (1 mm/min) in the temperature region where the strain to failure is 0.5 to 5.0 percent. In this region the asphalt cement binder acts in a brittle-ductile manner.

- Rotational Viscometer (RV) measurements at mixing and compaction temperatures.

- A pressure aging vessel (PAV) that simulates the long-term in-service aging that can occur in the field. This method does not account for aggregate or mixture effects but is used to compare or rank the long-term aging resistance of asphalt cement binders.

Each of the test methods are described in detail in this volume in chapters 1-5, and four of the test methods provisionally approved by the American Association of State Highway and Transportation Officials (AASHTO) are appended. Details regarding their development, data obtained, and the interpretation of the data can be found in volume 3 of this final report. These test methods and others developed by the SHRP asphalt research program are available in *The Superpave Mix Design System Manual of Specifications, Test Methods, and Practices* (SHRP-A-379).

The research methods described in chapters 6 through 12 were used at Western Research Institute and SRI International. These procedures were employed to study binder chemistry and for the most part represent extensions of methods used in other areas of fossil fuel science. In subsequent discussions, it has been the objective of the authors to provide as many details as possible. Equipment requirements are listed, and levels of skill of personnel required are indicated. Some hazards involved in performing the procedures have been emphasized.

Certain routine analytical methods have not been described in detail because it is unlikely that most highway testing facilities would find it cost-effective to perform them. For these procedures, the proper ASTM manuals are readily available.

The extraction of binders from pavement cores has long been a matter of concern to asphalt scientists. Methods currently in use employ chlorinated hydrocarbons and primarily are intended to be assay methods. An extensive study of binder extraction and recovery was conducted at Texas Transportation Institute concurrent with this research. The test method produced by this research is reprinted in appendix E. The method was developed to recover asphalts as completely and with as little change as possible. It is not an assay method and should not be used to recover aggregates.

1 Dynamic Shear Rheometry

Introduction

Purpose

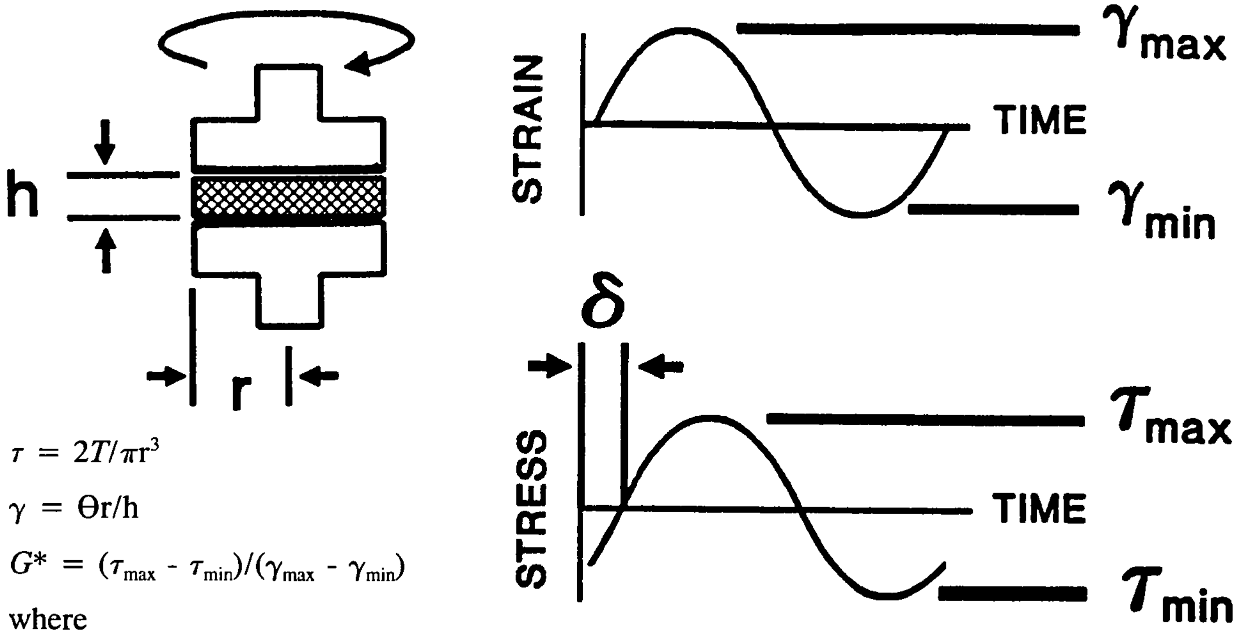
The dynamic shear rheometer is used to measure the linear viscoelastic moduli of asphalt cement binders in the sinusoidal (oscillatory) loading mode. Measurements may be obtained at different temperatures, strain and stress levels, and test frequencies.

Scope

The dynamic shear rheometer is used for specification purposes to measure the complex modulus and phase angle of asphalt binders at intermediate to upper pavement service temperatures and a frequency of 10 rad/s where the complex modulus is approximately 10 MPa (1,450 lb/in.^{2}) or larger. A typical measurement range for such devices is from 1.0 Pa to 100 MPa (0.000145 to 14,500 lb/in.^{2}). In addition to measuring the modulus and phase angle at a single frequency, the dynamic shear rheometer may also be used over a range of frequencies to determine the time (frequency) dependency of the modulus of asphalt binders. Thus, the device may be used to invoke time-temperature superposition and to construct thermorheologically simple linear viscoelastic master curves, as was done as part of this project (see chapter 2 in volume 3 of this report for details on developing master curves and models that describe the master curves). In this project the dynamic shear rheometer was used primarily to determine complex modulus and phase angle by means of parallel plate test geometry. Initally, limited testing was done with torsion bar geometry at low temperatures, although this technique was discontinued once the bending beam rheometer became operational.

Hardware

There are two general types of dynamic shear rheometers: controlled-strain and controlled-stress. Data obtained from the two types of rheometers are interchangeable. Controlled-strain rheometers, such as the Rheometrics models 803 (used on this project) or RAA, operate by applying a sinusoidally varying strain to the test specimen and measuring the magnitude and phase of the resulting stress. A controlled-stress instrument, such as the Bohlin CS, applies a sinusoidally varying stress and measures the magnitude and phase of the resulting strain. The parallel plate geometry and the associated data and equations are shown in figure 1.1.



$\tau = 2T/\pi r^3$

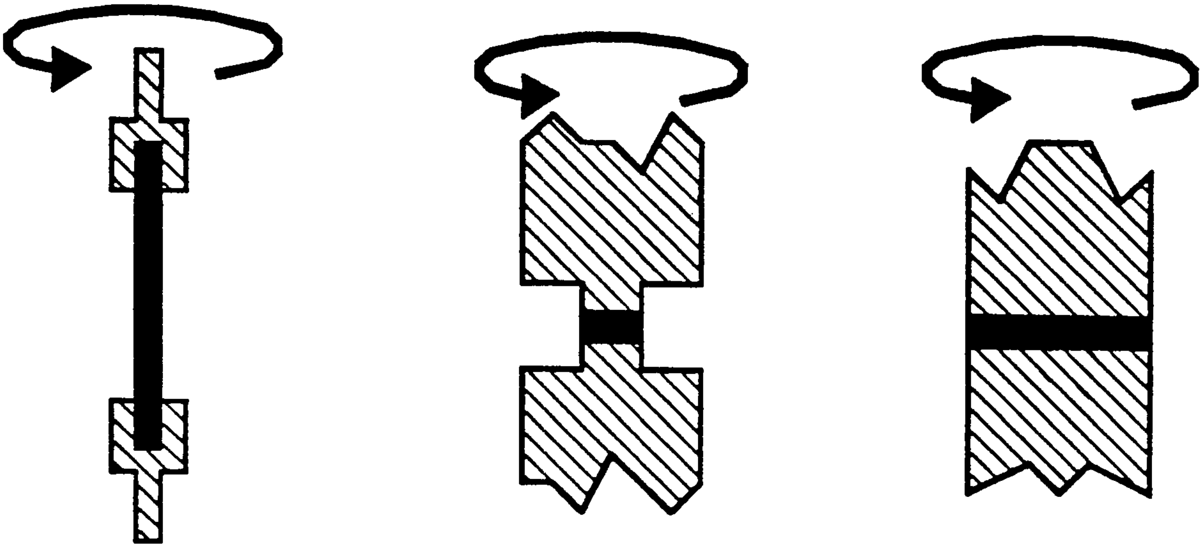
$\gamma = \Theta r/h$

$G^* = (\tau_{max} - \tau_{min})/(\gamma_{max} - \gamma_{min})$

where

γ = shear strain (%)
δ = phase angle (°)
Θ = deflection angle
τ = shear stress (Pa)
ω = angular frequency
G^* = complex modulus (Pa)
T = torque

Figure 1.1. The Dynamic Shear Rheometer and Related Test Data



Rectangular torsion

8-mm parallel plates

25-mm parallel plates

Figure 1.2. Geometries Used in Testing with the Dynamic Shear Rheometer

Various test geometries may be used, including parallel plates, cone and plate, and rectangular torsion. Parallel plate geometry is used for the specification testing because the specification measurements are in the region of linear behavior. Cone and plate geometry is required only when the test measurements are in the nonlinear region.

For specification testing, parallel plates 8 mm (0.32 in.) in diameter should be used at intermediate pavement design temperatures, 4 to 40°C (39 to 104°F), where the specification limit is 1.00 or 2.20 kPa (0.145 or 0.319 lb/in.^{2}) for tank and rolling thin film oven test (RTFOT) residue, respectively. At the maximum pavement design temperatures (46 to 82°C, 115 to 180°F), parallel plates 25 mm (1.0 in.) in diameter should be used where the specification limit is 5.00 MPa (7.25 lb/in.^{2}). The specific plate diameter and sample thickness (plate gap) used in testing a given asphalt depends not so much on temperature as on the modulus of the binder.

When the complex shear modulus of the binder is greater than approximately 30 MPa (4,350 lb/in.^{2}), parallel plate geometry should not be used because the compliance of the rheometer can be sufficient to cause errors in the measurements. Although the range of moduli that can be successfully measured with different size plates will vary according to the design (resolution and compliance) of each rheometer, the following guidelines may be used:

- Use the bending beam rheometer or torsion bar geometry when the complex modulus (G^*) $>$ 30 MPa.
- Use 8-mm parallel plates with a 2-mm gap when 0.1 MPa $< G^* <$ 30 MPa.
- Use 25-mm parallel plates with a 1-mm gap when 1.0 kPa $< G^* <$ 100 kPa.
- Use 50-mm parallel plates when $G^* <$ 1 kPa.

Schematics of several of the geometries used in the dynamic shear testing of asphalt binders as part of this project are shown in figure 1.2. Details regarding the torsion bar geometry can be found in volume 3, chapter 2, of this report.

Both controlled-strain and controlled-stress rheometers consist of three major parts: (1) the rheometer, (2) the controller, and (3) the computer. The rheometer normally includes a housing or frame, a motor for applying the strain or stress to the specimen, a transducer for measuring the response of the specimen, and a temperature control and measurement system. The controller is simply an interface between the rheometer and the computer and contains the data acquisition and signal conditioning hardware for the motors and transducers used in the rheometer. The rheometer is operated and programmed by a personal computer. Instrument-specific hardware and software are included with the computer for performing various types of tests and analyzing the resulting data.

Data Acquisition

Appropriate data acquisition systems and instructions for their use are included with commercially available rheometers. Normally, users of these devices need not be concerned with the details of data acquisition or reduction. To generate a single complex shear modulus

(G^*) and phase angle measurement (δ), multiple cycles of sinusoidally varying torque (controlled stress rheometer) or angular deflection (controlled strain rheometer) are applied to the specimen. The number of cycles and number of torque and angular deflection data points obtained depend on the hardware (data storage capacity) and software used by the manufacturer of the rheometer. A sufficient number of data points must be obtained to conduct a fast Fourier transform (FFT) so that the phase angle can be determined. Typically, data are obtained over six to ten cycles, and 200 or more torque and angular deflection data points may be captured.

The software for operating the rheometer will normally include provisions for selecting certain options such as the test frequency, rest period between measurements, and stress or strain amplitude. Anecdotal information such as the file name, the specimen identification, operator's name, date, and so forth may also be entered into the test file. For specification testing, the testing procedure has been standardized as follows: Prior to recording any data an initial measurement is obtained to "seat" the specimen and to be certain that the sample is properly mounted. After a few seconds' rest period, a second measurement is obtained and recorded as the measurement of record.

Testing Protocol

Sample Preparation

Prior to mounting the asphalt binder between the plates, the zero gap setting must be established. This should be done at the test temperature because the frame and fixtures in the dynamic shear rheometer change dimension with temperature. For most rheometers the change in gap with temperature may be neglected as long as the gap is set within ± 12°C (± 22°F) of the test temperature. Therefore, when tests are conducted over a range of temperatures, the gap should be set at the middle of the expected range of test temperatures. If, for a particular rheometer, the change in gap with temperature is sufficient to affect the accuracy of the measurements, a gap correction factor may be established. For most instruments, however, the gap may be considered constant within a ± 12°C (± 22°F) range. Making adjustments in the gap by moving the spindle between measurements when measurements are conducted at multiple temperatures is not recommended, especially at low temperatures where large normal stresses may occur when the gap is adjusted at the test temperature.

Some rheometers contain an autotension feature that automatically changes the gap to minimize normal forces when the test temperature is changed. The autotension feature was used with the Model 803 rheometer during the testing conducted as part of this project.

The specimen preparation procedure requires that the asphalt binder be heated until it is sufficiently fluid to pour. The required pouring temperature will vary according to the grade of the asphalt binder and its aging history, but heating in an oven set at 130 to 140°C (266 to 284°F) is usually sufficient. Heating is essential to remove any existing structuring caused by steric hardening (molecular associations) that can significantly increase the measured modulus. The annealing step was adopted as part of the test procedure to minimize the effect of steric hardening on test repeatability by producing a well-defined and reproducible reference condition. Results obtained during the project showed that steric hardening can, for some asphalts, increase the measured modulus by as much as 40 percent.

Test specimens may be formed by several procedures:

- Pouring hot asphalt binder on the lower plate. Hot asphalt binder may be poured directly onto the lower plate of the rheometer, after which the two plates are closed to the final gap plus 50 μm. Before or during the process of squeezing the asphalt binder between the plates, the lower plate (liquid bath) or the chamber (air oven) should be warmed to approximately 45°C (± 113°F) to ensure good adhesion between the asphalt binder and the plates.

- Preforming a sample in a silicone mold. Hot asphalt binder may be poured into a silicone rubber mold and allowed to cool to room temperature. The mold is chilled, then the asphalt binder disk is removed from the silicone mold and placed on the lower plate. Before or during the process of squeezing the asphalt binder between the plates, the lower plate (liquid bath) or the chamber (air oven) should be warmed to approximately 45°C (± 113°F) to ensure good adhesion between the asphalt binder and the plates.

- Pouring hot asphalt binder on removable upper plate. Hot asphalt binder may be poured directly onto the upper plate with the upper plate removed from the rheometer and at room temperature. This procedure will form a smooth, round specimen of asphalt binder approximately 3 mm thick, as shown in figure 1.3. The plate is immediately mounted in the rheometer with the lower plate warmed to approximately 45°C (± 113°F) in order to ensure good adhesion between the asphalt binder and the plates.

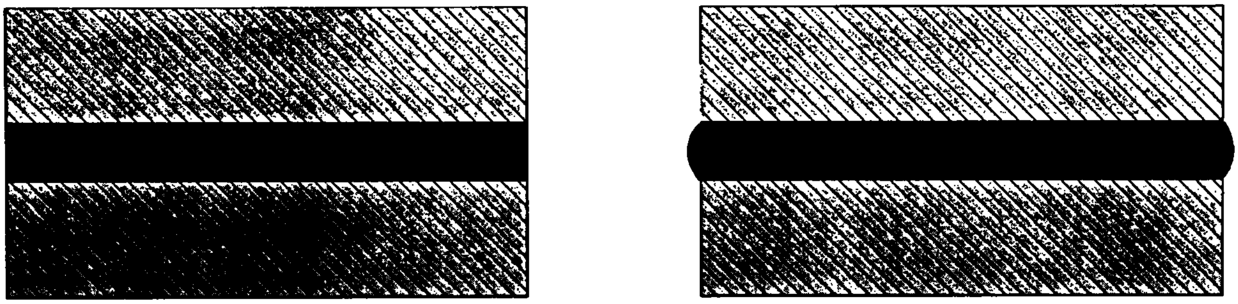
Once the plate or plates (lower plate for fluid bath and both plates for air oven) are sufficiently warmed that a good bond is achieved between the plates and the asphalt binder, the gap between the plates is gradually reduced to the target gap plus 50 μm. The asphalt specimen squeezed between the plates is then trimmed flush with the edge of the plate (figure 1.4). After trimming, the final adjustment is made to the designated gap (2.0 mm for the 8-mm plate, and 1.0 mm for the 25-mm plate). This procedure results in a slight bulge in the asphalt specimen, which is the desired configuration (figure 1.5). It is important that the periphery of the sample retain a convex (bulging outward) shape as the temperature is changed. The sample should not shrink to the point where the edge becomes concave.

Device Calibration

There are three transducers in a typical dynamic shear rheometer that must be calibrated on a regular basis: (1) the torque measurement transducer, (2) the deflection measurement transducer, and (3) the platinum resistance thermometer (PRT). The details of the transducers

Figure 1.3. Asphalt Specimen Poured on Testing Plate at Room Temperature

Figure 1.4. Specimen Squeezed between Testing Plates



Asphalt binder trimmed
flush with sides of plate

Slight bulge in asphalt binder
after closing gap by 50 μm

Figure 1.5. Sample Shape After Trimming and After Final Setting of Gap

and the required calibration vary among manufacturers. For specification as well as research use, dynamic shear rheometers must be supplied with a complete, accurate, and simple means of performing and verifying all required calibrations. This is essential if good within- and between-laboratory repeatability is to be obtained with dynamic shear rheometry. During the project no reference fluid was identified as being satisfactory for inter- or intra-laboratory use as a calibration fluid. Such a fluid would be very desirable and should become a part of the standard test procedure.

If the test temperature within the asphalt binder is to be maintained at the target test of ± 0.1°C (± 0.2°F), the calibration of the PRT mounted in the rheometer is of particular concern. The rheometer PRT is used to control the temperature of the test chamber; it also provides the test temperature readout. Because of difficulties in calibrating the PRT in situ as well as thermal gradients within the rheometer spindle and test plates, a secondary calibration of the PRT is required. This can be accomplished by inserting a thermocouple probe into a dummy test sample or by using a silicone wafer containing a thermistor. By comparing the temperature of the probe and the rheometer PRT, one can determine any offset that must be applied to the rheometer PRT to obtain the desired test temperature within the test sample. Details regarding calibration procedures are given in the proposed standard test method included at the end of this chapter. It is essential that the thermocouple probe be calibrated as indicated in the proposed standard. The probe must be calibrated with the same electronic readout and leads that are used during calibration.

Test Procedure

Two types of tests were performed during the project for the dynamic shear testing: strain sweeps and frequency sweeps. Strain sweeps were used to determine the region of linear behavior. In this procedure, the strain level to which a specimen was subjected was gradually increased until significant nonlinearity appeared in the response. Characterizations based on linear viscoelastic behavior, such as those used in this research, must be limited to strains within the linear region. Frequency sweeps were done at a fixed strain level at temperatures of -35, -25, -15, -5, 5, 15, 25, 35, 45, and 60° C (-31, -14, -5, 23, 41, 59, 77, 95, 113, and 140°F). In the initial testing of the core asphalts, three log decades of frequency were covered, from 0.1 to 100 rad/s. Each decade included ten points equally spaced on a logarithmic scale. In the later testing of the set of SHRP modified asphalts, testing at intermediate to high temperatures was done covering two log decades of frequency, from 1.0 to 100 rad/s. This procedure decreased the time required for testing and still provided sufficient overlap between temperatures to allow accurate shifting of the data.

In specification testing, data are acquired at only one frequency, 10 rad/s. Testing is done at temperatures ranging from 46 to 82°C (115 to 180°F) for the unaged and oven-aged asphalt and at temperatures ranging from approximately 4 to 40°C (39 to 104°F) for the pressure aging vessel (PAV) residue. The actual test temperatures and stress/strain levels used will depend on the *stiffness* of the binder, which depends on the grade and aging history of the asphalt binder being tested.

The dynamic shear modulus is relatively strain-independent at sufficiently small strains. The strain level at which nonlinearity is obtained varies significantly with the stiffness of the asphalt binder. During the testing for this project, the limit of linear viscoelastic behavior was defined as the point beyond which the measured value of *G** decreased to 95 percent of its zero-strain value. This point was determined by conducting a strain sweep, as shown in figure 1.6. Once the value of *G** was reduced by 5 percent (the strain sweep was stopped at that point), the strain was reduced to well within the linear region and a frequency sweep was obtained.

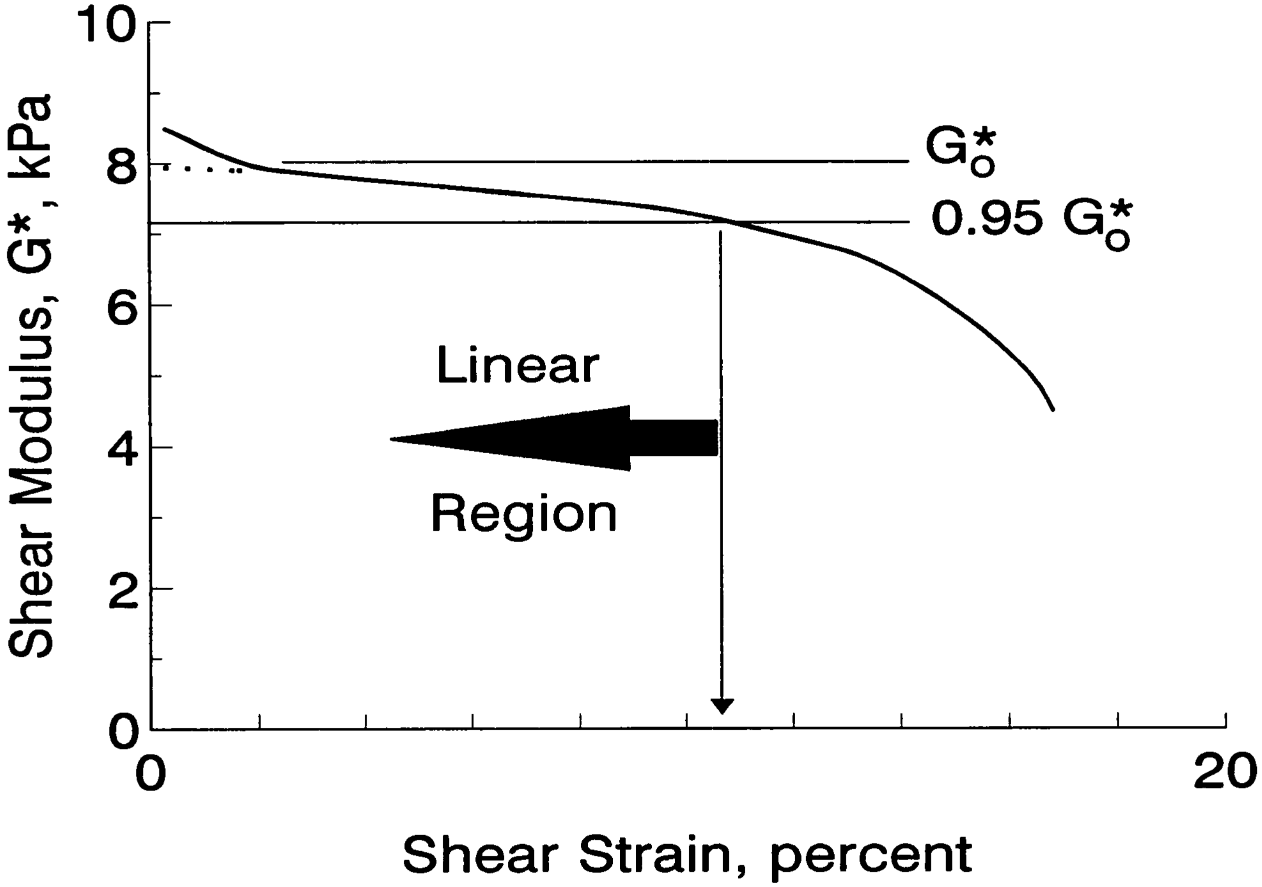


Figure 1.6. Strain Sweep Used to Determine Linear Region

The specification testing has to be conducted in such a way that the response measured is within the linear viscoelastic (LVE) range to ensure test repeatability. Therefore, the stress level (in case of a controlled-stress rheometer) or strain level (in case of a controlled-strain rheometer) at which testing is conducted must be selected so that the resulting response (G^*) is within the LVE limit. Conducting a strain sweep for each asphalt binder at each temperature is not practical for specification testing and there would undoubtedly be considerable operator variability in judging the point at which G^* decreases to 95 percent of the zero-strain value. Therefore, for specification purposes a "standard" set of strain values was established. The results of testing more than 40 asphalts at different temperatures and aging conditions are shown in figure 1.7. The plotted points represent the strain level at which the modulus is reduced to 95 percent of its zero-strain value. Using the data in figure 1.7 as a guide, the specification requires the strain to be controlled to ± 20 percent of the following:

$$\gamma = 12.0/(G^*)^{0.29} \tag{1.1}$$

where

γ = shear strain (%)
G^* = complex modulus (kPa)

When testing in the controlled-stress rheometer, the stress should be controlled to ± 20 percent of:

$$\tau = 0.12(G^*)^{0.71} \tag{1.2}$$

where

τ = shear stress (kPa).

Points of Caution

There are a number of operational factors that need to be strictly controlled because they may significantly affect the measured values. These factors are:

1. The gap between the testing plates. The zero gap setting should be established at a temperature as close as possible to the testing temperature. The fixtures and plates change their dimensions with temperature; therefore, different zero-gap settings will result at different temperatures. Rheometers from different manufacturers may require special consideration if the change in gap with temperature is excessive. The gap dimension enters into the calculation of G^* as a first-order term and the error resulting from an incorrect gap can be readily determined. For example, when the target gap is 2.00 mm, a 20 μm gap error will result in a 1 percent error in the measured shear modulus.

2. Trimming of the specimen. Excessive material or untrimmed material can cause the measurements to be considerably in error. Both under- and overtrimming are to be avoided. After the specimen has been trimmed and the gap has been closed to the target value, there should be a slight bulging at the periphery of the sample. A concave surface at the periphery of the sample is to be avoided, as it has a significant effect on the measured value of the shear modulus. To reiterate, if trimming is not done properly, the measurements may be considerably in error.

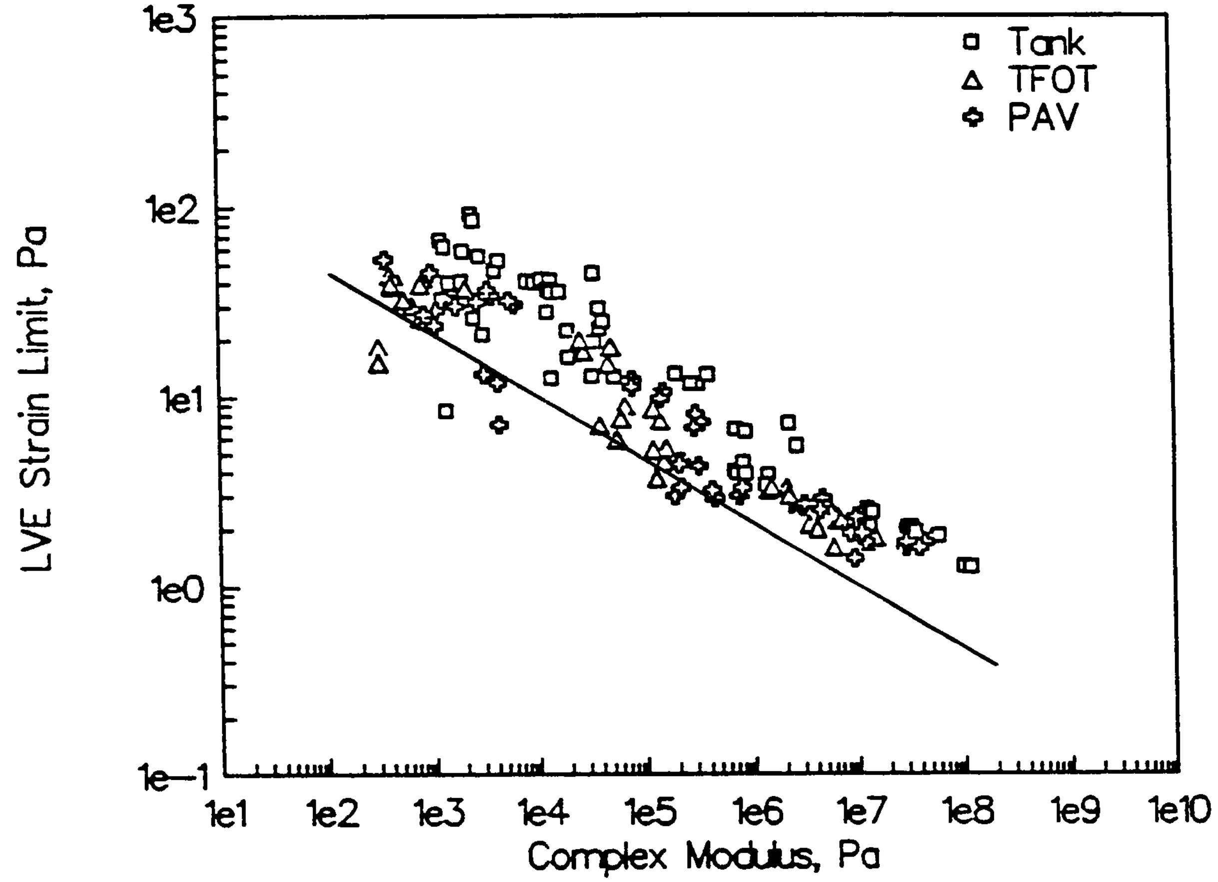


Figure 1.7. Linear Viscoelastic Strain Limit as a Function of Complex Modulus for Unaged and Aged Asphalts

3. Temperature of the specimen. Asphalt properties are very sensitive to temperature. Therefore, the temperature of the asphalt binder between the plates should be kept uniform and within ± 0.1°C (± 0.2°F) throughout the conditioning period and throughout the test. The plates and connecting shafts are potential heat sinks that create thermal gradients within the test chamber and across the test specimen. It is recommended that specimens as well as the upper and lower plates and spindles be submerged in a fluid bath or air oven that circulates fluid or air at a rate sufficient to keep the temperature of the specimen uniform and constant. Rheometers without fluid baths or ovens are unacceptable because thermal gradients will occur across the thickness and radius of the specimen. The temperature of the sample should be verified in trial runs using a calibrated temperature transducer as described above and in the proposed specification. The calibration should be done with a probe that is traceable to the National Institute of Standards and Technology.

4. Thermal treatment. Annealing (conditioning) times are important factors in testing asphalts. Annealing can reduce the measured modulus by as much as 40 percent (as observed with several asphalts during the project).

5. Cleanness of the plates. The testing plates should be clean and dry so that asphalt adheres to both plates uniformly and strongly.

Data Analysis

Theoretical

Calculation of the complex modulus, phase angle, and related rheological parameters for dynamic shear testing are normally performed automatically under the control of the personal computer included with the rheometer. In most cases, the specific parameters recorded in the data files and/or printed out can be selected by the operator. During this project, much data analysis was done using the principle of time-temperature superposition, which is used to generate a master curve of viscoelastic data, such as complex modulus or stiffness. Such data are not needed for specification testing. The details of this research testing and related analyses are presented in chapter 1 of volume 3 of this report.

Data Presentation

When dynamic shear rheometer data are to be used to *verify* the grade of an asphalt cement binder, it is necessary to conduct tests at three aging conditions to determine the complex modulus (G^*) and the phase angle (δ). The tests are done after different aging conditions and the data are used to calculate the specification parameters as follows:

1. Test original binder; $G^*/\sin\delta$ at 10 rad/s must be greater than or equal to 1 kPa.
2. Test RTFO-aged binder; $G^*/\sin\delta$ at 10 rad/s must be greater than or equal to 2.2 kPa.
3. Test PAV-aged binder; $G^* \sin\delta$ at 10 rad/s must be less than or equal to 5.0 MPa.

If any of the above requirements is not satisfied, the sample fails the specified grade. For verification or acceptance purposes the test data are used to make a "go or no-go" decision.

When dynamic shear data are used to *determine* the grade of an *unknown* binder, data should be obtained at two or more test temperatures for each of the aging conditions to determine the maximum temperature at which requirements 1 and 2 above are satisfied and the minimum temperature at which requirement 3 is satisfied. For an unknown asphalt, the following sequence of testing is suggested:

1. Test the original binder at 58°C (136°F) unless there is information to suggest another temperature at which $G^*/\sin\delta$ at 10 rad/s $\geq$ 1.0 kPa. For example, a soft grade intended for a northerly climate may be tested initially at 52°C (126°F). A grade intended for a hot climate may be tested initially at 64 or 72°C (147 or 162°F). If the measured value for $G^*/\sin\delta \leq$ 1.0 kPa, lower the test temperature by 6°C (11°F) (same specimen) and retest. Repeat in 6°C (11°F) increments until $G^*/\sin\delta \leq$ 1.0 kPa.

2. Start by testing the RTFOT-aged binder at the highest temperature at which $G^*/\sin\delta \leq$ 1.0 kPa in step 2 above. If $G^*/\sin\delta \leq$ 2.2 kPa, cool the specimen by 6°C (11°F) and retest. Repeat in 6°C (11°F) increments until $G^*/\sin\delta \geq$ 2.2 kPa. If $G^*/\sin\delta$ at the starting temperature $\geq$ 1.0 kPa, increase the temperature by 6°C (11°F) and retest. Repeat at 6°C (11°F) increments until $G^*/\sin\delta \leq$ 2.2 kPa.

3. The grading temperature for the maximum pavement design temperature is determined in step 1 above. This temperature determines the first number in the performance grade (PG), as in PG 64-XX. The second number is determined by testing at the intermediate pavement design temperature. The pavement design temperatures and the associated test temperatures are summarized in table 1.1 for the different grades.

   Once the maximum pavement design has been determined from steps 1 and 2, select the intermediate test temperature, using table 1.1 as a guide. For example, the PG-64 grade includes six intermediate pavement design temperatures: 16, 19, 22, 25, 28, 31°C (61, 66, 72, 77, 82, 88°F). Select a temperature at the middle of the range of temperatures, for example, 22 or 25°C (72 or 77°F) as the starting temperature unless there is information to suggest another temperature at which $G^*\sin\delta \leq 5.0$ MPa.

If $G^*\sin\delta \geq 5.0$ MPa, increase the test temperature (same specimen) by 3°C (5°F) and retest. Repeat in 3°C (5°F) increments until $G^*\sin\delta \leq 5.0$ MPa. If $G^*\sin\delta \leq 5.0$ MPa, cool the specimen by 3°C (5°F) and test. Repeat in 3°C (5°F) increments until $G^*\sin\delta \geq 5{,}000$ MPa.

A useful rule of thumb regarding the change in dynamic shear modulus is that $G^*/\sin\delta$ and $G^*\sin\delta$ change by three- to fourfold for every 10°C (18°F) change in test temperature. Different asphalt cements, however, often have quite different temperature dependencies and the rule of thumb must be considered an approximation.

Each set of measurements for the three steps above should give measurements at two or more temperatures. The data, $G^*/\sin\delta$ or $G^*\sin\delta$, can be plotted on a logarithmic axis versus temperature (isochronal plot). Over a short range in temperature, (e.g., 12°C [22°F]), the data plot very nearly as a linear function.

For research purposes, the dynamic shear rheometer can be used to conduct frequency sweeps at different temperatures. Data from such sweeps may be used to construct master curves, using the linear viscoelastic time-temperature shift functions. The reader is referred to volume 3 of this report for the use of bending beam data for research purposes.

Testing Variability

The coefficient of variation for dynamic shear testing conducted early in the project was found to range from 10 to 25 percent, depending on the modulus of the asphalt. Lower variability was observed at higher modulus levels. Although this level of variability is sufficient to differentiate between asphalts for research purposes, it is not acceptable for specification testing. Error analysis of the data collected, however, indicated that the variability can be reduced to levels appropriate for specification purposes.

Most of the variability in test data collected during the early part of the project was attributable to poor temperature control. The mechanical spectrometer, as originally equipped, had a guaranteed temperature stability of only ± 1°C (± 1.8°F); actual accuracy was less than this. Figure 1.8 illustrates the effect of temperature on the complex modulus.

Table 1.1. 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[a]	<46			<52							<58					<64					
Minimum Pavement Design Temperature, °C[a]	>-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:[b] Maximum, 3 Pa•s, Test Temp, °C	135																				
Dynamic Shear, TP5:[c] $G^*/\sin\delta$, 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: $G^*/\sin\delta$, Minimum, 2.20 kPa Test Temp @ 10 rad/s, °C	46			52							58					64					
PRESSURE AGING VESSEL RESIDUE (PP1)																					
PAV Aging Temperature, °C[d]	90			90							100					100					
Dynamic Shear, TP5: $G^*\sin\delta$, 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[e]	Report																				
Creep Stiffness, TP1:[f] 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:[f] 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

[a] 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.

[b] 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.

[c] 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 $G^*/\sin\delta$ 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).

[d] 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.

[e] 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.

[f] 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 1.1 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[b]	<70						<76					<82				
Minimum Pavement Design Temperature, °C[b]	>-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:[b] Maximum, 3 Pa•s, Test Temp, °C	135															
Dynamic Shear, TP5:[c] $G^*/\sin\delta$, 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: $G^*/\sin\delta$, Minimum, 2.20 kPa Test Temp @ 10 rad/s, °C	70						76					82				
PRESSURE AGING VESSEL RESIDUE (PP1)																
PAV Aging Temperature, °C[d]	100(110)						100(110)					100(110)				
Dynamic Shear, TP5: $G^*\sin\delta$, 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[e]	Report															
Creep Stiffness, TP1:[f] 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:[f] 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

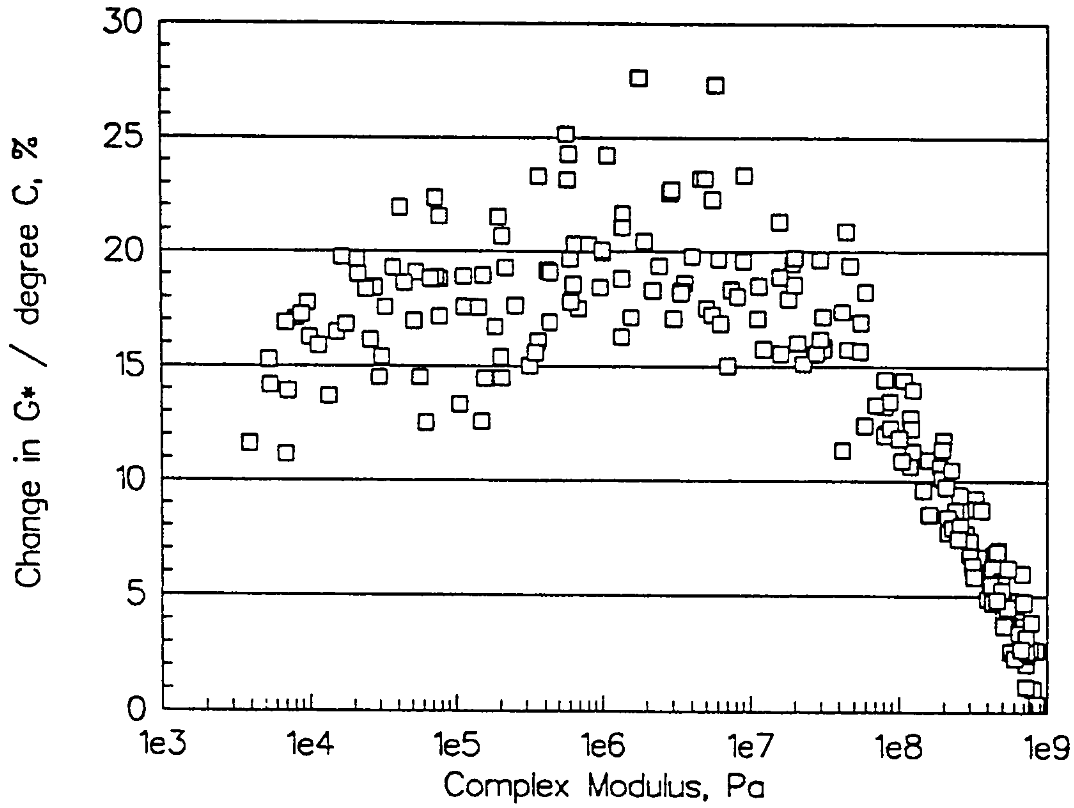


Figure 1.8. Percent Change in Complex Modulus per degree Celsius, as a Function of Complex Modulus

In this figure, the percentage change in complex modulus per degree Celsius is shown as a function of modulus for all core asphalts and all aging treatments. At very high modulus levels, there is very little change in modulus with temperature. However, over most of the region of interest for specification testing, there is a 15 to 25 percent change in modulus per degree. To obtain adequate precision for dynamic shear testing for specification purposes, the temperature of the specimen must be controlled to within ± 0.1°C (± 0.2°F). This will limit the temperature control's contribution to variation to no more than ± 2.5 percent. In later testing done as part of this project, as well as for data generated in other laboratories, a within-laboratory standard deviation of less than 5 percent is readily obtainable as long as adequate temperature control is maintained, as shown in table 1.2.

Another major source of variability is the trimming of the specimen. A raised pedestal in the lower plate facilitates trimming and is recommended for those rheometers that otherwise have a flat lower plate. With improved temperature control, better specimen trimming, and complete and regular calibration, it is anticipated that the coefficient of variation for dynamic shear testing can be reduced to 5 percent or less.

Table 1.2. Reproduceability of Dynamic Shear Measurements for Asphalts AAK-1 and AAM-1*

Run Number		G′ (kPa)	G″ (kPa)	Viscosity (kPa)	G* (kPa)	Tan δ (G″/G′)
AAK-1	1	161.6	392.7	81.33	424.6	2.43
	2	161.7	392.6	81.47	424.6	2.43
	3	160.3	393.9	84.07	425.2	2.46
	4	162.8	391.9	79.40	424.4	2.41
	5	162.5	391.3	79.00	423.7	2.41
Average		161.8	392.5	81.05	424.5	2.43
Standard Deviation		0.90	0.90	1.81	0.50	0.02
AAM-1	1	173.7	391.3	15.46	428.1	2.25
	2	171.0	393.2	16.52	428.7	2.30
	3	173.1	393.4	17.04	429.8	2.27
	4	172.7	391.5	15.60	427.9	2.27
Average		172.6	392.4	16.16	428.6	2.27
Standard Deviation		1.00	1.00	0.65	0.70	0.02

*Measurements were performed at 26 °C, 25-mm parallel plates, 2-mm film gap, and 400 g-cm torque.

Proposed Specification for Dynamic Shear Rheometer

The proposed specification for the dynamic shear rheometer was developed in draft form as part of this project and was further refined with the cooperation and input of the SHRP Asphalt Binder Rheology Expert Task Group, the A-001 contractor, and Federal Highway Administration (FHWA) and SHRP staff. Staff from the American Association of State Highway and Transportation Officials (AASHTO) were responsible for organizing the specification in its final format. The AASHTO version of the specification is presented in Appendix A.

2 Bending Beam Rheometer

Introduction

Purpose

The bending beam rheometer is used to measure the low-temperature creep response of asphalt binders. Creep stiffness and the slope of the log stiffness versus log time curve are obtained at several loading times ranging from 8 to 240 s.

Scope

The bending beam rheometer is used to apply a constant load to a prismatic beam loaded in simple bending at its midpoint. The device is useful for measuring moduli ranging from 30 MPa to 3 GPa (435 to 435,100 lb/in.^{2}). These moduli typically occur in the temperature range from -40 to 25°C (-40 to 77°F) depending on the grade and aging history of the binder.

Description of Equipment

Hardware

The main parts of the rheometer are shown in figure 2.1. The rheometer is operated by applying a constant load at the midspan of a small asphalt cement beam that is simply supported (supported at its two ends and loaded at the center). During the test, the deflection of the center point of the beam is measured continuously. The asphalt beam is supported at both ends by stainless steel half-rounds that are 102 mm (4.0 in.) apart. The beam is 125 mm (5.0 in.) long, 12.5 mm (0.50 in.) wide, and 6.25 mm (0.25 in.) thick. The specimen, the supports, and the lower part of the test frame are submerged in a constant-temperature fluid bath, which controls the test temperature. The fluid in the bath also provides a buoyant force to counterbalance the weight of the beam and to minimize deflections caused by the of the beam itself.

The loading unit in the device consists of an air bearing and a pneumatic piston that controls the movement of the loading shaft. The loading shaft serves a dual purpose; its upper end is attached to a linear variable differential transformer (LVDT) that precisely measures the shaft

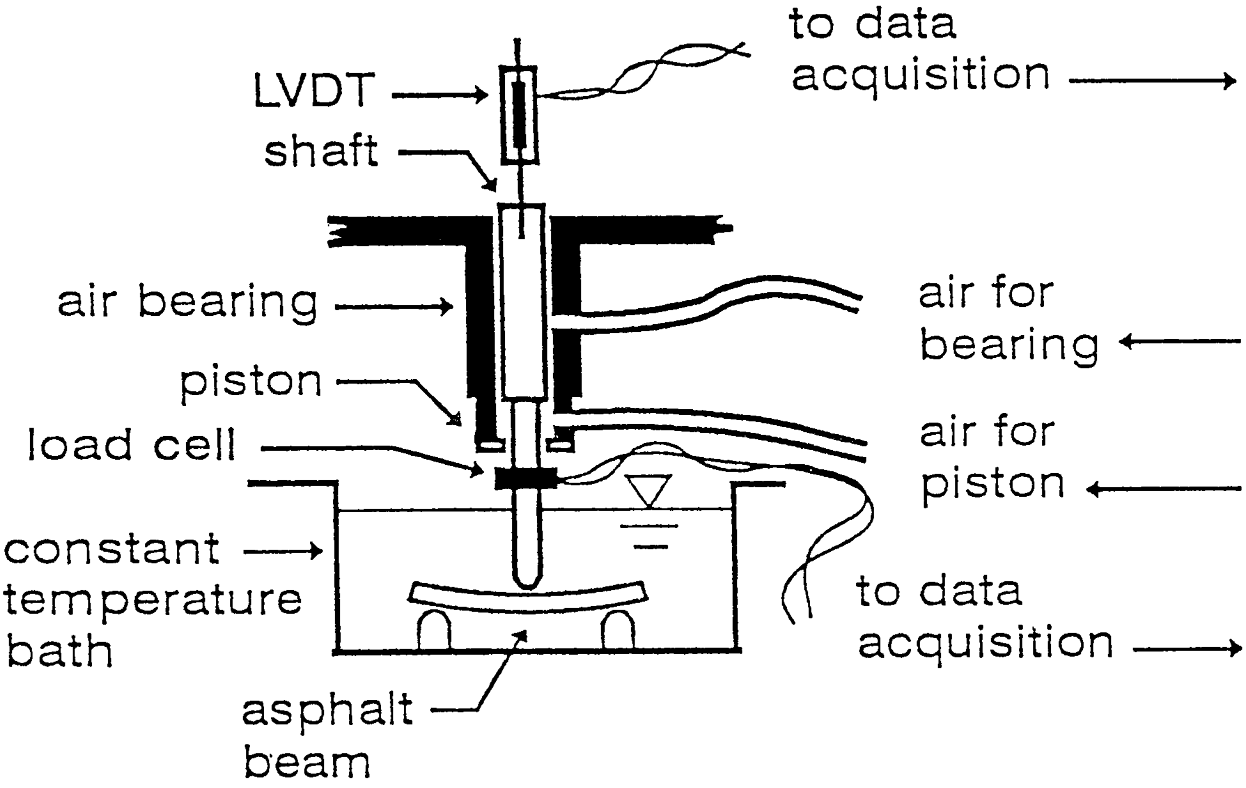


Figure 2.1. The Bending Beam Rheometer

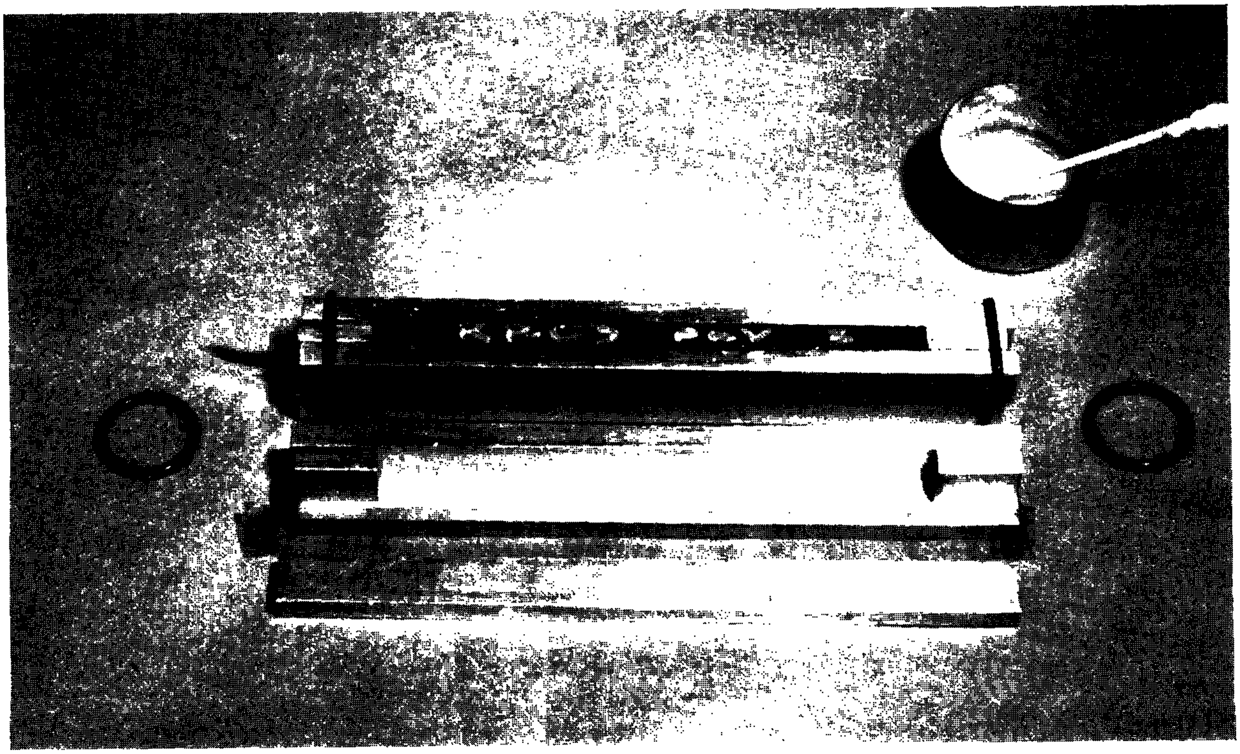


Figure 2.2. Aluminum Molds Used for the Preparation of Asphalt Beam Specimen

movement, and its own weight is used to apply the required load on the test specimen. The magnitude of the load is controlled by adjusting the pressure in the pneumatic piston.

Data Acquisition

Test data, which include deflection of the asphalt beam, load on the beam, and time of loading, are acquired by a personal computer through a digital/analog data acquisition board. The data collected are used to calculate the creep stiffness, $S(t)$, and the absolute value of the slope of the log stiffness versus log time curve where

$$m = |d \log S(t)/d \log(t)| \tag{2.1}$$

where

m = creep rate of the binder under load
$S(t)$ = time-dependent flexural creep stiffness
t = time

The values of m and $S(t)$ are reported at six loading times: 8, 15, 30, 60, 120, and 240 s. The creep stiffness is a measure of resistance of the binder to deformation, and m is a measure of the creep rate (loading time dependency) of the binder under load. Specific algorithms for calculating the stiffness and m are given in chapter 3 of volume 3 of this report and in the provisional specification at the end of this chapter. The software program supplied with the rheometer is written to perform the required calculations for $S(t)$ and $m(t)$ and to display the results together with input parameters at the end of each test.

Testing Protocol

Sample Preparation

1. Heat approximately 30 g of the asphalt binder in an oven until it has become sufficiently fluid to pour. The oven temperature is not to exceed 150°C (302°F), and the sample is to be stirred occasionally to ensure homogeneity and to remove air bubbles.

2. Pour the asphalt into the mold, starting from one end of the mold and moving toward the other. The sample container should be held close to the mold (20 to 50 mm [0.80 to 2.0 in.]), and the pouring should be continuous from one end to the other in one pass (figures 2.2 and 2.3). After pouring, allow the mold to cool to room temperature (≈60 min).

3. Once the asphalt cement binder has cooled, trim excess binder from the exposed face of the mold, using a hot knife or a heated spatula, to make the binder flush with the top of the mold.

4. Prepare the rheometer for operation by loading the data acquisition software and equilibrating the testing bath at the test temperature for at least 30 min.

Figure 2.3. Pouring the Asphalt Binder Specimen

5. Cool the mold by placing it in a freezer or an ice bath for a period of time sufficient to stiffen the beam so that it can be readily demolded. This can usually be accomplished in 15 to 60 s, depending on the testing temperature and the type of asphalt.

6. Remove the specimen from the bath and wipe it dry. Demolding should start immediately. After demolding, the specimen should be left in the bath at the testing temperature for 60 ± 5 min before testing. This equilibration time should be tightly controlled to ensure repeatability. Most asphalt binders show rapid hardening at low temperatures as a result of physical hardening (see volume 2 of this report). If the time of the test is not carefully controlled, low-temperature physical hardening may cause unacceptable variability in the test results.

Device Preparation and Calibration

1. Select the test temperature and adjust the bath temperature to the selected temperature. Wait until the temperature stabilizes and then allow the bath to equilibrate for 30 min.

2. Turn on the computer and the data acquisition system and load the software as explained in the rheometer software manual.

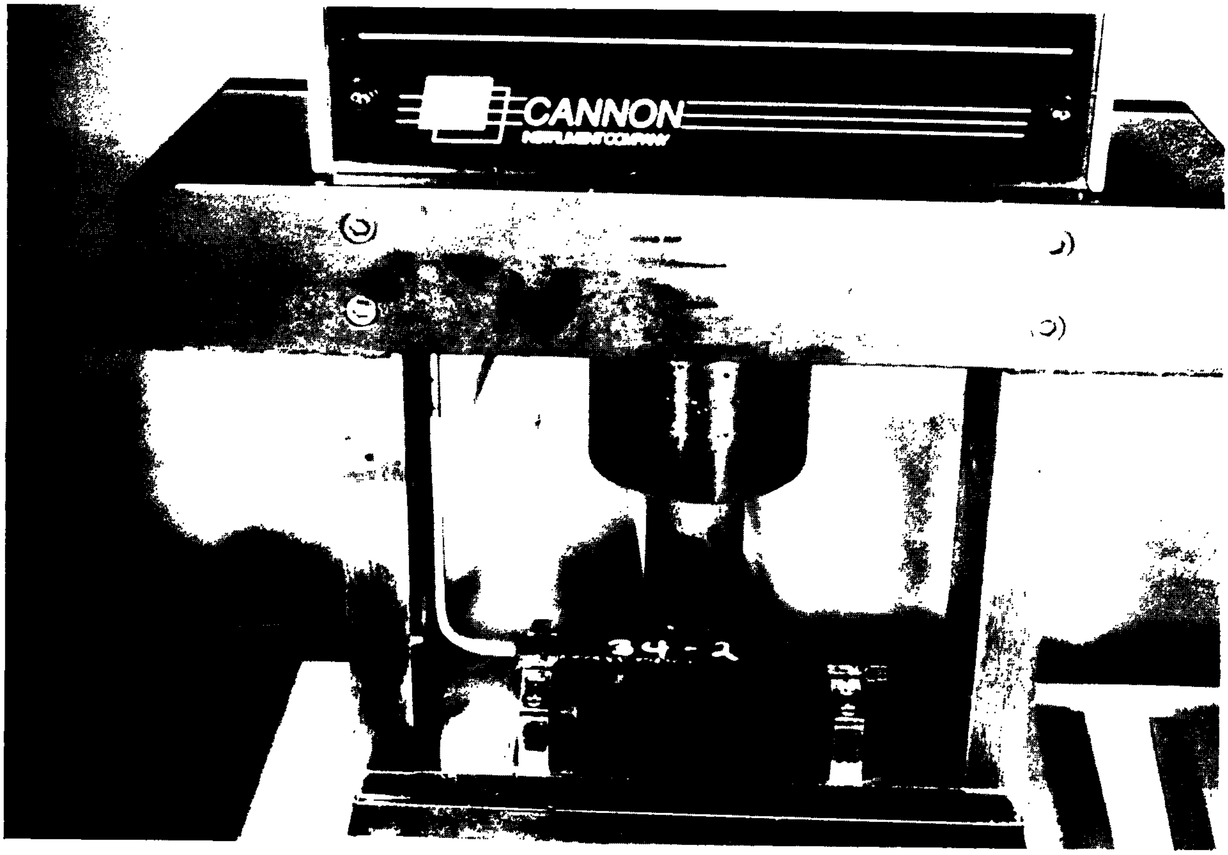


Figure 2.4. An Asphalt Binder Specimen on the Supports of the Rheometer for Testing

3. Open the compressed gas source and adjust the regulator to provide required pressure for the rheometer. Bottled compressed air or nitrogen may be used. Caution should be used with compressed laboratory air because it often contains excessive moisture or oil.

4. Place the 12.5-mm (0.5-in.) -thick steel beam on the beam supports (figure 2.4). Select "local" on the control panel and press the load button. Adjust the load applied to the beam by changing the air pressure to the pneumatic piston until the load is 100 ± 5 g. It is not necessary to adjust the load until it is precisely 100 g. The load measured by the load cell is used in the calculations.

5. From the main menu, select "calibration of the rheometer." Then select the calibration option and follow the steps displayed on the screen. The calibration takes less than 3 min. It automatically calculates and stores the calibration constants for the load cell and the LVDT. It also calculates the device compliance. After calibration, the rheometer is ready for testing. The calibration procedure is not a requirement for every test. The procedure needs to be run only at the beginning of the testing session.

6. Another important feature of the bending beam rheometer is the confidence check. This feature is used to check the overall performance of the system by applying 100 ± 5 g to a 1.6-mm (0.063-in.) -thick steel beam with a known modulus. The steel beam is supplied with the rheometer and the check can be done by selecting the "steel" option under the run test option.

The test procedure is performed by loading the steel beam for 20 s and calculating the elastic modulus. The modulus is compared with the known modulus of the steel beam. The result of the confidence check is displayed on the computer screen. If the modulus value reported for the beam differs from that supplied with the rheometer the calibration of the system is suspect or the system is not working properly. Both the calibration and the confidence check should be done on a daily basis.

Overview of Test Procedure

1. After conditioning the specimen for 60 ± 5 min, place the beam specimen on the supports and center it visually.

2. Type the specimen identification information, test load, test temperature, time the specimen has been at test temperature, and other information as appropriate.

3. Use a 3- to 4-g preload to establish contact between loading shaft and specimen. This is accomplished by carefully lowering the loading shaft until the load signal increases by 3 to 4 g (the load cell reading before the shaft contacts the beam should be approximately zero).

4. Apply an initial seating load of 100 ± 5 g for 1 s. Unload to the 3- to 4-g preload. Allow the beam to recover for 20 s. This load is applied to seat the beam on the supports and to remove any warping of the beam that may have occurred during handling.

5. Immediately after the 20-s recovery period, perform the stiffness measurement by loading the specimen with 100 ± 5 g for at least 240 s, after which the test should be stopped by unloading the specimen. The software will display plots of load and deflection versus loading time on the video screen for the 240-s loading period.

   Note: Once the preload has been adjusted, the computer automatically applies an initial seating load of the 100 ± 5 g for 1 s, allows the beam to recover for 20 s, and then applies the test load of 100 ± 5 g for 240 s. The load and deflection is displayed on the video screen only for the 240-s testing period. The remainder of the test sequence is transparent to the operator.

6. The software will perform the required calculations and a one-page report will appear on the screen summarizing the results and the input parameters.

7. Remove the specimen from the supports and proceed to the next test.

Points of Caution

A number of operational factors must be carefully controlled because they can significantly affect the reproducibility of the test measurements. These factors are:

1. Thickness of the beam specimen. The calculated stiffness is proportional to the third power of the thickness. For example, if the actual thickness is 6.5 mm and 6.0 mm is used in the calculations, the calculated stiffness will be 27 percent less than the correct value.

2. Shape of the beam specimen. Distortion of the specimen during demolding should be avoided. The analysis is based on the assumptions that the specimen at the supports is in full contact with the supports and that it is approximately horizontal between the supports.

3. Thermal treatment. Annealing (conditioning) times are important factors, particularly at low temperatures where physical hardening is dominant. The conditioning time after demolding the specimen should be kept within the limits of ± 5 min, as explained in the procedure.

4. Initial load on the specimen. The initial load on the specimen should be between 3 and 4 g. This load is required to ensure contact between loading shaft and specimen. Failure to establish the contact will lead to misleading results. An initial load that is too large also will give misleading measurements.

5. Temperature of bath. Asphalt properties are very sensitive to temperature. Therefore, temperature should be kept within ± 0.2°C (0.4°F) of the target test temperature throughout the conditioning period and throughout the test.

6. Cleanness of the supports and loading head. Because of the brittleness of asphalts, small fragments of asphalt may be present in the bath. If these fragments stick to the supports or the loading head, the measured deflection will not be accurate. These fragments will deform or cause poor seating of the beam and add an apparent deflection to the true deflection of the beam.

7. Limits of measurements. Any measurements for which the deflection of beam exceeds 4.0 mm (0.16 in.) should be considered suspect because at this point the maximum bending strain is approximately 1.0 percent and the linearity limit may be exceeded. When deflection is less than 0.08 mm (0.003 in.), the resolution of the device may not be sufficient to produce reliable test results.

Data Analysis

Theoretical

Using the elementary bending theory, the deflection for a prismatic beam of an elastic material in three-point loading mode is maximum at the center of the span and can be calculated using the following formula:

$$\delta = PL^3/48EI \qquad (2.2)$$

where

δ = deflection of beam at midspan
P = constant load applied, N (lb)
L = span length, mm (in.)
E = modulus of elasticity, Pa (psi)
I = moment of inertia of section = $bh^3/12$, mm^4
b = width of the beam
h = depth of the beam.

With a span-to-depth ratio of 16 to 1, the effects of shear can be neglected.

According to the elastic-viscoelastic correspondence principle, it can be assumed that if a viscoelastic beam is subjected to a constant load applied at $t = 0$ and held constant, the stress distribution is the same as that in an elastic beam under the same load. Further, the strains and displacements depend on time and are derived from those of the elastic problem by replacing E with $1/D(t)$. Since $1/D(t)$ is equivalent to $S(t)$ where $1/D(t)$ is equal to the extensional modulus in creep, rearranging the elastic solution results in the following:

$$S(t) = PL^3/4bh^3\delta(t) \tag{2.3}$$

where

$\delta(t)$ = time-dependent deflection of beam

The stress, σ, and strain, ϵ, in the outer fiber at midspan, using the span length of 102 mm (4.0 in.) and the selected beam dimensions, can be calculated as follows:

$$\sigma = 3PL/2bh^2 = 297.6{*}P \text{ kPa } (192{*}P \text{ lb/in}^2) \tag{2.4}$$

$$\epsilon = 6\delta(t)h/L^2 = 0.003691\text{-mm/mm } (0.09375{*}\delta(t)\text{-in./in.}) \tag{2.5}$$

According to the equations above, a deflection of 2.5 mm (0.10 in.) at the midspan, which is the maximum recommended deflection, will result in a maximum strain of 0.92 percent in the specimen. The deflection-to-depth ratio will be 1 to 2.5, and the deflection-to-span ratio will be 1 to 40. The maximum recommended deflection is within the known limits for the small strain criteria where the elementary bending theory is valid.

To illustrate the stiffness values with the selected dimensions, with a load of 100 g (0.221 lb), stiffness values range between 51 MPa (7,200 lb/in.^{2}) at the maximum recommended deflection of 4.0 mm (0.16 in.) and 2.5 GPa (360,000 lb/in.^{2}) at a deflection of 0.08 mm (0.003 in.).

Data Presentation

When bending beam test data are to be used to *verify* the grade of an asphalt cement binder, it is sufficient to conduct a single test (two replicate test specimens) at the specification temperature and to determine the stiffness and m at 60 s (see table 1.1). If $S(t) \leq 300$ MPa, and $m > 0.30$, the sample meets the specified grade. If $S(t) > 300$ MPa and/or $m < 0.30$, the sample fails the specified grade. For verification or acceptance purposes, the test data are used to make a "go or no-go" decision.

When bending beam test data are used to *determine* the grade of an *unknown* binder, it may be necessary to test at two or more test temperatures to determine the minimum temperature at which the specification requirement is satisfied. The initial test temperature for an unknown asphalt binder may be selected in several ways, as follows:

- The results of the dynamic shear rheometer (DSR) test at the intermediate test temperature can be used as a guideline for the initial test temperature. Select the initial test temperature in accordance with the grade indicated on the basis of the DSR measurements on the tank and rolling thin-film oven test (RTFOT) residue (measured at the maximum pavement temperature) and the pressure aging vessel- (PAV-) aged material (measured at the intermediate pavement temperature).

- If the DSR data for the PAV-aged material are not available, use the DSR data from the tank material to select the first number of the performance grade (for example, PG 64-XX). For the initial bending beam rheometer (BBR) test temperature, select a minimum test temperature in the midrange of the grade (table 1.1). For example, the PG-64 grade includes six minimum test temperatures: 0, -6, -12, -18, -24, and -30°C (32, 21, 10, 0, -11, and -22°F). Select a temperature at the middle of the range of temperatures (such as -12 or -18°C [10 or 0°F]) as the starting temperature, unless there is information to suggest another temperature at which $S(t) \leq 300$ MPa and $m \geq 0.30$.

- In the absence of any of the above conditions, use -12°C (10°F) as the initial test temperature.

Examine the results from the initial test temperature. If $S(t) \leq 300$ MPa and $m \geq 0.30$, select a new set of beams and decrease the test temperature by 6°C (11°F). Repeat until the $S(t)$ and m criteria are no longer met. If $S(t) \geq 300$ MPa and/or $m \leq 0.30$ at the initial test temperature, increase the test temperature in 6°C (11°F) increments until both criteria are met. Values of the log of $S(t)$ and m versus temperature are very linear over a limited range of temperatures.

For research purposes, the entire 4-min creep curve may be useful. Data may also be obtained at different conditioning times and test temperatures. Such data may be used to study physical hardening potential and to determine temperature shift functions. The reader is referred to volume 3 of this report for the use of bending beam data for research purposes. It should be noted that the BBR is not designed for creep recovery testing. The slight preload needed to keep the loading shaft in contact with the beam will result in unreliable recovery data.

Testing Variability

To evaluate the precision of the rheometer data collected for the eight core asphalts, four temperatures and four isothermal storage times were used. The data set consisted of 1,256 measurements, with 2 independent replications in 628 cells. To measure the size of experimental error, the standard deviation is usually used. However, because of the wide range in measured stiffness values, it is more appropriate to use the coefficient of variation. Furthermore, it was expected that the coefficient of variation would depend on the stiffness level, because the LVDT has a certain level of resolution; the lower the deflections, the higher the expected experimental noise. To solve this problem, the stiffness values were divided into sets representing different ranges of stiffness values. The range in measured values included in the analysis was between 16.5 MPa and 1.85 GPa (2,400 and 268,000 lb/in.^{2}). The ranges were selected so that approximately equal numbers of measurements would be contained in each range. The stiffness ranges selected, the number of replicate measurements, and the results of the statistical analysis are summarized in table 2.1. The coefficients of variation were obtained by calculating the average of the sample means and standard deviations for the paired replicates in each of these stiffness intervals.

Because of the large number of paired replicates used to provide the estimate of the pure experimental error variance, the estimates of the coefficient of variation can be considered very accurate. However, it is important to recognize that the analysis here represents a measure of the variability in a well-controlled setting, in one laboratory, with a well-trained operator. The values of the coefficient of variations shown in table 2.1 are very low and show a trend relative to the stiffness interval: the higher the stiffness mean, the higher the coefficient of variation. The variability levels reflect experimental error involving not only the testing operation, but also variation due to specimen preparation procedure, temperature control, and isothermal age control.

Table 2.1 Statistical Summary of Stiffness Repeatability for the Bending Beam Rheometer.

Stiffness Range (MPa)	Mean Stiffness (MPa)	Number of Test Cells	Standard Deviation (MPa)	Coefficient of Variation (%)
< 0.124	71	142	1.16	1.6
0.124 to 320	211	154	5.47	2.6
320 to 620	457	146	13.7	3.0
> 620	1,000	186	37.8	3.8

Proposed Specification for Bending Beam Rheometer

The proposed specification for the bending beam rheometer was developed in draft form as part of this project and was further refined with the cooperation and input of the SHRP Asphalt Binder Rheology Expert Task Group, the A-001 contractor, and Federal Highway Administration and SHRP staff. Staff of the American Association of State Highway and Transportation Officials (AASHTO) were responsible for organizing the specification in its final format. The AASHTO provisional specification is presented in Appendix B.

3 Direct Tension

Introduction

Purpose

The purpose of the direct tension test is to provide tensile failure properties of asphalt binder at low in-service temperatures. The test procedure is used in the SHRP binder specification to ensure that the strain at failure at the minimum pavement design temperature is greater than 1.0 percent. At temperatures and loading rates where the strain to failure is less than approximately 1.0 percent, asphalt binders act as a brittle material.

Scope

This test method has been designed to measure tensile strength and strain to failure as required for the SHRP binder specification (table 1.1). Dog-bone-shaped specimens are cast in a silicone rubber mold and pulled in tension until rupture occurs. The specification test is designed to capture only the strain at failure and is conducted at a single temperature and rate of elongation. With appropriate recording (data acquisition) equipment it is also possible to determine a stress-strain curve, stress at failure, and energy to failure. Approximately 2 g of asphalt binder are required per specimen, making the test procedure acceptable for use with various binder aging tests. The test is valid when the asphalt binder fails in a brittle-ductile mode where the strain to failure ranges from 0.1 to 10 percent. Failure strains of less than 0.1 percent cannot be reliably measured with the equipment and no provision for change in cross-section of the sample is included in the test procedure, limiting the test to relatively small strains.

As part of this study, the stress-strain curve stress at failure, energy to failure, and tensile modulus were also obtained. Tests were conducted at several strain rates and temperatures so that failure master curves could be constructed.

Description of Equipment

Hardware

Grips

The gripping mechanism consists of specially designed pins precisely centered in the top and bottom loading grips. Figure 3.1 shows the specially designed pins, and the grip with the pin

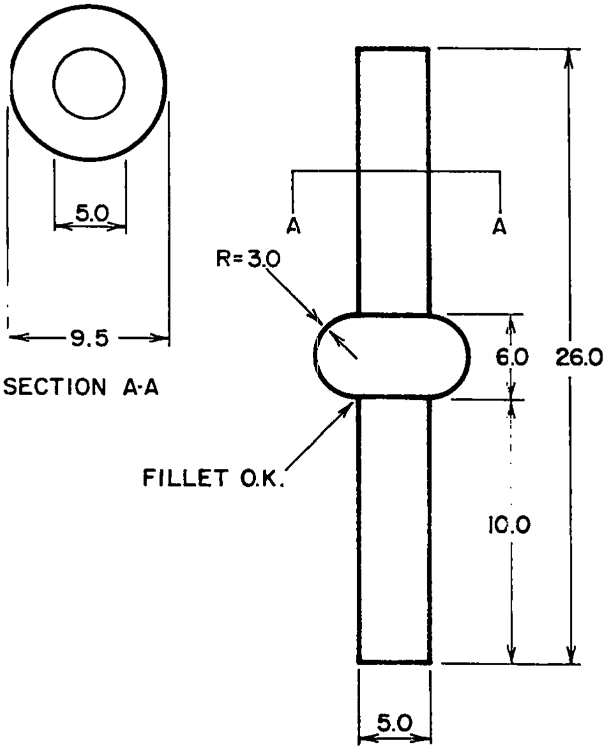


Figure 3.1. Specially Designed Pins Used to Mount the Direct Tension Specimen.

Figure 3.3. The Top Grip with a Specimen Attached.

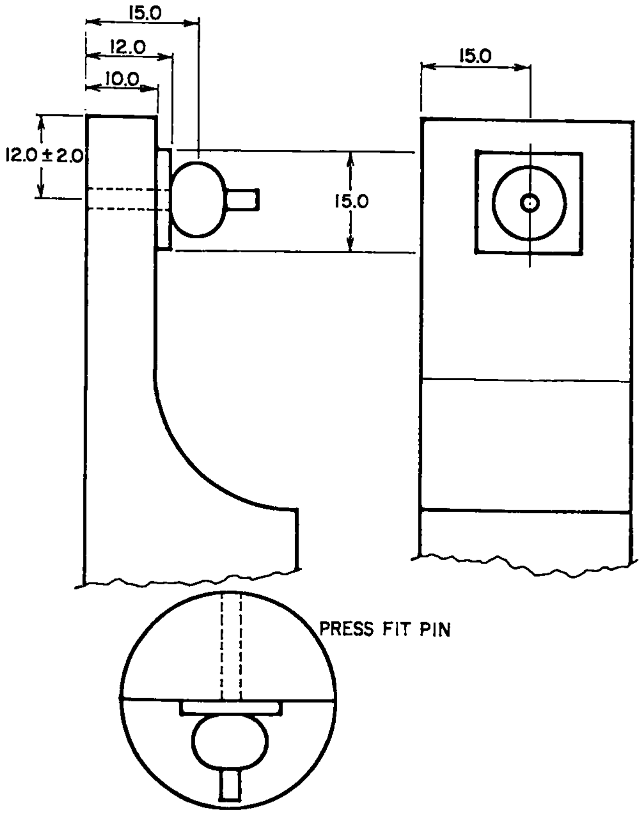


Figure 3.2. Top Grip Showing the Pin Press-Fitted.

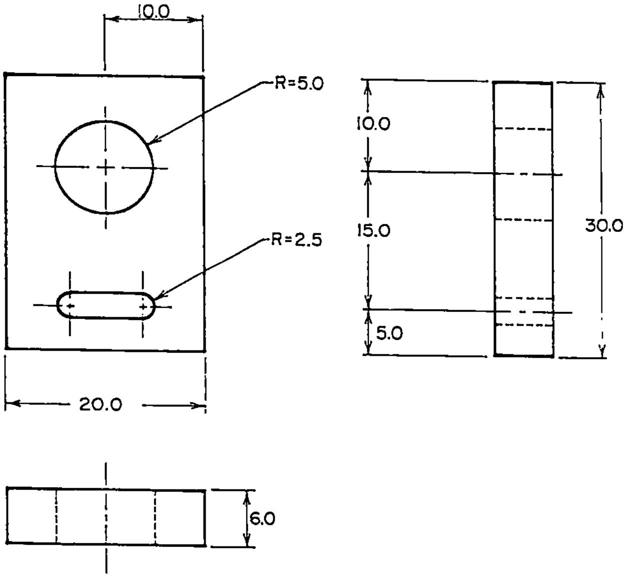


Figure 3.4. Plexiglas End Inserts.

All dimensions in millimeters
Not to scale

is shown in figure 3.2. The top and bottom grips are identical. The lower grip remains stationary while the upper grip is pulled at a specified rate of 1.0 mm/min (0.04 in./min) for the specification test. The asphalt binder bonds to the plastic inserts during the fabrication of the test specimen. Each end insert has a precisely machined hole with a diameter slightly larger than the pin and a horizontal slot below the hole, as shown in figures 3.3 through 3.5. The slot is used as a reference edge for the laser beam used for the elongation measurement.

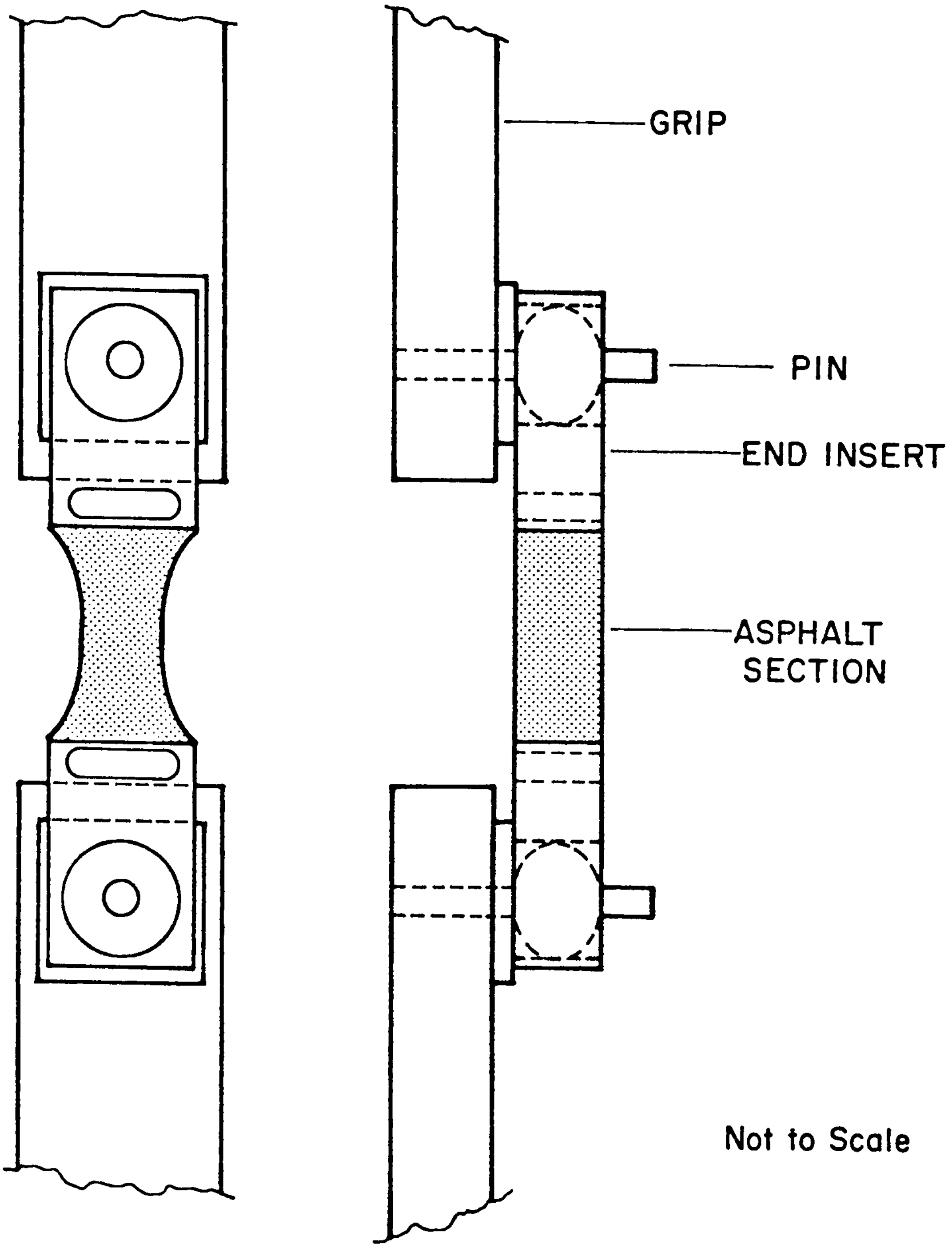


Figure 3.5. Mounting of the Specification Type Specimen.

The specimen is attached to the top and bottom grips by sliding the plastic inserts onto the pins, as shown in figure 3.6. The raised portion of the pins, the vertical axis of the pull rods, and the holes in the end inserts (bonded to the specimen) must be precisely aligned with the center line of the heads of the testing machine to ensure axial tensile stresses within the test section (asphalt portion). Even a slight misalignment will introduce bending stresses that are not considered in the usual stress computation (load divided by the cross-sectional area) and will cause the test results to be variable.

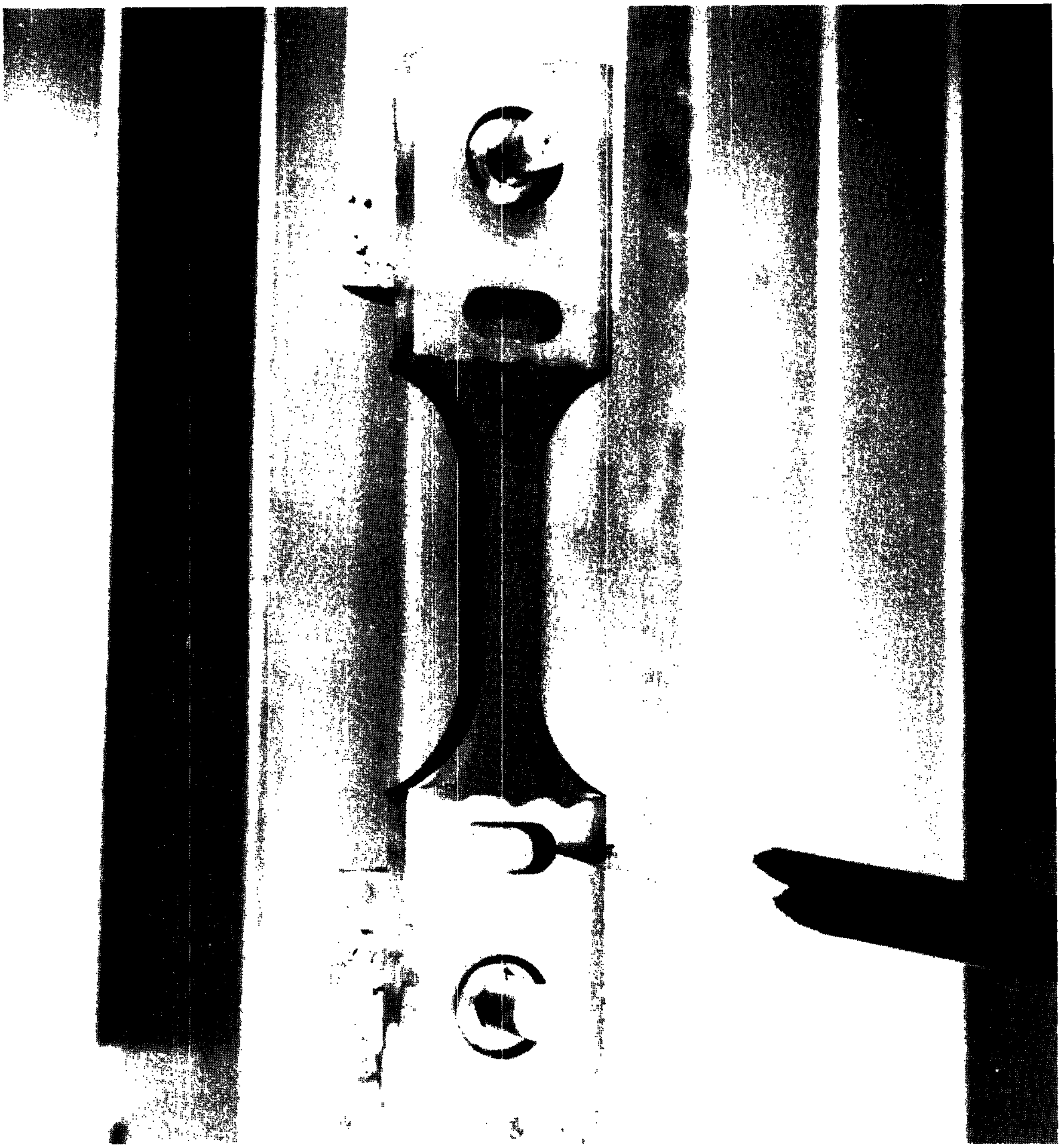


Figure 3.6. The Specimen Attached to the Top and Bottom Grips

Specimen Molds

The molds are manufactured from silicone rubber. The Dow Corning HSII RTV Moldmaking Rubber 20:1 Kit (white) has been found to be acceptable for this purpose. Silicone rubber is used because it provides an excellent nonstick surface for asphalt cement. The dog-bone-shaped female silicone rubber mold is cast in a precisely machined aluminum male mold. The aluminum mold consists of the entire specimen, including the end inserts portion. To prepare an asphalt binder specimen in the silicone rubber mold, shown in figure 3.7, asphalt cement is poured from one end insert of the mold to the other, slightly overfilling, while the mold is placed flat on a plate. This requires trimming the molded specimen to obtain the required flat top surface. For trimming the filled molds, a flat cheese shaver was found to work well.

After use, the silicone rubber mold can be easily cleaned by heating and wiping with a piece of cloth. Solvents like acetone and trichloroethylene (TCE) must never be used for cleaning the silicone molds or the inserts.

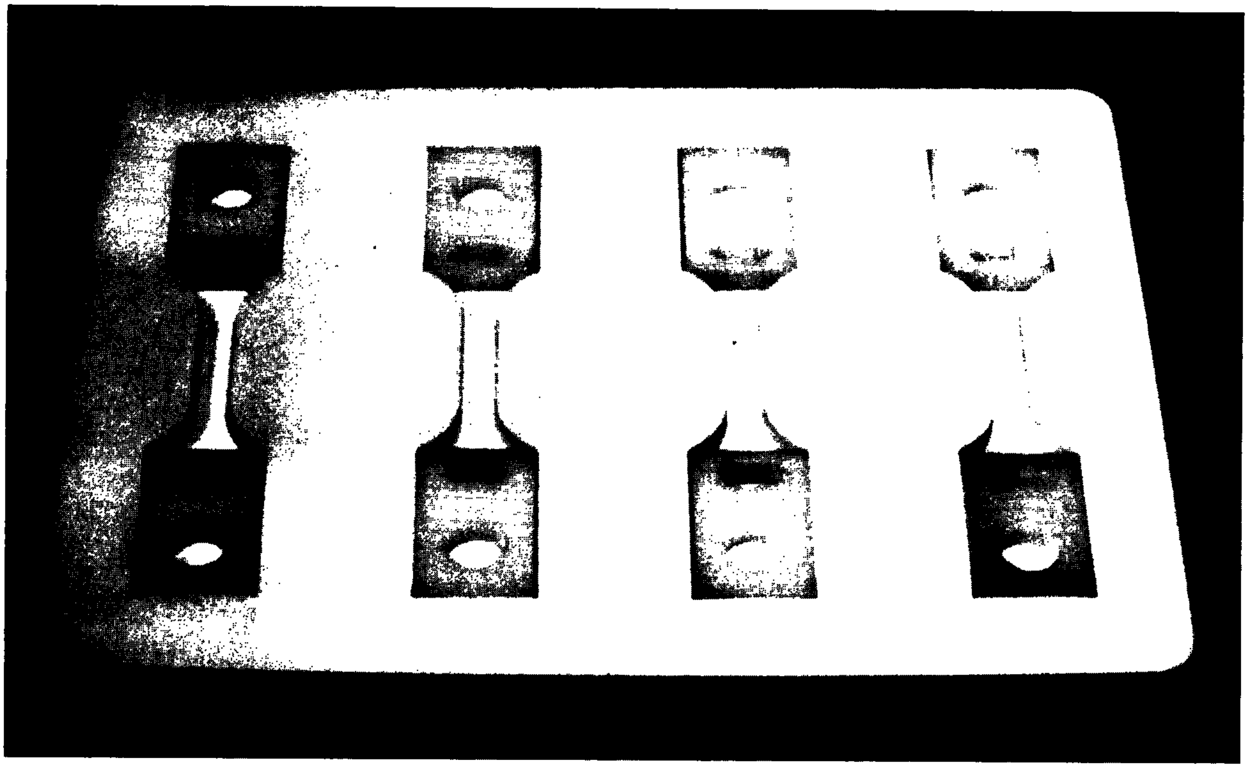


Figure 3.7. Silicone Rubber Molds Used to Prepare the Specimen.

Specimen Configuration

Each specimen requires approximately 2 g of asphalt. The specimen is 100 mm (3.94 in.) in overall length, including the end inserts. The end inserts are each 30 mm (1.18 in.) long by 20 mm (0.79 in.) wide. The asphalt portion of the specimen is therefore 40 mm (1.58 in.) long with an effective gauge length of 27 mm (0.71 in.) and cross-sectional dimensions of 6 mm (0.55 in.) wide by 6 mm (0.55 in.) thick. The constant cross-section widens at each end with a radius of 12 (2.0 times its thickness) to provide a gradual transition with the end inserts.

In the development work, polypropylene was used to make end inserts because it has a linear thermal coefficient of expansion (6.8×10^{-4} mm/mm/°C; 12.2×10^{-4} in./in./°F) relatively close to that of asphalt cement (0.6×10^{-4} mm/mm/°C; 1.1×10^{-4} in./in./°F). Matching the expansion coefficients of the asphalt binder and the inserts reduces thermal shrinkage stresses at the interface that otherwise cause bond failures at the interface. Because it is much easier to machine, plexiglass (PMMA), which has a slightly higher coefficient of expansion, was substituted for the polypropylene and found to be acceptable.

Loading System

For the specimen size selected, a loading frame capable of producing a 400- to 500-N (approximately 100-lb) load was found to be adequate for testing neat, unmodified asphalt cement. Modified asphalt cement systems may require a somewhat larger load capacity. In addition, the loading system must be able to reproduce various platen speeds in the range of 1.0 mm/min (0.05 in./min) to 50.0 mm/min (approximately 2.0 in./min), although a single elongation rate, 1.0 mm/min (0.05 in./min), is needed for specification purposes. A screw-driven machine such as that made by Instron (Model 4201) is the preferred type of testing machine. A conventional hydraulic testing machine is not suitable for this test method because the rate of elongation cannot be readily controlled. However, a closed-loop electro-hydraulic testing machine operating in stroke-controlled mode could be used.

Load Measuring System

The load should be monitored with an electronic load cell with an electronic readout and a resolution of ± 0.5 N (± 0.1 lb). For specification purposes, the ability to capture the maximum stress (load) is sufficient. For research purposes, a continuous recording of the load is desirable.

Deflection Measuring System

Experiments showed that such measurements are reliable only above 1 to 2 percent strain; therefore, a laser-based, noncontact deformation measuring system (extensometer) was used. Because of the brittle nature of asphalt binder, traditional contact extensometers are not suitable for the direct tension test. Therefore, a new technology was employed for measuring specimen elongation. This system uses a visible semiconductor laser beam (wavelength of 670 nm) as its light source.

This system consists of a laser light transmitter and receiver combination. The transmitter produces a vertical plane of laser light, which is monitored by the receiver. For measuring deformation, the specimen and the grip assembly are arranged so that they interrupt this plane of laser light, except for the slots in the inserts. Thus, the receiver sees only four edges produced by the slots in the end inserts. The receiver constantly monitors the movement between the two inner edges to produce a proportional voltage. This voltage is converted to deformation by a controller attached to the receiver using a prescribed calibration factor.

Environment Control

A temperature-controlled chamber completely enclosing the specimen and the gripping system is required. Such a chamber must be able to produce temperatures between -40°C (-40°F) and ambient temperature with a variation of no more than ± 0.2°C (± 0.4°F). Most importantly, the environmental chamber must be accessible through a porthole so that the specimen may be introduced for testing without opening the chamber door. Such an arrangement prevents excessive temperature variations due to opening and closing the door. An insulated chamber using liquid nitrogen coolant, with appropriate temperature controlling equipment, was found to be adequate. This system ensures a moisture-free environment within the chamber and therefore minimizes problems with moisture condensation. Alternatively, mechanical refrigeration may be used as long as the air within the charger is kept sufficiently dry to eliminate the formation of frost. When mechanical refrigeration is used, the chamber may have to be purged occasionally with nitrogen or other dry gas to prevent the buildup of frost.

Data Acquisition

Peak indicators (load and deflection or stress and strain) are adequate for specification testing. Within this project, the data were digitized and acquired by means of an IBM-compatible computer and an analog/digital data acquisition board. Two channels, one for load and one for elongation, were acquired and stored in ASCII format.

Testing Protocol

Sample Preparation

The following steps are necessary to prepare specimens.

1. Heating sample. Heat the asphalt in an oven at a temperature not over 135°C (275°F) until it has become sufficiently fluid to pour. The time and temperature required to prepare the sample for pouring will depend on the size of the sample and the hardness of the asphalt. For virgin (tank) asphalt, and for a sample of about 50 g (3 oz) tin, 60 min at 135°C (275°F) has been found to be sufficient. The sample should be stirred from time to time to aid heat transfer and to ensure uniformity. Before pouring, stir the sample of asphalt to remove any air bubbles. Clean and place the mold on a flat horizontal surface.

2. Pouring sample. Place the plexiglass end inserts at both ends of the mold. To facilitate the proper filling of the molds without preheating, the molds should be supported on a

flat aluminum plate 6 mm (0.25 in.) thick. After the test specimen is poured, the entire assembly is allowed to cool to ambient temperature. Cooling should be done in air at ambient temperature—quenching to ambient temperature should not be allowed.

Pour hot asphalt in the mold starting from one end of the plexiglass insert and moving slowly along the mold to the other end in a single pass. The specimen should be poured in a continuous stream to avoid entraining air bubbles or gaps. The pouring operation should be accomplished as quickly as possible to avoid excessive changes in asphalt temperature. Stop pouring when the asphalt is slightly higher than level with the top of the mold.

3. Trimming. Allow the specimen to come to room temperature (about 1 h). Once the specimen is at room temperature, trim off the excess asphalt cement with a heated flat (spatula-type) cheese cutter so that the asphalt is flush with the top of the mold. Take care during the trimming operation that the specimen is not pulled away from the mold.

4. Demolding. Before demolding, the environment chamber should be equilibrated at the test temperature. Place the specimen with the mold in the test chamber for 5 to 10 min. Remove and demold the specimen. It is not necessary to measure the dimensions of the specimen because they are closely controlled in the molding process.

Device Calibration

The loading system and the noncontact, laser-based deformation measuring system are factory calibrated. It is, however, necessary to validate these calibrations. The load cell can be calibrated with dead weights. The extensometer can be calibrated by moving the crosshead a known amount and comparing the extensometer reading with the known movement.

Test Procedure

The following steps were followed when conducting a typical test.

1. Set the environmental chamber at the desired testing temperature and wait until it stabilizes at that temperature (about 1/2 to 1 h).

2. Place the specimen in the chamber and wait 1 h ± 10 min. It is essential to follow the 1 h ± 10 min schedule very carefully to avoid variability caused by physical hardening.

3. After 1 h, mount the specimen on the pins by reaching through the porthole. Do not open the chamber door to mount the specimens because excessive temperature fluctuations will occur.

4. Select the desired deformation rate and load the specimen to failure.

After testing, the asphalt portion of the spent specimen is discarded. The plexiglass end inserts can be cleaned and reused. The plexiglass end inserts can be cleaned by soaking in

Varsol (MS-Solvent or mineral spirit for cleaning asphalt) and wiping with a soft cloth. Acetone, trichloroethylene, or toluene should not be used, as they will dissolve the plexiglass inserts. After wiping the inserts, use a detergent solution to remove any oil residue left by the mineral spirit cleaner. Alternatively, degreasing spray cleaners (safe on plastics) may be used.

Data Analysis

Theoretical

Failure stress is computed by dividing the failure load and the original area of cross-section as shown in equation 3.1:

$$\sigma_f = P_f/A \tag{3.1}$$

where

σ_f = failure stress, MPa (psi)
P_f = failure load, N (lb)
A = original area of cross-section, m^2 (in.^{2}).

Note that for this specimen geometry A = 3.6 E-5 m^2 (0.056 in.^{2})

Failure strain is computed by dividing the elongation at failure and the original gauge length, as shown in equation 3.2:

$$\epsilon_f = \delta_f/L \tag{3.2}$$

where

ϵ_f = failure strain, mm/mm (in./in.)
δ_f = elongation at failure, mm (in.)
L = gauge length, mm (in.)

Note that for this specimen geometry the gauge length L = 27 mm (1.1 in.).

Failure energy, although it is not a specification requirement, can be determined numerically by computing the area under the stress-strain curve to failure. The digitized stress-strain data may be integrated using Simpson's rule or other appropriate numerical method to determine the area under the stress-strain curve.

Failure is defined as that point on the stress-strain curve where the load reaches a maximum value as shown in figure 3.8. When the specimen exhibits brittle or brittle-ductile behavior, as shown in figure 3.9, the specimen will rupture, the maximum load will be very obvious, and, for plain asphalt binders, the maximum stress will typically be obtained at strains less than 10 percent. At higher temperatures, where the asphalt does not rupture but extends to

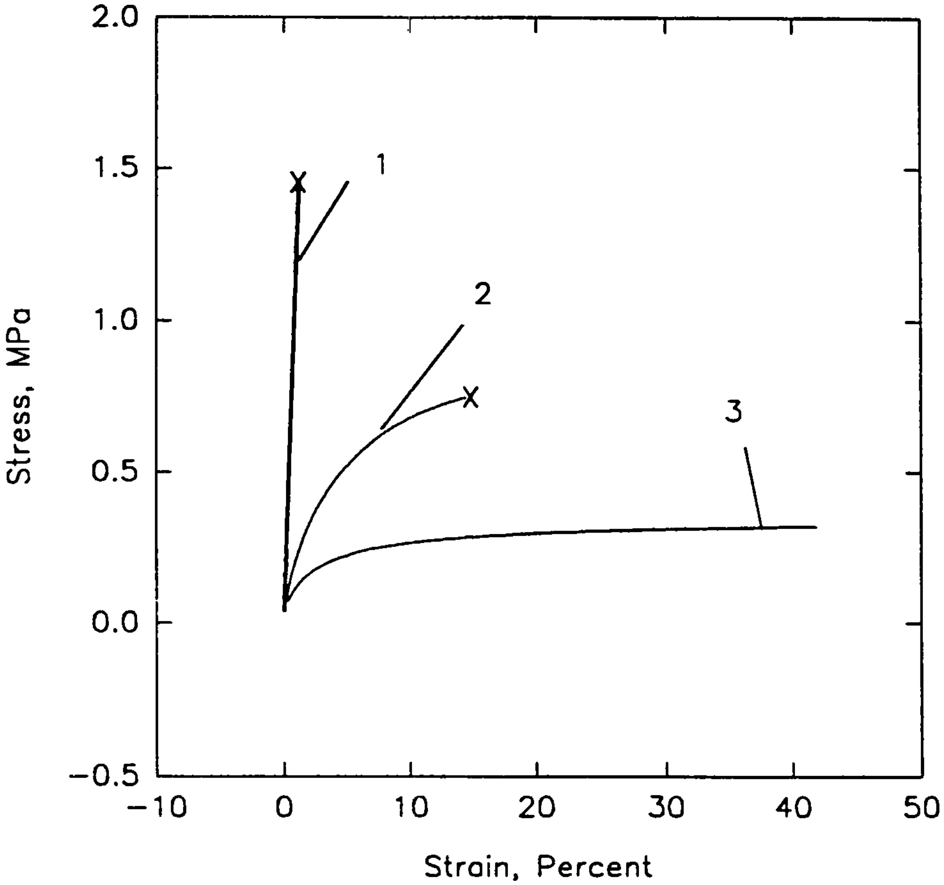


Figure 3.8. Typical Stress Versus Strain Curves.

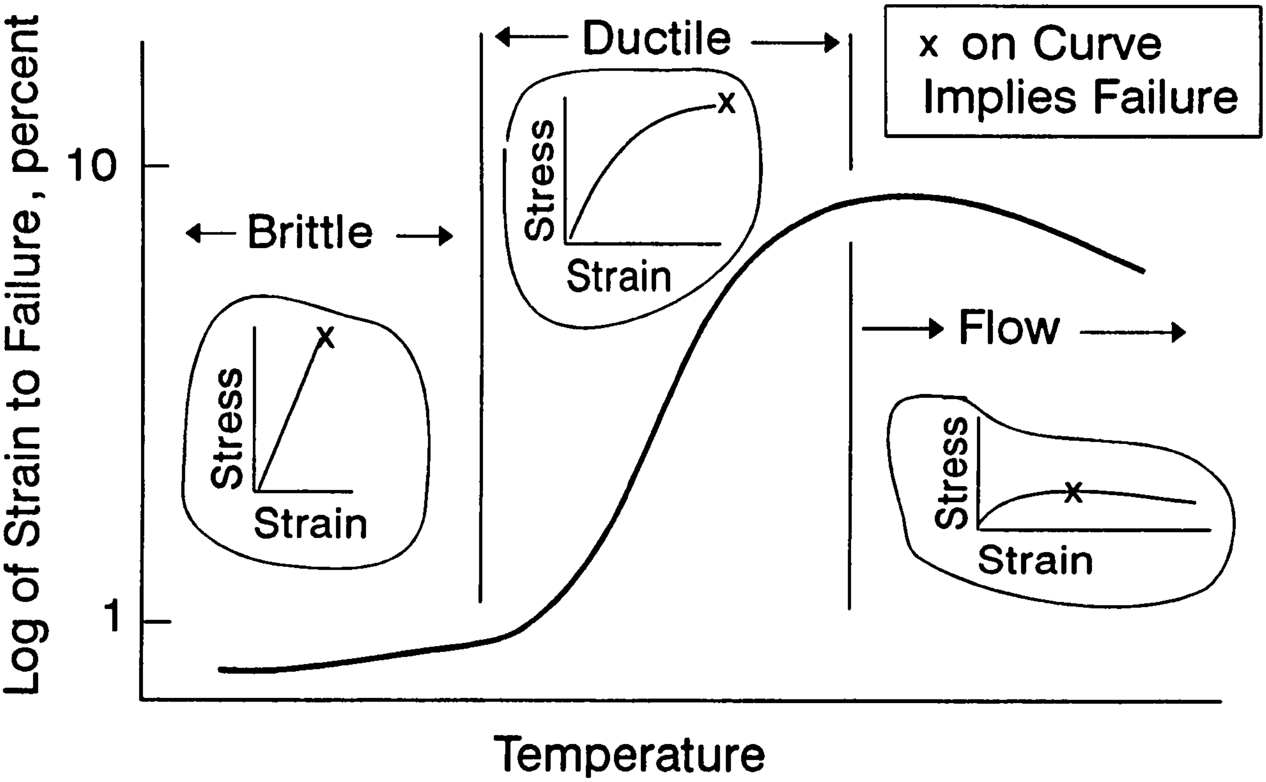


Figure 3.9. Strain Behavior as a Function of Temperature.

larger strains, the maximum load often will be difficult to determine (figure 3.9). The test procedure was developed for small strains (less than 10 percent) and is not considered valid at large strains where an accomodation for the reduction in cross section during loading must be made. The small-strain assumption is not a shortcoming for specification purposes because the test is designed to identify the brittle-ductile transition which occurs at strains of approximately 1.0 percent.

The data acquisition system myst be able to capture the specimen elongation when the load is at maximum. This requires that the load and the strain be indexed to each other in real time. Details regarding the test procedure are given in the specification in appendix C.

The temperature at which the strain-to-failure is 1.0 percent can be determined by plotting the logarithm of the failure strain versus the test temperature. In the range from 0.5 to 10 percent strain, the logarithm of the failure versus temperature generally plots as a linear relationship. This was the case for the plain asphalts tested as part of this project. A sample plot showing the determination of the temperature where the failure strain is 1.0 percent is shown in figure 3.10.

Operator: RD
Date: 10/7/92
Sample ID.: XYZ PAV aged
Comments:

Temperature (°C)	Replicate No.	Failure Strain (%)	Failure Stress MPa
-20	1	0.45	1.40
	2	0.54	1.18
	3	0.39	1.29
	4	0.42	1.16
	Average	0.45	1.26
-10	1	2.31	1.10
	2	2.05	0.89
	3	1.89	1.02
	4	1.65	0.96
	Average	1.98	0.99
0	1	8.0	0.51
	2	7.6	0.49
	3	8.4	0.56
	4	7.3	0.52
	Average	7.8	0.52

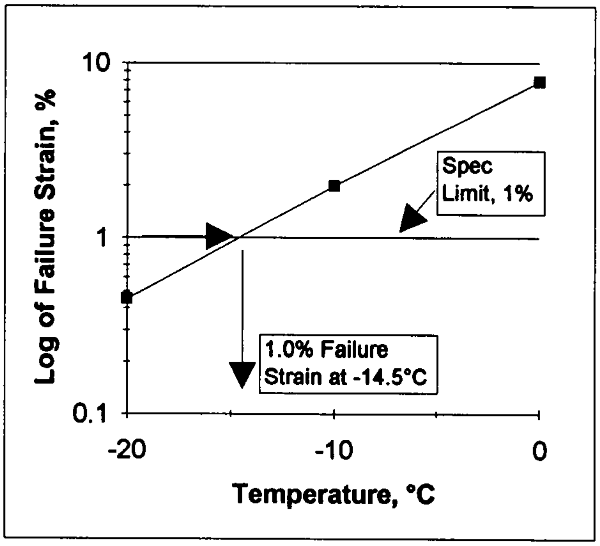


Figure 3.10. Data Sheet Used for Analyzing and Reporting Direct Tension Specification Test Data

Testing Variability

The variability of this test was determined from the following experiment. This experiment contained four replications of an 8 (core asphalts) by 3 (age condition) factorial experiment. However, it should be noted that within each of these 96 primary cells three completely independent experiments were carried out to produce one value of the response variable of interest (the estimated failure strain, stress, or energy for that asphalt at its limiting stiffness condition). Thus, a total of 288 specimens were tested to failure in this experiment. The coefficient of variation was determined from replicate measurements in each cell. It was found that the failure stresses have a coefficient of variation between 5 and 10 percent, whereas failure strains show a 20- to 25-percent coefficient of variation.

Proposed Specification for Direct Tension Test

The proposed specification for the direct tension test was developed in draft form as part of this project and further refined with the cooperation and input of the SHRP Asphalt Binder Rheology Expert Task Group, the A-001 contractor, the Federal Highway Administration and the SHRP staff. Staff from the American Association of State Highway and Transportation Officials (AASHTO) were responsible for organizing the specification in its final format. An AASHTO version of the specification is given in appendix C.

4 Pressure Aging Vessel Procedure

Introduction

Purpose

The pressure aging vessel (PAV) is used to simulate the physical and chemical property changes that occur in asphalt binders as a result of long-term, in-service oxidative aging in the field. The test accounts for temperature effects but is not intended to account for mixture variables such as air voids, aggregate type, and aggregate adsorption.

Scope

The PAV procedure is conducted by placing the asphalt binder in a heated vessel pressurized with air to 2.1 ± 0.1 MPa (305 ± 15 psi) for 20 h. The temperature of the test is varied depending on the climate (grade) in which the asphalt will be used (asphalt binder grade). A temperature range of 90 to 110°C (194 to 230°F) is recommended to represent conditions (in particular the temperature regime) ranging from cold mountain to hot desert temperature regimes. Ten asphalts can be aged in the same vessel with 50 g (0.11 lb) of asphalt in each pan. The aging process is accelerated by the combination of the elevated temperature and the pressure that forces oxygen into the asphalt cement binder thereby accelerating the oxidative aging process.

Description of Equipment

Hardware

The PAV procedure requires, in addition to the pressure vessel, an oven or chamber surrounding the vessel that can maintain precise control of the temperature of the asphalt cement binder; a temperature monitoring system that monitors the temperature inside the vessel; a source of clean, dry, pressurized air; and a set of standard thin film oven pans (ASTM D 1754). Each pan holds 50 g (0.11 lb) of asphalt cement binder to give a film thickness of 3.18 mm (1/8 in.). The levelness of the pans must be maintained during the test to ensure uniform film thickness. The temperature should be controlled to within ± 0.5°C (1.0°F) throughout the 20 h of the procedure. Figure 4.1 shows a schematic of the PAV equipment.

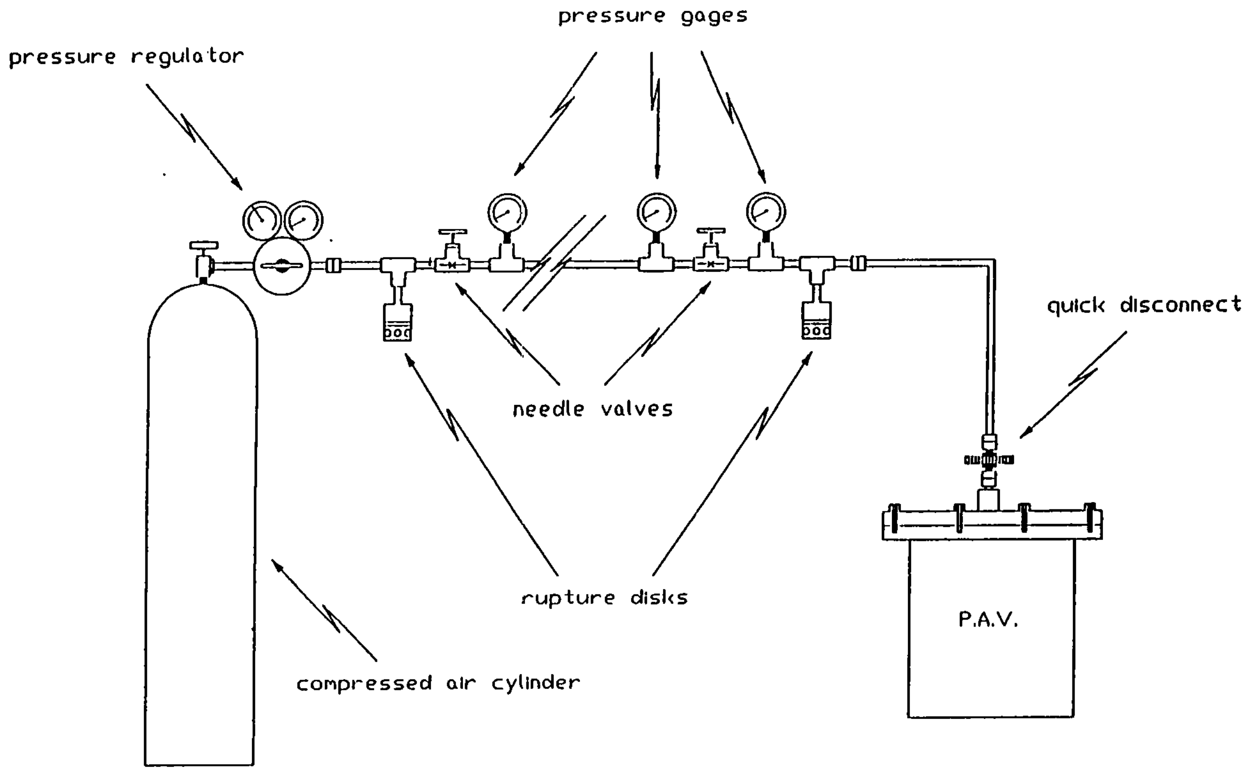


Figure 4.1. The Pressure Aging Vessel Equipment.

The hardware that was used to conduct the pressure aging test during the research and development part of this project is unwieldy because of the need to handle the hot, heavy pressure vessel. Several manufacturers are developing heated pressure vessels that should eliminate the need to handle the vessel. Internally heated vessels, top opening ovens, or other alterations will eliminate the need to transfer the test vessel to and from the oven. Caution should be used to ensure that the temperature within the vessel is uniform. Uniformity will be of particular concern in designs that include a heating mantle as opposed to a fluid or air bath to control the temperature of the vessel.

Data Acquisition

The PAV test is a conditioning test that requires no response recording. However, the temperature and pressure must be monitored throughout the test. Monitoring may be done with a high-low pressure detector or with a recording device. The pressure can be read from a pressure regulator mounted in line with the pressure source. The temperature is measured with a platinum resistance thermometer (PRT) placed inside the vessel. The user is cautioned to be certain that the temperature transducer is properly calibrated. Thermocouples, unless they are calibrated against a standard, are typically reliable to only ± 2°C (± 4°F). PRTs meeting the German Industrial Standards (DIN) 43760 (Class A) are accurate to ± 0.2°C (± 0.4°F) without calibration.

Testing Protocol

Details of the test method are given in the draft specification presented at the end of this chapter. The following is a summary of the test method developed as part of this contract.

Sample Preparation

The PAV procedure is conducted on asphalt binders after aging according to the standard rolling thin film oven test (RTFOT) (ASTM D 2872). Although much of the work done during the project was with the thin film oven test (TFOT) (ASTM D 1754), the RTFOT was selected as the recommended procedure (see below). Samples aged in multiple bottles within a single RTFOT run should be combined directly after the test is run and mixed to produce one homogeneous sample. To prepare samples for the PAV, 50 ± 0.5 g (0.11 ± 0.0011 lb) of the combined material is poured from the combined sample into the PAV pans. Standard stainless steel pans from ASTM D 1754 are used for this purpose.

Two pans of PAV-aged material are sufficient for conducting the specification tests. Additional pans may be aged to allow for wastage and the retention of material for additional testing if needed. Research conducted as part of this study has shown that samples from different sources or of different grades can be commingled in the PAV without adverse effects (see volume 3 of this report).

Device Calibration

Temperature sensor, pressure regulator, and weighing balance are the three units that need to be calibrated. The temperature should be within ± 0.5°C (± 1.0°F) throughout the test. Pressure should be maintained at 2.1 ± 0.1 MPa (305 ± 15 psi) during the test and the balance used to weigh the asphalt binder should be calibrated to ± 0.1 g (± 0.0011 lb).

Test Procedure

1. Turn on the oven, adjust its temperature to the test temperature, and heat the vessel (unpressurized) in the oven until it has reached test temperature.

2. Place the TFOT pans in the pan holder, which typically holds up to ten pans, and place them inside the hot vessel (figure 4.2). Close the vessel and return it to the oven. This step should be carried out quickly so that the change in temperature of the pressure vessel is kept to a minimum.

3. Connect the pressure hose and the PRT to the vessel and leave for approximately 30 min to equilibrate the asphalt samples and pan holder to test temperature. The waiting period will depend on the heat capacity and size of the oven. The waiting period should be sufficient to cause the PRT to read within 2°C (4°F) of the aging temperature.

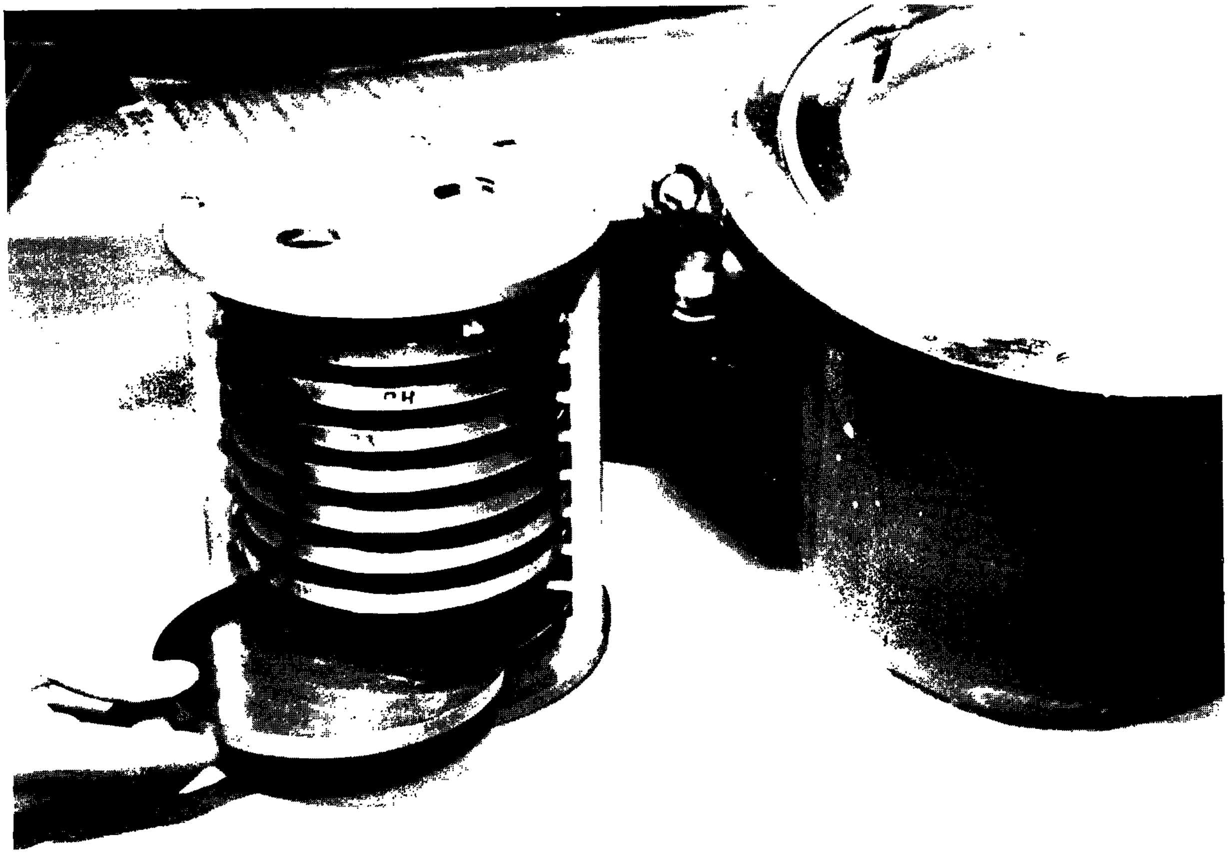


Figure 4.2. The Pressure Aging Vessel and the Pan Holder, Ready for Assembly.

4. Apply a pressure of 2.1 ± 0.1 MPa (305 ± 15 psi) and start timing the test. Keep the pressure and temperature constant for 20 h.

5. After 20 h, release the pressure at a slow rate (10 min to go from 2.1 MPa [305 psi] to atmospheric pressure). Open the oven and let the vessel cool for 30 min. If the pressure is not released slowly, the absorbed gasses will cause the asphalt binder to foam.

6. Remove the vessel from the oven, open the vessel lid and remove the pan holder.

7. Heat the asphalt pans in an oven for 30 min at 135°C (275°F) to allow air entrapped in the samples to reach the surface. Pour the sample from the pans into storage containers.

Points of Caution

The oxidative aging resulting from the PAV procedure is sensitive to a number of factors that need to be controlled to obtain repeatable, reliable results. The following are important factors.

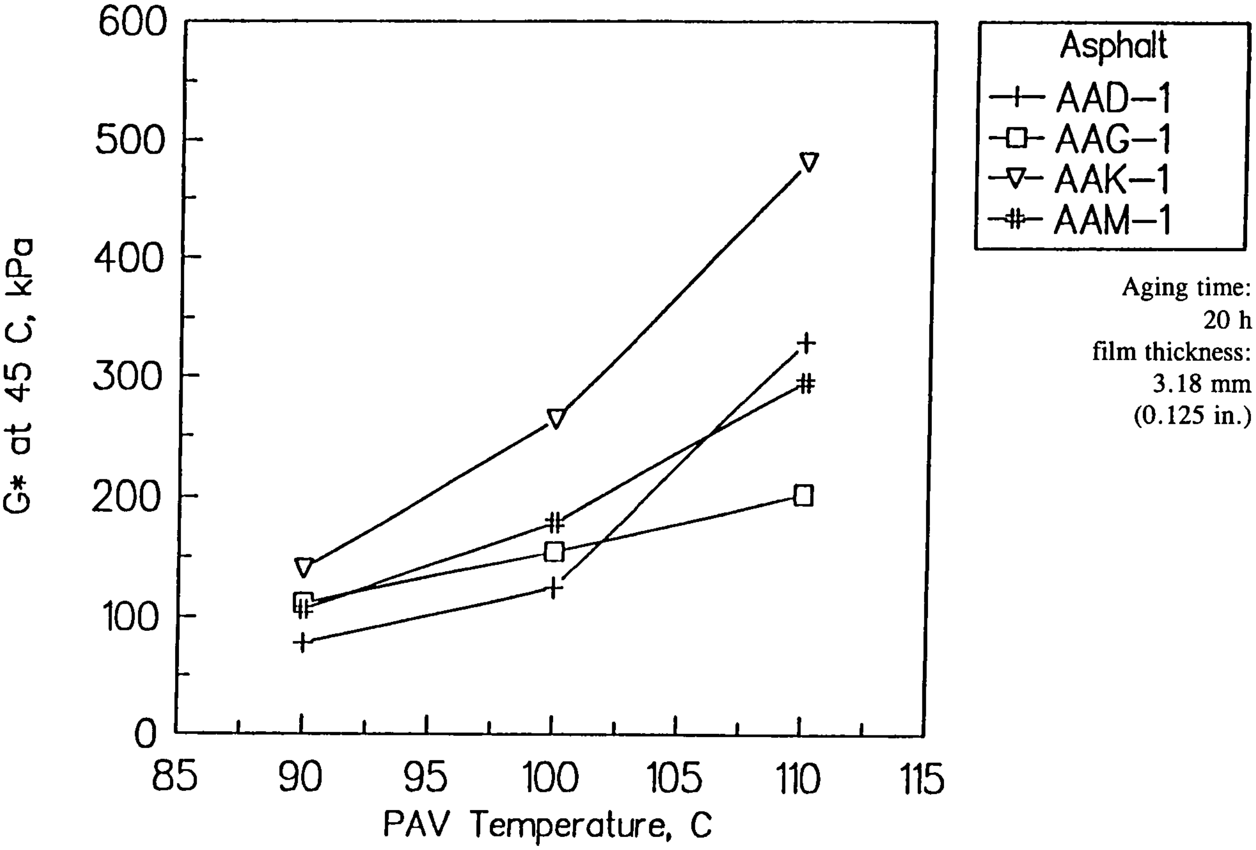


Figure 4.3. Effect of PAV Temperature on Aging of Asphalts for the 20-H Procedure.

1. Film thickness. Oxidation of asphalts is diffusion limited. Therefore, the film thickness of the asphalt binder is very important. For heavily modified asphalts, the specific gravity should be measured such that the weight of binder in each aging pan is adjusted to result in a film thickness of 3.18 mm (1/8 in.).

2. Temperature. Temperature of the asphalt during pressure aging should be controlled to within ± 0.5°C (1°F). Test temperature has a strong effect on the accelerating effect of the pressurized aging and must be carefully controlled (figure 4.3).

3. Levelness of aging pans. Since film thickness is an important factor, and since aging is related to film thickness, maintaining a uniform film thickness in each pan is important to ensure uniform aging that is repeatable. Thus it is important that the pans in the PAV be level when placed in the oven. When a separate vessel is used in an oven the shelves in the oven should be reinforced so that they do not bend under the weight of the PAV.

4. Time of test. When the pans and pan holder are placed in the oven, the PAV and its contents will be below the test temperature. The temperature of the PRT inside the PAV should read within 2°C (4°F) of the test temperature before the pressure is applied. Once pressurized, the temperature inside the PAV will equilibrate very rapidly. The time under pressure is the aging time (20 h required). Relatively little aging occurs at ambient pressure given that RTFOT residue is being tested.

Data Analysis

There is no data analysis involved with the PAV aging procedure. Temperature during aging must be recorded but no analysis of this data is needed.

Data Presentation

The PAV procedure is not a test. It is a conditioning step designed to simulate oxidation in the field. The only data that must be collected during the procedure are the temperature and the pressure used during aging. The data do not reflect behavior of the material but indicate that the temperature and pressure during the test are within the required limits. In the SHRP specification the aging pressure is 2.1 ± 0.1 MPa (305 ± 15 psi) irrespective of the grade of the asphalt. The aging temperature, however, varies according to the grade.

If the aging is being done to *verify* the grade, the temperature of aging is defined by the temperature of the environment. If the grade is not known, then the aging should be done after the results from dynamic shear rheometry on the original binder and the RTFOT-aged binder are known. The first number in the grading (the 64 in PG 64-22) is determined from the dynamic shear measurements on the tank and RTFOT residue. The first number dictates the PAV aging temperature.

Testing Variability

Data needed to determine the repeatability of the PAV aging procedure for the specification time-temperature schedule described above, 90 to 110°C (194 to 230°F) for 20 h were not available at the end of the project and obtaining such data was not within the scope of the project. However, an earlier experiment was conducted to evaluate the repeatability of the PAV procedure using 144 hours at 60°C (140°F). The results are shown in table 4.1. The experiment was based on three asphalts, and nine laboratories were included in the program.

In evaluating the variability of the results from 60°C (140°F) multiple-lab testing, it was concluded that the TFOT (ASTM D 1754) rather than the PAV was the primary source of the variability. ASTM is currently in the process of revising the TFOT. Revisions to the test should improve the reliability of the TFOT. The binder specification as recommended by SHRP considered only the RTFOT with the rationale that allowing both the TFOT and RTFOT procedures would effectively double the number of specifications because the two tests differ in severity for different asphalt binders. The RTFOT was selected because it is more repeatable and apparently better suited to polymer-modified asphalts.

Proposed Specification for Pressure Aging Test

The proposed specification for the pressure aging test was developed in draft form as part of this project and was further refined with the cooperation and input of the SHRP Asphalt Binder Rheology Expert Task Group, the A-001 contractor, the Federal Highway Administration, and SHRP staff. Staff of the American Association of State Highway and Transportation Officials (AASHTO) were responsible for organizing the specification in its final format. An AASHTO version of the specification is given in Appendix D.

Table 4.1. Summary of Statistical Analyses of Pressure Aging Vessel Round-Robin Test Data.

Response Variable	Within-Lab Std. Dev.	Within-Lab CV (%)	Lab-to-Lab Dev.	Overall Dev.	Overall CV (%)
$(\mathrm{Pen}_{\mathrm{TFOT}}/\mathrm{Pen}_{\mathrm{Tank}})100\%$	5.88	9.6	1.8	6.14	10
$(\mathrm{Pen}_{\mathrm{TFOT+PAV}}/\mathrm{Pen}_{\mathrm{Tank}})100\%$	2.52	8.7	2.1	3.2	11.3
$(\mathrm{Vis}_{\mathrm{TFOT}}/\mathrm{Vis}_{\mathrm{Tank}})100\%$	25.0	10.8	9.4	26.7	11.5
$(\mathrm{Vis}_{\mathrm{TFOT+PAV}}/\mathrm{Vis}_{\mathrm{Tank}})100\%$	197.7	16.7	102.8	222.8	18.8

Notes: SD = standard deviation; CV = coefficient of variation

Two replications at nine laboratories; asphalts AAC-1, AAD-1, and AAG-1.

Note that the lab-to-lab variation appears to be reasonable for this experiment. The within-lab standard deviation includes both the experimental error and the measurement error variation but the major part is likely to be the experimental error.

For an overall standard deviation, the square root of the sum of squared lab-to-lab and within-lab standard deviations is the appropriate quantity. This overall standard deviation corresponds to the uncertainty if one selects a laboratory (such as the ones included in this study) at random and sends it a sample of asphalt to be measured, aged, and measured. Repeating such a process would result in values with this overall standard deviation.

5 Rotational Viscometry

Introduction

Purpose

The rotational viscometer is used to determine the coefficient of viscosity of asphalt cement binders at the high temperatures that typically occur during blending and shipping, during the plant mixing of hot-mix asphalt concrete, and during hot-mix laydown and field compaction operations.

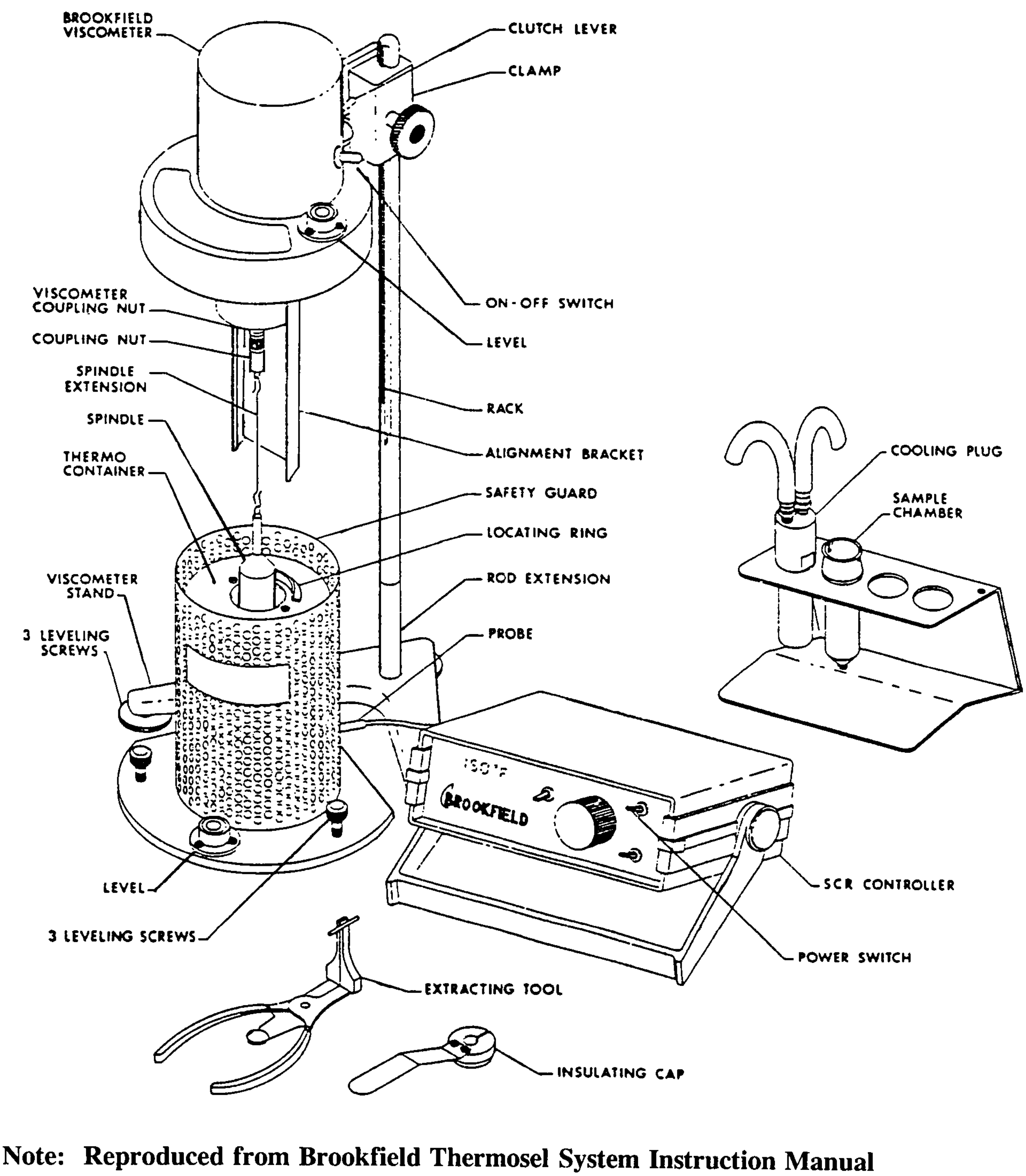
Scope

The rotational viscometer is a rotating spindle-type viscometer that meets the requirements of the ASTM Standard Test Method for Viscosity Determination of Unfilled Asphalts Using the Brookfield Thermosel Apparatus (ASTM D 4402-87). The viscometer can be used to measure the viscosity of asphalt cement binders in the range of 0.01 Pa·s (0.1 poise) to 200 Pa·s (2000 poise). These coefficients of viscosity are typically measured within the temperature range of 100 to 260°C (212 to 500°F). This test method can be used for general specification and is especially convenient for use at a field laboratory or plant site. The method is also used in the proposed SHRP binder specifications for the determination of viscosity–temperature profiles by obtaining test data at two test temperatures.

Description of Equipment

Hardware

The Brookfield Model DV-II viscometer and Thermosel temperature control system or their equivalents are used for this test method. A schematic of the main parts of the viscometer and the Thermosel (temperature-controlled cell) is shown in figure 5.1. A viscosity measurement is obtained by inserting the spindle into a sample of asphalt binder contained in the temperature-controlled cup or Thermosel. The viscometer is then operated by rotating the spindle until the required torque becomes constant. The sample size depends on the size of the spindle; a 10.5 mL sample is required for the SC4-27 spindle recommended by the Texas Transportation Institute research team (see volume 3, chapter 6 of this report).



Note: Reproduced from Brookfield Thermosel System Instruction Manual

Figure 5.1. Schematic of the Brookfield Thermosel System.

During the test the spindle is rotated by a motor. The torque necessary to rotate the spindle is measured by applying the torque through a beryllium copper spring. The degree to which the spring is wound, detected by a rotational transducer, is used to calculate the torque. Given the torque, the rotational speed of the spindle, and the geometry of the spindle and cup, it is possible to calculate a coefficient of viscosity for the sample. The viscometer is powered by a precision synchronous motor that is mounted on a stand. The viscometer must be leveled to ensure that the spindle is aligned with the center of the Thermosel.

Data Acquisition

The rotational viscometer contains electronic circuitry that monitors the applied torque and automatically displays the calculated viscosity (figure 5.2). The keypad on the instrument is used to enter the spindle number, zero the signal, and run the test at a selected speed. Torque and viscosity can be recorded manually or an interface (optional software) can be used to send the signal from the instrument to a personal computer. Optional software is also available that can be used to program preselected thermal profiles. This software is not needed for the specification test. However, it is mandatory that the Thermosel be used to control the temperature and thereby obtain acceptable reproducibility.

Testing Protocol

Sample Preparation

The following protocol has been found to be adequate for measuring the coefficient of viscosity at a preselected temperature. When it is necessary to obtain a temperature-viscosity profile, two temperature measurements are required, as discussed below. The SHRP binder specification provides guidelines for selecting the appropriate test temperatures (table 1.1).

1. Oven-heat approximately 30 g of the asphalt binder *only* until it has become sufficiently fluid to pour. Use caution to avoid overheating the sample. For most asphalt binders, the oven temperature should not exceed 150°C (302°F). The sample should be stirred occasionally to ensure homogeneity and to remove air bubbles. Caution should be used to avoid entrapping air during the stirring.

2. Weigh 10.5 ± 0.1 g of the asphalt binder into the Thermosel sample chamber. The sample weight must be carefully controlled to obtain reproducible results, because the sample volume, as determined by the weight of the sample, is used in the calculation of the viscosity.

3. Using the extraction tool, place the filled chamber containing the reweighed sample of asphalt binder into the Thermosel. Lock the chamber into position as shown in figure 5.3.

4. Turn the Thermosel controller on and set the temperature to the selected test temperature. Approximately 20 min are required to bring the sample to thermal equilibrium. Allow the spindle to rotate until a constant torque or viscosity value is obtained. Typically, 20 to 30 sec are required for the measuring system to equilibrate so that constant torque or viscosity values can be observed.

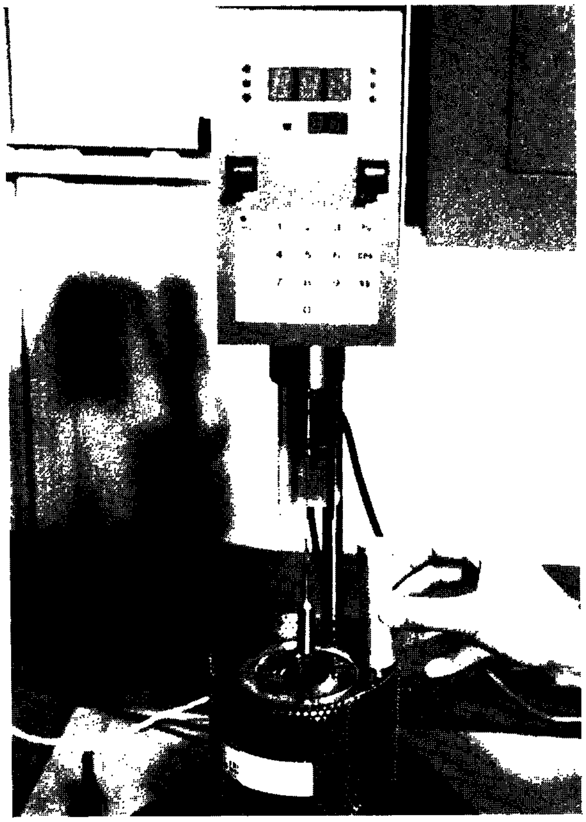


Figure 5.2. The Viscometer Digital Pad.

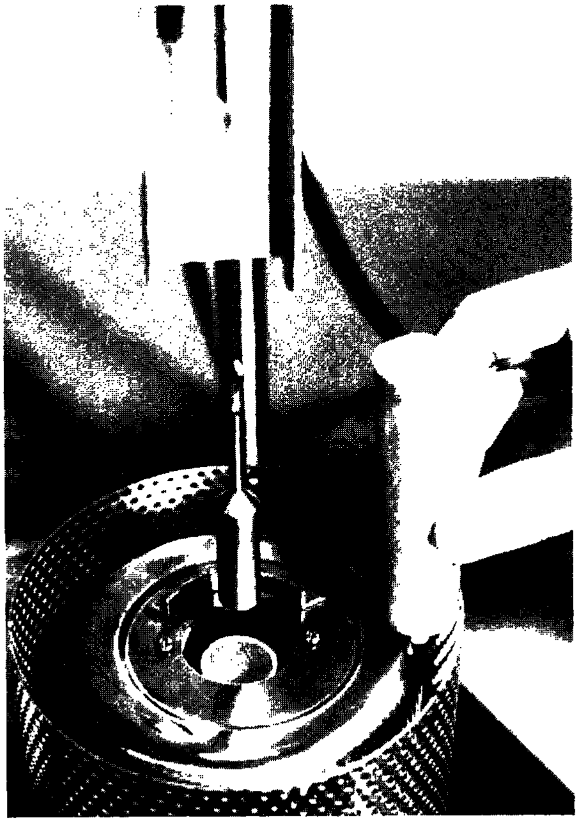


Figure 5.3. Sample Chamber Being Placed Inside the Thermosel Apparatus.

5. If a measurement is to be made at a second temperature, set the Thermosel controller for the desired temperature. Wait until the Thermosel comes to thermal equilibrium and repeat the testing process at the new test temperature.

Device Preparation and Test Procedure

Preparing the device, leveling and aligning of the viscometer on the stand, and setting the temperature of the temperature controller of the Thermosel are explained in the operation instructions provided by the manufacturer. The calibration of the temperature controller and the calibration of the viscometer are also explained in those instructions. The detailed steps for testing are specified in the ASTM Standard Test Method for Viscosity Determination of Unfilled Asphalts Using the Brookfield Thermosel Apparatus (ASTM D 4402-87), section 7. Based on the work done at the Texas Transportation Institute, spindle type SC4-27 and 20 rpm were recommended in the standard method.

Points of Caution

The rotational viscometer test is an ASTM standard method (ASTM D 4402). The reader is referred to the standard method for points of caution and details regarding the test method.

1. Shear rates. Viscosity data obtained with this test method are used to ensure pumpability, mixibility, and compactibility. Ideally, the shear rates during the test should match, as closely as possible, the shear rates associated with each of these processes. Therefore, a zero shear rate condition or apparent shear rate is not desired. The rotational speed of the spindle was selected to maximize the shear rate for the device. Changing spindle sizes and rotational speeds affect both the shear rate and, for shear-rate-dependent materials, the measured viscosity.

2. Pretreatment of the sample. Pretreatment of the sample may affect the measured coefficient of viscosity for some asphalt binders, especially those modified with some polymers. For materials that are shear-rate-dependent, the sample to be tested should be heated to above the test temperature and stirred vigorously. After stirring, care should be taken to remove all air bubbles from the specimen. At this time there are insufficient data upon which to base a more specific pretreatment of the sample.

3. Excessive heating. Excessive heating may cause volatiles to be lost from the sample thereby decreasing the viscosity. Some modified systems may also be irreversibly altered by excessive heating. In general, during the preparation and measurement process the sample should not be heated to temperatures greater than those used during handling, pumping, storage, or mixing and compaction.

Data Analysis

Theoretical

The Thermosel system contains an inner spindle and an outer cylinder and is properly referred to as a rotational coaxial cylinder viscometer. The following formulas are used to calculate shear rate, shear stress, and viscosity:

Shear rate (s^{-1}): $$S' = (2R_c^2 / R_c^2 - R_b^2) \tag{5.1}$$

Shear stress ($dynes/cm^2$): $$F' = (M / \pi R_b^2 L) \tag{5.2}$$

Viscosity (poise): $$\eta = F' / S' \tag{5.3}$$

where F' = shear stress ($dynes/cm^2$)
S' = shear rate at surface of spindle (s^{-1})
ω = angular velocity of spindle (rad/s)
R_c = radius of container (0.9525 cm, 0.372 in.)
R_b = radius of spindle (spindle selected is SC4-27 with R_b = 1.176 cm, 0.453 in.)
M = torque input by instrument
L = effective length of spindle (for SC4-27, L =3.302 mm, 1.3 in.)
η = viscosity (poise)

The Brookfield viscometer displays the coefficient of viscosity in centipoise. The coefficient may be converted to pascal seconds by using the conversion factor 1 cps = 0.001 Pa·s.

Data Presentation

Rotational viscometer data are used to ensure that asphalt cement binders at pumping and mixing temperature are sufficiently fluid to handle. Therefore the testing temperature is the same regardless of the grade of the asphalt or the climatic conditions at which the asphalt will be used. If data from the rotational viscometer are used to *verify* the specification requirements, it is sufficient to conduct a single test (two replicate test specimens) at the specification temperature of 135°C (275°F) and to determine the steady state viscosity. If the viscosity is less than 3 Pa·s (≈ 3,000 cSt), the sample meets the specification requirement; otherwise it fails the specification.

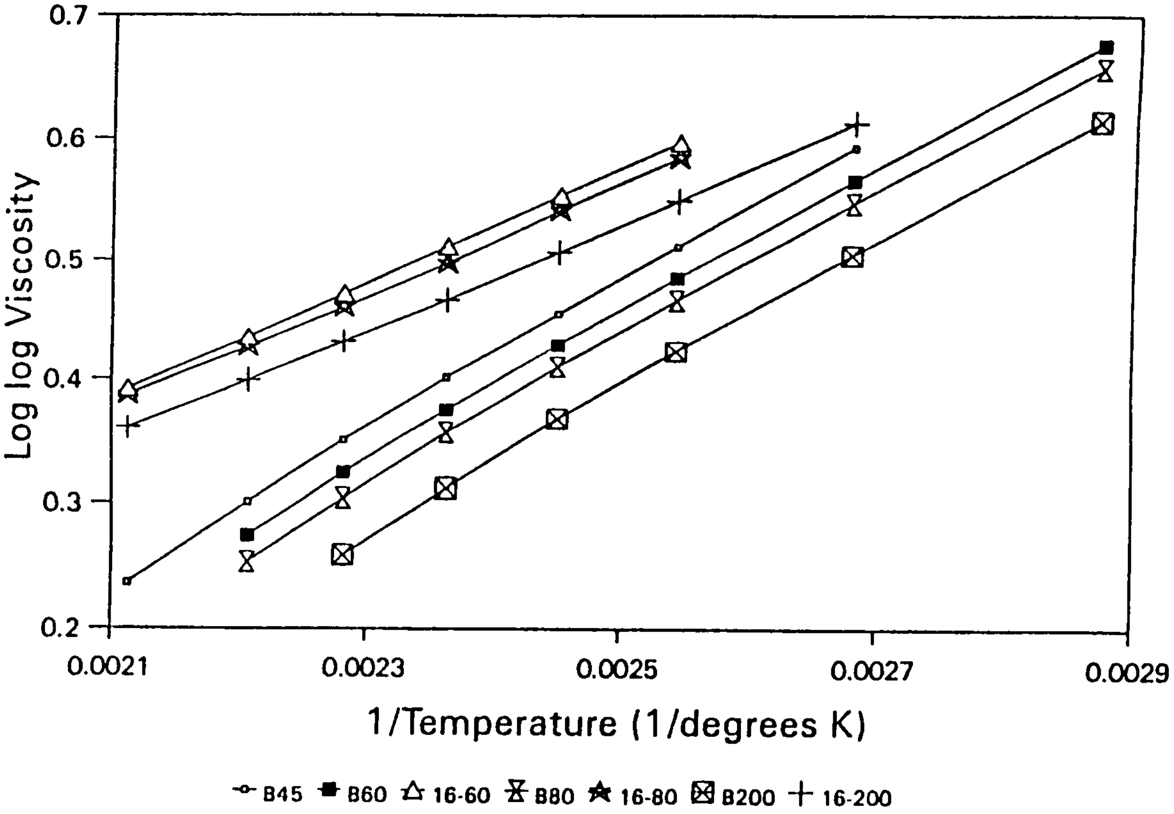
The rotational viscometer can also be used to establish viscosity–temperature profiles for compaction purposes. Viscosity–temperature profiles are often required for determining mixing and compaction temperatures and for other purposes. Originally, the researchers attempted to establish viscosity–temperature profiles by continuously changing the temperature of the Thermosel, thereby yielding a continuous recording of viscosity versus temperature. This procedure proved to be unacceptable because of thermal lag between the indicated temperature (measured in the Thermosel) and the actual temperature of the sample. A continuous viscosity–temperature profile is still a valid objective; however, the device requires considerable redesign before this objective can be accomplished. Such development work was outside the scope of this project.

At the higher temperatures typical of mixing and compaction, the coefficient of viscosity is generally plotted as a linear relationship when the axes are transformed to the log–log of viscosity versus the reciprocal of the absolute temperature. A representative plot for a number of asphalt binders is shown in figure 5.4. Coefficients of regression, R^2, for such plots typically exceed 0.999.

When a viscosity–temperature curve is required it may be more expeditious to obtain the first data point at the lower temperature rather than the higher temperature. The Thermosel does not have well-controlled cooling capabilities and thus the temperature of the test sample may be increased more rapidly than it can be cooled. Considerable time may be required to cool the sample to a lower test temperature. Until additional experience is gained, temperature differentials much in excess of 50°C (90°F) between measurements should be avoided because the log–log viscosity versus reciprocal of absolute temperature may not be linear over the entire range from 60°C (140°F) to 165°C (329°F). A standard viscosity-temperature chart is also given by ASTM D 2493 and may be used to plot viscosity data (figure 5.5). The current chart is given in terms of centistokes but is being modified by ASTM to include a viscosity scale in pascal seconds.

Testing Variability

The Brookfield DV-II viscometer and Thermosel system have proven to be extremely reliable with regard to the accuracy and reproducibility of results. ASTM Standard Test Method D 4402-87 requires that the 95 percent confidence level for duplicate values by the same



Coefficient of correlation (R_2) > 0.999 for all lines

Figure 5.4. Plots of Logarithm-Logarithm Coefficient of Viscosity versus Reciprocal of Absolute Temperature.

operator be considered suspect if the values differ by more than 3.5 percent. The arithmetic average of duplicate measurements reported by two laboratories should not differ by more than 14.5 percent.

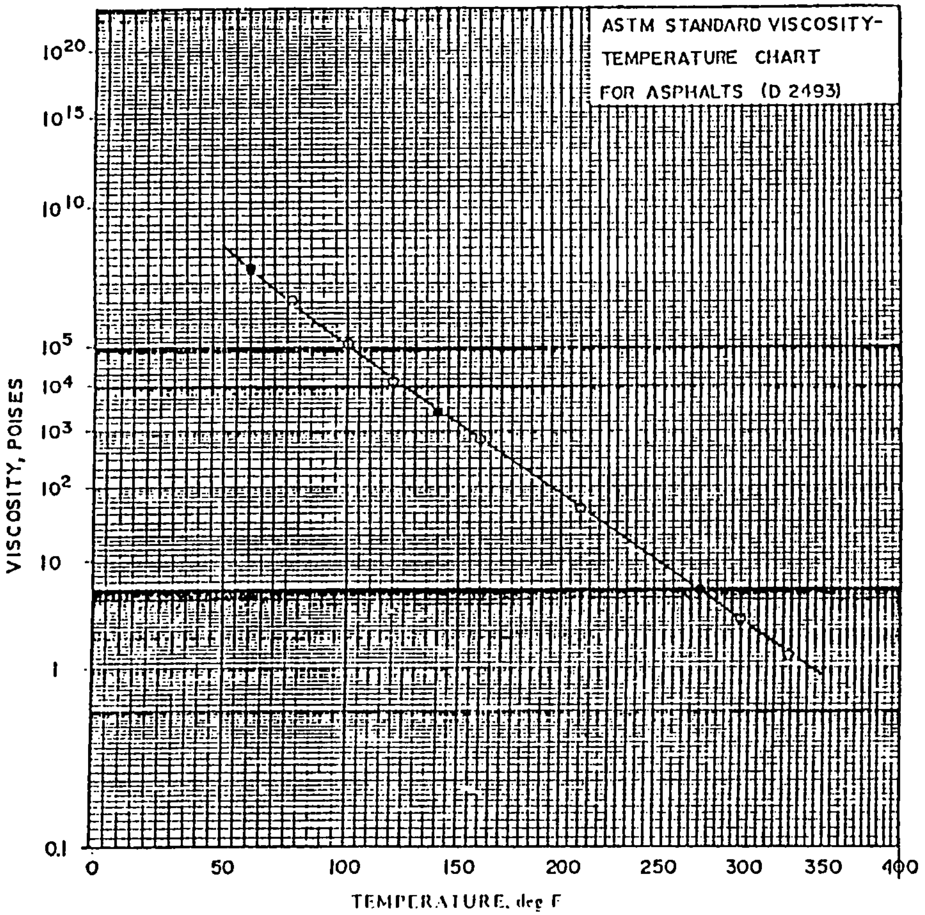
Viscosity as a function of temperature for a high temperature-viscosity standard oil is shown in figure 5.6. The standard values for the oil are 8.875 Pa·s (88.75 poise) at 93.3°C (200°F) and 4.39 Pa·s (43.9 poise) at 148.9°C (300°F). The instrument was capable of measuring viscosity within 2 percent of the standard value. Viscosity standards, therefore, provide an acceptable means for checking the calibration of the device and variability resulting from viscometer or operator effects.

Statistical analyses were performed by the Texas Transportation Institute (TTI) to determine the within-laboratory repeatability of the Brookfield viscometer and test procedure. The data consist of two replicate viscosity measurements of eight different sources of asphalt, with approximately five measurements, each at a different temperature. Repeatability for this paired data set was determined by means of the paired t test. The two sets of the paired data are assumed to be no different from each other; that is, their means are the same ($\mu_1 - \mu_2 = 0$, the null hypothesis). This hypothesis was checked to determine whether, for a given confidence level, it could be rejected. If there was sufficient evidence to disprove the hypothesis, it was rejected; otherwise, it was accepted.

Operator :

Date :

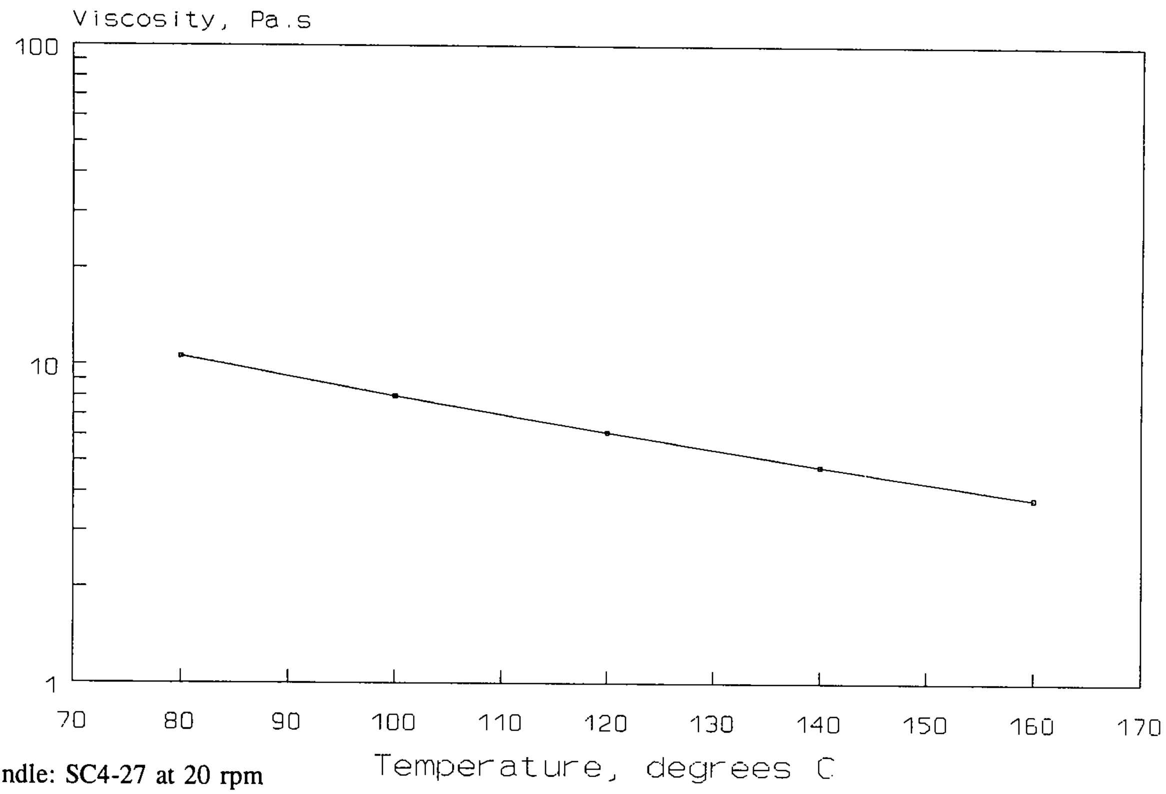
Asphalt :



Test Data

Spindle No	*Speed RPM*	*Temperature C*	*Capillary Viscosity Pa.s*

Figure 5.5. Data Sheet for Plotting Viscosity-Temperature Profile.



Spindle: SC4-27 at 20 rpm

Figure 5.6. Brookfield Viscosity versus Temperature for a Commercial High-Temperature Viscosity Standard Oil

For the Brookfield viscosity data, test 1 and test 2 had mean values of 1.384 and 1.363 Pa·s (13.84 and 136.3 poise), respectively. The difference in means, μ_D, was 0.0215 Pa·s (0.215 poise) and the standard deviation of the differences, s_D, was 0.1455 Pa·s (1.455 poise). Using the following relationship:

$$t_{paired} = (\mu_D \ / \ s_D)\cdot\sqrt{n} \tag{5.4}$$

where n = number of pairs, t_{paired} was calculated to be 0.9091. For a 95 percent confidence level, and 38 data points, the $t_{a/2,n-1}$ value was given as 2.025. According to the statistical procedure, for the hypothesis to be rejected, the necessary condition is $t_{paired} \geq t_{a/2,n-1}$. Since this condition was not satisfied, there was insufficient evidence to reject the null hypothesis. Hence it can be stated, with a 95 percent confidence, that the two test runs are not different from each other. These results reinforce the acceptability of the Brookfield viscometer as a specification device.

Specification

The work done during this project did not involve any additional development or refinement of the existing text method.

6 Analyses of Asphalts by Standard Analytical Techniques

Introduction

The analytical methods described below are standard research techniques used in the study of fossil fuels and other organic materials. Two techniques, infrared functional group analysis (IR-FGA) and Heithaus titration, had been specifically developed for the study of asphalts before the beginning of the SHRP research activities. A large number of data exists in the literature for asphalts studied using the techniques described below. Therefore, to permit a comparison of SHRP work with other studies, the classical methods of chemical analysis were performed on the SHRP asphalts.

Elemental, infrared, molecular weight, and nuclear magnetic resonance (NMR) analyses provide chemists with useful information about any organic substance. With the exception of the infrared method, it is anticipated that highway testing laboratories would not perform these analyses, but will use the facilities of numerous commercial analytical laboratories.

Elemental Analysis

Most elemental analyses were performed by the Analytical Services Division of Western Research Institute, using standard methods. Carbon, hydrogen, and nitrogen analyses were obtained with a Perkin-Elmer 2400 C-H-N Analyzer. Trace nitrogen analyses were obtained with a Dohrmann nitrogen analyzer. Sulfur analyses were obtained with a Fisher 470 Sulfur Analyzer. Oxygen analyses were obtained with a Coulometrics Inc. analyzer. Metal analyses were obtained with a Jarrel-Ash 1100 ICP following digestion in sulfuric acid. For these elemental analyses, replicate determinations were performed from randomly selected samples to serve as quality controls. The original asphalts were also analyzed for carbon, hydrogen, and nitrogen with a Leco C-H-N 600 (Wyoming Analytical Laboratories).

Infrared Analysis

IR-FGA were obtained on a Perkin-Elmer 983G infrared spectrophotometer using a method developed by Petersen (1986). Because of differences among spectrophotometer sources, extinction coefficients must be calculated using model compounds before the method can be implemented in a laboratory. Before undertaking the quantitative IR-FGA of asphalts, one should read and thoroughly understand Petersen and the references cited therein. An understanding of the principles of infrared spectrometry is necessary to carry out these analyses.

Infrared spectrometry is used to identify and quantify several chemical functional groups of interest to the asphalt scientist. Among these are the hydroxyl groups of phenols, imino groups of pyrrolic compounds, carbonyl groups of carboxylic acids, and carbonyl groups of 2-quinolones, all of which are found in neat asphalts. Upon oxidation, ketone, carboxylic acid anhydride, and sulfoxide groups form in asphalts. Structures of these functional groups are illustrated in volume 2, figure 9.1. The measurement of the carbonyl functionality of an asphalt is of particular importance, because of the correlation with viscosity for a given asphalt. Infrared carbonyl absorbance contains contributions from ketones, carboxylic acids, and carboxylic acid anhydrides. The IR-FGA method was devised to measure relative amounts of each of these species. The total carbonyl absorbance in the infrared spectrum at approximately 1,700 cm^{-1} of a solution of asphalt in carbon disulfide is measured, and then another sample of the asphalt is treated with sodium hydroxide solution. The result of this treatment is the conversion of carboxylic acids and carboxylic acid anhydrides to sodium salts of carboxylic acids. Ketones are not affected by the treatment, so comparison of carbonyl absorbance after sodium hydroxide treatment with carbonyl absorbance of untreated asphalts yields a direct measurement of ketone content. The sodium hydroxide reagent also converts phenols to phenolate salts, but does not react with pyrroles. Phenolic hydroxide and pyrrolic imino peaks overlap in untreated materials, and so the base treatment allows for a direct measurement of imino groups, from which phenolic hydroxide may be calculated.

The reagent triphenyl tin hydroxide reacts with carboxylic acids. After a sample of asphalt is treated with this reagent, carbonyl absorbance in the 1,700 cm^{-1} region is composed of contributions of ketones and carboxylic acid anhydrides. Thus, by comparing areas under carbonyl peaks in neat asphalts, sodium hydroxide-treated asphalts, and triphenyl tin hydroxide-treated asphalts, amounts of ketones, carboxylic acids, and carboxylic acid anhydrides may be estimated.

Sulfoxides also are separately quantified in the above procedure.

In oxidatively aged asphalts, ketones are the dominant carbonyl functional group. In many cases, it may not be essential to measure carboxylic acid and anhydride concentrations, as ketone concentration alone provides a good estimate of the extent of aging. Therefore, a simplification of the IR-FGA method has been developed for estimation of the ketone content of asphalts. A 50 mg sample of asphalt is dissolved in 1.00 mL carbon disulfide, and an infrared spectrum of this solution versus carbon disulfide is obtained. If substantial amounts of ketones are present, a peak centered at approximately 1,700 cm^{-1} will be observed. The height of the peak is measured from a baseline drawn from peak minima at 1,750-1,780 cm^{-1} to 1,630-1,640 cm^{-1}. Another solution of the asphalt in tetrahydrofuran (50 mg asphalt in 1.00 mL) is made, and a differential spectrum of this solution versus the carbon disulfide solution is taken. If any carboxylic acids are present, as evidenced by the differential spectrum, the peak height of the differential spectrum is multiplied by 1.5 and this value is subtracted from the carbon disulfide peak height. The remaining absorbance units are converted to moles per liter of ketones using the correlation curve illustrated in figure 6.1.

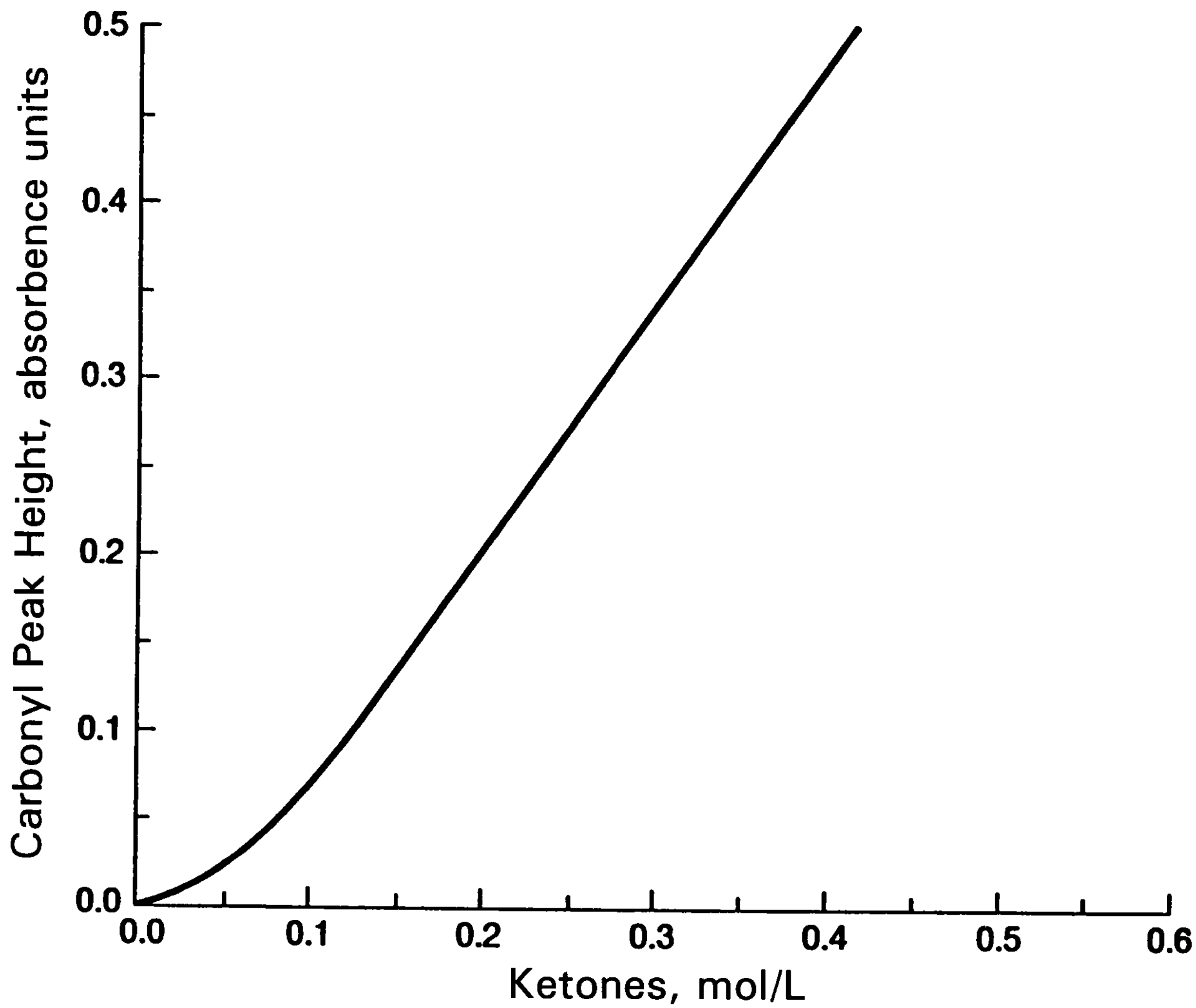


Figure 6.1.Correlation Curve for Conversion of Infrared Carbonyl Peak Heights into Ketone Concentrations.

Molecular Weight Analysis

Molecular weights were determined by vapor phase osmometry in toluene or pyridine at 60°C (140°F) using ASTM Method D 2503.

Metalloporphyrin Analysis

Metalloporphyrin analyses were performed by the method of Sugihara and Bean (1962) using a Beckman DB spectrophotometer with an attached Beckman Linear Recorder, model 385. Samples of asphalt weighing about 0.050 g were dissolved in chloroform (EM Sciences) and the solution was transferred to a 100 mL volumetric flask. Chloroform was added to the flask to the volume mark. A 5.0 mL aliquot of this solution was pipetted into another 100 mL volumetric flask. Chloroform was added to this flask to the volume mark. An aliquot of this solution was transferred to a 1.0 quartz cell, and the spectrum was recorded between 350 and 550 nm. The reference cell contained chloroform. Recorder chart speed was 5 cm/min.

A base line was drawn under the peak centered at 400 nm in the recorded spectrum. The area under this peak was compared with the area under the same peak in a spectrum of 0.050 g Boscan asphaltenes (prepared by precipitation from an n-pentane solution of Boscan crude oil) known to contain 29.0 μM/g porphyrins. This material has been used as a reference material for porphyrin analyses in crude oils because Boscan crude contains large amounts of these compounds. A weighed sample of a model vanadyl porphyrin such as vanadyloctaethylporphine or etioporphyrin dissolved in chloroform could also be used as a standard. If a model vanadyl porphyrin is used, only small amounts are required, as porphyrin extinction coefficients at 400 nm are large ($\epsilon \approx 10^5$).

Nuclear Magnetic Resonance

Liquid-state ^{1}H and ^{13}C NMR measurements were made on a JEOL GSX-270 NMR spectrometer. The experimental conditions for recording a ^{1}H spectrum were 8 scans, a pulse width of 5.4 μs (45°), an acquisition time of 1.5 s, a pulse delay of 20 s, and 16K time-domain data points. The conditions for recording a ^{13}C NMR spectrum were 320 scans, 9.3 μs pulse width (90°), 0.8 s acquisition time, a pulse delay of 10 s, 32K time-domain data points, and gated decoupling with the decoupler on during data acquisition. Carbon-13 spectra were obtained on samples containing $\approx$ 0.05 M chromium (III) acetylacetonate as a relaxation agent.

Silica Gel Separations

Separations using silica gel were performed on a column (50 cm × 1.0 cm ID) dry-packed with Silicar-CC-7 Special (Mallinckrodt Chemical Co.). This product is no longer available. About 100 mg neutral fraction obtained by ion exchange chromatography (chapter 7) was dissolved in a few milliliters of n-pentane (EM Sciences), and this solution was poured on the top of the bed of silica gel. Approximately 10 g silica gel was used, a charge-to-gel ratio of 100:1. The aliphatic fraction was eluted with 100 mL n-pentane. This was followed by 100 mL benzene (EM Sciences), which eluted the aromatic fraction. The very small amount of remaining material can be eluted with methanol-benzene (1:5).

Asphaltene Precipitation

Asphaltenes are prepared by transferring approximately 50 g of asphalt into a 4 L Erlenmeyer flask. A top loading balance is used. Forty volumes of n-heptane (EM Sciences) are added to the flask, 40 mL per gram of asphalt. The flask is then swirled occasionally for 16 h, after which the contents are filtered through a Buchner funnel with a sintered glass plate (medium porosity), placed on a 1 L filter flask. The side of the Erlenmeyer flask is washed several times with n-heptane and the filter cake containing the asphaltenes is washed with small portions of n-heptane until the filtrate has very little color. This generally takes several washings. All washings should be combined with the filtrate.

The filtrate is transferred to a round-bottom flask and the n-heptane is removed on a rotary evaporator using heat and reduced pressure. Before all n-heptane is removed, the maltenes should be transferred to a tared 100 or 125 mL round-bottom flask. The remainder of the n-heptane is then removed on the same rotary evaporator, but in an oil bath at approximately 125°C (257°F). Weighings are performed about once per hour until a constant weight is obtained.

The asphaltenes (the filter cake) are dried under vacuum and then scraped into a tared 100 mL beaker. An aluminum foil cap is placed over the top of the beaker and a dry nitrogen gas stream directed over the asphaltenes is used to dry them overnight. The residual asphaltenes that could not be removed by scraping are dissolved in methylene chloride (EM Sciences) and the filtrate is poured into a 50 ml tared beaker. An aluminum foil cap is placed over the top of the beaker and the liquid asphaltenes are placed under the nitrogen gas stream overnight. When a constant weight is achieved in both beakers the two batches of asphaltenes are then combined into a vial.

Five grams of the maltene fraction is removed for further analysis. The remainder of the maltenes are used to make iso-octane (2,2,4-trimethylpentane, Burdick & Jackson) asphaltenes. Forty milliliters of iso-octane per gram of maltene fraction is mixed in a 2 L Erlenmeyer flask. The flask is swirled until the maltenes are dissolved in the iso-octane. Dissolution of maltenes is generally time consuming. The flask and contents are allowed to stand overnight. The next morning the solution is filtered through a Buchner funnel with a sintered glass plate (medium porosity), placed on a 1 L filter flask. The filter cake (iso-octane asphaltenes) is rinsed with iso-octane until the filtrate has little or no color. The solvent is removed from the filtrate (iso-octane maltene fraction) as was described for the heptane maltenes. If any material in the Erlenmeyer flask is not soluble in iso-octane and cannot be removed by scraping, the material is rinsed and dissolved with methylene chloride. The methylene chloride solution is placed in a tared beaker and evaporated under a stream of nitrogen gas. The filter cake from the Buchner funnel is added to the beaker to combine all the iso-octane asphaltenes in one container. The iso-octane asphaltenes are dried under nitrogen until a constant weight is obtained. The mass percent heptane asphaltenes, mass percent iso-octane asphaltenes, and mass percent maltenes are then calculated.

Heithaus Titration

Heithaus titrations were performed using a method developed by Heithaus (1960; 1962) and modified by Kiggundu et al. (1984) and in these laboratories. In this improved procedure, four 1.0 g samples of the test asphalt were weighed into 125 mL Erlenmeyer flasks. To the four flasks were added amounts of 1.0, 2.0, 4.0, or 6.0 mL toluene (Burdick & Jackson, redistilled prior to use). Dissolution of the asphalt in toluene may take several hours at ambient temperatures. Use of heat is not advised because it may result in loss of solvent. After dissolution was complete, a stirring bar was added to each flask, and the flasks were immersed in a water bath maintained at 25°C (77°F) for 30 min. The flasks were then titrated with 1.0 mL aliquots of n-heptane (Phillips Petroleum Co., 99 percent, redistilled over calcium hydride prior to use). After each addition of n-heptane, the contents of the flask were stirred for 5 minutes on a magnetic stirrer. Flocculation was determined by transferring a drop of the solution to a filter paper with a glass rod. The development of two rings on the filter paper is indicative of flocculation. Otherwise, only one ring is observed. For replicate determinations of an asphalt, all but 1 mL of the amount of n-heptane required for flocculation may be added at once, followed by addition of 0.1 mL increments. For some asphalts, flocculation points could not be determined for the samples mixed with 1.0 mL toluene. In these cases, 1.0 g asphalt was dissolved in 8.0 mL toluene, so that the four flasks contained 2.0, 4.0, 6.0, and 8.0 mL toluene respectively.

If and when asphaltene flocculation was observed, Heithaus parameters were calculated as follows:

Flocculation Ratio: $$FR = V_T / (V_T + V_H) \tag{6.1}$$

Dilution Ratio: $$X = (V_T + V_H) / W_A \tag{6.2}$$

where

V_T = volume of toluene in flask
V_H = volume of n-heptane required for flocculation
W_A = weight of asphalt in flask (1.00 ± 0.05 g).

These calculations resulted in four values of FR and four values of X. A graph in which FR is plotted versus $1/X$ was prepared. A straight line was drawn through the data points and extrapolated to both axes. The intercept with the ordinate is FR_{max}. The intercept with the abscissa is $1/X_{min}$, from which X_{min} is calculated. These two values were used to calculate P_a, P_o, and P as follows:

Peptizability of asphaltenes: $$P_a = 1 - FR_{max} \tag{6.3}$$

Peptizing power of maltenes: $$P_o = FR_{max}(X_{min} + 1) \tag{6.4}$$

State of peptization of asphalt: $$P = P_o / (1 - P_a) = X_{min} + 1. \tag{6.5}$$

Reduced Specific Viscosity Experimental Procedure

Reduced specific viscosity measurements of mixtures composed of varying amounts of natural maltenes as the solvent and natural asphaltenes as solute provide a measure of the state of dispersion and thickening power of the asphaltenes. These data are acquired by first separating asphaltenes and maltenes from an asphalt, unaged or aged, then preparing blends with varying asphaltene contents, and then measuring the viscosities of the blends. The procedure for preparing asphaltenes and maltenes was described previously in this chapter. All asphaltenes and maltenes used in blends were prepared by n-heptane precipitation.

The blends may be prepared by either of two methods. In the first method, calculated amounts of maltenes and asphaltenes, maltenes and asphalts, or asphalts and asphaltenes are introduced into a flask and enough dichloromethane is added to dissolve the mixture. The solvent then is removed by attaching the neck of the flask to a rotary evaporator and immersing the flask in a hot water bath. Most solvent can be removed without the use of a vacuum. Reduced pressure must be used to remove the last traces of solvent. In some cases solvent is tenaciously retained, and heating in a hot oil bath at 125°C (257°F) under vacuum may be necessary. Absence of solvent may be monitored by examining the infrared spectrum of a portion of the mixture. Dichloromethane has a strong peak at 740 cm^{-1}. This method of blending is used for mixtures of maltenes and asphaltenes, and asphalts and asphaltenes. In the second method, calculated amounts of maltenes and asphalts are mixed in a flask, and the stoppered flask is placed in an oven heated to 150°C (302°F) until the mixture becomes liquid. The mixture is removed from the oven and thoroughly shaken. Heating and shaking were repeated twice.

In calculating the amounts of components of mixtures to be weighed out, it should be borne in mind that 4.0 g of material are required for rheological analysis. This is a minimum value for a mixture, particularly because stiffer mixtures are not readily removed from flasks. After viscosities of the mixtures have been determined at low shear rates, reduced specific viscosities are then calculated by using the following equation:

$$<\eta> = (\eta - \eta_o) / (\eta_o \times c) \tag{6.6}$$

where

η = viscosity of the solution (blend)
η_o = viscosity of the solvent (maltenes)
c = concentration of the solute (asphaltenes), mass fraction.

Viscosity measurements were performed on a Rheometrics Mechanical Spectrometer. Asphaltenes and maltenes measured were flooded with argon and placed in an oven at 110°C (230°F) for 1 h 10 min. After the samples were removed from the oven, rheological measurements were made within 40 to 60 h. This annealing step must be performed in order to obtain consistent viscosity determinations. Relative viscosities were calculated by dividing absolute viscosities of asphalts by absolute viscosities of their n-heptane maltenes determined at the same temperature and rate of shear.

7 Separation of Asphalts by Ion Exchange Chromatography

Introduction

One of the principal objectives of this research was to correlate asphalt chemical and physical properties. To accomplish this objective, it is necessary to divide asphalts into defined chemical fractions and determine the influence of the fractions on selected physical properties for a number of asphalts. Asphalts are known to consist of relatively nonpolar hydrocarbons and acidic and basic heteroatom-containing molecules of varying polarity. These components cannot be completely separated by solvent precipitation methods or techniques that separate molecules according to molecular size. Ion exchange chromatography (IEC) can be used to separate solutions of asphalts into defined neutral, acidic, and basic fractions. Amounts of samples may be processed in one experiment so that fractions are obtained of sufficient size that various physical property measurements can be performed. The IEC separation can be varied to isolate specific fractions of interest.

The procedure consists of pumping solutions of asphalts through columns filled with activated anion or cation resins. The procedure is exacting and time-consuming and depends for success on proper resin activation. One week (assuming 8-h work days) is required to activate substantial amounts of resins as described below. Another week is required to separate asphalt solutions into four fractions and remove solvents. Highly trained personnel are essential.

In the procedures described below, chemicals and equipment used in IEC separations during the SHRP program were obtained from suppliers that are specifically mentioned. Mention of these suppliers does not constitute an endorsement by SHRP or the Western Research Institute. Most of the chemicals and supplies may be obtained from other vendors, but inferior grades of chemicals should not be substituted. Some of the chromatographic equipment used is no longer stocked by the vendors mentioned, so other suppliers must be found.

Activation of the Resins

Activation of the cation and anion resins is the first step in IEC. This procedure requires 4 days to complete. The day before the experiment is started, glassware and chemicals are collected. The solutions to be used are prepared as needed prior to the beginning of the activation process.

Five hundred grams of analytical grade macroporous cation resin AG MP-50, 100–200 mesh, hydrogen form (Bio Rad Laboratories), stored in an amber bottle, is poured into a 3 L Buchner funnel with a coarse-porosity sintered glass plate. The Buchner funnel rests on a 4 L filter flask. The resin is washed successively with the solutions listed below. The washing of the resin proceeds rapidly enough without the use of suction.

The first wash solution is 11.7 L of 1.5 N NaOH, prepared by adding sodium hydroxide pellets (700 grams, Baker analyzed reagent) to distilled water. The amber resin bottle is rinsed with some of the NaOH solution to remove residual resin. The NaOH wash solution is then poured over the resin bed portionwise. The resin bed is stirred occasionally with a stainless steel spatula throughout the activation to allow all the resin particles to contact the solutions evenly. Any resin particles adhering to the spatula are transferred to the resin bed by rinsing with distilled water. After the last portion of each of the different wash solutions has been added to the Buchner funnel, the resin bed is allowed to drain to near dryness and then a portion of the next wash solution is added.

The second wash solution is approximately 1.3 L of distilled water. After the resin has been washed with the distilled water, 11.7 L of 1.5 N hydrochloric acid (1,727 mL of 36.5-38.0 percent Baker analyzed reagent) is added to the resin in portions. When half of the HCl solution has been added, filtration is interrupted and the resin is allowed to soak in the HCl solution for 1 h to neutralize residual NaOH. This is accomplished by inserting a Nalgene stopper in the stem of the Buchner funnel. After washing of the resin with HCl is completed, the resin bed is washed with 4.0 L of distilled water, followed by 8.3 L of a 1-propanol-water solution (1:1 by volume). The 1-propanol can be obtained from redistillation of 1-propanol used in previous activations.

When the 1-propanol-water wash is completed, the resin should not contact water for the remainder of the activation or else the resin will not be properly activated. The filter flask is rinsed with a small amount of the 1-propanol-water solution.

The resin is then washed with 8.3 L of 1-propanol (Burdick & Jackson, HPLC Grade). The 1-propanol is allowed to filter slowly and is stoppered for 1 h after 4 L has filtered through. It has been determined that both the HCl and 1-propanol soak are essential to proper activation. When the contact time was too short and the resin was not allowed to soak for a time in the solvents, the resin was not fully activated. When approximately 2 L of 1-propanol remains to be filtered, the Buchner funnel is stoppered and the activation may be suspended until the following day. The 1-propanol that passes through the resin bed is collected in the filter flask and is redistilled for use in the 1-propanol-water solutions in future activations.

The next day, preparations are made for the Soxhlet extraction of the resin with diethyl ether (Baker analyzed reagent). A complete diagram of the Soxhlet extraction apparatus is shown in figure 7.1. Before the remaining 2 L of 1-propanol is filtered, the ether is cooled in ice for 15 min. Then the 1-propanol filtration is begun. When approximately 1 L remains to be filtered in the Buchner funnel, the ether is transferred to a 3 L round bottom two-neck flask and is degassed by bubbling argon into the ether. Enough ether is added to allow for convenient flushing during extraction (approximately 2 L). When the 1-propanol filtration is complete, the resin is spooned into a glass extraction thimble having a coarse-porosity

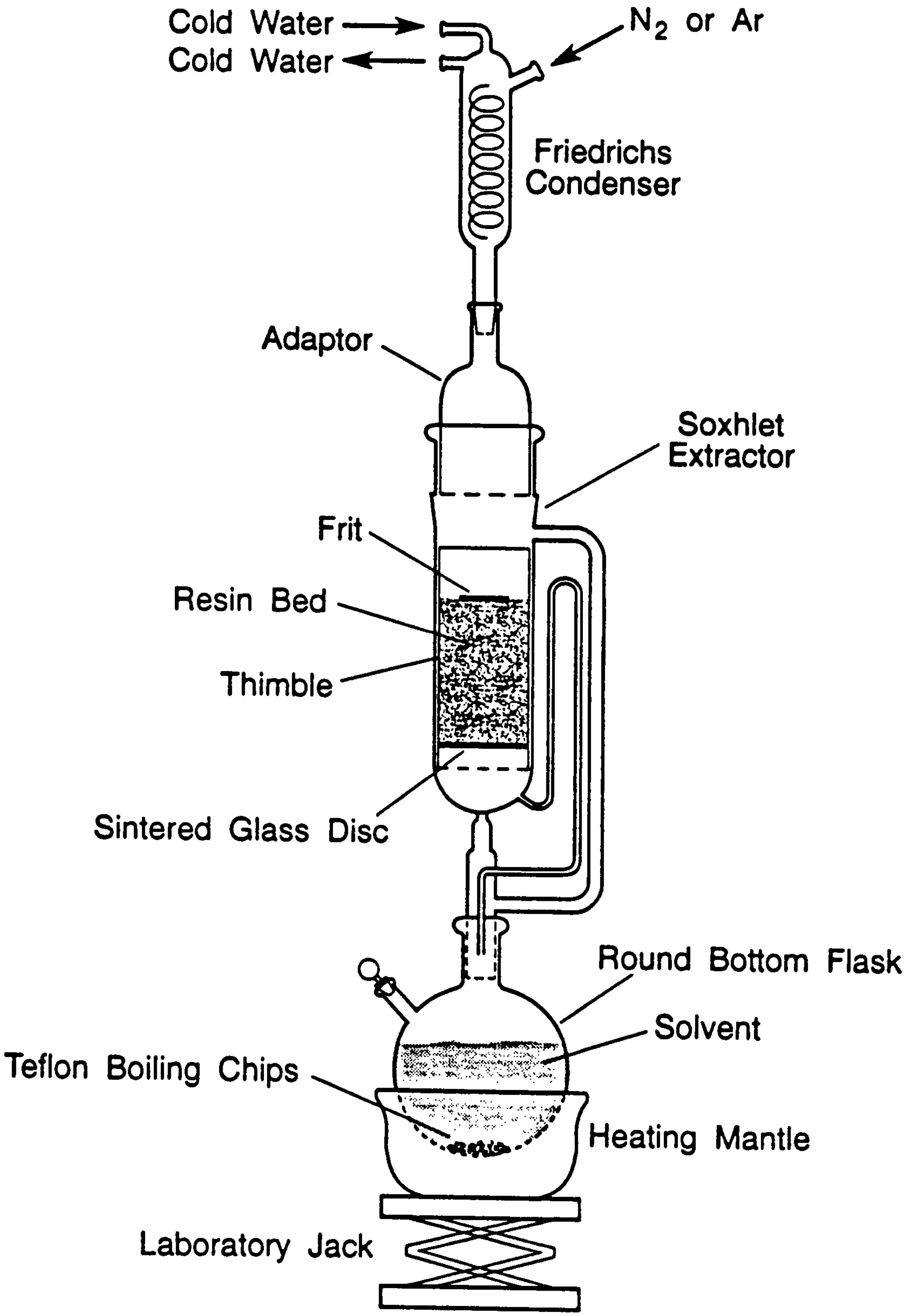


Figure 7.1. Apparatus for the Extraction of Activated Resins

sintered glass disc (8.5 cm I.D. and 19.5 cm height above the disc), and a glass frit is placed on top of resin bed to reduce resin loss during flushing. The thimble is placed into a large Soxhlet extraction apparatus 17.5 cm in height and 9.0 cm I.D. (Rocky Mountain Scientific Glassblowing Co.). The extraction apparatus is setup in a walk-in fume hood. The Soxhlet extractor rests on the 3 L round bottom flask nested in a heating mantle, which rests on a laboratory jack, and a Friedrichs condenser is connected to the top of the extractor by means of an adaptor. A stream of nitrogen or argon is added to the top condenser to prevent oxygen from contacting the resin. Teflon boiling chips are added to the flask through a side neck and the ether is heated to reflux for 24 h.

After 24 h reflux, the extraction ether is allowed to cool for approximately 30 min by turning off the heating mantle, removing the mantle by lowering the lab jack, and immersing the round bottom flask in ice. Concurrently, n-pentane (EM Sciences) is cooled in ice and degassed with argon. The thimble is then carefully removed from the Soxhlet extractor and rinsed 5 times with portions of n-pentane to remove ether. The round bottom flask is emptied of ether, rinsed with pentane, and then filled with n-pentane to a level that allows convenient flushing (approximately 2 L). Nitrogen (or argon) is used to further degas the n-pentane. Teflon boiling chips are added, heating is begun, and the n-pentane is allowed to reflux for 24 h.

The next day, after the reflux period has elapsed, the n-pentane is cooled for 30 min and the thimble is removed from the Soxhlet extractor. The resin is transferred by means of a spoon into a plastic funnel, the neck of which is inserted into the mouth of an amber bottle. Degassed cyclohexane (EM Sciences) in a wash bottle is used to assist the transfer of the resin into the amber bottle. The amber bottle is filled with cyclohexane and blanketed with argon. The lid is closed and taped to prevent any leakage of argon. The date of resin preparation should be noted on the bottle. The activated resins should be used within 6 months. After this period of time, the resins should be tested for activity as discussed below, using Wilmington distillate (370–535°C; 698–995°F) or other materials previously separated.

Activation of the analytical grade macroporous anion resin AG MP-1, 100–200 mesh, chloride form (500 g) is similar to the cation resin, with a few changes in procedure. The HCl and NaOH washes are reversed in order. The activation is performed in a fume hood. The resin is first washed with a HCl mixture, 8.3 L of 1.5 N HCl (1,233 mL concentrated HCl diluted in water to 8.3 L = 1.5 N). Distilled water (1.3 L) is added to the resin, followed by 8.3 L 1.5 N NaOH (500 grams in 8.3 L aqueous solution = 1.5 N). The NaOH solution is prepared during the HCl wash and is degassed with argon to assure adequate removal of dissolved carbon dioxide and oxygen. For the remainder of the activation the solvents should be rigorously degassed to minimize contact of the resin with air. During the introduction of the NaOH, the resin bed is also blanketed with argon to protect it from the air. After the NaOH wash, the succession is the same as for the cation resin. Argon is continuously bubbled into the solvent above the resin bed when filtration is interrupted. The ether and n-pentane Soxhlet extractions are the same as for the cation resin. The anion resin turns a pinkish color during the ether extraction, which seems to be an indication of proper activation. Occasionally, batches of resin cannot be properly activated. These resins never develop proper color after activation. If they are used to separate asphalts, excessive irreversible adsorption is encountered, resulting in virtual cessation of flow through columns packed with the resins. The reason some batches of resin do not become properly activated is not known. For this reason, batch numbers of resins from the supplier should be monitored.

Column Packing

Activated resins are packed into columns by means of helium pressure. Reasonable safety considerations dictate that the packing operation must be performed behind a protective shield. The procedure can be completed in about 30 min.

A packing reservoir (Rainin) is attached to the top of a 25-mm I.D. × 500 mm Altex Prep column fitted with end caps. A filter disc, size 30-60 μ (Rainin), and Teflon screen (Rainin) are placed on the flat end of a bed support (Rainin) fitted with two Viton O-rings, size 2-116 (Rocket Seals Corp). This assembly is held together with a Teflon sleeve (Rainin), and the entire assembly is inserted into the bottom of the column (figure 7.2). The packing reservoir is connected to the column with a column extender and then the whole assembly is mounted vertically. Degassed cyclohexane is poured into the top of the packing reservoir until the solvent level reaches the neck of the reservoir. A bed support connected to a helium tank by Teflon tubing is inserted into the top of the reservoir. Pressure of up to 50 psi helium in 10 psi increments is applied, and any leakage or loose connection is identified and corrected.

About 240 mL activated anion or cation resin slurried in cyclohexane is poured into a graduated cylinder. Helium pressure is relieved from the column, and more degassed cyclohexane is added to fill the packing reservoir halfway. The resin-cyclohexane slurry is poured into the top of the packing reservoir, followed by cyclohexane rinses until the reservoir is filled. The bed support connected to the helium tank is reinserted into the top of the packing reservoir, and a pressure of no more than 50 psi is applied. Cyclohexane flows out of the column by means of Teflon tubing connected to the bed support at the bottom of the column. When the solvent level is reduced to about 10 mm above the resin bed level in the column, the packing reservoir is detached from the column and replaced with a plunger. The components of the plunger are also illustrated in figure 7.2.

Filled columns are allowed to stand 24 h before use. Gas bubbles that form are maneuvered to the top of the columns by gently tapping the sides of the columns. Gas is released by opening the tube that runs through the plunger and lowering the plunger until it makes contact with the liquid in the column.

Testing of Activated Resin

Portions of some batches of the activated anion and cation resins were occasionally tested with a Wilmington distillate (370-535°C; 698-995°F) to determine whether the resins were activated completely. The procedure used is the same as described by Green et al. (1984) for the separation of asphalts into acidic, basic, and neutral fractions using cyclohexane as eluant. Green et al. (1984) reported normalized recoveries of 10.1 mass percent acids, 8.0 mass percent bases, and 81.8 mass percent neutrals for this material. When columns of different dimensions were used and the Wilmington distillate was separated on batches of

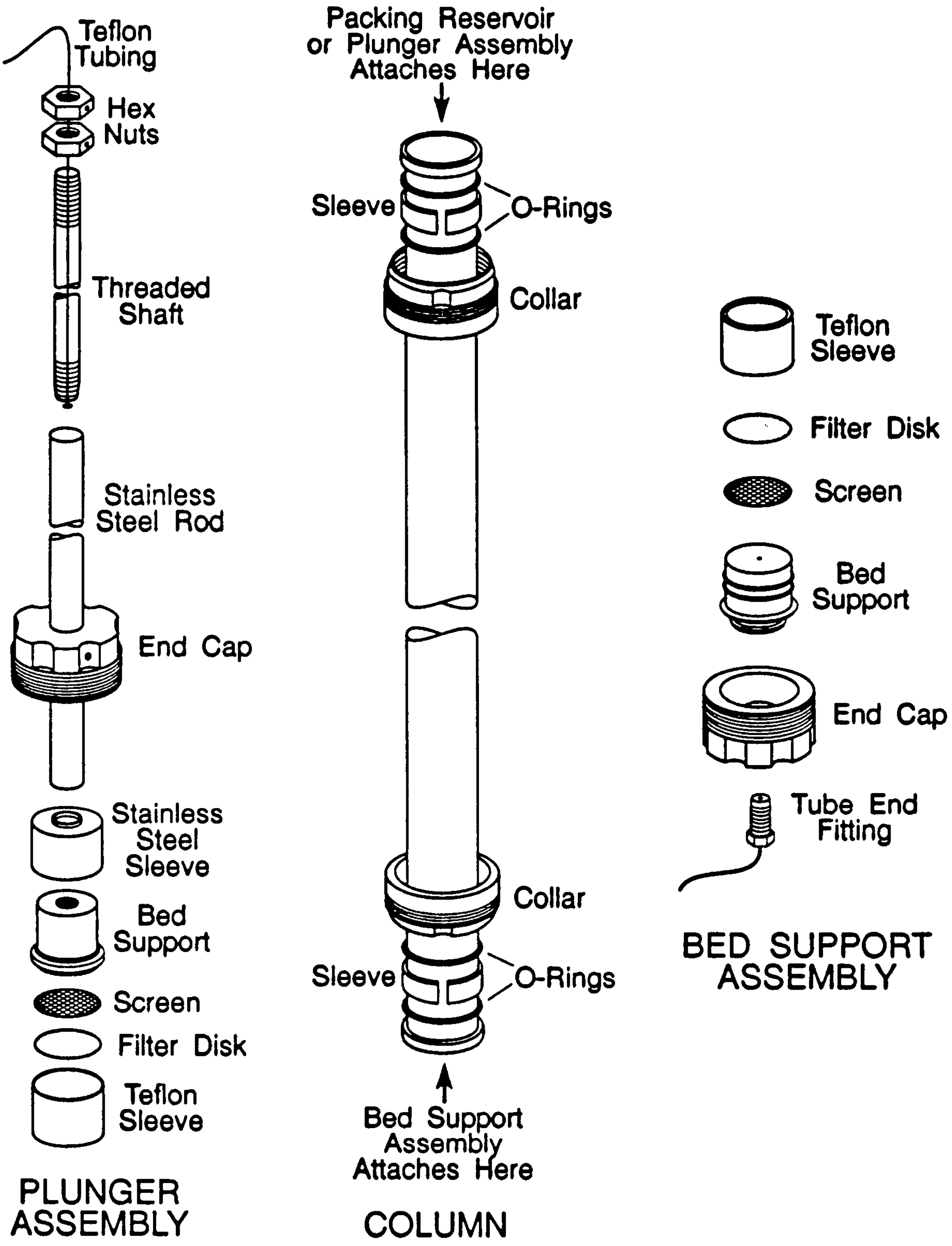


Figure 7.2. Column, Plunger Assembly, and Bed Support Assembly for Columns Used in Ion Exchange Chromatography Separations

resins activated during the SHRP A-002A program, normalized recoveries of 10.7 percent acids, 7.1 percent bases, and 82.2 percent neutrals were observed. The two values of the neutral fractions vary by only 0.5 percent. The two determinations of the polar fractions are reasonably close considering that columns of different dimensions were used. In the separation of the Wilmington distillate, small (~ 2 percent) losses during workup are encountered, but only negligible amounts of irreversible absorption on resins are observed. Separation of nondistilled materials results in some irreversible absorption. If yields of neutral and polar fractions differ from these results by over 5 percent, the resins may not have been properly activated, or for unknown reasons are unsuitable.

Resins may also be tested with asphalts from the Materials Reference Library of the Federal Highway Administration Long-Term Pavement Performance program.

Separation of Asphalts into Neutral, Acid, Base, and Amphoteric Fractions

The IEC separation of asphalts into neutral, acid, base, and amphoteric fractions differs from the procedure of Green et al. (1984). Solutions of asphalts contact cation resins first instead of anion resins, as in the Green et al. (1984) procedure. A flow sheet for this separation is illustrated in figure 7.3.

Chromatographic separation of asphalts into neutrals, acids, bases, and amphoterics is performed with cyclohexane as the solvent at 37°C (98.6°F). Use of cyclohexane allows basic and amphoteric functionalities to adsorb on a cation resin while acids adsorb on an anion resin and the neutrals are eluted. Amphoteric fractions are then separated from bases with an anion column in a separate operation. The use of cyclohexane for IEC separation was reported by Boduszynski et al. (1977). The IEC separation can be performed in approximately 5 h.

Sixteen grams of asphalt is dissolved in 64 mL of degassed cyclohexane. Two columns, one filled with activated cation resin and the other filled with activated anion resin, are used. The plungers are adjusted to remove any voids. A ¼ in. gap is left between the resin bed and the plunger in each column to prevent pressure buildup. Two FMI lab pumps, model RP-SY are connected to two FMI pulse dampeners, model PD-60-LF, which are then connected to the bottom of the columns. Approximately 250 mL of degassed cyclohexane is pumped through each column individually at a flow rate of 5 mL/min. Water jackets (not illustrated in the schematic diagram of the column, plunger assembly, and bed support assembly in figure 7.2) are fitted onto the columns. The water jackets are connected to a constant temperature bath maintained at 37°C (98.6°F). The columns are arranged in series, with the top of the cation column connected to the bottom of the anion column, and 50 mL of degassed cyclohexane then is pumped through them. It is necessary to remove the pulse dampener from the system before the asphalt solution is introduced. The dissolved asphalt is introduced into the system via Teflon tubing, followed by rinsing of the flask that contained the asphalt solution with approximately 30 mL of degassed cyclohexane. The pulse dampener is reconnected to the system and 750 mL of degassed cyclohexane is pumped through both columns. Another 200 mL of degassed cyclohexane is pumped through the anion column alone. All eluates are collected as the neutral fraction. These eluates are filtered through a 350 mL Buchner funnel

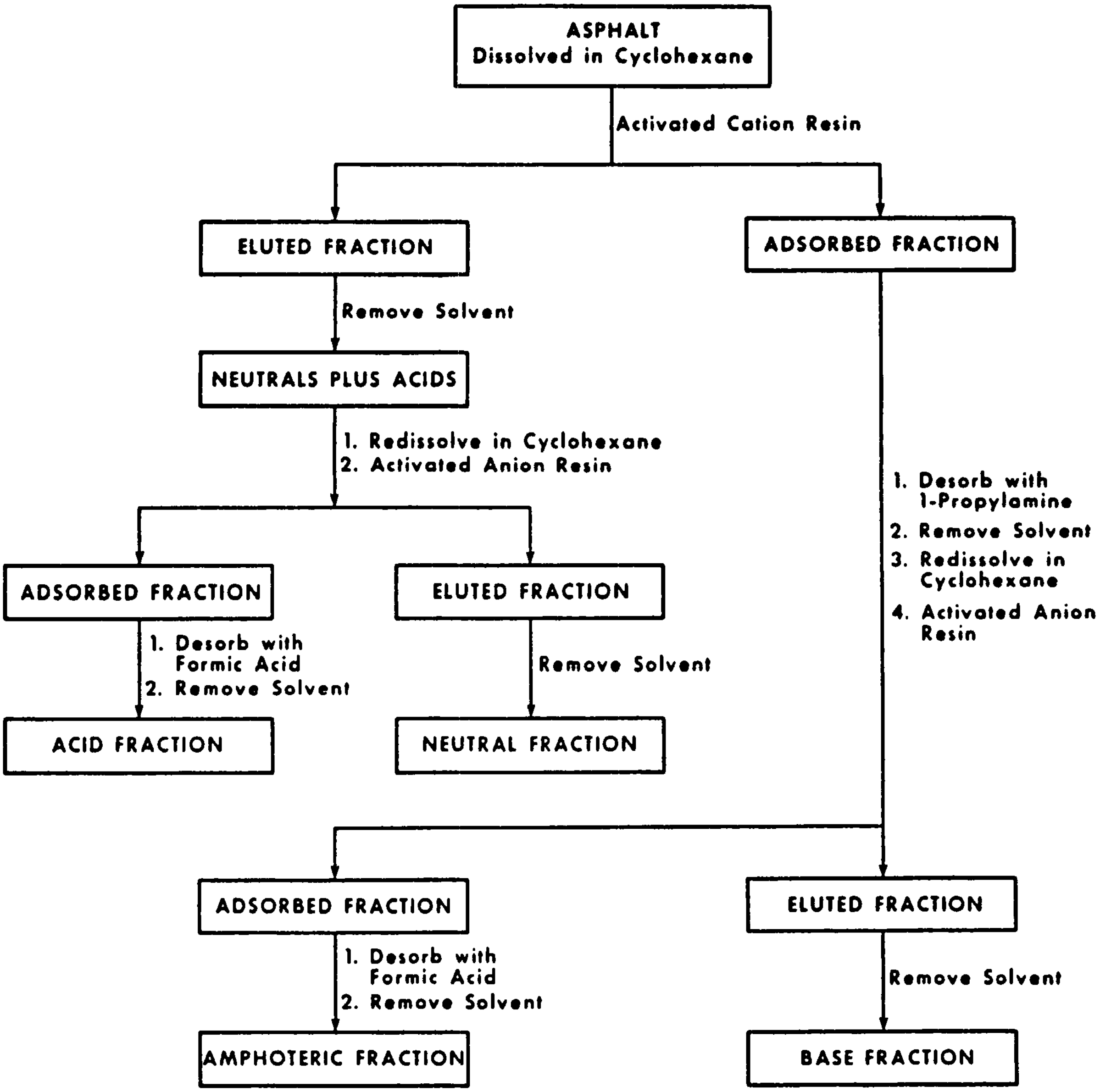


Figure 7.3. Isolation of Amphoterics by Ion Exchange Chromatography.

with a medium-porosity sintered glass plate to remove resin particles. The filtrate is then divested of solvent on a rotary evaporator (Buchi). After most cyclohexane has been removed, the neutral fraction is transferred to a 100 mL round bottom flask with methylene chloride (EM Sciences) and again is divested of the solvent on the rotary evaporator. The flask and contents are then rotated in a boiling water bath under reduced pressure until a constant weight is reached (approximately 2 h). The water bath is replaced by an oil bath, which is heated to 125°C (257°F). During heating, reduced pressure (2 torr) is applied for 2 h. After this treatment, the flask is removed from the rotary evaporator. The neutral fraction is blanketed with nitrogen and the flask is stoppered. The flask and contents are stored in a cool, dark cabinet.

Extraction of Asphalt Fractions Adsorbed on Resins

The combination of amphoteric and basic fractions is adsorbed on the cation resin, and these materials must be desorbed. The procedure follows. The plunger on the top of the column is removed and rinsed with benzene (EM Sciences) in a 1 L beaker. This and subsequent operations must be performed in a good fume hood to avoid exposure to vapors. The plunger is removed from the beaker and the column is inverted over the beaker. Approximately 30 mL benzene is pumped into the column. The pump is then detached from the column and a syringe containing about 25 mL benzene is inserted into the Teflon tube that leads into the top of the column. Hand pressure on the syringe should be sufficient to dislodge the resin into the beaker. Several rinses are required to fully remove the resin from the column. Pumping the syringe with air may speed up the process. The end cap at the top of the column is unscrewed and the bed support assembly is removed and rinsed into the beaker. Fifteen milliliters of a mixture of 1-propylamine (Aldrich Chemical Co., 98 percent) and benzene is then added to the beaker. This mixture, which desorbs asphaltic materials from the cation resin, should be prepared previously. It consists of 50 mL 1-propylamine and 100 mL benzene. After 15 mL of the mixture is added to the beaker, the remainder is reserved.

The cation resin in the beaker is poured into a Soxhlet thimble resting in another beaker. After the solvent has drained from the thimble, a glass frit is placed on top of the resin bed. The liquids drained from the resin are poured into a 2 L round bottom, two-necked flask with a vertical side arm containing a magnetic stirring bar. More benzene is added to the flask to allow for convenient flushing. A Soxhlet extraction apparatus similar to the one used in the resin activation, only on a smaller scale, is set up. A stirring plate (Sargent-Welch Scientific Co.) is set under the heating mantle in place of the laboratory jack. A drip funnel with a pressure bypass is placed in the second neck of the flask to allow the remainder of the 1-propylamine-benzene mixture to be slowly added to the system, approximately 5 mL every 15 min. The amine-benzene mixture must be added cautiously or "bumping" of the resin will result, causing resin to be ejected from the extractor. The solvent is allowed to reflux for approximately 12 h (which need not be continuous), after which the resin should be clean of most adsorbed material. During the addition of the 1-propylamine and the extraction, dry argon is introduced into the mouth of the condenser. This procedure minimizes contact of water and oxygen with the contents of the extractor.

When the extraction is finished, the thimble is carefully removed from the Soxhlet extraction apparatus, and the resin is removed as a slurry into a beaker. The solution of desorbed IEC fraction in the round bottom flask is then filtered through a 350 mL medium-porosity Buchner funnel by gravity filtration. The resin in the flask, if any (some usually escapes from the thimble as a result of bumping), is washed with benzene until the filtrate is clean. The resin from the thimble is then poured into the Buchner funnel and rinsed with benzene until a clean filtrate appears.

After desorption is complete the solution containing the desorbed amphoteric and basic fractions is transferred to a pear-shaped flask and *carefully* divested of solvent by means of a rotary evaporator. These fractions are highly surface active and tend to form rigid foams that enter the rotary evaporator from the flasks. After almost all solvent has been removed, the residue concentrated in the flask is rinsed three times with benzene to remove 1-propylamine. The desorbed materials are then transferred to a 100 mL round bottom flask and dried to a constant weight, as for the neutral fraction. These desorbed materials comprise the base and amphoteric fractions. They are stored under a blanket of inert gas in the dark.

The desorption of the anion resin is similar to the procedure described above with a few changes. The column is emptied of resin as described above and the anion resin is desorbed with 50 mL of formic acid (Aldrich Chemical Co., Inc., 96 percent A.C.S. reagent). Approximately 15 mL of formic acid is mixed with the anion resin slurry before the resin is transferred to the Soxhlet thimble and the remaining 35 mL is added to a 1 L round bottom, single-necked flask. Enough benzene is then added to allow for convenient refluxing. The anion resin is placed in an extraction thimble. The thimble and contents are placed in a Soxhlet extractor, which is mounted on the round bottom flask. A condenser is mounted on top of the Soxhlet extractor. The benzene-formic acid mixture will reflux for approximately 12 h or until the resin is cleaned of adsorbed material. Dry argon is introduced into the mouth of the condenser during addition of formic acid and refluxing. The filtration procedures after the extraction are the same.

To separate the base from the amphoteric fraction, a second separation is required. The mixture of the two fractions is dissolved in cyclohexane (4 mL cyclohexane for each 1.0 g mixture) and the solution is pumped through a column of activated anion resin, as described above. The base fraction is eluted, and the amphoteric fraction is adsorbed on the resin. Isolation of each fraction is the same as described above for the anion resin.

Separation of Asphalts into Strong Acid, Strong Base, Weak Acid, Weak Base, and Neutral Fractions

IEC separation of the asphalts into strong acid, strong base, weak acid, weak base, and neutral fractions is based on the method reported by Green et al. (1984). A flow sheet for this separation is illustrated in figure 7.4. This separation uses a mixed solvent consisting of 810 mL benzene, 810 mL tetrahydrofuran (Burdick & Jackson), and 180 mL ethanol (Aldrich Chemical Co.). In this separation, 64 g of this mixed solvent are used to dissolve 16 g of asphalt for each experiment. One column filled with activated anion resin and one column filled with activated cation resin are connected in series. The asphalt solution is pumped into the column filled with anion resin first. Use of the mixed solvent allows strong acids to adsorb on an anion resin while strong bases adsorb on a cation column, and the

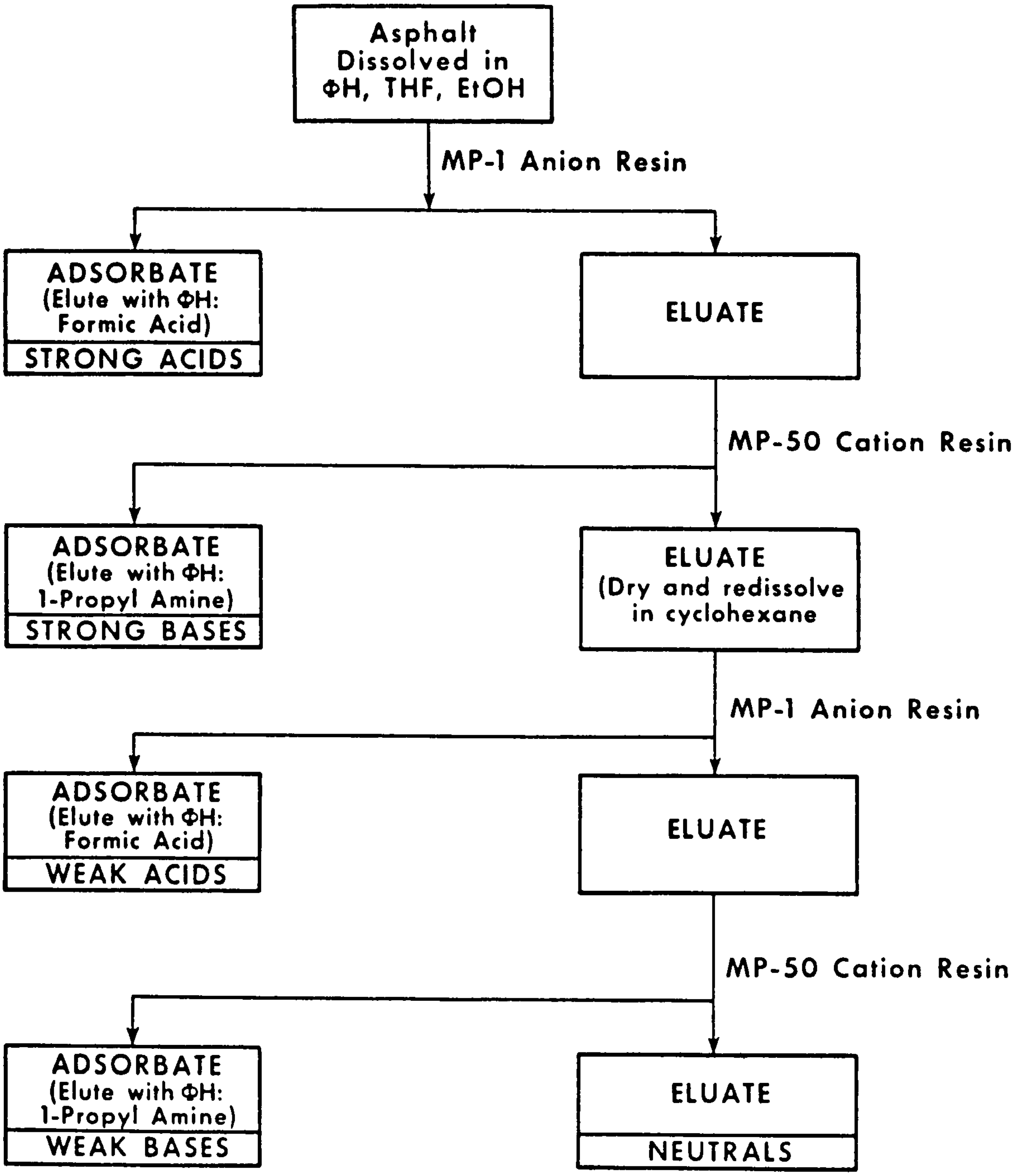


Figure 7.4. Separation of Asphalts into 5 Fractions by Ion Exchange Chromatography.

neutrals, weak acids, and weak bases are eluted. The eluates are divested of solvent and redissolved in cyclohexane (four volumes per gram of substrate) and the solution is pumped through two different columns of activated anion and cation resins, the solution contacting the anion resin first. Weak acids, adsorbing on an anion column, and weak bases, adsorbing on a cation column, are then separated from the eluted neutrals. The details of this separation and subsequent operations are essentially the same as those explained more fully in the previous two sections.

Results of IEC of SHRP asphalts are presented and discussed in volume 2, chapter 1.

8 Analysis of Non-Polar Fractions of Asphalts by Supercritical Fluid Chromatography

Introduction

Supercritical fluid chromatography (SFC) is a relatively new analytical method that has seen limited application in fossil fuel science. Near their critical points, fluids have the solvent power of a liquid but the mobility of a gas. In most SFC separations, carbon dioxide is the mobile phase, which limits application of the method to analysis of relatively nonpolar molecules. Asphalts contain large amounts of nonpolar molecules of relatively high molecular weight. Many of the components are chemically similar and differ mainly in molecular size. Conventional gas chromatographic separations are restricted to nonpolar molecules of below carbon number 40, because most molecules larger than this are involatile. Volatility is not a prerequisite for SFC separation. The method permits quantification of nonpolar species in the carbon number range of 40 to over 100, which occur in asphalts in significant amounts and about which little is known.

SFC Analyses of Asphalt Nonpolar Fractions

The SFC separations reported in volume 2 were performed on a CCS 5000 supercritical fluid chromatograph equipped with a flame ionization detector. A polysiloxane PM packer column, 100 × 1 mm I.D. (Brownlee Labs) was used for this work. Carbon dioxide was the mobile phase (SFC grade, Scott Specialty Gases).

Samples to be analyzed were dissolved in toluene (spectral grade, EM Sciences) in concentrations of 20–40 mg/mL. Sample masses are about 8 μg for a given run. Toluene masks any hydrocarbons of carbon number 18 or below, but few of these are found in asphalts. The column temperature program was 125°C (257°F) for 5 min, after which the temperature was raised to 150°C (302°F) at a rate of 2°C (3.6°F) per minute. The final temperature was maintained for 22 min. The column pressure program was 2,000 psi for 5.5 min, rising to 5,500 psi at 140 psi per minute. Higher temperatures and pressures than these cause column deterioration. These conditions limit the analysis of hydrocarbons by SFC to those having carbon numbers in the range of 18 to 110.

Calibration was accomplished with a polyethylene standard consisting of even-number oligomers ranging from carbon number 18 to 110 (Pressure Chemical Co.). The standard was spiked with normal alkanes of carbon numbers 26, 50, and 60 (Fluka Chemical Co.). The retention times of the oligomers were used to define cut points for every five carbon numbers. The area slices between these cut points were accumulated, and the background of the appropriate area slice from a blank solvent run was subtracted. The area slices were then reduced to area per sample concentration to compare different runs. Data for maltenes and size exclusion chromatography fractions were adjusted for detector response.

The response of the flame ionization detector (FID) was checked for linearity over the carbon number range from 20 to 60. The response of mineral oil detected during SFC analysis was compared to that of a gas chromatography simulated distillation analysis. Since mineral oil is totally distillable by 538°C (1,000.4°F), the end of the ASTM D 2887 simulated distillation method, it provides a good sample for comparison in the carbon number range from 20 to 44. Comparison of the normalized data for the two methods was quite good with the SFC data practically overlaying that from the GC method and indicating that there was no discrimination in detector response for the entire carbon number range represented by mineral oil. A further check on the linearity of the SFC detector was done by comparing the responses of normal pentacontane ($n\text{-}C_{50}$) and hexacontane ($n\text{-}C_{60}$) with that of normal pentaconsane ($n\text{-}C_{25}$). When these comparisons were made on a response-per-unit concentration basis, the relative response factors were very close to unity. The lack of hydrocarbon standards beyond C_{60} made it impossible to check the linearity of responses above C_{60}, and a drop in detector response with increasing carbon number may be possible. Reproducibilities of the separations are good (volume 2, chapters 1 and 2).

9 Separation and Analysis of Asphalts by Size Exclusion Chromatography

Introduction

Size exclusion chromatography (SEC) is a method used to separate solutions of mixtures according to the molecular size of the components. Solutions to be analyzed are percolated through columns filled with gel particles swollen in organic solvents. The gel particles are porous, and the pore diameters vary in size. Large molecules or extensive associations of molecules do not enter gel pores, but pass through gel columns between particles. Unlike most chromatographic methods, larger entities elute first. Somewhat smaller molecules, depending on their size, spend varying amounts of time within the gel particles during an SEC separation. The smallest molecules enter all pores in gel particles and are not separated from each other. If the chemical properties of a mixture vary along with molecular size, an SEC separation effects a chemical separation; otherwise, it does not.

The method has seen wide application in fossil fuel science particularly in the separation of heavy crude oils and derived materials. One model of the structure of heavy crude oils holds that these materials are composed of associations of polar molecules dispersed in a relatively non-polar solvent phase. The same model has been proposed for asphalts and is discussed at length in volume 1, chapter 1. Any extensive associations of polar molecules must be of fairly large size, and so it should be possible to separate associated from non-associated components by preparative size exclusion chromatography (PSEC) (and analyze differences between the components by analytical SEC) if associations are stable in solvents used for SEC separations. The SEC separation methods do not suffer from irreversible absorption, as do ion exchange chromatographic and liquid chromatographic procedures. In SEC, recoveries of charged materials usually are quantitative. Therefore SEC can be used to separate highly aged asphalts, containing many highly polar functional groups, for which other chromatographic separations and analyses are unsuitable. The method is inherently incapable of the resolution of other chromatographic methods, but it is one of the only effective tools for the fingerprinting of the larger components of fossil fuels.

A variety of gels of widely different pore sizes are commercially available. Most are categorized according to average pore diameters. A gel having a large average pore diameter will not efficiently separate mixtures of small molecules, and vice versa.

The SEC method can be adapted as an analytical technique for separating minute amounts of sample or as a preparative separation of samples weighing several grams.

Preparative Size Exclusion Chromatography Experimental Procedure

PSEC is used to provide fractions of asphalts large enough to permit rheological analysis. In addition, gram quantities of asphalt PSEC fractions are needed to perform blending experiments. The procedure developed in the SHRP A-002A program is described below.

The equipment required for the PSEC separation consists of the following. An Andrews Glass Company Lab Crest (5.08 cm I.D. × 100 cm long) water-jacketed column, connected to end fittings with stopcocks, is packed with Bio-Rad Bio-Beads S-X1 (200–400 mesh) gel swelled in toluene (EM Sciences, HPLC grade). The end fittings contain fritted glass discs to contain the gel and add 2.4 cm to the total length of the column. A water circulation bath connected to the column water jacket by Tygon tubing provides 40°C (104°F) temperature control for the column. The column is vertically mounted in a well-ventilated space. The pump used is an FMI model RPG-50 (¼ in. piston), and an FMI model PD-60-LF pulse dampener is placed in the solvent stream between the pump and the column. Teflon tubing is used to conduct solvent from one piece of equipment to another. Graduated cylinders are used as receivers and Erlenmeyer flasks are used as sample and solvent reservoirs. Similar pumps, pulse dampeners, and columns are available from other manufacturers. A diagram of the PSEC apparatus is shown in figure 9.1.

The column is packed by making a slurry of most of the required amount of gel with toluene. The amount of gel needed can be calculated from the volume of the column (about 2,000 mL), estimating that the gel swells in toluene to about 7.9 mL/g and also compresses under the pressure of solvent pumping to about 75 percent of its unconfined swelled volume. For the column used in most experiments, about 330–340 g of dry gel is needed. A few grams of dry gel is reserved for the final packing step after all of the slurry has been poured into the column. To fill the column, toluene is poured into the top of the column to about one-half the column height. Then the gel slurry is added in increments while the solvent drains out of the bottom of the column by gravity. After all of the slurry has been added the column appears to be thoroughly packed. However, pumping solvent through the top of the column will pack the gel further so that a gap between the top of the gel bed and the glass frit develops. For best results, this gap must be filled with gel. Therefore, it is necessary to pump a few milliliters of methanol into the top of the column, which shrinks the gel so that the reserved dry gel can be added to the top of the column. Toluene is then pumped into the bottom of the column, which flushes out the methanol and swells the shrunken gel and the added dry gel.

Before a sample is introduced into the column, toluene is pumped into the bottom of the column at 3.5 mL/min for about 1 h to allow the gel bed to settle. The toluene is contained in an Erlenmeyer flask, and one end of a tube connected to the pump inlet is placed in the flask below the liquid level. The sample, 16 ± 0.5 g of either unaged or aged asphalt, is dissolved in 150 mL toluene in an Erlenmeyer flask and is introduced into the bottom of the column through the pump. The delivery tube is placed inside a 500 mL graduated cylinder. During sample injection, the pulse dampener is removed from the sample stream and the pump setting is not changed even if the flow rate slows down, as increasing pressure may break the glass frit. After sample injection has been completed, the pulse dampener is

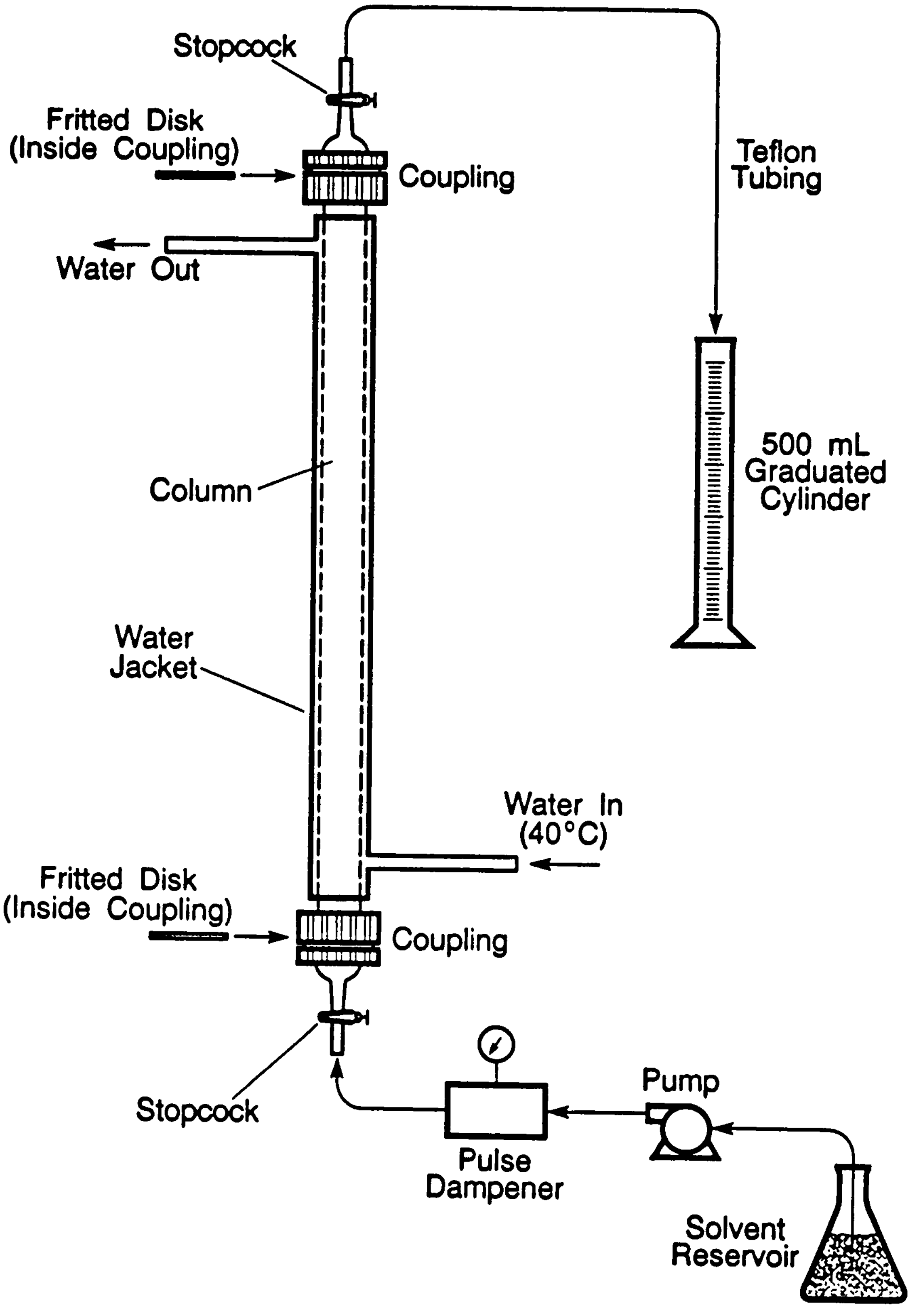


Figure 9.1. Apparatus Used for Preparative Size Exclusion Chromatography Separations.

replaced in the sample stream. The removal of the pulse dampener may be accomplished either directly or be setting up an alternate stream and switching between the two. The reason for removal of the pulse dampener is that portions of the charges are retained in it.

When color is detected at the outlet of the column (this occurs after about 450–530 mL of eluate has been collected after sample introduction; the amount varies with the column because no two columns are packed exactly alike and there is also variation among asphalts), the delivery tube is put into a second 500 mL graduated cylinder and placed so that eluates flow down the side of the collecting cylinder. The first material emerging from the column is a black solution and does not vividly fluoresce when exposed to light of 350 nm wavelength. After about 240–275 mL additional eluate is collected, stronger fluorescence begins to be detected. When an additional 25–60 mL has been collected (making a total of about 300–325 mL; this total, again, can vary among asphalts) the transition between relative nonfluorescence and uniformly bright fluorescence is complete and the delivery tube is transferred to a third graduated cylinder. This is the cutpoint between SEC Fraction-I and subsequent fractions. The exact determination of the cutpoint depends on the judgement of the operator. In the separations described herein, a Gelman-Camag Universal ultraviolet lamp was used. Other lamps generating light in the 350–360 nm range may be used. The lamp is normally held 10 cm from the material irradiated, and white paper is placed behind it. The nonfluorescent material contains the associated molecular species. The transition zone is the result of materials flowing up the outside of the column of gel faster than the inside. If the eluate is allowed to stand for about 1 h in the graduated cylinder, layers will form of gradually increasing brightness until uniform brightness occurs. This allows the operator to make the judgement between transition and uniformly bright eluate, in other words, between the associated species and the nonassociated species. Also at this point the operator must decide (if such a decision has not already been made) whether to perform a two-fraction run or a multifraction run. If a two-fraction run is required, then all of the remaining eluate collected will be SEC Fraction-II. If a multifraction run is required, then the size of each fraction must be decided on and the run will proceed accordingly. After SEC Fraction-I has been eluted, the separation can be interrupted and the remainder of the asphalt sample can be eluted at a later time. In the multifraction runs performed in the SHRP A-002A program, the SEC Fraction-II was divided into eight subfractions consisting of successive 200 mL volumes of eluates.

The fractions collected are then divested of solvent by pouring eluates from the collecting cylinders into round bottom flasks. Most of the solvent is removed by attaching the flasks to a rotary evaporator with a hot water bath. To remove toluene, a vacuum is required. After most solvent is removed, the eluates are transferred to weighed vials and the residual solvent is removed. The mass of each fraction is determined. The mass percent of each fraction is then calculated with the following equation:

$$\text{mass \%} = (\text{mass of fraction} \times 100) / \text{wt asphalt} \qquad (9.1)$$

About 1 ½ days are required to perform one preparative SEC separation for a 16.0 g sample of asphalt. This estimate assumes that the column has been packed and calibrated and that all solid material has been removed from the asphalt solution by filtration. The duration of the solvent removal step depends on the number of fractions collected and the number of rotary evaporators available. Customarily, in multifraction runs, masses of each of the fractions are plotted versus cumulative column bed volumes; after which each of the fractions has been collected, in order to construct chromatograms. The first point in such a chromatogram corresponds to the breakthrough of colored materials, which is zero mass.

Streamlined Preparative Size Exclusion Chromatography Experimental Procedure

The streamlined preparative size exclusion chromatography (SPSEC) procedure was devised to shorten the time necessary to obtain results comparable to those obtained from the large-scale PSEC procedure. The techniques are basically the same except for time and scale. The PSEC procedure takes about 2 working days from sample introduction to final weighing of fractions. The SPSEC procedure takes about 3 h. In both cases toluene (EM Sciences, HPLC grade) is used as the eluant and Bio-Rad Bio-Beads S-X1 are used as the column packing.

The equipment required for the SPSEC separation consists of the following. A Lab-Crest water-jacketed column 0.9 cm I.D. × 50 cm long, fitted with stopcocks at both ends, is packed with Bio-Rad Bio-Beads S-X1 (200–400 mesh) gel beads. The end fittings contain fritted glass discs that hold the resin in place and add about 2 cm to the length of the column. The columns presently in use were purchased from Andrews Glass Company, but similar columns are available elsewhere. A water circulation bath connected to the column water jacket by Tygon tubing provides 40°C (104°F) temperature control. The pump used is an FMI model RPG-50 (1/8 in. piston) with an FMI PD-60-LF pulse dampener in the solvent stream between the pump and the column. Teflon tubing is used in the sample stream. Small (10 and 25 mL) graduated cylinders are used as receivers. Erlenmeyer flasks are used as solvent reservoirs. Graduated test tubes are used as sample reservoirs.

The gel swells about 7.9 mL/g in toluene, but compresses in the column under the influence of the pressure from solvent pumping to about 75 percent of that volume. A calculation of the volume of the column, including end fittings, yields a volume of about 33 mL. Therefore, it takes approximately 5.6 g of the gel to fill a column. The column can be packed in either of two ways. The first involves swelling the gel with toluene before putting it into the column, pouring some of the slurry into the column, allowing the gel to settle, and then adding more gel slurry as the gel settles. However, the gel compresses as solvent is pumped through the column, and so a small amount of dry gel must be added at the very end of the column filling process to compensate for not being able to fill the column completely with swelled gel. The second way to pack the column is to partially fill the column from the top with dry resin and then pump toluene in from the bottom and alternate addition of gel with toluene finishing, again, with dry resin.

After the column is filled, solvent is pumped through the column from the bottom, whereupon a gap may develop at the bottom of the column between the surface of the gel bed and the glass frit. For best results, this gap must be filled with gel. Therefore, pumping is reversed so that the gap forms at the top of the column and shrinks when pumping is discontinued and the gel swells. It thus will be impossible to add the right amount of gel for proper operation without shrinking the gel. This is accomplished by pumping in a few milliliters of methanol at the top of the column. The calculated amount of dry gel can then be added by removing the fitting at the top of the column. The amount of gel to be added is calculated from the volume of the gap and assuming the known swelling ratio of the gel of 7.9 mL/g and the 75 percent compression of the gel under pressure. Occasionally another gap may develop after prolonged use of the column. This can be corrected in the same way. It should also be mentioned that if the column is overpacked, one or both of the frits at the ends of the column may break and need to be replaced.

The columns are mounted vertically in a well-ventilated space and solvent is pumped into the bottom. The pulse dampener is taken out of the solvent stream when sample is being pumped into the column, after which it is put back into the solvent stream. The eluate is piped to a graduated cylinder collector immediately after the column. The toluene flow rate is 0.26 ± 0.04 mL/min.

The sample (0.15 ± 0.0025 g) is dissolved in enough toluene to make 3.0 mL of solution in a graduated test tube. The sample solution is introduced through the pump into the bottom of the column. The delivery tube is put into a 25 mL graduated cylinder at that point; the tip of the delivery tube is placed so that as the liquid level rises the tip is immersed in the liquid. The receiver is placed on a white piece of paper to allow easy detection of color when the first of the sample starts to emerge. When the first color is observed in the receiver the delivery tube is transferred to a 10 mL graduated cylinder. The next 5.5 to 6.0 mL of eluate contains SEC Fraction-I, which corresponds to the associated or the dispersed part of the asphalt. The next 25 mL of eluates are collected in a second 25 mL graduated cylinder and contain SEC Fraction-II of the asphalt. The fractions are transferred to weighed 30 mL vials.

The fractions are divested of solvent overnight by means of a static solvent evaporator, such as an Organomation N-Evap with an inert gas flow and a hot water bath; if results are needed sooner, a rotary evaporator can be used. The vials are then weighed and the results are calculated by using the following formula:

$$\text{mass \%} = (\text{mass of fraction} \times 100) \,/\, \text{wt asphalt} \tag{9.2}$$

The important datum to be obtained is the mass percent of SEC Fraction-I. That means that the determination of the cutpoint between Fraction-I and Fraction-II is critical. There are two ways that this cutpoint can be ascertained during a run. Initially, the onset of fluorescence to 350 nm light was used to determine the cutpoint. Then it was found that for small samples all asphalts gave essentially the same cutpoint, so the use of the volume of 5.5 mL collected as the cutpoint was established. This gave reproducible and accurate results, when compared with results from the PSEC. However, as we continued to use the columns, it was discovered that results deviated slightly from the PSEC results and so the volume of SEC Fraction-I was increased to 6.0 mL. This cutpoint gives good results but suggests that a "standard" asphalt be run weekly to ensure that results are staying within acceptable bounds.

Fast Size Exclusion Chromatography Procedure

The PSEC procedure described previously was developed to give samples that are large enough to analyze and to use in other experiments. For an analysis that gives numbers only, a faster procedure was desired that could give results in minutes instead of the hours required by the PSEC procedure. This procedure uses high-performance liquid chromatography (HPLC) equipment with its associated software and hardware.

The equipment used here is a Hewlett-Packard (HP) 1090A equipped with a UV-visible diode array detector (DAD), a DR5 solvent delivery system, and an autoinjector. The system operates from an HP 85B personal computer equipped with an HP 9121B dual disk drive and uses the HP 1090 B-2517 version software. The system is also equipped with an HP 7470A plotter and an HP Thinkjet printer.

The sample is injected into the system and passes through a guard column into a Phenomenex Phenogel 10,000 Å (5 μm particle size) column, followed by a Phenomenex Phenogel 1,000 Å (10 μm particle size) column. The sample loop is then led outside the HPLC mainframe to an HP 1046A fluorescence detector (FD), back to the mainframe to the DAD, and outside again to a Waters R401 differential refractive index detector (DRID). The order of the detectors is dictated by the pressures under which each is able to operate.

The FD and the DRID are each equipped with an HP 3393A integrator, and each integrator is equipped with an HP 9114B disk drive. The disk drives allow storage of the raw data on 3.5 in. double-sided double-density floppy disks for further analysis if necessary. The DAD puts out enough raw data that only two runs can be stored on one 3.5 in. disk. However, data from hundreds of runs from the other detectors can be stored on one disk. Each integrator is programmed to report data as 30 sec data slices. Evaluation routines allow preparation of either two- or three-dimensional plots of the DAD data.

Column conditions include a flow rate of 2.0 mL/min toluene at a temperature of 30°C (86°F). Samples (1.25 mg) are injected into 50 μL of a solution prepared by dissolving 50 mg sample in 2.0 mL toluene. A run is complete in 18 min and it takes about another 2 min to run the BASIC programs on the FD and DRID integrators. The program for the DAD is run automatically. Some examples of the 30 sec slice data are available in the SHRP database.

Results of SEC separations of SHRP asphalts are presented and discussed in volume 2, chapter 2.

10 Oxidation of Asphalts by Thermal, Catalytic, and High Pressure Methods

Introduction

The purposes of oxidative aging experiments are to simulate in the laboratory asphalt aging in the field and to investigate the chemical changes occurring in asphalts during oxidation over the range of temperatures experienced in highways. Two research methods used to simulate field aging are described in this chapter. One is a pressure vessel procedure (designated TFO-POV) similar to the test method described in chapter 4. In this method, greatly increased oxygen pressure is used to accelerate asphalt aging processes. The difference between the test method and the research procedure is that the latter is performed over longer periods of time and at lower temperatures. Formal test methods for asphalts cannot take several days to complete, so they must operate at somewhat higher temperatures than research procedures. The temperatures in the research TFO-PAV procedure were chosen to approximate pavement service temperature maxima. A second research method simulating field aging is an oven procedure designated the thin film accelerated aging test (TFAAT). This procedure operates at atmospheric pressure and uses somewhat elevated temperatures to accelerate asphalt aging processes. Reaction times are too long for the procedure to be used as a formal test method unless reaction temperatures are raised such that maximum service temperatures are greatly exceeded.

This chapter also contains detailed instructions for the measurement of rates of oxidation of model compounds in the presence of asphalts, chemiluminescence measurements on asphalts, measurements of oxygen uptake in asphalts, and other methods used during the investigation of the mechanism of asphalt oxidation at SRI International.

TFO-POV and TFO-PAV

The conditions described below for the aging of asphalts by thin film oven followed by pressure vessel oxidation using either oxygen (TFO-POV method) or air (TFO-PAV method) were used at Western Research Institute to obtain the data reported in volume 2. Conditions used for asphalts aged at The Pennsylvania State University are reported in chapter 4. In performing these experiments, special care must be taken in handling pressurized equipment.

Pressure oxidation vessel aging experiments were performed by first weighing 50.0 g asphalt into TFO pans. Smaller samples were aged maintaining the same mass-to-surface area ratio

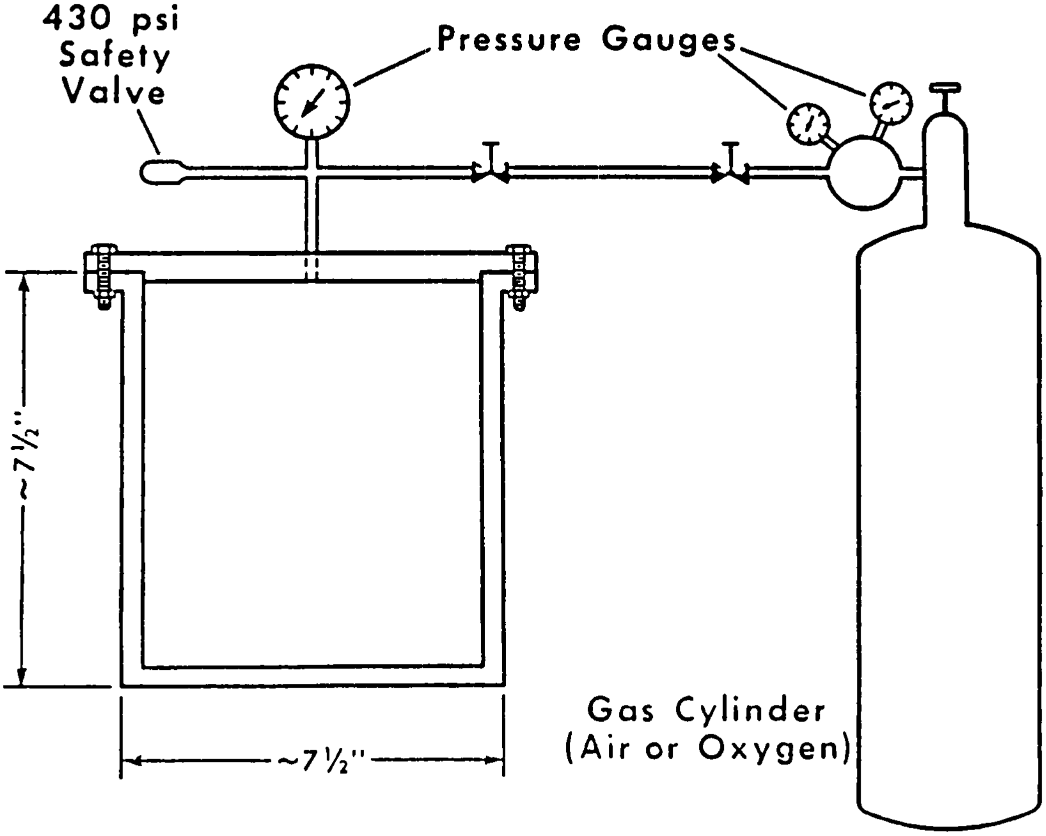


Figure 10.1. Equipment for Pressure Aging (POV and PAV) Experiments.

so that the sample film thickness was always 0.3175 cm (0.125 in.). Most samples underwent a TFO treatment at 163°C (235.4°F) for 5 h (ASTM Procedure D 1754) prior to pressure aging. Then, the TFO pans were placed in one of two pressure aging vessels constructed of stainless steel. One of the vessels was generously provided by Dr. D.Y. Lee of Iowa State University and the other was fabricated by Kent Allen and Daughters. The pressure aging vessels are cylindrical, approximately 19.05 cm I.D. × 19.05 cm high (7.5 in. I.D. × 7.5 in. high). The pressure aging apparatus is shown in figure 10.1.

The pressure aging vessel was filled with either air or oxygen (Great Plains Welding) so that the pressure inside the vessel would be 300 psi (2.07×10^6 Pa) at reaction temperature. The vessel and contents were placed in a VWR 1630 forced draft oven. The temperature of the oven was adjusted to produce the appropriate temperature inside the pressure oxidation vessel as measured by a thermocouple placed inside the pressure vessel. After 6 days (in some instances other lengths of time were used) at a temperature of 60, 70, or 80°C (140, 158, or 176°F), the pressure oxidation vessel was removed from the oven, cooled, and slowly vented. When the vessel was opened, the samples displayed evidence of some frothing caused by escape of dissolved gases from the asphalt samples. The oxidized asphalts were stored in sealed plastic bags in the TFO pans until required for study. In no case was a skin observed to form on any asphalt after storage.

Thin Film Accelerated Aging Test

Thin film accelerated aging test (TFAAT) oxidations were performed as described by Petersen (1989), using standard rolling thin film oven test (RTFOT) bottles and a standard RTFOT oven (James Cox and Sons) without air injection. To prepare samples for aging, 4.0 g of asphalt was weighed into each of several RTFOT bottles to the nearest 0.1 mg, using an analytical balance. The samples were deposited on the sides of the bottles to facilitate subsequent dissolution. Ten milliliters of redistilled toluene (EM Sciences, Omni Solv, glass distilled) was added to the bottles, which were each plugged with a silicone stopper.

A house vacuum line was attached to the top air vents of the oven to capture any solvent vapors. The stoppered bottles were placed in the oven and rotated for 45 min to dissolve the asphalt, and then the stoppers were removed. The bottles were again rotated for 1 h with no heat and with the vacuum applied to vent the oven of solvent. This procedure removes all but traces of the toluene from the asphalt and deposits a uniform asphalt film on the inside surface of the bottles. With the vacuum on and the bottles rotating, the oven was heated to about 85°C (185°F) and held at this temperature for 30 min. At this point, all solvent had been removed from the asphalt film (confirmed initially by infrared spectroscopy). With the bottles rotating, silicone stoppers containing glass capillary tubes 0.3 I.D. × 5.2 cm (0.118 I.D. × 2.04 in.) were inserted snugly into the bottle openings. Then the vacuum line was removed from the oven vents. It is essential to keep the bottles rotating at all times when the asphalt is hot to maintain uniformly deposited films of asphalt on the inside surfaces of the bottles. The oven was then heated to either 85, 113, or 130°C (185, 235, or 266°F). The asphalt samples were aged for the following times:

85°C: 0, 24, 48, 96, 144, and 400 h

113°C: 0, 24, 48, 72, and 120 h

130°C: 0, 4, 12, 20, and 36 h

After aging, the bottles were removed from the oven while they were still warm. The warm sample was scraped from the inside surface of each bottle with a single-edged razor blade attached to a handle (or other suitable tool), deposited in a small glass bottle, and blanketed with argon gas. The sample was then consolidated and made uniform by placing the bottle in a 135°C (275°F) sand bath and stirring the contents with a spatula. The sample was again blanketed with argon gas, and the bottle was sealed.

Asphalt-Aggregate Aging Experiments

Asphalt-aggregate aging experiments were conducted by coating 5 mass percent asphalt on 95 mass percent aggregate particles. Ten grams of asphalt were weighed into a porcelain weighing dish and heated for 20 minutes at 150°C (302°F). Approximately 190 g of 20–35 mesh aggregate (previously washed and dried) was placed in a clean oven (no organic contamination) at 150°C (302°F) overnight and left in the oven until used. After the asphalt was heated, 190 g of hot aggregate was added to the asphalt using a top loading balance. The mixture was mixed quickly and completely and returned to the oven for 5 min, after which the mixture was stirred again and then split into two 100 g aliquots. One aliquot was extracted immediately after completion of mixing and cooling for about 1 h.

The other aliquot was placed in one of two pressure oxidation vessels (POV) constructed of stainless steel. The vessels are cylindrical, approximately 19.05 I.D. × 19.05 cm in height. The POV was filled with air so that the pressure would be 300 psi (2.07×10^6 Pa) at reaction temperature. The vessel and contents were placed in a VWR 1630 forced draft oven. The temperature of the oven was adjusted to produce the appropriate temperature as measured by a thermocouple placed inside the vessel. After 144 h at 60°C (140°F), the POV was slowly vented and removed from the oven. This aliquot was then extracted after cooling about 1 h.

Both aliquots were extracted with 15 percent ethanol in toluene, using a medium frit Buchner funnel placed on a filter flask. The mixture was washed until the filtrate was colorless. The solvent was removed from the extracted asphalt on a rotary evaporator using heat and reduced pressure. An argon gas stream was connected to the rotary evaporator and the sample was continuously flushed to prevent oxidation of the sample. Before all solvent was removed, the extracted asphalt was transferred to a tared 30 mL vial. The remainder of the solvent was removed by rotary evaporation using a 105°C (222°F) oil bath for 90 min. Infrared spectra of each sample dissolved in carbon disulfide were obtained to detect residual solvent in samples before rheological measurements (chapter 12) were performed.

Rates of Oxidation of p-methoxyphenol

Solutions of p-methoxyphenol (MP), azobisisobutyronitrile (ABN), and asphalt in t-butyl benzene (TBB) were made up in 25 mL flasks with ground glass stoppers. Reactions were immersed in a 50 ± 0.05°C (122 ± 32°F) oil bath. Aliquots of 1 mL were withdrawn each hour and immediately cooled to 20°C (68°F). Each solution was immediately extracted with 0.1 M aqueous NaOH by shaking for 10 min to remove the MP anion. The extracted solution was neutralized to pH 5 with 20 μL of 3.6 M sulfuric acid and analyzed for MP by HPLC on a HP-1090 chromatograph equipped with a diode array detector set at 230 nm. The HPLC separation required a 2 m C-18 reverse phase column with 40:60 acetonitrile:pH 5 phosphate buffer as eluent. At a flow rate of 0.4 mL/min^{-1}, MP elutes at 2.8 min. Trial mixtures with MP in TBB showed that efficiency of extraction was about 80 percent in the concentration range of 5 to 30 μM. The HPLC detection limit was close to 2 μM. Procedures for oxidation of hydroxynaphthoic acid (HNA) were identical to those used for MP. HPLC analyses for HNA also were similar, except that HNA elutes at 1.8 min where MP elutes in 2.8 min. Trial mixtures with HNA in TBB showed that efficiency of extraction was greater than 95 percent in the concentration range of 5 to 30 μM using pH 8 phosphate buffer was used. The HPLC detection limit for HNA was less than 1 μM.

Pressure Transducer, Calibration and Oxidation

The differential pressure transducer used for cumene oxidations is shown in figure 10.2. Five milliliters of 0.010 M ABN in cumene was introduced into one of two reaction flasks

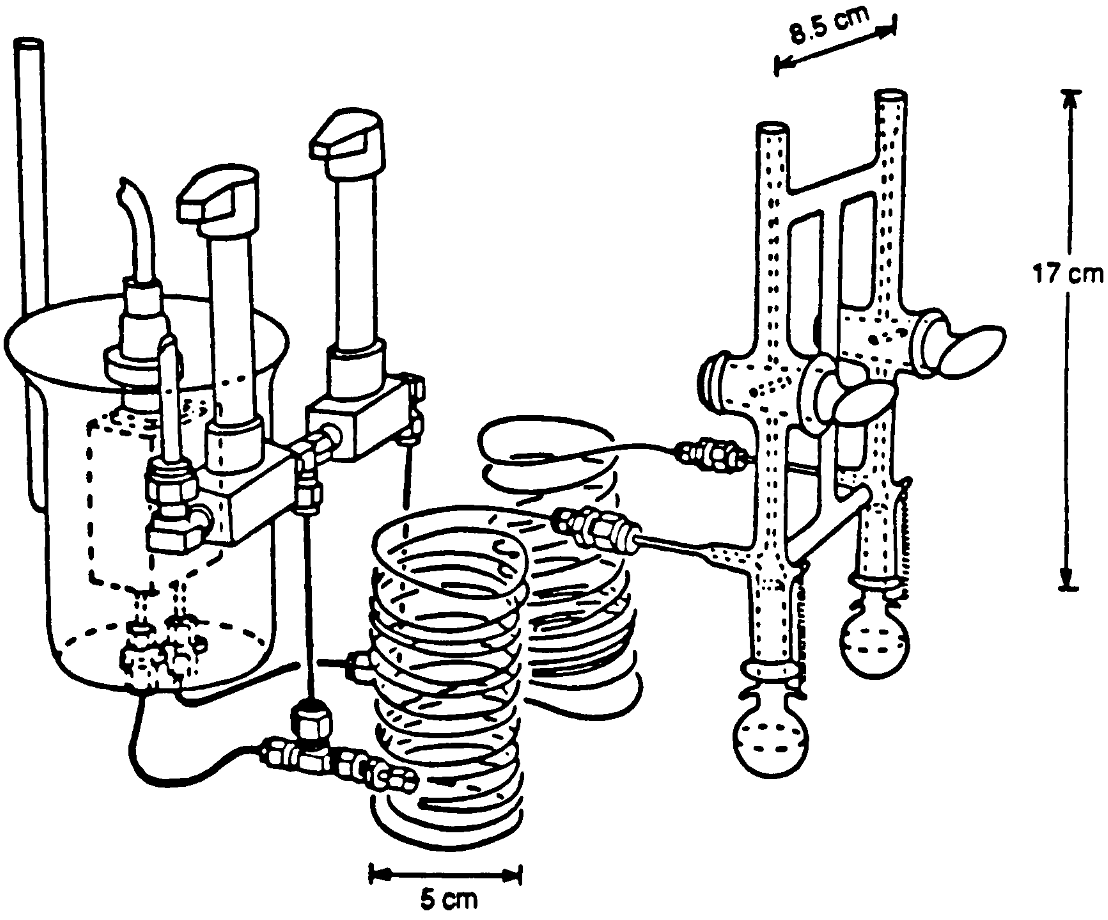


Figure 10.2. Pressure Transducer and Reaction Flasks for Oxygen Uptake Measurements.

attached to the pressure transducer system to calibrate the pressure change in nanomoles of gas. The reference flask contained only cumene; both flasks were immersed in the water bath at 60°C (140°F). Changes in pressure with time were noted over 1, 3, 6, or 8 h for duplicate runs. ABN decomposed during this period to evolve 45, 133, 430 or 578 pmoles of nitrogen, which corresponded to output readings over a range from 0.13 to 1.6 on a scale of 100.0.

Oxidation experiments were conducted with 1 to 5 mL of cumene in the transducer system, first flushed with oxygen and then loaded with pure cumene in both reaction flasks. After equilibrating for 10 min to reach 60°C (140°F), a solution of ABN and inhibitor in cumene was introduced through the top of the apparatus with a long-needled syringe. Stopcocks were closed on both the reaction and reference sides and the transducer readout was set to zero as was the recorder attached to the readout. The reaction flasks were agitated with an eccentric shaker to ensure rapid mixing of oxygen with the cumene. Oxygen uptake began only when the inhibitor was exhausted and the recorder traced the pressure change with time. The time of inhibition is defined as the point where the slope of the pressure change line intersects the x-axis on extending the line.

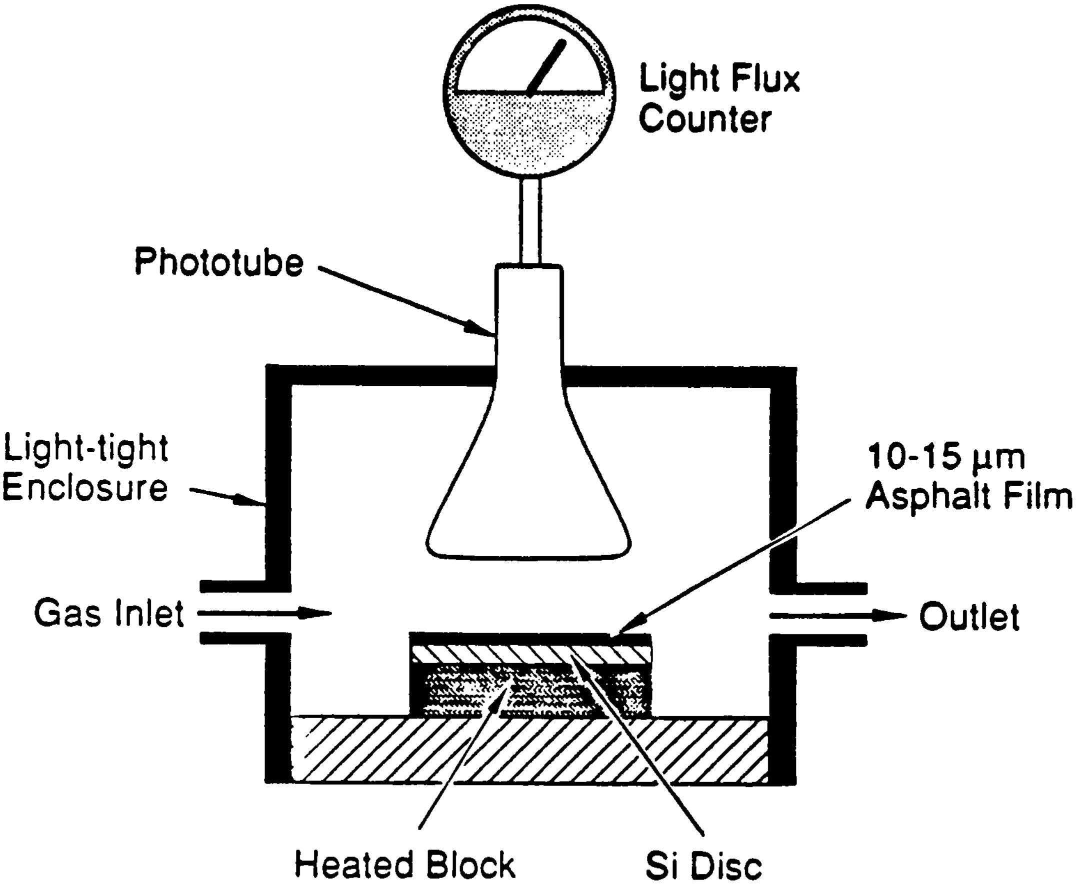


Figure 10.3. Chemiluminescence Detector.

Chemiluminescence

The chemiluminescence apparatus consists of a light-tight container outfitted with gas inlet and outlet tubes, a resistance heater, and a photomultiplier to count near-UV-visible photons, (figure 10.3). Films of asphalts 8 to 30 μm thick cast from toluene onto 5-cm-diameter silicon wafers and dried under vacuum ($<$ 0.1 torr) at 25 to 30°C (77 to 86°F) were examined for chemiluminescence emission in the chemiluminescence apparatus at temperatures ranging from 25 to 145°C (77 to 293°F).

Sulfoxide Measurements and Pyrolysis

Oxidized asphalt films were dissolved in carbon disulfide (CS_2) and analyzed by FTIR as described below. Oxidized films for pyrolysis were degassed at 30°C (86°F) under a 25 μm vacuum and cooled and pumped for 1 h, then repressured to one atmosphere with argon containing less than 10 ppmv oxygen and sealed. The films were heated for 5 to 10 h at 165°C (329°F), cooled, opened, and dissolved in CS_2. Films were analyzed by FTIR by cutting and weighing the area under the sulfoxide band near 1,000 cm^{-1} and comparing the result with a calibration curve prepared with spectra of di-n-butyl sulfoxide solutions in CS_2, cut and weighed in the same way. Reproducibility of the method is ± 2 percent for the same investigator, ± 3 to 4 percent among investigators.

Carbonyl Measurements

Films were analyzed by FTIR for carbonyl by cutting and weighing the area under the difference spectra for the carbonyl band near 1700 cm^{-1} and comparing the result with a calibration curve prepared with spectra of valerophenone in CS_2 solution, cut and weighed in the same way.

Oxygen Oxidation of Aliphatic Sulfides

The model sulfides dibenzyl sulfide and n-butyl sulfide in 50 mg amounts were loaded into 50 mL Pyrex glass volumetric flasks, sealed under air or pure oxygen, and heated at 130°C (266°F) for 3 days. The samples were then analyzed for sulfoxide by FTIR.

Oxygen Uptake Measurements

Glass bottles 60 mL in volume were loaded with 100 to 300 mg of asphalt in CH_2Cl_2 and coated on the vessel walls as 40 μm films. Vessels were sealed with rubber serum caps, wired, and placed in the 100°C (212°F) oil bath. After heating for the required time, samples were withdrawn and cooled. The volume percent oxygen was measured by withdrawing 70 to 100 μL of gas with a gas-tight syringe and injecting it into a gas chromatograph equipped with a 2-m zeolite column and a thermal conductivity detector.

The integrated areas under the nitrogen and oxygen peaks were converted to percent oxygen ($\%O_2$) and compared with $\%O_2$ in an empty control vessel fitted with the same septum and heated for the same time. Calculation of the micromoles of oxygen consumed requires that the vessel volume V and the barometric pressure p in centimeters be known on the day the reaction is started.

$$\mu\text{moles } O_2 \text{ consumed} = (pV/RT)\%O_{2\text{control}} - (pV/RT)\%O_{2\text{reaction}} \qquad (10.1)$$

where $RT = 1.8585$ $(\text{cm mL}/\mu\text{mole})^{-1}$ at 298°K. Reproducibility of the method is very good. Replicate analyses have errors of ± 0.3 to 0.4 percent; replicate experiments have errors of ± 3 to 5 percent.

11 Potentiometric Titrations of Asphalts

Introduction

Nonaqueous potentiometric titration of solutions of fossil fuels is a method that is used for rapid quantification of acidic and basic species present. Before the SHRP Binder Characterization and Evaluation Program, the method had seen limited use with asphalts. Nonaqueous potentiometric titration can be used routinely to quantify strong and weak organic bases in tank and aged asphalts. There is no other method available for rapid quantification of strong organic bases in asphalts. Nonaqueous potentiometric titration of acids in asphalts is still in the development stage. A procedure is included for use in research. At this time, quantification of acids in asphalts might best be performed by infrared methods (chapter 6).

Characterization of Bases: Perchloric Acid Titration of Asphalts

The method developed for the titration of bases is a modification of a method originally developed by Buell (1967b) for the titration of crude oils and their distillate fractions, of ASTM method 2896-85, and of a method developed by Dutta and Holland (1984) for the characterization of bases in petroleum asphaltenes. These methods used perchloric acid as the titrant so that the weaker bases could be titrated. The titration solvent of choice for asphalts was determined to be a 9:1 (v:v) solution of chlorobenzene (Aldrich, HPLC grade) and acetic anhydride (EM Sciences, reagent grade). The acetic anhydride was added to increase the potential range of the solvent and to scavenge any water that might get into the system. The titrant of choice was 0.1 N perchloric acid in acetic acid (Aldrich Chemical). The manufacturers of chlorobenzene and perchloric acid provide data sheets outlining the hazards involved in handling these reagents and proper methods for their disposal. Perchloric acid requires neutralization, and chlorobenzene is disposed of with other halogenated hydrocarbons.

The data reported earlier in this program were produced on an older model Mettler autotitrator with a glass pH electrode and a calomel reference electrode filled with methanolic potassium chloride. The instrument currently in use is a Metrohm 670 Titroprocessor used in conjunction with the 665 Dosimat titrating unit. The electrodes of choice were a glass pH electrode and a silver chloride reference electrode filled with ethanolic lithium chloride. Although the calomel reference has been used extensively in the past, the silver chloride reference was found to be more sensitive at the higher potentials.

A 150 mL portion of material to be titrated (asphalt or asphalt fraction) was accurately weighed into a 50 mL beaker. Thirty milliliters of the titration solvent were added to the beaker. When the sample was completely dissolved it was placed on a magnetic stirrer, the electrodes and burette tip were placed in the solution, and the titration was started. With the old Mettler titrator the titration was carried out at a rate of 0.24 mL/min and the titration curve was produced on a strip chart recorder plotting electrode potential in millivolts against volume of titrant in milliliters. At the end of the titration the end points and the calculations that followed had to be determined manually. With the new Metrohm titrator, the titration is carried out at a rate of 1.00 mL/min and the plot is produced on the screen of the titroprocessor as the titration progresses. The instrument locates the end points and carries out the necessary calculations, which are then printed out at the end of the run along with the titration curve. The base quantities at each end point were calculated with the following formula:

$$\text{meq/g base} = N(S - B)/M \qquad (11.1)$$

where

N = Normality of the titrant (meq/mL)
S = Volume of titrant to end point (mL) for sample
B = Volume of titrant to end point (mL) for blank
M = Mass of sample (g)

The amounts of moderately strong bases (end point 1) were subtracted from the total bases to obtain weak base concentrations (end point 2).

The key factor to succeeding with nonaqueous titrations is proper electrode maintenance. The pH electrode should be soaked in distilled water when not in use. Prior to the start of a titration, it should be rinsed with acetone and then chlorobenzene. After the titration, the electrodes and the burette tip should be rinsed with chlorobenzene to remove any adhering sample. The pH electrode should be rinsed again with acetone and then water, and it should be soaked in water until it is needed again. This particular type of titration stresses the pH electrode because the electrode becomes dehydrated and because asphalts are known to be high in surfactants, which cling to electrodes and are difficult to remove. This problem has been solved by soaking the pH electrode in distilled water for at least 1 h between runs. To keep up productivity, three electrodes were used in rotation.

At the start of each day, titrations were done on blank titration solvent to condition the electrodes and to ensure that the system was working properly. New batches of titrant were standardized against 0.02 N solutions of select model compounds such as caffeine and hydroxyquinoline. This titration was also used on occasion as a check for electrode stability.

Characterization of Acids: Tetrabutylammonium Hydroxide Titration of Asphalts

The method developed for the titration of acids is a modification of procedures developed by Dutta and Holland (1983) for the titration of acidic groups in coal and coal-derived materials and of a procedure developed by Buell (1967a) for the titration of acids in petroleum. Both methods used tetrabutylammonium hydroxide (TBAH) as the titrant. The titrant of choice for asphalts was determined to be a 0.1 N solution of TBAH in toluene/2-propanol. It was prepared by mixing 10 mL of a 1.0 M solution of TBAH in methanol (Aldrich) with 4 mL of 2-propanol in a 100 mL volumetric flask and then diluting to the mark with toluene. This titrant is sensitive to carbon dioxide so it was kept under argon at all times. The titration solvent used has been chlorobenzene (Aldrich, HPLC Grade).

The technique used for the TBAH titrations was the same as the perchloric acid technique. Titrations were done initially on a variety of model carboxylic acids and phenols. These titrations were also used for standardizing new batches of titrant.

12 Rheological Measurements of Asphalts

Introduction

Most physical property measurements obtained during the course of the SHRP Binder Characterization and Evaluation Program were performed at The Pennsylvania State University. It was necessary to generate some rheological data in-house for the study of binder chemistry at Western Research Institute (WRI) because of the large number of samples generated. Protocols used during the rheological studies at WRI are described below. As a result of research in the Binder Characterization and Evaluation Program, SHRP recommends that routine rheological measurements be performed as described in chapter 1. This method was used at The Pennsylvania State University, and employs a different instrument from the one used at WRI.

Equipment

The rheological measurements obtained at WRI were performed with the Rheometrics Mechanical Spectrometer model 605. This dynamic shear rheometer is used to determine linear viscoelastic moduli at various temperatures and frequencies of asphalts, aged asphalts, asphalt fractions, and modified asphalts. The temperatures of measurement range from 0—60°C (32—140°F), and test frequencies vary from 0.1 to 100.0 rad/s. Viscosities (η^*) are usually reported at 0.1 or 1.0 rad/s. Phase angles (δ) and their tangents (tan δ) also are calculated from these measurements. Other variables in rheological determinations of asphalt samples are parallel plate sizes, gap size, and strain level. These parameters must be taken into consideration before the sample is tested.

Annealing Procedure Initially Used

At the beginning of the A-002A program, there was no set procedure for preparing (annealing) samples before rheological measurements. Consequently, annealing procedures were developed for the different types of samples that were generated during the course of the program. Among these different kinds of samples are core asphalts, aged asphalts, and various fractions of asphalts. The annealing procedure initially used consisted of heating samples to 110°C (230°F) for 1 h, and then performing rheological measurements 48 h later. The relatively low temperature was chosen to minimize sulfoxide decomposition in aged asphalts. The decision to measure rheological properties 2 days later was based on the assumption that most molecular structuring would have occurred by this time (see volume 2, chapter 6). Initially, aged samples also were annealed as described above, except that samples catalytically aged with vanadyl complexes were later annealed for 1 h 15 min at 50°C (122°F) and tested rheologically 24 h later. The lower temperature was used because of the high catalytic activity of vanadyl complexes at 110°C (230°F).

Unfortunately, use of these annealing procedures not only limited the number of samples to be tested on a daily basis, but also resulted in great scatter among the data that were obtained. Consequently, new annealing procedures were adopted.

Standard Annealing Procedure for the Neat Asphalts

A sample of asphalt weighing between 6 and 7 g was taken directly from its container and transferred into a small vial. The vial was flooded with argon to prevent oxidation during the annealing procedure. The vial and its contents were placed in a vacuum oven that was heated at 150°C (302°F) for 1 h. After this treatment, the vial was removed from the oven and cooled to room temperature for about 30 min. After 30 min the sample was loaded onto the mechanical spectrometer to be tested.

Annealing Procedure for Thin Film Accelerated Aging Test–Aged Samples, Mixed with Vanadyl Acetoacetonate

Vials containing samples were placed in a vacuum oven for 1 h 15 min at 50°C (122°F), and then removed. They were maintained at room temperature for about 24 h, after which rheological testing was performed.

High–Temperature Annealing Procedure

A 16 g sample of asphalt was transferred to a container, and the container was flooded with argon and sealed. The container was heated to 163°C (325.4°F) and maintained at that temperature for 2 h. This temperature was chosen because aged asphalts are heated to this temperature in the TFO. The container was placed in a paint shaker for 5 min, and then was allowed to cool to room temperature. Rheological measurements on a mechanical spectrometer were performed within 2 h after the container was removed from the paint shaker.

Mechanical Parameters for Rheometrics Mechanical Spectrometer Model 605

- Heat the plates of the instrument to the testing temperature and allow temperature to stabilize for 30—45 min.

- Check the transducer temperature to make sure it is in the range from 39.9—40.1°C (103.8—104.2°F); if not, adjust accordingly.

- Check instrument parameters (test geometry, sweep parameters, printer setup, and plotter setup).

Sample Loading/Temperature Stabilization

- Take 1—2 g of sample and place it onto the bottom plate of the pair of parallel plates.
- Lock the oven around the sample. Heat sample to a temperature at which the sample is fluid and can be worked to get rid of air bubbles.
- After working the sample so that the sample is uniform, with plates apart and sample in the middle, turn on the instrument motor.
- Set the testing temperature to the required value.
- Apply normal force to the sample so that the distance between the plates is decreased to about 2.2 mm, trimming the sample every 0.20 mm with a spatula, starting from around 3.0 mm distance between the plates.
- After the last trim, which would be at a 2.20 mm gap, close the instrument oven; loosen the spindle and apply normal force to the sample until the gap between plates becomes 2.0 mm. Check to make sure there is an observable bulge of the sample around the plates.
- The sample is loaded and ready to undergo test temperature stabilization. After it reaches testing temperature, allow sample to set for 20 min.

Operating Instructions for Rheological Measurements

- Push *Start* buttons on instrument panel; wait for the *Measurement in Progress* button to come on; press the *Hold* button.
- After the *Measure in Progress* button has been lit for two cycles, press *Hold* button again to turn it off.
- Enable the graphics mode on the computer.
- Enable the plotter on the instrument.
- When the sample measurement is completed, store the run in the computer.
- Label the run and enter the following information into the computer: loading temperature; transducer temperature; run temperature; sample description, what sample contains, when sample was received and annealed, and so forth.

To illustrate the above points, the rheological properties of asphalts AAK-1 and AAM-1 at 25°C (77°F) were measured to determine the standard deviations for rheological parameters. The asphalts were annealed according to the high-temperature annealing procedure. Measurements were performed at 400 g-cm torque and 3 percent strain using 25 mm parallel plates with 2 mm film thickness. The results of these experiments are listed in table 12.1.

Table 12.1 Multiple Rheological Analyses[1] of Asphalts AAK-1 and AAM-1.

Run Number	G' (dyne/cm^2)	G'' (dyne/cm^2)	Viscosity (Pa·s)	G^* (dyne/cm^2)	Tan δ (G''/G')
			AAK-1[1]		
1	1.616×10^6	3.927×10^6	8.133×10^4	4.246×10^6	2.429
2	1.617×10^6	3.926×10^6	8.147×10^4	4.246×10^6	2.428
3	1.603×10^6	3.939×10^6	8.407×10^4	4.252×10^6	2.458
4	1.628×10^6	3.919×10^6	7.940×10^4	4.244×10^6	2.407
5	1.625×10^6	3.913×10^6	7.900×10^4	4.237×10^6	2.408
Average ±	$1.618 \times 10^6 \pm$	$3.925 \times 10^6 \pm$	$8.105 \times 10^4 \pm$	$4.245 \times 10^6 \pm$	$2.426 \pm$
St. Dev.	0.010×10^6	0.010×10^6	0.202×10^4	0.005×10^6	0.021
			AAM-1[1]		
1	1.737×10^6	3.913×10^6	1.546×10^5	4.281×10^6	2.254
2	1.710×10^6	3.932×10^6	1.652×10^5	4.287×10^6	2.299
3	1.731×10^6	3.934×10^6	1.704×10^5	4.298×10^6	2.273
4	1.727×10^6	3.915×10^6	1.560×10^5	4.279×10^6	2.268
Average ±	$1.726 \times 10^6 \pm$	$3.924 \times 10^6 \pm$	$1.616 \times 10^5 \pm$	$4.286 \times 10^6 \pm$	$2.274 \pm$
St. Dev.	0.012×10^6	0.011×10^6	0.075×10^5	0.009×10^6	0.019

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[1] Measurements were performed at 25°C, 25-mm parallel plates, 2-mm film gap, and 400 g·cm torque

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Appendix A

Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer (DSR)

AASHTO Designation: TP5

Standard Method of Test for

Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer (DSR)

AASHTO Designation: TP5[1]

1. SCOPE

1.1 This test method covers the determination of the dynamic shear modulus and phase angle of asphalt binder when tested in dynamic (oscillatory) shear using parallel plate test geometry. It is applicable to asphalt binders that have dynamic shear modulus values from 100 Pa to 10 MPa. This range in modulus is typically obtained between 5°C and 85°C. This test method is intended for determining the linear viscoelastic properties of asphalt binders as required for specification testing and is not intended as a comprehensive procedure for the full characterization of the viscoelastic properties of asphalt binder.

1.2 This standard is appropriate for unaged material or material aged in accordance with T240, T179, or PP1.

1.3 Particulate material in the asphalt binder is limited to particles with longest dimensions less than 250 μm.

1.4 The values stated in SI units are to be regarded as the standard.

1.5 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this procedure to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.*

2. REFERENCE DOCUMENTS

2.1 *AASHTO Standards*

MP1	Test Method for Performance-Graded Asphalt Binder
T40	Practice for Sampling Bituminous Materials
T179	Test Method for Effect of Heat and Air on Asphalt Materials (Thin Film Oven Test)

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[1] This standard is based on SHRP Product 1007.

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 an Asphalt Binder Using the Bending Beam Rheometer
PP1	Practice for Accelerated Aging of an Asphalt Binder Using a Pressurized Aging Vessel
PP6	Practice for Grading or Verifying the Performance Grade of an Asphalt Binder

2.2 *ASTM Standards*

E1	Specification for ASTM Thermometers
E220	Method for Calibration of Thermocouples by Comparison Techniques

2.3 *DIN Standards*

43760

3. TERMINOLOGY

3.1 *Definitions*

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

3.2 *Descriptions of Terms Specific to this Standard*

3.2.1 complex shear modulus, G^*—ratio calculated by dividing the absolute value of the peak-to-peak shear stress, τ, by the absolute value of the peak-to-peak shear strain, γ.

3.2.2 phase angle, δ—the angle in radians or degrees between a sinusoidally applied strain and the resultant sinusoidal stress in a controlled-strain testing mode, or between the applied stress and the resultant strain in a controlled-stress testing mode.

3.2.3 loss shear modulus, G''—the complex shear modulus multiplied by the sine of the phase angle expressed in degrees. It represents the component of the complex modulus that is a measure of the energy lost (dissipated during a loading cycle).

3.2.4 storage shear modulus, G'—the complex shear modulus multiplied by the cosine of the phase angle expressed in degrees. It represents the in-phase component of the complex modulus that is a measure of the energy stored during a loading cycle.

3.2.5 parallel plate geometry, *n*—a testing geometry in which the test sample is sandwiched between two relatively rigid parallel plates and subjected to oscillatory shear.

3.2.6 oscillatory shear, *n*—refers to a type of loading in which a shear stress or shear strain is applied to a test sample in an oscillatory manner such that the shear stress or strain varies in amplitude about zero in a sinusoidal manner.

3.2.7 linear viscoelastic, *adj*—refers to a region of behavior in which the dynamic shear modulus is independent of shear stress or strain.

3.2.8 molecular association, *n*—refers to associations that occur between asphalt binder molecules during storage at ambient temperature. Often referred to as steric hardening in the asphalt literature, molecular associations can increase the dynamic shear modulus of asphalt binders. The extent of molecular association is asphalt specific and may be apparent even after a few hours of storage.

4. SUMMARY OF TEST METHOD

4.1 This standard contains the procedure used to measure the complex shear modulus (G^*) and phase angle (δ) of asphalt binders using a dynamic shear rheometer and parallel plate test geometry.

4.2 The standard is suitable for use when the dynamic shear modulus varies between 100 Pa and 10 MPa. This range in modulus is typically obtained between 5°C and 85°C, dependent upon the grade, test temperature, and conditioning (aging) of the asphalt binder.

4.3 Test specimens 1 mm thick by 25 mm in diameter, or 2 mm thick by 8 mm in diameter, are formed between parallel metal plates. During testing, one of the parallel plates is oscillated with respect to the other at preselected frequencies and rotational deformation amplitudes (or torque amplitudes). The required amplitude depends upon the value of the complex shear modulus of the asphalt binder being tested. The required amplitudes have been selected to ensure that the measurements are within the region of linear behavior.

4.4 The test specimen is maintained at the test temperature ± 0.1°C by positive heating and cooling of the upper and lower plates.

4.5 Oscillatory loading frequencies using this standard can range from 1 to 100 rad/s using a sinusoidal waveform. Specification testing is performed at a test frequency of 10 rad/s. The complex modulus (G^*) and phase angle (δ) are calculated automatically as part of the operation of the rheometer using proprietary computer software supplied by the equipment manufacturer.

5. SIGNIFICANCE AND USE

5.1 The test temperature for this test is related to the temperature experienced by the pavement in the geographical area for which the asphalt binder is intended.

5.2 The complex shear modulus is an indicator of the stiffness or resistance of asphalt binder to deformation under load. The complex shear modulus and the phase angle define the resistance to shear deformation of the asphalt binder in the linear viscoelastic region. Other linear viscoelastic properties, such as the storage modulus (G'), or the loss modulus (G''), can be calculated from the complex modulus and the phase angle. The loss modulus is a measure of the energy dissipated during each loading cycle.

5.3 The complex modulus and the phase angle are used to calculate performance-related criteria in accordance with MP1.

6. APPARATUS

6.1 *Dynamic Shear Rheometer Test System*—A dynamic shear rheometer test system consisting of parallel metal plates, an environmental chamber, a loading device, and a control and data acquisition system.

6.1.1 *Test plates*—Metal test plates with smooth polished surfaces. One 8.00 ± 0.05 mm in diameter and one 25.00 ± 0.05 mm in diameter. The base plate in some rheometers is a flat plate. A raised portion 2 to 5 mm high with the same radius as the upper plate is recommended. The raised portion makes it easier to trim the specimen and may improve test repeatability.

6.1.2 *Environmental Chamber*—A chamber for controlling the test specimen temperature, by heating (in steps or ramps), or cooling (in steps or ramps), to maintain a constant specimen environment. The medium for heating and cooling the specimen in the environmental chamber is a gas or liquid (note 1) that will not affect asphalt binder properties. The temperature in the chamber may be controlled by the circulation of fluid or conditioned gas; nitrogen or water is acceptable. When air is used, a suitable drier must be included to prevent condensation of moisture on the plates and fixtures and, if operating below freezing, the formation of ice. The environmental chamber and the temperature controller shall control the temperature of the specimen, including thermal gradients within the sample, to an accuracy of ± 0.1°C. The chamber shall completely enclose the top and the bottom plates to minimize thermal gradients.

NOTE 1.—A circulating bath unit separate from the dynamic shear rheometer which pumps the bath fluid through the test chamber may be required if a fluid medium is used.

6.1.2.1 *Temperature Controller*—A temperature controller capable of maintaining specimen temperatures within 0.1°C for test temperatures ranging from 5 to 85°C.

6.1.2.2 *Temperature Detector*—A reference thermal detector (RTD) mounted inside the environmental chamber, in intimate contact with the fixed plate, with a range of 5 to 85°C, readable and accurate to the nearest 0.1°C. This detector shall be used to control the temperature in the chamber and provide a continuous readout of temperature during the mounting, conditioning, and testing of the specimen.

NOTE 2.—Platinum RTDs meeting DIN Standard 43760 (Class A) or equal are recommended for this purpose. The RTD shall be calibrated as an integral unit with its respective meter or electronic circuitry.

6.1.2.3 *Reference Temperature Sensing Device*—A thermistor, RTD, or thermocouple as described in sections 9.1.1.2.1, 9.1.1.2.2, or 9.1.1.2.3 shall be used.

6.1.3 *Loading device*—The loading device shall apply a sinusoidal oscillatory load to the specimen at a frequency of 10.0 ± 0.1 rad/s. If frequencies other than 10 rad/s are used, the frequency shall be accurate to 1%. The loading device shall be capable of providing either a stress-controlled or strain-controlled load. If the load is strain controlled, the loading device shall apply a cyclic torque sufficient to cause an angular rotational strain accurate to within 100 μrad of the strain specified. If the load is stress controlled, the loading device shall apply a cyclic torque accurate to within 10 mN·m of the torque specified. Total system compliance at 100 N·m torque shall be $<$ 2 mrad/N·m.

6.1.4 *Control and Data Acquisition System*—The control and data acquisition system shall provide a record of temperature, frequency, deflection angle and torque. Devices used to measure these quantities shall meet the accuracy requirements specified in table 1. In addition, the system shall calculate and record the shear stress, shear strain, complex shear modulus (G^*) and phase angle (δ). The system shall measure and record G^*, in the range of 100 Pa to 10 MPa, to an accuracy of 0.5% or less. The system shall measure and record the phase angle, in the range from 0 to 90°, ± 0.1°.

Table 1. Control and Data Acquisition System Requirements

Quantity	Accuracy
Temperature	0.1°C
Frequency	1%
Torque	10 mN·m
Deflection angle	100 μrad

6.2 *Specimen Mold (Optional)*—A silicone rubber mold for forming asphalt binder test specimens having a diameter approximately equal to the diameter of the upper test plate and a height approximately equal to 1.5 times the width of the test gap.

6.3 *Specimen Trimmer*—A specimen trimmer with a straight edge at least 4 mm wide.

6.4 *Calibrated Temperature Detector*—A calibrated thermocouple, thermistor, or RTD with a thickness or diameter $\leq$ 2.0 mm is suitable for measuring the temperature of a dummy specimen or sample of asphalt binder. Thermocouples and thermistors are not reliable to ± 0.1°C unless calibrated to a standard traceable to the National Institute of Standards and Technology (NIST) and must be calibrated with associated meters or electronic circuitry. Platinum RTDs are typically not suitable because they are too large to fit in the gap between the test plates in the DSR.

7. HAZARDS

7.1 Standard laboratory caution should be used in preparing the test specimens of the hot asphalt binder.

8. PREPARATION OF APPARATUS

8.1 Prepare the apparatus for testing in accordance with the manufacturer's recommendations. Specific requirements will vary for different DSR models and manufacturers.

8.2 Mount the test plates on the test fixtures and tighten firmly.

8.3 Select the testing temperature according to the grade of the asphalt binder or according to the preselected testing schedule (note 3). Allow the DSR to reach a stabilized temperature ± 0.1°C of the test temperature.

NOTE 3.—Specification MP1 and Practice PP6 provide guidance on the selection of test temperatures.

8.4 With the test plates at the test temperature or the middle of the expected testing range, establish the zero gap level by one of two methods. One method is to manually spin the moveable plate. While the moveable plate is spinning, close the gap until the movable plate touches the fixed plate. The zero gap is reached when the plate stops spinning completely. The other method, for rheometers with normal force transducers, is to close the gap and observe the normal force. After establishing contact between the plates, set the zero gap at approximately zero normal force.

8.5 Move the plates apart and establish a gap setting of 1 mm plus 0.05 mm (for 25-mm diameter test specimens) or 2 mm plus 0.05 mm (for 8-mm diameter test specimens).

NOTE 4.—The frame, detectors, and fixtures in the DSR change dimension with temperature, which causes the zero gap. Adjustments in the gap are not necessary when measurements are made over a limited range of temperatures. The gap should be set with the test apparatus at the test temperature. When tests are to be conducted over a range of temperatures, the gap should be set with the test apparatus at the middle of the expected range of test temperatures. For most instruments, no gap adjustment is needed if the test temperature will be ± 12°C of the temperature at which the gap is set.

9. CALIBRATION AND STANDARDIZATION

9.1 Perform the following calibration and verification procedures at least every six months:

9.1.1 *Temperature*—Prepare a dummy specimen of asphalt binder or use a silicone wafer following standard procedures. Use the dummy specimen only for temperature verification measurements. (Dynamic shear measurements are not valid if a temperature detector is inserted into the asphalt binder.) Verify the specimen temperature indicated by the DSR RTD in trial runs by using a calibrated temperature detector inserted into the dummy specimen.

9.1.1.1 Compare temperature measurements obtained from the dummy specimen and the DSR RTD. Use the temperature measured inside the dummy specimen as the reference temperature. If the temperatures are not equal, apply an appropriate temperature correction to the temperature measurement indicated by the DSR RTD.

9.1.1.2 Thermal gradients within the rheometer and the difficulty of calibrating the instrument RTD while it is mounted in the rheometer (see note 5) require a direct measurement of the temperature between the plates using a dummy specimen and a reference temperature sensing device. This is accomplished by placing a dummy specimen between the plates and reading the temperature in the dummy specimen with a reference temperature sensing device. A thermistor, RTD, or thermocouple as described in sections 9.1.1.2.1, 9.1.1.2.2, or 9.1.1.2.3 shall be used as the reference temperature sensing device. Adjust the temperature in the chamber to the minimum temperature that will be used for testing and allow the chamber to come to thermal equilibrium. Read the instrument RTD and the temperature of the dummy specimen. Increase the temperature in increments of no more than 6°C and repeat the measurements to cover the range of test temperatures. Using these measurements, obtain the temperature difference between the instrument RTD and the reference temperature sensing device inserted between the plates. This difference will not be a constant but will vary with test temperature. Offset the thermal controller on the rheometer so that the target test temperature is obtained between the plates.

NOTE 5.—The RTD and its meter can be calibrated by a commercial vendor. Verification of calibration can be obtained by comparing the output from the RTD with a calibrated ASTM mercury-in-glass thermometer in accordance with ASTM E220. A stirred water bath is suitable for calibrating the thermal detector. Select a partial immersion mercury-in-glass thermometer with an appropriate range (ASTM 90C; 0 to 30°C or ASTM 91C; 20 to 50°C) and place the thermal detector and the thermometer in the stirred water bath. Fasten the detector to the glass thermometer with a rubber band or rubber O-ring. Allow the bath, detector, and thermometer to come to thermal equilibrium and record the temperature of the glass thermometer and the readout from the thermal detector. The temperature in the bath shall be constant to within 0.1 degree.

9.1.1.2.1 A silicone wafer 2 mm thick by 25 mm in diameter containing a thermistor calibrated to the nearest 0.1°C shall be inserted between the plates as the dummy specimen. Use a thin coating of petroleum jelly to ensure good thermal contact. A suitable thermistor mounted in a silicone wafer is available from Cannon Instruments as part number 9728-V95.

9.1.1.2.2 A wafer-shaped RTD shall be mounted between the plates and used as described in section 6.1.2.2. The RTD must be calibrated as described in note 5 to the nearest 0.1°C. A suitable RTD is available from Omega as part number RTD FN105. This RTD is not waterproof and must be dipped in hot asphalt prior to calibration. To obtain measurements, the RTD is mounted in the rheometer within the asphalt binder sample. After mounting the sample and trimming excess asphalt binder, proceed with the temperature measurements as described in section 6.1.2.2.

9.1.1.2.3 A thermocouple probe shall be used to measure the sample temperature by inserting the probe into a sample that has been mounted in the rheometer (this procedure is described in section 10). The thermocouple must be calibrated at 3 month intervals using the procedure described in note 5 to the nearest 0.1°C. When obtaining the sample temperature the cabling and instrumentation must remain unchanged from that used during the calibration. To make a sample temperature reading insert the thermocouple in the asphalt binder between the plates and proceed as described in section 6.1.2.3. A suitable thermocouple probe is available from Omega as part number HYP1-30-1/2-T-G-60-SMP-M.

9.1.2 Calibrate the load transducer in accordance with the directions and fixtures supplied with the apparatus.

9.1.3 Calibrate the strain transducer in accordance with the directions and fixtures supplied with the apparatus.

9.1.4 Verify the overall calibration of the DSR using suitable reference fluids with viscoelastic properties similar to asphalt binder. Do not attempt to verify individual load or deflection detectors with a reference fluid. Suitable standards have not been identified.

NOTE 6.—Reference fluids exhibiting moduli and phase angles within the range of measurement may be used for verification purposes. Because reference fluids do not have the same temperature dependency as asphalt binder, caution must be used when interpreting the results obtained from such fluids.

10. PREPARING SAMPLES AND TEST SPECIMENS

10.1 *Preparing Test Samples*—If unaged binder is to be tested, obtain test samples according to T40.

10.1.1 Anneal the asphalt binder from which the test specimen is to be obtained by heating until it is sufficiently fluid to pour the required specimens. Annealing prior to testing removes reversible molecular associations (steric hardening) that occur during normal storage at ambient temperature. Do not exceed a temperature of 163°C. Cover the sample and stir it occasionally during the heating process to ensure homogeneity and to remove air bubbles. Minimize the heating temperature and time to avoid hardening the sample.

NOTE 7.—Minimum pouring temperatures that produce a consistency equivalent to that of SAE 10W30 motor oil (readily pours but not overly fluid) at room temperature are recommended. Heating unaged asphalt to temperatures above 135°C should be avoided. With some modified asphalts or heavily aged binders, however, pouring temperatures above 135°C may be required.

10.1.2 Cold material from storage containers must be annealed prior to usage. Structure developed during storage can result in overestimating the modulus by as much as 50%.

10.2 *Preparing Test Specimens*—Carefully clean and dry the surfaces of the test plates so that the specimen adheres to both plates uniformly and strongly. Bring the chamber to approximately 45°C so that the plates are preheated prior to the mounting of the test specimen. This will provide sufficient heat so that the asphalt binder may be squeezed between the plates for trimming and to ensure that the asphalt binder adheres to the plates. Serrated plates or otherwise roughened plates are not necessary to ensure load transfer between the asphalt binder and the plates as long as the plates are clean and dry when the test specimen is prepared. Prepare a test specimen using one of the methods specified in sections 10.2.1 or 10.2.2.

10.2.1 *Alternate 1*—Remove the removable plate and, while holding the sample container approximately 15 mm above the test plate surface, pour the asphalt binder at the center of the upper test plate continuously until it covers the entire plate except for an approximate 2-mm-wide strip at the perimeter (note 8). Carefully insert the RTD. Wait several minutes for the specimen to stiffen, then mount the test plate in the rheometer for testing.

NOTE 8.—An eye dropper or syringe may be used to transfer the hot asphalt binder to the plate.

10.2.2 *Alternate 2*—Pour the hot asphalt binder into a silicone rubber mold that will form a pellet that has a diameter approximately equal to the diameter of the upper test plate and a height approximately equal to 1.5 times the width of the test gap. Carefully insert the RTD. Allow the silicone rubber mold to cool to room temperature. Remove the specimen from the mold and center the pellet on the lower plate of the DSR.

NOTE 9.—The filled mold may be chilled in a freezer to facilitate demolding of softer grades of asphalt binder. Chill the mold in the freezer for only the minimum time needed to facilitate demolding the specimen.

10.3 *Test Specimen Trimming*—After the specimen has been placed on one of the test plates as described above, move the test plates together to squeeze the asphalt mass between the two plates. Move the plates together until the gap between plates equals the testing gap plus 0.05 mm.

10.3.1 Trim excess asphalt from the specimen by moving a heated trimming tool around the upper and lower plate perimeters. The tool may be heated on a hot plate or with a flame.

NOTE 10.—The calculated modulus is proportional to the fourth power of the specimen radius. Carefully trim the specimen to insure that the measurements are reliable.

10.3.2 When the trimming is completed, decrease the gap by 0.05 mm to the desired testing gap. This will cause a slight bulging of the asphalt binder at the periphery of the test specimen.

11. PROCEDURE

11.1 Bring the specimen to the test temperature ± 0.1°C. See note 4.

NOTE 11.—The gap should be set at the starting test temperature (section 11.1.1) or at the middle of the expected range of test temperatures (section 11.1.2). See sections 8.4 and 8.5 for guidance on setting the gap.

Typically, reliable test results may be obtained with a single sample, in an 8-mm or 25-mm plate, using temperatures within 12°C of the temperature at which the gap is set.

11.1.1 When testing a binder for compliance with MP1, select the appropriate test temperature from table 1 of MP1.

11.1.2 When conducting a temperature sweep, start at a mid-range test temperature and increase or decrease the test temperature to cover the desired range of test temperatures. (See sections 6 and 7 in PP6.)

11.2 Set the temperature controller to the desired test temperature, including any difference as required by section 9.1.1.2. Allow the temperature indicated by the RTD to come to the desired temperature. The test shall be started only after the temperature has remained at the desired temperature ± 0.1°C for at least 10 minutes. After temperature equilibration, anneal the specimen for 5 minutes.

NOTE 12.—It is impossible to specify a single equilibration time that is valid for different manufacturers' DSRs. The design (fluid bath or air oven) of the environmental control system and the starting temperature will dictate the time required to reach the test temperature.

11.3 *Strain Control Mode*—When operating in a strain controlled mode, determine the strain value according to the value of the complex modulus. Control the strain within 20% of the target value calculated by equation 1.

$$\gamma = 12.0/(G^*)^{0.29} \tag{1}$$

where

γ = shear strain in percent
G^* = complex modulus in kPa

11.3.1 When testing specimens for compliance with MP1, select an appropriate strain value from table 2. Software is available with the dynamic shear rheometers that will control the strain automatically.

Table 2. Target Strain Values

Material	G* (kPa)	Strain (%) Target Value	Range
Original Binder	1.0	12	9 to 15
RTFO Residue	2.2	10	8 to 12
PAV Residue	5.0	1	0.8 to 1.2

11.4 *Stress-Controlled Mode*—When operating in a stress-controlled mode, determine the stress level according to the value of the complex modulus. Control the stress within 20% of the target value calculated by equation 2.

$$\tau = 0.12(G^*)^{0.71} \tag{2}$$

where

τ = shear stress in kPa
G^* = complex modulus in kPa

11.4.1 When testing specimens for compliance with MP1, select an appropriate stress level from table 3. Software is available with the dynamic shear rheometers that will control the stress level automatically without control by the operator.

Table 3. Target Stress Levels

Material	G* (kPa)	Stress (kPa)	
		Target Level	Range
Original Binder	1.0	0.12	0.09 to 0.15
RTFO Residue	2.2	0.22	0.18 to 0.26
PAV Residue	5.0	50.0	40 to 60

11.5 When the temperature has equilibrated, condition the specimen by applying the required strain for 10 cycles at a frequency of 10 rad/s (note 13). Obtain test measurements by recording data for an additional 10 cycles. Reduce the data obtained for the second 10 cycles to produce a value for the complex modulus and phase angle. Typically a Fast Fourier Transform (FFT) is used to reduce the data. The data acquisition system automatically acquires and reduces the data when properly activated. When conducting tests at more than one frequency, start testing at the lowest frequency and increase to the highest frequency.

NOTE 13.—The standard frequency of 10 rad/s is used when testing binder for compliance with MP1.

11.6 The data acquisition system specified in section 6.1.4 automatically calculates G^* and δ from test data acquired when properly activated.

11.7 Initiate the testing immediately after preparing and trimming the specimen. The testing at subsequent temperatures should be done as quickly as possible to minimize the effect of molecular associations (steric hardening) that can cause an increase in modulus if the specimen is held in the rheometer for a prolonged period of time. When testing at multiple temperatures, all testing should be completed within 4 hours.

12. INTERPRETATION OF RESULTS

12.1 The dynamic modulus and phase angle depend upon the magnitude of the shear strain; the modulus and phase angle for both unmodified and modified asphalt cement decrease with increasing shear strain as shown in figure 1. A plot such as that shown in figure 1 can be generated by gradually increasing the load or strain amplitude, thereby producing a strain sweep. It is not necessary to generate such sweeps during normal specification testing; however, such plots are useful for verifying the limits of the linear region.

12.2 A linear region may be defined at small strains where the modulus is relatively independent of shear strain. This region will vary with the magnitude of the complex modulus. The linear region is defined as the range in strains where the complex modulus is 95% or more of the zero-strain value.

12.3 The shear stress varies linearly from zero at the center of the plates to a maximum at the extremities of the plate perimeter. The shear stress is calculated from the applied or measured torque, measured or applied strain, and the geometry of the test specimen.

13. REPORT

13.1 Provide a complete identification and description of the material tested including name code, source, and type of sample container.

13.2 Describe the instrument used for the test. Include the model number, whether it is a constant strain or constant stress rheometer, the type of environmental chamber, and other information needed to describe the rheometer.

13.3 The strain and stress levels specified in tables 2 and 3 have been selected to ensure a common reference point that has been shown to be within the linear region for plain and modified asphalt binders. Some systems may not be linear within this region. When this situation is observed, report the modulus at the recommended stress or strain levels but report that the test conditions were outside the linear region.

13.4 For each test, report the following:

13.4.1 the test plate diameter, to the nearest 0.1 mm;

13.4.2 the test gap, to the nearest 1μm;

13.4.3 the test temperature, to the nearest 0.1°C;

13.4.4 the test frequency, to the nearest 0.1 rad/s;

13.4.5 the strain amplitude, to the nearest 0.01%, or the torque, to the nearest mN·m;

13.4.6 the complex modulus (*G**) for the ten measurements, in kPa to three significant figures; and

13.4.6 the phase angle (δ) for the second ten cycles, to the nearest 0.1 degrees.

14. PRECISION AND BIAS

14.1 *Precision*—The research required to develop estimates of precision has not been conducted.

14.2 *Bias*—The research required to establish the bias of this method has not been conducted.

15. KEY WORDS

Asphalt binder, complex modulus, dynamic shear rheometer.

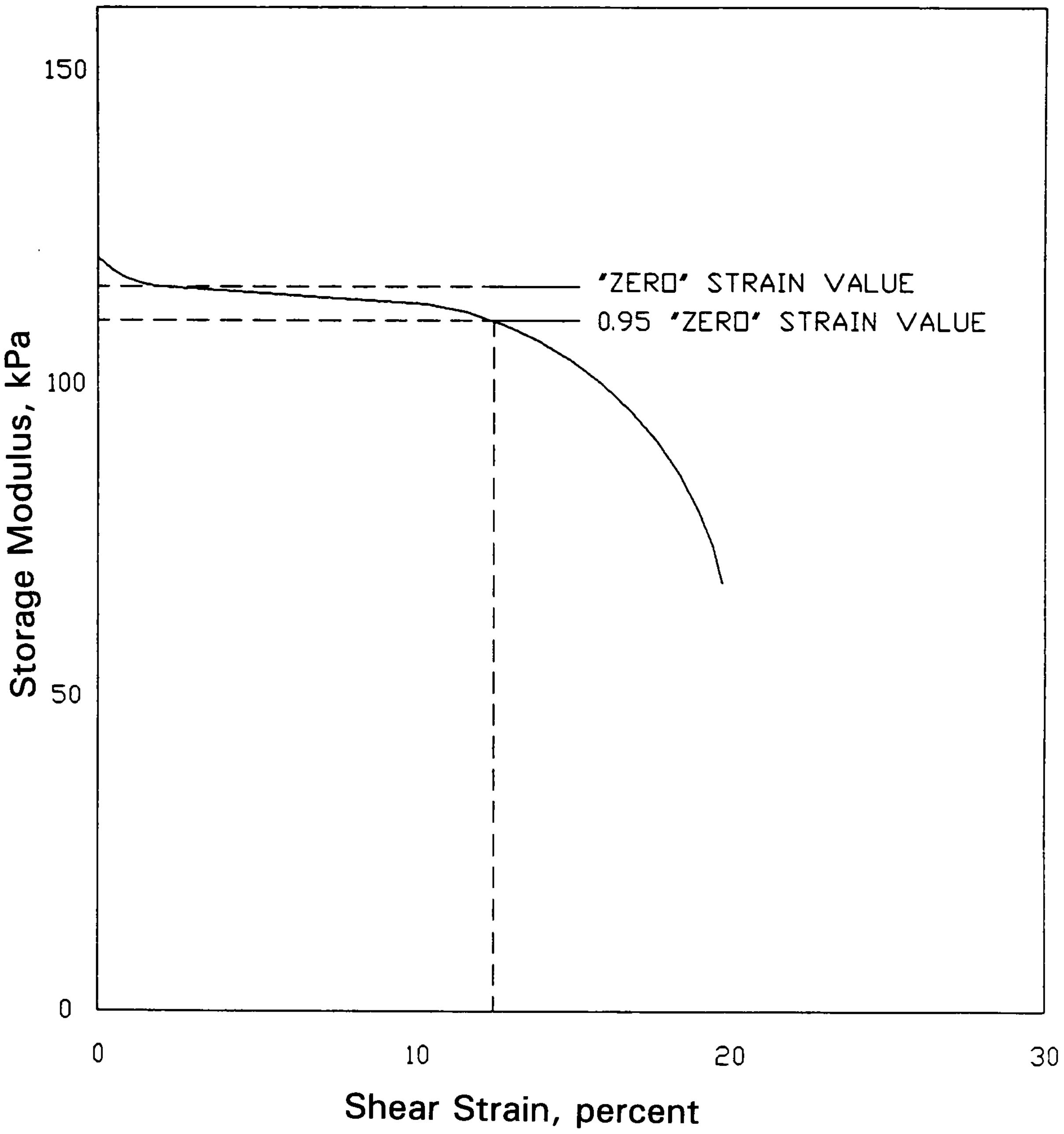

Figure 1. Example of a Strain Sweep Test Used to Define the Linear Viscoelastic Limit for Dynamic Mechanical Testing of Asphalt

Appendix B

Determining the Flexural Creep Stiffness of Asphalt Binder Using the Bending Beam Rheometer

AASHTO Designation: TP1

Standard Method of Test for

Determining the Flexural Creep Stiffness of Asphalt Binder Using the Bending Beam Rheometer

AASHTO Designation: TP1[1]

1. SCOPE

1.1 This test method covers the determination of the flexural creep stiffness or compliance of asphalt binders by means of a bending beam rheometer. It is applicable to material having flexural creep stiffness values from 30 MPa to 1 GPa (creep compliance values in the range of 300 mPa^{-1} to 1 nPa^{-1}). It can be used with unaged material or with material aged using T240, T179, or PP1. The test apparatus is designed for testing within the temperature range of −40 to 25°C.

1.2 Test results are not valid for beams of asphalt binder that deflect more than 4 mm when tested in accordance with this method.

1.3 The values stated in SI units are to be regarded as the standard.

1.4 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this procedure to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.*

2. REFERENCE DOCUMENTS

2.1 *AASHTO Standards:*

MP1	Standard Method of Test for Performance-Graded Asphalt Binder
PP1	Practice for Accelerated Aging of an Asphalt Binder Using a Pressurized Aging Vessel
T40	Practice for Sampling Bituminous Materials
T179	Test Method for Effect of Heat and Air on Asphalt Materials (Thin Film Oven Test)
T240	Test Method for Effect of Heat and Air on Rolling Film of Asphalt (Rolling Thin Film Oven Test)

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[1] This standard is based on SHRP Product 1002.

2.2 *ASTM Standards:*

C802 Conducting an Interlaboratory Test Program to Determine the Precision of Test Methods for Construction Materials
E1 Specification for ASTM Thermometers
E77 Standard Test Method for Inspection and Verification of Liquid-in-Glass Thermometers

2.3 *DIN Standards:*

43760

3. TERMINOLOGY

3.1 *Definitions:*

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

3.1.2 physical hardening, *n*—a time-dependent stiffening of asphalt binder that results from time-delayed increase in stiffness when the asphalt binder is stored at low temperatures.

3.2 *Descriptions of Terms Specific to this Standard:*

3.2.1 flexural creep, *n*—a material characteristic determined by a test in which a simply-supported beam is loaded with a constant load at its midpoint and the deflection of the beam is measured with respect to loading time.

3.2.2 flexural creep stiffness, $S(t)$—ratio obtained by dividing the maximum bending stress in the beam by the maximum bending strain.

3.2.3 flexural creep compliance, $D(t)$—ratio obtained by dividing the maximum bending strain in the beam by the maximum bending stress. $D(t)$ is the inverse of $S(t)$. $S(t)$ has been used historically in asphalt technology while $D(t)$ is commonly used in studies of viscoelasticity.

3.2.4 m—absolute value of the slope of the logarithm of the stiffness curve versus the logarithm of time.

3.2.5 preload, *n*—load required to maintain positive contact between the beam and the loading shaft; 30 ± 5 mN.

3.2.6 initial seating load, *n*—load of 1-s duration required to seat the beam; 980 ± 50 mN.

3.2.7 test load, *n*—load of 240-s duration required to determine the stiffness of the material being tested; 980 ± 50 mN.

4. SUMMARY OF TEST METHOD

4.1 The bending beam rheometer measures the midpoint deflection of a simply-supported prismatic beam of asphalt binder that is subjected to a constant load applied to the midpoint of the beam. The device operates only in the loading mode. Recovery measurements are not obtained.

4.2 A test beam is placed in the controlled temperature fluid bath and loaded with a constant load for 240 seconds. The test load (980 ± 50 mN) and the midpoint deflection of the beam are monitored versus time using a computerized data acquisition system.

4.3 The maximum bending stress at the midpoint of the beam is calculated from the dimensions of the beam, the span length, and the load applied to the beam for loading times of 8, 15, 30, 60, 120, and 240 seconds. The maximum bending strain in the beam is calculated for the same loading times from the dimensions of the beam and the deflection of the beam. The stiffness of the beam for the loading times specified above is calculated by dividing the maximum stress by the maximum strain.

5. SIGNIFICANCE AND USE

5.1 The test temperature for this test is related to the temperature experienced by the pavement in the geographical area for which the asphalt binder is intended.

5.2 The flexural creep stiffness or flexural creep compliance determined from this test describes the low-temperature stress-strain-time response of asphalt binder at the test temperature within the linear viscoelastic response range.

5.3 The low-temperature thermal cracking performance of paving mixtures is related to the creep stiffness and the slope of the logarithm of the creep stiffness versus the logarithm of the time curve of the asphalt binder contained in the mix.

5.4 The creep stiffness and the slope of the logarithm of the stiffness versus the logarithm of the time curve are used as performance-based specification criteria for asphalt binders in accordance with MP1.

6. INTERFERENCES

6.1 Measurements wherein the beam deflection is greater than 4.0 mm are suspect. Strains in excess of this value may exceed the linear response of asphalt binders.

6.2 Measurements wherein the beam deflection is less than 0.08 mm are suspect. When the beam deflection is less than 0.08 mm, the test system resolution may not be sufficient to produce reliable test results.

7. APPARATUS

7.1 *Bending Beam Rheometer (BBR) Test System*—A bending beam rheometer (BBR) test system consisting of (1) a loading frame which permits the test beam, supports, and the lower part of the test frame to be submerged in a constant temperature fluid bath, (2) a controlled temperature liquid bath which maintains the test beam at the test temperature and provides a buoyant force to counterbalance the force resulting from the mass of the beam, and (3) a computer-controlled automated data acquisition component.

7.1.1 *Loading Frame*—A frame consisting of a set of sample supports, a blunt-nosed shaft that applies the load to the midpoint of the test specimen, a load cell mounted on the loading shaft, a means for zeroing the load on the test specimen, a means for applying a constant load to the loading shaft, and a deflection-measuring transducer attached to the loading shaft. A schematic of the device is shown in figure 1.

7.1.1.1 *Sample Supports*—Sample supports consisting of two stainless steel half-rounds 25 mm in diameter that are spaced 102 ± 0.5 mm apart.

7.1.1.2 *Loading Shaft*—A blunt-nosed loading shaft continuous with the load cell and deflection-measuring transducer that is capable of applying a preload of 30 ± 5 mN and maintaining a test load of 980 ± 50 mN within ± 5 mN using differential air pressure or other means, such as electro-hydraulic, for adjustment. The rise time for the test load shall be less than 0.1 s, where the rise time is the time required for the load to rise from the 30 ± 5 mN preload to the 980 ± 50 mN test load. During the rise time the system shall dampen the test load to a constant ± 5 mN value.

7.1.1.3 *Load Cell*—A load cell with a minimum capacity of 2000 mN having a sensitivity of 1 mN, mounted in line with the loading shaft and above the fluid to measure the preload and the test load.

7.1.1.4 *Linear Variable Differential Transducer*—A linear variable differential transducer (LVDT) or other suitable device mounted axially above the loading shaft, capable of resolving a linear movement $\leq 2.5\ \mu m$ with a range of at least 10 mm, to measure the deflection of the test beam. Digital or analog smoothing of the load and deflection data may be required to eliminate electronic noise that could otherwise affect the ability of the second order polynomial to fit the data with sufficient accuracy to provide a reliable estimate of the m-value. Averaging five or more load or deflection signals equally spaced over a range ± 0.2 s from the reported time is acceptable to smooth the load or deflection signal.

7.1.2 *Controlled-Temperature Fluid Bath*—A controlled-temperature liquid bath capable of maintaining the temperature at all points within the bath between −40 and 25°C within ± 0.1°C. Placing a cold specimen in the bath may cause the bath temperature to fluctuate ± 0.2°C from the target test temperature. Consequently bath fluctuations of ± 0.2°C during testing and isothermal conditioning shall be allowed.

7.1.2.1 *Bath Fluid*—A bath fluid that is not absorbed by or does not affect the properties of the asphalt binder tested.

7.1.2.2 *Bath Agitator*—A bath agitator for maintaining the required temperature homogeneity with agitation intensity such that the fluid currents do not disturb the testing process and mechanical noise caused by vibrations is less than the resolution specified in 7.1.1.4.

7.1.2.3 *Circulating Bath (Optional)*—A circulating bath unit separate from the test frame that pumps the bath fluid through the test bath. If used, vibrations from the circulating system shall be isolated from the bath test chamber so that mechanical noise is less than the resolution specified in section 7.1.1.4.

7.1.3 *Data Acquisition System*—A data acquisition system that resolves loads to the nearest 0.1 mN, beam deflection to the nearest 2.5 μm, and bath fluid temperature to the nearest 0.1 °C. The system shall sense the point in time when the load is first applied (zero time) and, using this time as a reference, shall provide a record of subsequent load and deflection measurements relative to this time within ± 0.20 s. The system shall record the load and deflection at loading times of 8, 15, 30, 60, 120 and 240 s, with less than 0.1 s between load and deflection measurement times. All readings shall be an average of five or more points within ± 0.2 s from the loading time, e.g., for a loading time of 8 s, average 7.8, 7.9, 8.0, 8.1 and 8.2 s.

7.2 *Temperature Measuring Equipment*—A calibrated temperature transducer capable of measuring the temperature to 0.1 °C over the range −40 to 25 °C mounted in the immediate vicinity of the midpoint of the test specimen.

NOTE 1.—Required temperature measurement can be accomplished with an appropriately calibrated platinum resistance thermometer (RTD) or a thermistor. Calibration of the RTD or thermistor can be verified as per section 7.6. The RTDs meeting DIN Standard 43760 (Class A) are recommended for this purpose. The required precision and accuracy cannot be obtained unless each RTD is calibrated as a system with its respective meter or electronic circuitry.

7.3 *Test Beam Molds*—Test beam molds of suitable dimensions to yield demolded test beams 6.35 ± 0.05 mm thick by 12.70 ± 0.05 mm wide by 127 ± 0.5 mm long fabricated from aluminum flat stock as shown in figure 2, or from silicone rubber as shown in figure 3.

7.4 *Stainless Steel Beams*—One stainless steel beam 6.4 ± 0.1 mm thick by 12.7 ± 0.1 mm wide by 127 ± 0.5 mm long for measuring system compliance and one stainless steel beam 1.0 to 1.6 mm thick by 6.35 mm wide measured to ± 0.02 mm by 127 mm long measured to ± 0.5 mm with a known stiffness modulus, for performing periodic checks on the performance of the BBR.

7.5 *Standard Masses*—Four standard masses 50.0 or 100.0 ± 0.2 g masses for periodic BBR calibration verification.

7.6 *Calibrated Thermometers*—Calibrated liquid-in-glass thermometers for verification of the temperature transducer of suitable range with subdivisions of 0.1 °C. These thermometers shall be calibrated in accordance with ASTM E77. ASTM thermometers 89C and 119C are suitable thermometers.

7.7 *Thickness Gauge*—A stepped-thickness gauge for verifying the calibration of the displacement transducer as described in figure 4.

8. MATERIALS

8.1 *Plastic Sheeting*—Clear plastic sheeting 0.12 to 0.15 mm thick, for lining the interior faces of the three long aluminum mold sections. Sheeting should not be distorted by hot asphalt binder. Transparency film sold for use with laser printers has been found suitable.

8.2 *Petroleum-Based Grease*—A petroleum-based grease used to hold the plastic sheeting to the interior faces of the three long aluminum mold sections. **(Warning: do not use any silicone-based products.)**

8.3 *Glycerol-Talc Mixture*—Used to coat the end pieces of aluminum molds.

8.4 Suitable bath fluids include ethanol and glycol-methanol mixtures (e.g., 60% glycol, 15% methanol, 25% water).

9. HAZARDS

9.1 Observe standard laboratory safety procedures when handling hot asphalt binder and preparing test specimens.

10. PREPARATION OF APPARATUS

10.1 Clean the supports, loading head and bath fluid of any particulates and coatings as necessary.

NOTE 2.—Because of the brittleness of asphalt binder at the specified test temperatures, small fragments of asphalt binder can be introduced into the bath fluid. If these fragments are present on the supports or the loading head, they will affect the measured deflection. Because of their small size, the fragments will deform under load and add an apparent deflection to the true deflection of the beam. Filtration of the bath fluid will aid in preserving the required cleanliness.

10.2 Select the test temperature and adjust the bath fluid to the selected temperature. Wait until the temperature stabilizes and then allow the bath to equilibrate to the test temperature ± 0.2°C.

10.3 Activate the data acquisition system and load the software as explained in the manufacturer's manual for the test system.

11. STANDARDIZATION

11.1 Verify calibration of the displacement transducer, load cell, and temperature transducer. Conduct each of the steps in this section each day before conducting any tests.

NOTE 3.—Calibration is usually performed by a calibration service agency. Calibration verification and quality checks may be performed by the manufacturer, other agencies providing such services, or in-house personnel using the procedures described below.

11.1.1 Verify calibration of the displacement transducer using a stepped thickness gauge of known dimensions similar to the one shown in figure 4. Remove the loading frame from the bath. Place the gauge on a reference platform underneath the loading shaft. Measure the rise of the steps relative to the top surface of the gauge with the displacement transducer. Compare the measured values with the known dimensions of the gauge. If the difference is $\geq 4\ \mu m$, further calibration or maintenance is required. Report the calibration constants ($\mu m/mV$) for the displacement transducers to three significant figures. The calibration constants should be repeatable from day to day. Otherwise, the operation of the system may be suspect.

11.1.2 Verify calibration of the load cell using four standard dead masses evenly distributed over the range of the load cell. Perform the verification by resting the loading shaft against the 6.35-mm thick standard steel beam, loading it with the four standard masses sequentially in four steps, while recording the load after each step. If the load indicated by the data acquisition system does not agree with the force imposed by the standard masses within ± 2 mN at all steps, further calibration or maintenance is required. Report the calibration constants (mN/m) for the load transducers to three significant figures. The calibration constants should be repeatable from day to day. Otherwise, the operation of the system may be suspect.

11.1.3 Verify calibration of the temperature detector by using a calibrated thermometer of suitable range meeting the requirements of section 7.6. Immerse the thermometer in the liquid bath close to the thermal detector and compare the temperature indicated by the calibrated thermometer to the detector signal being displayed. If the temperature indicated by the thermal detector does not agree with the liquid-in-glass thermometer within ± 0.1°C, further calibration or maintenance is required.

11.2 Determine the compliance of the loading system by placing the 6.35-mm–thick stainless steel beam on the testing supports, resting the loading tip of the loading shaft against the stainless steel beam, and applying a load to the shaft of 980 ± 50 mN measured to the nearest 2 mN. The beam is relatively rigid within the range of loading applied and the range of deflection measurement specified. Therefore, any measured deflection is caused by the load cell or other parts of the test system. Divide the deflection measured under this load by the applied load. The quotient is the compliance of the loading system in $\mu m/mN$. Use this result to calculate the deflection component that is not due to the compliance of the system. This component is automatically subtracted from the deflection measured during a test.

11.3 Perform a daily quality control check on the operation of the overall system using the 1.0- to 1.6-mm-thick stainless steel beam of known modulus. Load the steel beam with 981 and 1961 mN using the standard masses (100 and 200 g) and measure the deflection at the midpoint. Using the load applied and deflection measured, calculate the elastic modulus of the beam. Compare the calculated modulus to the known modulus of the beam. If the calculated modulus differs from the known modulus by 10% or more, the operation of the system is suspect. Perform required maintenance on the system and then repeat section 11.

12. PREPARATION OF MOLDS AND TEST SPECIMENS

12.1 To prepare aluminum molds, spread a very thin layer of petroleum-based grease, only sufficient to hold the plastic strips to the aluminum, on the interior faces of the three long aluminum mold sections. Place the plastic strips over the aluminum faces and rub the plastic with firm finger pressure. Assemble the mold as shown in figure 2 using the rubber 0-rings to hold the pieces of the mold together. Inspect the mold and press the plastic film against the aluminum to force out any air bubbles. If air bubbles remain, disassemble the mold and recoat the aluminum faces with grease. Cover the inside faces of the mold's two end pieces with a thin film of glycerol to prevent the asphalt binder from sticking to the aluminum end pieces. After assembly, keep the mold at room temperature until pouring the asphalt binder.

12.2 To prepare silicone rubber molds, assemble the two mold sections.

12.3 If unaged binder is to be tested, obtain test samples according to T40.

12.4 Heat the material until it is sufficiently fluid to pour.

NOTE 4.—Minimum pouring temperatures that produce a consistency equivalent to that of SAE 10W30 motor oil (readily pours but not overly fluid) at room temperature are recommended. Heating unaged asphalt binders to temperatures above 135°C should be avoided. Some modified asphalts or heavily aged binders,however, may require pouring temperatures above 135°C may be required. PAV residues shall be placed in TFOT pans and may be heated up to 163°C. In all cases, heating time should be minimized. These precautions avoid oxidative hardening and volatile loss that will further harden the sample. During the heating process, the sample should be covered and stirred occasionally to ensure homogeneity.

12.5 *Molding (aluminum mold)*—If an aluminum mold is used, begin pouring the binder from one end of the mold and move toward the other end, slightly overfilling the mold. When pouring, hold the sample container 20 to 100 mm from the top of the mold and pour continuously toward the other end in a single pass. After pouring, allow the mold to cool 45 to 60 minutes to room temperature. Trim the exposed face of the cooled specimens flush with the top of the mold using a hot knife or a heated spatula. Discard the plastic sheeting (lining the mold sections) if it becomes distorted.

12.6 *Molding (silicone rubber mold)*—If a silicone rubber mold is used, fill the mold from the top of the mold in a slow, steady manner, taking care not to entrap air bubbles. Fill the mold to the top with no appreciable overfilling. After pouring, allow the mold to cool to room temperature for at least 45 minutes.

12.7 Store all test specimens in their molds at room temperature prior to testing. Schedule testing so that it is completed within 4 hours after specimens are poured.

NOTE 5.—Time-dependent increases in stiffness can occur when asphalt binders are stored at room temperature for even short periods of time. This increase in stiffness is the result of molecular associations and is referred to as steric hardening in the literature.

12.8 Just prior to testing, cool the aluminum or silicone mold containing the test specimen in a freezer or ice bath at −5°C ± 5°C for 5 to 10 minutes, only long enough to stiffen the asphalt binder beam so that it can be readily demolded without distortion (note 6). Some softer grades may require lower temperatures. Do not cool the molds containing the specimens in the test bath because it may cause temperature fluctuations in the bath to exceed ± 0.2°C.

NOTE 6.—Excessive cooling may cause unwanted hardening of the beam, thereby causing increased variability in the test data.

12.9 Immediately demold the specimen when it is sufficiently stiff to demold without distortion by disassembling the aluminum mold or by removing the test specimen from the silicone rubber mold.

NOTE 7.—Minimize distortion of the specimen during demolding. Full contact at specimen supports is assumed in the analysis. A warped test beam yields a measured stiffness less than the actual stiffness.

13. PROCEDURE

13.1 When testing a specimen for compliance with MP1, select the appropriate test temperature from table 1 of MP1. After demolding, immediately place the test specimen in the testing bath and condition it at the testing temperature for 60 ± 5 minutes.

NOTE 8.—Asphalt binders may harden rapidly when held at low temperatures. This effect, which is called physical hardening, is reversible when the asphalt binder is heated to room temperature or slightly above. Because of physical hardening, conditioning time must be carefully controlled if repeatable results are to be obtained.

13.2 After conditioning, place the test beam on the test supports and initiate the test. Maintain the bath at test temperature ± 0.2°C during testing.

13.3 Enter the specimen identification information, test load, test temperature, time the specimen is placed in bath test temperature, and other information as appropriate into the computer that controls the test system.

13.4 Manually apply a 30 ± 5 mN preload to the beam to ensure contact between the beam and the loading head.

NOTE 9.—The specified preload on the specimen is required to ensure continuous contact between the loading shaft and the specimen. Failure to establish continuous contact within the required load range gives misleading results.

13.5 Activate the automatic test system that is programmed to proceed as follows.

13.5.1 Apply a 980 ± 50 mN initial seating load for 1 ± 0.1 second.

NOTE 10.—The actual load on the beam as measured by the load cell is used in calculating the stress in the beam. The 980 ± 50 mN initial seating and test load includes the 30 ± 5 mN preload.

13.5.2 Reduce the load to 30 ± 5 mN and allow the beam to recover for 20 ± 0.1 seconds.

NOTE 11.—The initial seating loads described in sections 13.5.1 and 13.5.2 are applied and removed automatically by the computer-controlled loading system and are transparent to the operator. Data are not recorded during initial loading.

13.5.3 Apply a test load ranging from 980 ± 50 mN, and maintain the load constant to ± 5 mN for 240 s.

13.5.4 Remove the test load and terminate the test.

13.5.5 At the end of the initial seating, load and at the end of the test, monitor the computer screen to verify that the load on the beam in each case returns to 30 ± 5 mN.

13.6 Remove the specimen from the supports and proceed to the next test.

14. CALCULATION AND INTERPRETATION OF RESULTS

See Annex.

15. REPORT

15.1 Report data as shown in figure A1 that describes individual tests, including:

15.1.1 Temperature of the test bath measured 60 s after the test load is first applied, to the nearest 0.1 °C;

15.1.2 Date and time when test load is applied;

15.1.3 File name of test data;

15.1.4 Name of operator;

15.1.5 Sample identification number;

15.1.6 Any flags issued by software during test;

15.1.7 Correlation coefficient, R^2 for log stiffness versus log time, expressed to nearest 0.000001;

15.1.8 Anecdotal comments (maximum 256 characters);

15.1.9 Report constants A, B, and C to three significant figures;

15.1.10 Difference between measured and estimated stiffness calculated as:

$$(\text{Measured} - \text{Estimated}) \times 100\% \, / \, \text{Estimated}$$

15.2 Report data as shown in figure A1 for time intervals of 8, 15, 30, 60, 120, and 240 seconds including:

15.2.1 Time beam is placed in bath;

15.2.2 Time test started;

15.2.3 Loading time, to the nearest 0.1 second;

15.2.4 Load, to the nearest 0.1 mN;

15.2.5 Beam deflection, to the nearest 2 μm;

15.2.6 Measured Stiffness modulus, in MPa, expressed to three significant figures;

15.2.7 Estimated Stiffness modulus, in MPa, expressed to three significant figures;

15.2.8 Estimated m, to the nearest 0.001.

16. PRECISION AND BIAS

16.1 *Precision*—The research required to develop precision values in accordance with ASTM C802 has not been conducted.

16.2 *Bias*—The research required to establish the bias of this method has not been conducted.

17. KEY WORDS

Bending beam rheometer, flexural creep compliance, flexural creep stiffness.

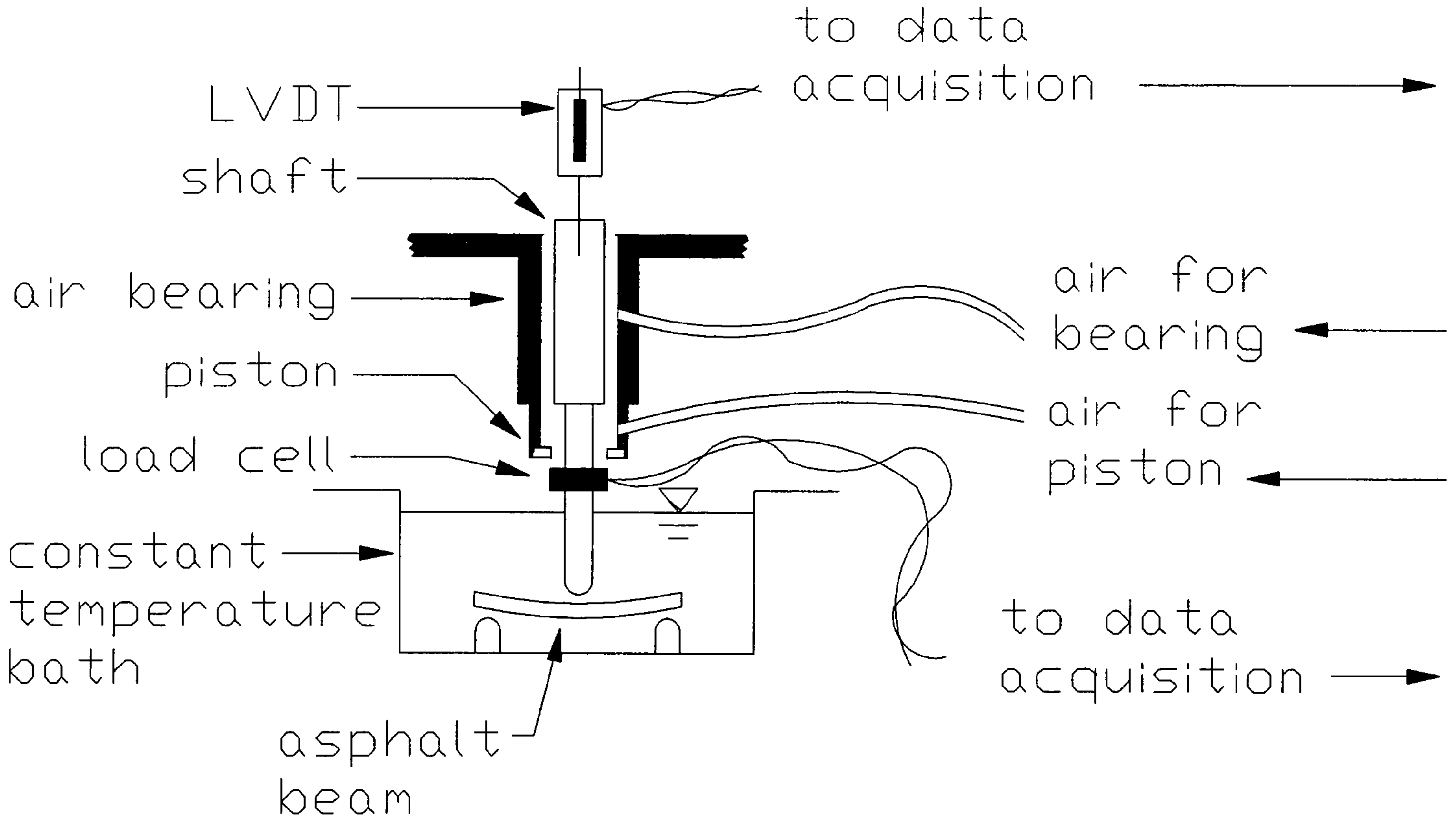


Figure 1 Schematic of the bending beam rheometer

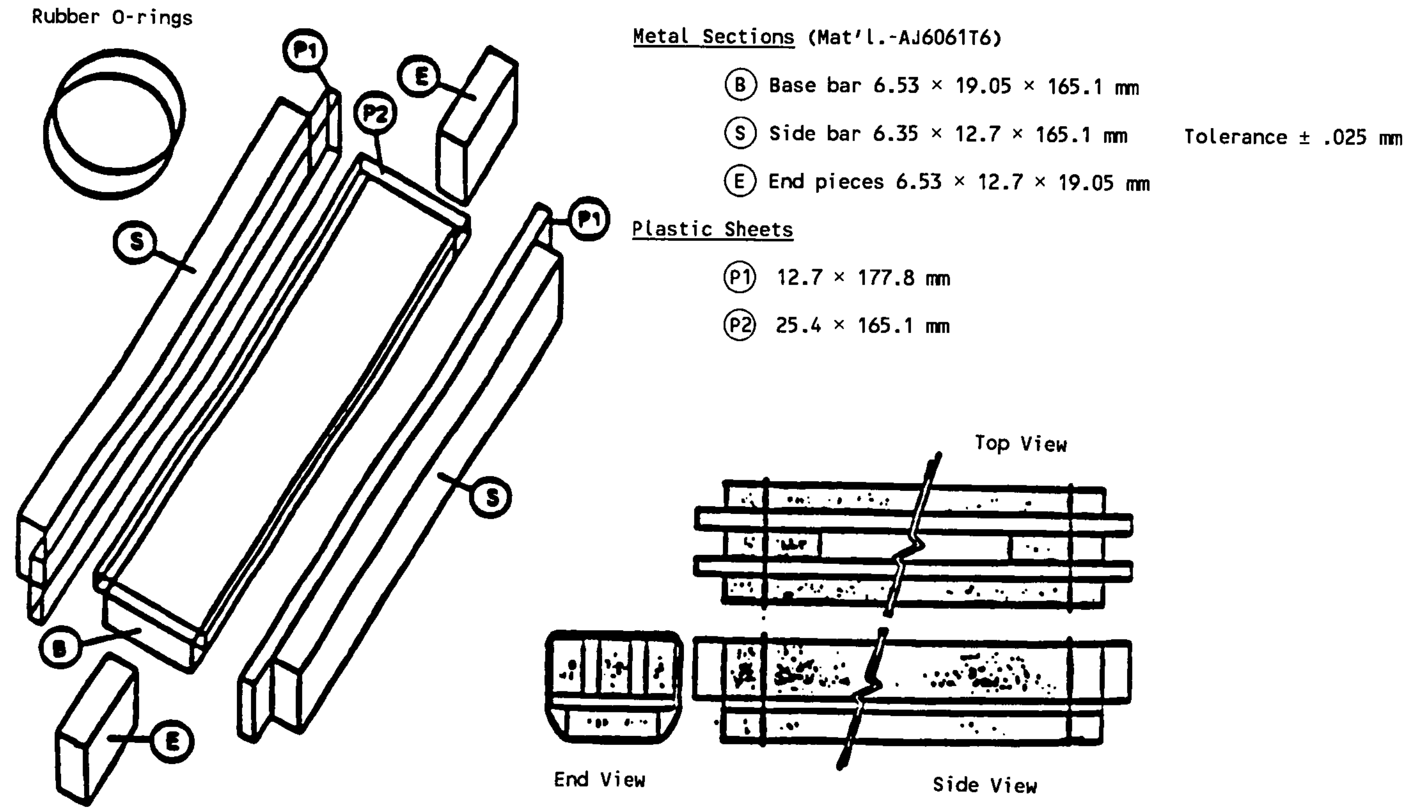


Figure 2 Dimensions and specifications for aluminum molds

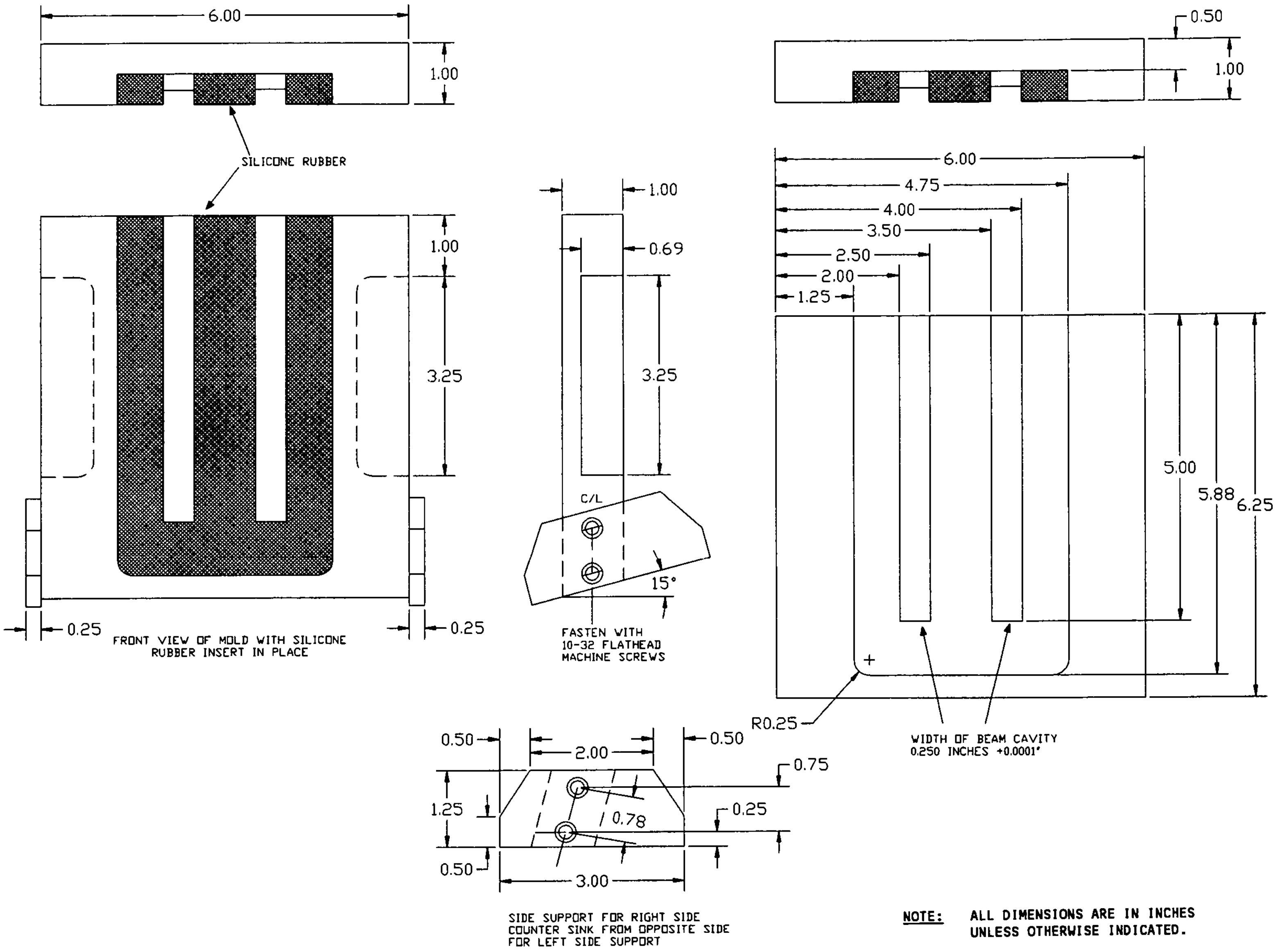
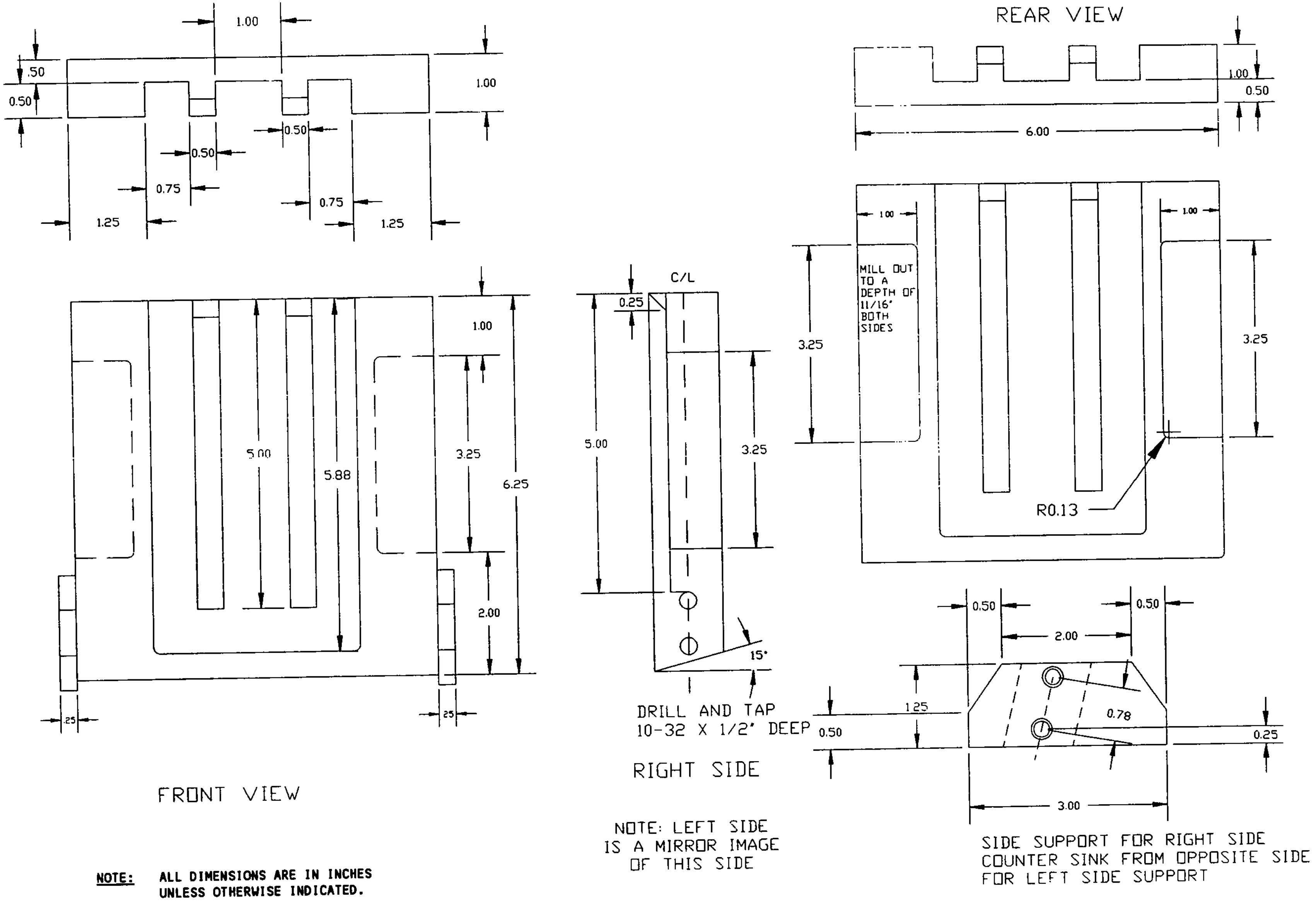


Figure 3 Schematic of silicone rubber molds

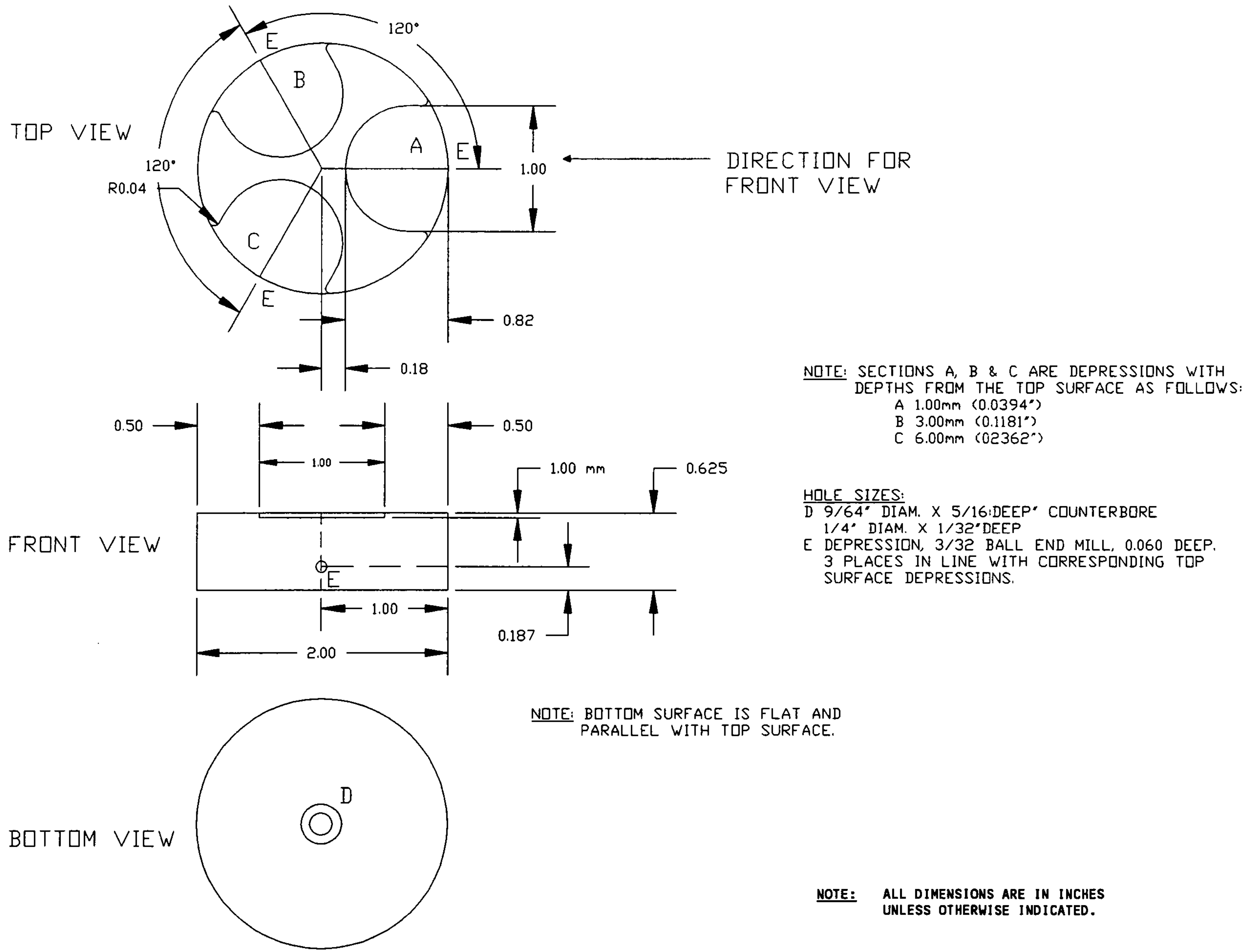


NOTE: LEFT SIDE IS A MIRROR IMAGE OF THIS SIDE

SIDE SUPPORT FOR RIGHT SIDE
COUNTER SINK FROM OPPOSITE SIDE
FOR LEFT SIDE SUPPORT

NOTE: ALL DIMENSIONS ARE IN INCHES UNLESS OTHERWISE INDICATED.

Figure 3 Schematic of silicone rubber molds (cont.)



NOTE: SECTIONS A, B & C ARE DEPRESSIONS WITH
DEPTHS FROM THE TOP SURFACE AS FOLLOWS:
A 1.00mm (0.0394")
B 3.00mm (0.1181")
C 6.00mm (02362")

HOLE SIZES:
D 9/64" DIAM. X 5/16:DEEP" COUNTERBORE
1/4" DIAM. X 1/32"DEEP
E DEPRESSION, 3/32 BALL END MILL, 0.060 DEEP.
3 PLACES IN LINE WITH CORRESPONDING TOP
SURFACE DEPRESSIONS.

NOTE: BOTTOM SURFACE IS FLAT AND
PARALLEL WITH TOP SURFACE.

NOTE: ALL DIMENSIONS ARE IN INCHES
UNLESS OTHERWISE INDICATED.

Figure 4 Schematic of thickness gauge used to calibrate deflection detector

ANNEX

1.1 A typical test result is shown in figure A1. Disregard measurements obtained and the curves projected on the computer screen during the initial 8 s application of the test load. Data from a creep test obtained immediately after the application of the test load may not be valid because of dynamic loading effects and the finite rise time. Use only the data obtained between 8 and 240 s loading time for calculating $S(t)$ and m.

1.2 *Deflection of an elastic beam*—Using the elementary bending theory, the midpoint deflection of an elastic prismatic beam of constant cross section loaded in three-point loading can be obtained by applying equations (1) and (2) as follows:

$$\delta = PL^3/48EI \tag{1}$$

where

δ = deflection of beam at the midpoint, mm
P = load applied, N
L = span length, mm
E = modulus of elasticity, MPa
I = moment of inertia, mm^4

and

$$I = bh^3/12 \tag{2}$$

where

I = moment of inertia of cross section of test beam, mm^4
b = width of beam, mm
h = thickness of beam, mm

NOTE 12.—The test specimen has a span-to-depth ratio of 16 to 1 and the contribution of shear to deflection of the beam can be neglected.

1.3 *Elastic flexural modulus*—According to elastic theory, calculate the flexural modulus of a prismatic beam of constant cross section loaded at its midpoint thus:

$$E = PL^3/4bh^3\delta \tag{3}$$

where

E = time-dependent flexural creep stiffness, MPa
P = constant load, N
L = span length, mm
b = width of beam, mm
h = depth of beam, mm
δ = deflection of beam, mm

1.4 *Maximum bending stress*—The maximum bending stress in the beam occurs at the midpoint at the top and bottom of the beam. Calculate σ thus:

$$\sigma = 3PL/2bh^2 \tag{4}$$

where

σ = maximum bending stress in beam, MPa
P = constant load, N
L = span length, mm
b = width of beam, mm
h = depth of beam, mm

1.5 *Maximum bending strain*—The maximum bending strain in the beam occurs at the midpoint at the top and bottom of the beam. Calculate ϵ thus:

$$\epsilon = 6\delta h/L^2 \text{ mm/mm} \tag{5}$$

where

ϵ = maximum bending strain in beam, mm/mm
δ = deflection of beam, mm
h = thickness of beam, mm
L = span length, mm

1.6 *Linear Viscoelastic Stiffness Modulus*—According to the elastic-viscoelastic correspondence principle, it can be assumed that if a linear viscoelastic beam is subjected to a constant load applied at $t = 0$ and held constant, the stress distribution is the same as that in a linear elastic beam under the same load. Further, the strains and displacements depend on time and are derived from those of the elastic case by replacing E with 1/D(t). Since 1/D(t) is equivalent to S(t), rearranging the elastic solution results in the following relationship for the stiffness:

$$S(t) = PL^3/4bh^3\delta(t) \tag{6}$$

where

$S(t)$ = time-dependent flexural creep stiffness, MPa
P = constant load, N
L = span length, mm
b = width of beam, mm
h = depth of beam, mm
$\delta(t)$ = deflection of beam, mm, and
$\delta(t)$ and $S(t)$ indicate that the deflection and stiffness, respectively, are functions of time.

1.7 *Presentation of Data*

1.7.1 Plot the response of the test beam to the creep loading as the logarithm of stiffness with respect to the logarithm of loading time. A typical representation of test data is shown in figure A2. Over the limited testing time from 8 to 240 s, the plotted data shown in figure A2 can be represented by a second order polynomial as follows:

$$\log S(t) = A + B[\log(t)] + C[\log(t)]^2 \tag{7}$$

and, the slope, *m*, of the logarithm of stiffness versus logarithm time curve is equal to (absolute value):

$$|\,m(t)\,| = \mathrm{d}[\log S(t)]/\mathrm{d}[\log(t)] = B + 2C[\log(t)] \tag{8}$$

where

$S(t)$ = time-dependent flexural creep stiffness, MPa
t = time in seconds
A, B, and C = regression coefficients

Smoothing the data may be required to obtain smooth curves for the regression analysis as required to determine an *m* value. This can be done by averaging 5 readings taken at the reported time ± 0.1 and ± 0.2 seconds.

1.7.2 Obtain the constants *A*, *B*, and *C* from the least squares fit of equation 7. Use data equally spaced with respect to the logarithm of time to determine the regression coefficients in equations 7 and 8. Determine experimentally the stiffness values used for the regression to derive the coefficients *A*, *B*, and *C* and to, in turn, calculate values of *m* after loading times of 8, 15, 30, 60, 120, and 240 s.

1.8 Calculation of Regression Coefficients, estimated stiffness values and *m*.

1.8.1 Calculate the regression coefficients *A*, *B*, and *C* in equations 7 and 8 and the denominator *D* as follows:

$$A = [S_y(S_{x2}S_{x4} - Sx_3^{2}) - S_{xy}(S_{x1}S_{x4} - S_{x2}S_{x3}) + S_{xxy}(S_{x1}S_{x3} - S_{x2}^{2})] \;/\; D \tag{9}$$

$$B = [6(S_{xy}S_{x4} - S_{xxy}S_{x3}) - S_{x1}(S_yS_{x4} - S_{xxy}S_{x2}) + S_{x2}(S_yS_{x3} - S_{xy}S_{x2})] \;/\; D \tag{10}$$

$$C = [6(S_{x2}S_{xxy} - S_{x3}S_{xy}) - S_{x1}(S_{x1}S_{xxy} - S_{x3}S_y) + S_{x2}(S_{x1}S_{xy} - S_{x2}S_y)] \;/\; D \tag{11}$$

$$D = 6(S_{x2}S_{x4} - S_{x3}^{2}) - S_{x1}(S_{x1}S_{x4} - S_{x2}S_{x3}) + S_{x2}(S_{x1}S_{x3} - S_{x2}^{2}) \tag{12}$$

where, for loading times of 8, 15, 30, 60, 120, and 240 seconds:

S_{x1} = $\log 8 + \log 15 + \ldots \log 240$
S_{x2} = $(\log 8)^2 + (\log 15)^2 + \ldots (\log 240)^2$
S_{x3} = $(\log 8)^3 + (\log 15)^3 + \ldots (\log 240)^3$
S_{x4} = $(\log 8)^4 + (\log 15)^4 + \ldots (\log 240)^4$

S_y = log S(8) + log S(15) + ... log S (240)
S_{xy} = log S(8)(log (8)) + log S(15) log (15) + ... log S(240) log (240)
S_{xxy}= [log (8)]^2 log S(8) + [log (15)]^2 log S(15) + ... [log (240)]^2 log S(240)

1.8.2 Calculate the estimated stiffness at 8, 15, 30, 60, 120, and 240 seconds as:

$$\log S(t) = A + B[\log(t)] + C[\log(t)]^2 \tag{13}$$

1.8.3 Calculate the estimated m value at 8, 15, 30, 60, 120, and 240 s as the absolute value of

$$|m| = B \quad 2C[\log(t)] \tag{14}$$

1.8.4 Calculate the fraction of the variation in the stiffness explained by the quadratic model as:

$$R^2 = 1.00 - \left[\frac{[\log S(8) - \log S(8)]^2 + ...[\log S(240) - \log S(240)]^2}{[\log S(8) - \log(\bar{S})]^2 + ...[\log S(240) - \log(\bar{S})]^2} \right] \tag{15}$$

1.8.5 Calculate $\overline{S}$ the average of the stiffness values at 8, 15, 30, 60, 120, and 240 s as:

$$\log \overline{S} = [\log S(8) + ...\log S(240)]/6 \tag{16}$$

1.8.6 Use the estimated values of the stiffness and m at 60 s for specification purposes. Measured and estimated stiffness values should agree to within 2%. Otherwise, the test is considered suspect.

Test Information

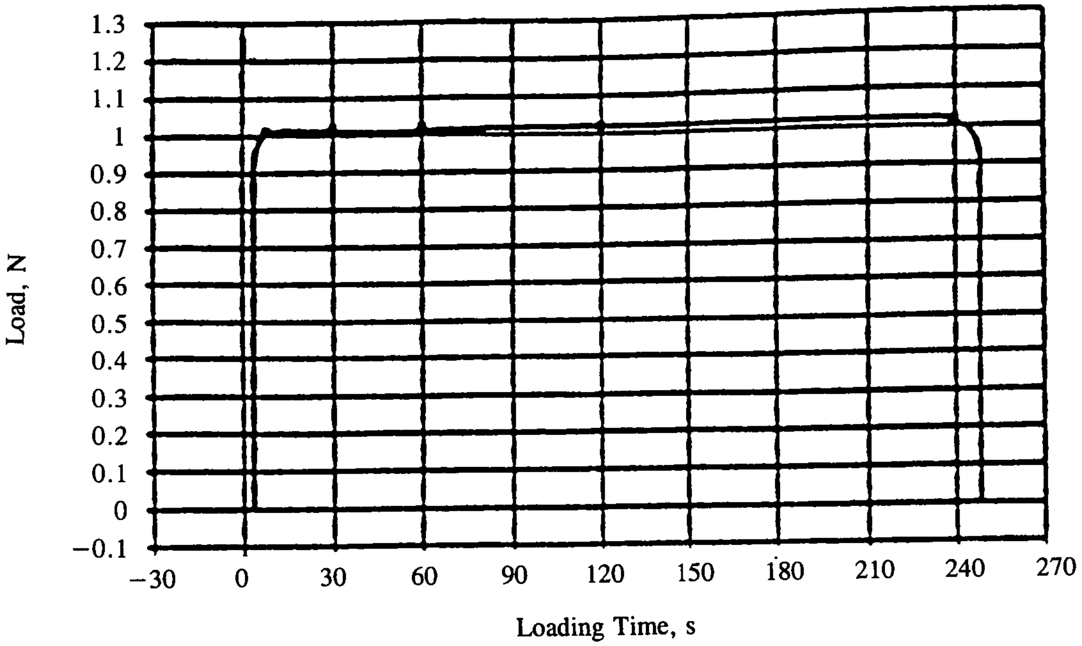
Project:	testing	Target Temp:	23.0°C	Conf. Test:	2.199e+008
Operator:	jsy	Actual Temp:	14.8°C	Date:	09/17/93
Specimen:	plastic beam b	Soak Time:	0.0 sec	Load Const:	0.24
Time:	11:47:03	Beam Width:	12.70 mm	Defl Const:	0.0024
Date:	09/18/93	Thickness:	6.35 mm	Date:	09/17/93
File:	0818934.DAT				

Results

t Time (sec)	P Force (N)	d Defl (mm)	Measured Stiffness (kPa)	Estimated Stiffness (kPa)	Difference %	m-value
8	.9859	.9126	87030.0	87060.0	.03532	0.176
15	.9894	1.022	77990.0	77930.0	−.08120	0.175
30	.9913	1.158	68960.0	68990.0	.04809	0.175
60	.9910	1.308	61110.0	61110.0	.004487	0.174
120	.9908	1.475	54150.0	54150.0	−.001551	0.174
240	.9906	1.664	48010.0	48000.0	−.005077	0.174

Regression Coefficients:
$a = 5.100$ $b = -.1784$ $c = .001020$ R^2 = 0.999996

Figure A1 Typical Test Report



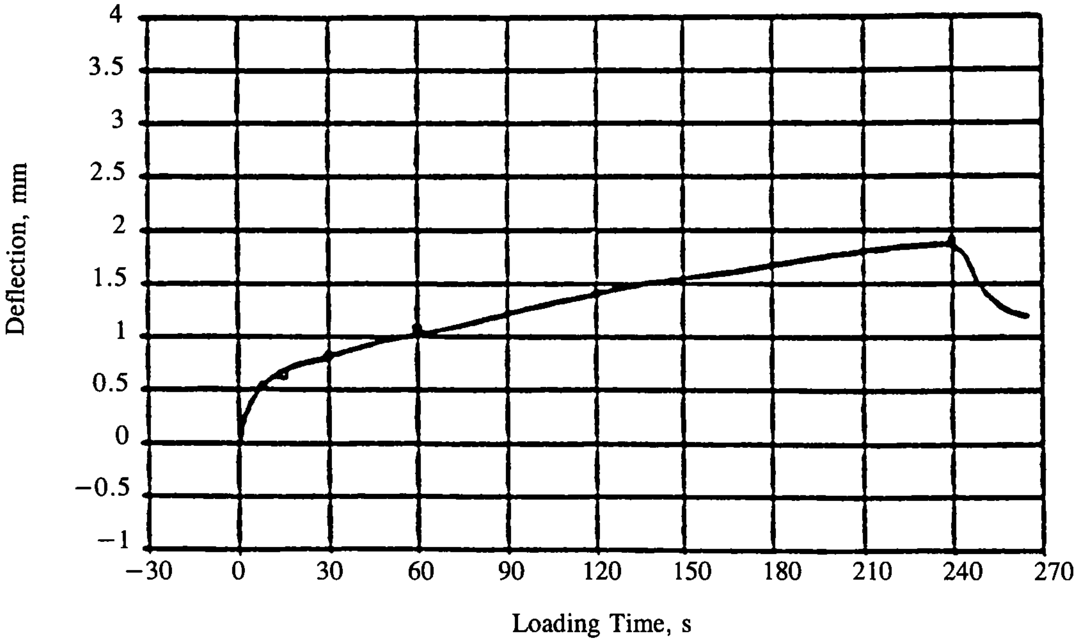


Figure A2 Typical Load and Deflection Plots for the Bending Beam Rheometer

Appendix C

Determining the Fracture Properties of Asphalt Binder in Direct Tension

AASHTO Designation: TP3

Standard Method of Test for

Determining the Fracture Properties of Asphalt Binder in Direct Tension

AASHTO Designation: TP3[1]

1. SCOPE

1.1 This test method covers the determination of the failure strain and failure stress of asphalt binders by means of a direct tension test. It is applicable to material that has a failure strain less than 10% and can be used with unaged material or with material aged using T240 (RTFOT), T179 (TFOT), or PP1 (PAV). The test apparatus is designed for testing within the temperature range from −40°C to 25°C.

1.2 This test method is limited to asphalt binders that contain particulate material less than 250 μm in diameter.

1.3 This test method is not valid for specimens that exhibit a strain to failure outside the defined brittle-ductile range ($\geq$ 10%).

1.4 The values stated in SI units are to be regarded as the standard.

1.5 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this procedure to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.*

2. REFERENCE DOCUMENTS

2.1 *AASHTO Standards:*

MP1	Specification for Performance-Graded Asphalt Binder
PP1	Practice for Accelerated Oxidative Aging of Asphalt Binder Using a Pressurized Aging Vessel
T40	Practice for Sampling Bituminous Materials

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[1] This standard is based on SHRP Product 1005.

T179	Test Method for Effect of Heat and Air on Asphalt Materials (Thin-Film Oven Test)
T240	Test Method for Effect of Heat and Air on Rolling Film of Asphalt (Rolling Thin-Film Oven Test)

2.2 *ASTM Standards:*

E1	Specification for ASTM Thermometers
E4	Practice for Load Verification of Testing Machines
E83	Method of Verification and Classification of Extensometers
E220	Method for Calibration of Thermocouples by Comparison Techniques

2.3 *DIN Standards*

43760

2.4 *MIL Standards*

5545

45662

45662A

3. TERMINOLOGY

3.1 *Definitions*

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

3.2 *Description of Terms Specific to This Standard*

3.2.1 brittle, *adj*—refers to a type of failure in a direct tension test where the stress-strain curve is essentially linear up to the point of failure and the failure is by sudden rupture of the test specimen without appreciable reduction in the cross section of the specimen.

3.2.2 brittle-ductile, *adj*—refers to type of failure in a direct tension test where the stress-strain curve is curvilinear and the failure is by sudden rupture of the test specimen. A limited reduction in the cross section of the specimen occurs before rupture.

3.2.3 ductile, *adj*—refers to a type of failure in a direct tension test where the specimen does not rupture but fails by flow at large strains.

3.2.4 engineering strain, *n*—refers to the axial strain resulting from the application of a tensile load and calculated as the change in length caused by the application of the tensile load divided by the original unloaded length of the specimen without any correction for reduction in its cross section.

3.2.5 failure, *n*—refers to the point at which the tensile load reaches a maximum value as the test specimen is pulled at a constant rate of elongation.

3.2.6 failure stress, *n*—the tensile stress on the test specimen when the load reaches a maximum value during the test method specified in this standard.

3.2.7 failure strain, *n*—the tensile strain corresponding to the failure stress.

4. SUMMARY OF TEST METHOD

4.1 This method describes the procedure used to measure the strain at failure and stress at failure in an asphalt binder test specimen pulled at a constant rate of elongation. Test specimens are prepared by pouring hot asphalt binder into a suitable mold. Two plastic inserts are used to grip the asphalt binder during the test and to transfer the tensile load from the test machine to the test specimen.

4.2 This test procedure was developed for asphalt binders at temperatures where they exhibit brittle or brittle-ductile failure. A brittle or brittle-ductile failure will result in a fracture of the test specimen as opposed to a ductile failure in which the specimen simply stretches without fracturing. The test is not applicable at temperatures where failure is by ductile flow.

4.3 A non-contact extensometer is used to measure the elongation of the test specimen as it is pulled in tension at a constant rate of elongation of 1 mm/min. The maximum load developed during the test is monitored. The tensile strain and stress in the test specimen when the load reaches a maximum is reported as the failure strain and failure stress, respectively.

5. SIGNIFICANCE AND USE

5.1 The strain at failure is a measure of the amount of elongation that an asphalt binder can sustain without cracking. Strain at failure is used as a criterion for specifying the low-temperature properties of asphalt binder in accordance with MP1.

5.2 The test is designed to identify the temperature region where the asphalt binder has limited ability to elongate without cracking. In the asphalt binder specification, a lower limit is placed on the allowable strain to failure at a specified temperature and rate of elongation.

5.3 For evaluating an asphalt binder for conformance to MP1, the elongation rate is 1.0 mm/min and the test temperature is selected from table 1 of MP1 according to the grade of asphalt binder. Other rates of elongation and test temperatures may be used to test asphalt binders.

6. APPARATUS

6.1 *Direct Tension Test System*—A direct tension test system consisting of (1) a displacement-controlled tensile loading machine, (2) a specimen gripping system, (3) a chamber for environmental conditioning and testing, (4) load measuring and recording devices, (5) elongation measuring and recording devices, (6) a temperature detection device, and (7) data acquisition and display devices.

6.1.1 *Tensile Loading Machine*—A tensile loading machine with a controlled-displacement loading frame capable of producing at least a 500 N load is required. The platen movement shall be controlled with either one or two motor-driven screws or with a hydraulic-controlled actuator. Screw-type loading frames are typically used for this test, although a hydraulic closed-loop testing frame is acceptable if the requirements specified in this standard are met. The loading frame shall produce a crosshead speed of 1.00 ± 0.05 mm/min. Additional crosshead speeds may be supplied but are not required. The testing frame shall be equipped with an automatic return feature that returns the crosshead to a reference position such that the center-to-center spacing of the loading pins is 100.0 mm ± 0.1 mm. The testing frame shall be equipped with two standards with sufficient clear space between the standards so that an environmentally controlled chamber with dimensions given in section 6.1.3 can be placed between the standards.

6.1.2 *Specimen Gripping System*—The gripping system shall produce a self-aligning uniaxial test load, accept the plastic end units described in section 6.1.2.1 and be designed so that test specimens can be easily mounted in the machine. The system shall include two grips. Each grip shall include a specially-shaped pin that is mounted rigidly to the upper and lower platens of the testing machine. Figure 1 specifies the dimensions of the top and bottom grips. One grip shall be fixed and remain stationary during the test while the other grip is displaced at the desired rate. Figure 2 specifies the dimensions of the loading pins used with the grips.

6.1.2.1 *Specimen Plastic End Inserts*—PMMA (Plexiglas®) end inserts having the dimensions specified in figure 3 shall be used on both ends of the test specimen to transfer the tensile load to the asphalt binder. Each end insert contains a precisely machined hole and slot. The diameter of the hole is slightly larger than the diameter of the pin. The slots on the top and bottom inserts allow two spots of laser light to pass the test specimen and shine upon the receiver. Gripping of the specimen is accomplished through the bond (adhesion) between the asphalt binder test specimen and the plastic end insert. Each end insert mounts on a specially shaped pin that is part of the gripping system. The specimen is attached to the top and bottom grips by positioning the end inserts in the test machine such that the plastic inserts fit onto the pins and are indexed against the face of the grips. Matching the coefficient of thermal expansion of the asphalt binder and the inserts is necessary to reduce thermal shrinkage stresses at the interface that otherwise cause bond failures.

NOTE 1.—PMMA (Plexiglas®), meeting MIL STD-5545, has been found acceptable for making the inserts. It is readily available, opaque to the laser beam, has a satisfactory coefficient of thermal expansion, and is easy to machine.

6.1.3 *Environmental Conditioning and Testing Chamber*—The environmental conditioning and testing chamber shall be capable of controlling temperature and humidity and performing isothermal conditioning of test specimens prior to testing. It should be on the order of 300 mm wide by 200 mm deep by 450 mm high and shall completely enclose the specimen and gripping system. It shall be capable of controlling test temperatures between −40°C and ambient with variations within the chamber ≤ 0.2°C. It shall be equipped with a cooling system that has the capacity to reduce the chamber temperature from ambient to −40°C within 40 minutes and to change the chamber temperature from −30 to −40°C or from −40 to −30°C within 10 minutes. Mechanical cooling or liquid nitrogen may be used to cool the chamber. It shall have a dehumidifying system with a capacity such that the formation of frost on the interior of the chamber, the test specimen, or any of the test fixtures is eliminated.

6.1.3.1 The chamber shall be capable of storing a minimum of 16 test specimens on a rack which is thermally isolated from the walls and floors of the chamber such that heat conducted from the walls and floors of the chamber does not affect the temperature of the stored specimens.

NOTE 2.—A demolded test specimen is placed on Plexiglas®, Teflon® or other plastic plate (with approximate dimensions of 6 mm thick by 20 mm wide by 100 mm long) and transferred to the environmentally controlled test chamber for thermal conditioning. The use of a transfer plate will minimize deformation during handling. Each plate, when the above dimensions are used, accommodates up to four demolded test specimens.

6.1.3.2 The chamber shall be fitted with a front-opening door for maintenance and standardization purposes and an access port that allows for insertion of the operator's hand and forearm to position test specimens on the storage shelf for conditioning and to position test specimens on the grips for testing. The access port shall be designed so that changes in chamber temperature are ≤ 0.2°C during an operation in which the operator's hand or forearm is inserted into or removed from the chamber. Visual access to the interior of the test chamber shall be provided to permit proper mounting of test specimens and test monitoring. The test specimen elongation is measured with an optical laser. Use of the laser requires optical glass windows on two sides of the temperature chamber so that a beam of laser light can be passed through the chamber without distorting the beam.

6.1.4 *Load Measuring and Recording Devices*—Load shall be measured with a load cell having a minimum capacity of 500 N and a sensitivity of 0.1 N. The load cell shall be calibrated at least annually in accordance with ASTM E4. The load and elongation shall be monitored with the data acquisition system such that they can be resolved to 1% of the failure load and elongation, respectively. Once the test has started, the data acquisition system shall be able to detect the point in time when the load starts to change as a result of elongation in the sample. This shall be accomplished by monitoring the load cell signal with time. A change in the load signal equivalent to 1 to 2 N (threshold load) shall be used to mark the point in time where zero reading of the extensometer is obtained. The point in time where the peak load is obtained will be captured by the data acquisition system and the accumulated elongation from the zero reading to the elongation corresponding to the peak load shall be used to calculate the failure strain. Once the test is complete, the device shall display the strain at failure. Peak load typically ranges from 10 to 100 N depending on the test temperature, grade, aging, and source of the binder. Stress and strain shall be displayed to the nearest 0.1 N.

6.1.5 *Elongation Measuring and Recording Devices*—Specimen elongation shall be measured with a laser light transmitter and receiver. The non-contact laser extensometer shall be calibrated at least annually according to ASTM E83, MIL-STD 45662 and MIL-STD 45662A. The transmitter shall produce a vertical plane of laser light that is monitored by the receiver and shall be arranged so that the test specimen interrupts the plane of laser light except for the slots in the insert. Thus, two spots of laser light are transmitted to the receiver. The receiver shall constantly monitor the relative position of the two spots of laser light to produce a voltage proportional to the distance between the two nearest edges of the spots of light. This voltage shall be converted to elongation by a controller attached to the receiver using a calibration factor determined by the manufacturer and verified when the extensometer is calibrated. The laser measurement range shall be 30 to 60 mm with an accuracy $\leq$ 0.005 mm. Elongations shall be recorded to the nearest 0.005 mm.

6.1.6 *Temperature Detection Device*—The temperature detection device shall be a calibrated resistance thermal detector (RTD) readable and accurate to 0.1°C (note 3). The RTD shall be mounted inside the environmental chamber in the immediate vicinity of the test specimen. Cabling to the RTD shall be of sufficient length that the bulb of a total immersion mercury-in-glass thermometer can be held adjacent to the RTD for standardization purposes (See section 9.1.3).

NOTE 3.—Required temperature measurement can be accomplished with an appropriately calibrated platinum resistance thermometer (RTD) or thermistor. Platinum resistance thermometers meeting DIN Standard 43760 (Class A) are recommended for this purpose. The required precision and accuracy cannot be obtained unless each RTD or thermistor is calibrated as a system with its respective meter or electronic circuitry (See section 9.1.3).

6.1.7 *Data Acquisition and Display Device*—The data acquisition and display device shall display the load and elongation selected by the operator (stress and strain) on an LED (or other appropriate computer controlled display) during the time the test specimen is loaded. It shall detect the peak load and capture the elongation associated with the peak load. The maximum skew time between the load and corresponding elongation shall be 0.015 s.

6.1.7.1 The data acquisition component shall consist of an IBM-compatible computer with three A/D channels; one for load (the load cell), one for elongation (the laser), and one for temperature (the RTD). Data shall be stored in ASCII format.

6.1.7.2 *Display of Stress-Strain Curve*—The data acquisition and display system shall be capable of displaying a stress-strain curve in units of stress (MPa) versus strain (percent). This may be accomplished using the video screen of the data acquisition computer or with an *x-y* recorder. If a recorder is used, the units may be recored in volts but the test file shall contain the calibration factor in megapascals/volt and percent strain/volt for both the *x* and *y* axes.

6.2 *Specimen Molds*—The specimen molds shall be manufactured from silicone rubber available from Dow Corning (HSII RTV Moldmaking Rubber 20:1 Kit, white in color). Silicone rubber is used because it is dimensionally stable, provides an excellent non-stick surface for asphalt binder, and is easy to clean. Specimens and molds shall have the dimensions specified in figures 4 (silicone rubber molds) and 5 (aluminum molds).

6.3 *Specimen Mold Support Plates*—Aluminum plates 5 to 10 mm thick to support the rubber molds when molding test specimens are required.

6.4 *Specimen Storage Plates*—Plexiglas, Teflon, or other plastic plates for transferring and storing test specimens in the environmental chamber.

6.5 *Calibrated thermometer*—A calibrated liquid-in-glass thermometer of suitable range with subdivisions of 0.1°C is required for verification of the temperature transducer. This thermometer shall be calibrated in accordance with ASTM E77. An ASTM 62C thermometer is suitable.

6.6 *Load Verification Equipment*—Known dead masses (traceable to NIST) ranging 10 to 500 ±0.1 N (1 to 50 ± 0.1 kg) are required for verifying the calibration of the load cell.

7. MATERIALS

7.1 Solvent (Varsol or mineral spirits) or a degreasing spray cleaner formulated for use on plastic for cleaning molds, plastic end inserts and aluminum plates

7.2 Cleaning cloths (cotton) for wiping molds, end inserts and plates

8. HAZARDS—Use the standard laboratory safety procedures required for handling the hot asphalt binder when preparing test specimens and the required safety procedures when cleaning with solvents or degreasers.

9. CALIBRATION AND STANDARDIZATION

9.1 Verify calibration of the extensiometer, load cell, and temperature transducer.

NOTE 4.—Calibration is usually performed by a calibration service agency. Calibration verification, system standardization, and quality checks may be performed by the manufacturer, other agencies providing such services, or in-house personnel using the procedures described below.

9.1.1 *Load cell*—Verify calibration of the load cell at least every 6 months using dead masses suspended from the load cell.

9.1.2 *Non-Contact Extensometer*—Verify calibration of the non-contact extensometer at least every month using the fixture shown in figure 6. Place the fixture in the test machine and apply a 20 to 50 N load on the fixture to hold the fixture firmly in the grips. Insert the gauge in the fixture and measure the short dimension of the gauge with the laser. Remove the gauge from the fixture and measure the long dimension. Check the length of the gauge as measured with a similar reference measurement made on the gauge during the last calibration. If the verification measurement and the reference measurement differ by more than 0.006 mm, either calibration or maintenance is required.

NOTE 5.—Measurements should be made at −12°C. Allow sufficient time for gauge to achieve thermal equilibrium.

9.1.3 *Temperature Detector*—Verify calibration of the temperature detector at least every six months by comparing the output of the RTD with a calibrated mercury-in-glass thermometer in accordance with ASTM E220. Place the thermometer in the environmentally controlled chamber. Hold the RTD in intimate contact with the bulb of the thermometer with a rubber O-ring or other suitable technique. When the thermometer and the temperature detection device have reached equilibrium, compare the temperature indicated on the detector's readout to the temperature indictated on the thermometer by reading through the observation port on the door of the chamber. If the temperature indicated by the thermal detector does not agree with the mercury-in-glass thermometer ± 0.1°C, further calibration or maintenance is required.

9.1.4 Verify the speed of the crosshead by using a dial gauge and a stopwatch. Mount a dial gauge on a fixed portion of the testing machine in a manner such that the stem of the dial gauge senses the movement of the crosshead. Be careful to ensure that the movement of the stem of the dial gauge is parallel to the movement of the crosshead and that the dial gauge is firmly attached to the fixed portion of the testing machine. Mounting the dial gauge on a magnetic base is a convenient method for attaching the dial gauge to the testing machine. Select the desired crosshead speed and start operating the machine at the desired speed. As the machine is running, start the stopwatch and simultaneously obtain an initial reading of the dial gauge. Approximately one minute later, obtain a second reading and simultaneously stop the stopwatch. Calculate the speed of the crosshead by dividing the difference between the initial and final dial gauge reading in millimeters by the stopwatch time in minutes.

10. PREPARATION OF SAMPLES AND TEST SPECIMENS

10.1 *Preparing Test Samples*—If unaged binder is to be tested, obtain test samples according to T40.

10.2 Anneal the asphalt binder for the test specimen by heating until it is sufficiently fluid to pour. Annealing prior to testing removes reversible molecular associations (steric hardening) that occur during normal storage at ambient temperature.

NOTE 6.—Minimum pouring temperatures that produce a consistency equivalent to that of SAE 10W30 motor oil (readily pours but not overly fluid) at room temperature are recommended. The specific temperature will depend on the grade of binder and its prior aging history, if any. Temperatures less than 135°C are desirable. Temperatures above 135°C may be required, however, for some modified asphalt binders or heavily aged binders.

10.3 Place the plastic end inserts into both ends of the mold. Place the molds and inserts into a 163°C oven for 30 minutes.

10.4 After heating, place the mold on a 6- to 7-mm-thick aluminum plate. Do not preheat the aluminum plate. Pour hot asphalt binder into the mold by starting at one end of the mold and moving across the mold in a single pass. Pour the specimen in a continuous stream to avoid entraining air bubbles or gaps. Complete the pouring operation as quickly as possible to avoid any excessive drop in the temperature of the asphalt binder. Stop pouring when the asphalt is slightly above the top surface of the mold.

10.5 After pouring the test specimen, allow the entire assembly to cool on the benchtop at ambient temperature for approximately one hour. Do not quench the specimen to achieve ambient temperature.

10.6 As soon as the specimen has cooled to room temperature, trim off the excess asphalt binder with a straight cutting edge (e.g., a flat cheese cutter or spatula) so that the asphalt binder is flush with the top of the mold. Use care during the trimming operation so that the asphalt binder is not pulled away from the mold and that the bond between the plastic inserts and the asphalt binder is not damaged. Trim the specimen in a consistent manner. Pull the cutting edge along the long axis of the sample flush with the surface of the mold to remove the excess asphalt binder. After trimming, remove all debris or extraneous asphalt binder from the holes or slots in the plastic insert.

NOTE 7.—Caution: Excessive downward pressure during trimming will distort the sample mold. If this occurs, discard the sample.

10.7 Immediately prior to demolding, place the mold containing the specimen in a freezer at -5 ± 5°C until the specimen is sufficiently stiff to demold without distorting the sample. Some softer grades may require lower temperatures. Time in the freezer should not exceed 15 minutes. After demolding, place the sample on the specimen storage plate (see section 6.4). Measurement of specimen dimensions after demolding is not necessary since dimensional tolerances are closely controlled in the molding process.

11. PROCEDURE

11.1 Set the environmental chamber at the desired testing temperature and wait until it stabilizes to within ± 0.2°C of the desired test temperature. When testing for compliance with MP1, use the test temperatures specified in table 1 of MP1.

11.2 Immediately after demolding, place the test specimens in the chamber on the plastic storage plate and condition the specimens at the test temperature for 1 hour ± 10 minutes. Adhere carefully to time schedule to avoid testing variability that is caused by physical hardening.

11.3 After 1 hour ± 10 minutes, mount the specimen on the pins using the environmental chamber hand access port, centering the back face of the insert on the mounting pin. Do not open the chamber door to handle or mount the specimen because that will produce excessive temperature fluctuations that will take time to stabilize and lead to variable thermal histories. Handle the specimens with latex surgical gloves to protect the operator's fingers and to minimize heating of the specimen. Handle the specimen by touching only the plastic inserts—do not touch the asphalt binder.

NOTE 8.—Air currents from the circulation fan may cause the inserts to move after being placed on the mounting pins. A silicone rubber or foam washer that remains flexible at the test temperature will help to hold the insert against the face of the grip. It is important that the insert be centered on the pin (flush against the face of the grip) in order for the load to be applied axially through the center of the test specimen. A suitable washer may be cut from silicone rubber or foam sheeting with a cork borer. The washer may be 5-10 mm thick with an outer diameter of approximately 10 mm. The inside diameter of the washer shall be sufficient to provide a friction fit on the 5-mm portion of the pin. The washer should slide easily on the pin providing only sufficient force to hold the insert in place during the test.

11.4 Select the desired deformation rate and load the specimen to failure. Select a deformation rate of 1.00 ± 0.05 mm/min when testing for compliance with MP1. If a test specimen fails outside the gauge area of the specimen (from throat to throat), discard the test.

11.5 *Alternate loading procedure*—Apply a preload to the test specimen by mounting the specimen as previously described and applying an elongation sufficient to develop a 10 to 20 N load; this may reduce testing variability. As soon as the 10 to 20 N load is reached, stop the movement of the platen and allow the load to relax until it is no longer detectable. The time required to relax the load will depend on the stiffness of the test specimen. Once the load has relaxed, continue the test as described in section 11.4.

11.6 The strain at failure is easily identified as the strain at peak load (maximum stress) when the failure is by fracture (i.e., the specimen breaks into two pieces). However, if the specimen does not fracture but reaches a maximum stress and then flows without fracture, the strain at failure is recorded as the strain corresponding to the maximum stress. In some cases, the maximum stress may occur at strains greater than 10%. In this case, do not continue the test beyond 10% strain. Simply record the failure stress as "greater than 10%." If the asphalt binder can be stretched to 10% without fracture, it meets the requirements of MP1 at the test temperature.

11.7 If the plastic specimen end inserts are to be reused, break them off the asphalt binder while the asphalt binder is still cold. Discard the asphalt binder and clean the end inserts by soaking them in solvent and wiping with a soft cloth. Do not use acetone, TCE, or toluene, since such solvents will dissolve the plastic inserts. After wiping the inserts, use a detergent solution to remove oil film residue left by the mineral spirit cleaner. Alternatively, use a degreasing spray cleaner formulated for use on plastic. Clean the plastic inserts thoroughly. Grease on the asphalt bonding area can reduce bonding and cause bond failures.

12. CALCULATION

12.1 Compute the failure stress by dividing the failure load by the original area of the test specimen cross section as shown in equation 1:

$$\sigma_f = P_f/A \tag{1}$$

where

σ_f = failure stress, MPa
P_f = failure load, N
A = original area of cross section, mm^2

NOTE 9.—For specimens used in this test, A = 3.6 mm^2.

12.2 Compute the failure strain by dividing the elongation at failure by the original gauge length, as shown in equation 2:

$$\epsilon_f = \delta_f/L \tag{2}$$

where

ϵ_f = failure strain, mm/mm
δ_f = elongation at failure, mm
L = gauge length, mm

NOTE 10.—For specimens used in this test, the effective gauge length, L, is assumed to be 27.0 mm. This is an effective gauge length that represents the portion of the specimen that contributes to the majority of the strain. Strain values determined in this test may vary slightly from the actual strain at the point of fracture because of the assumed value for the gauge length.

13. REPORT

13.1 Report the following information:

13.1.1 the sample identification;

13.1.2 the date and time of test;

13.1.3 the test temperature, to the nearest 0.1 °C;

13.1.4 the average rate of elongation, to the nearest 0.01 mm/min.;

13.1.5 the average failure strain, to the nearest 0.01%;

NOTE 11.—Direct tension testing of multiple specimens may produce obvious outliers. Until a statistically valid procedure is developed for considering outliers, discard any strain at failure values that are obvious outliers.

13.1.6 the average failure stress, to the nearest 0.01 MPa;

13.1.7 the average peak load, to the nearest N; and

13.1.8 the type of fracture observed (fracture or no fracture).

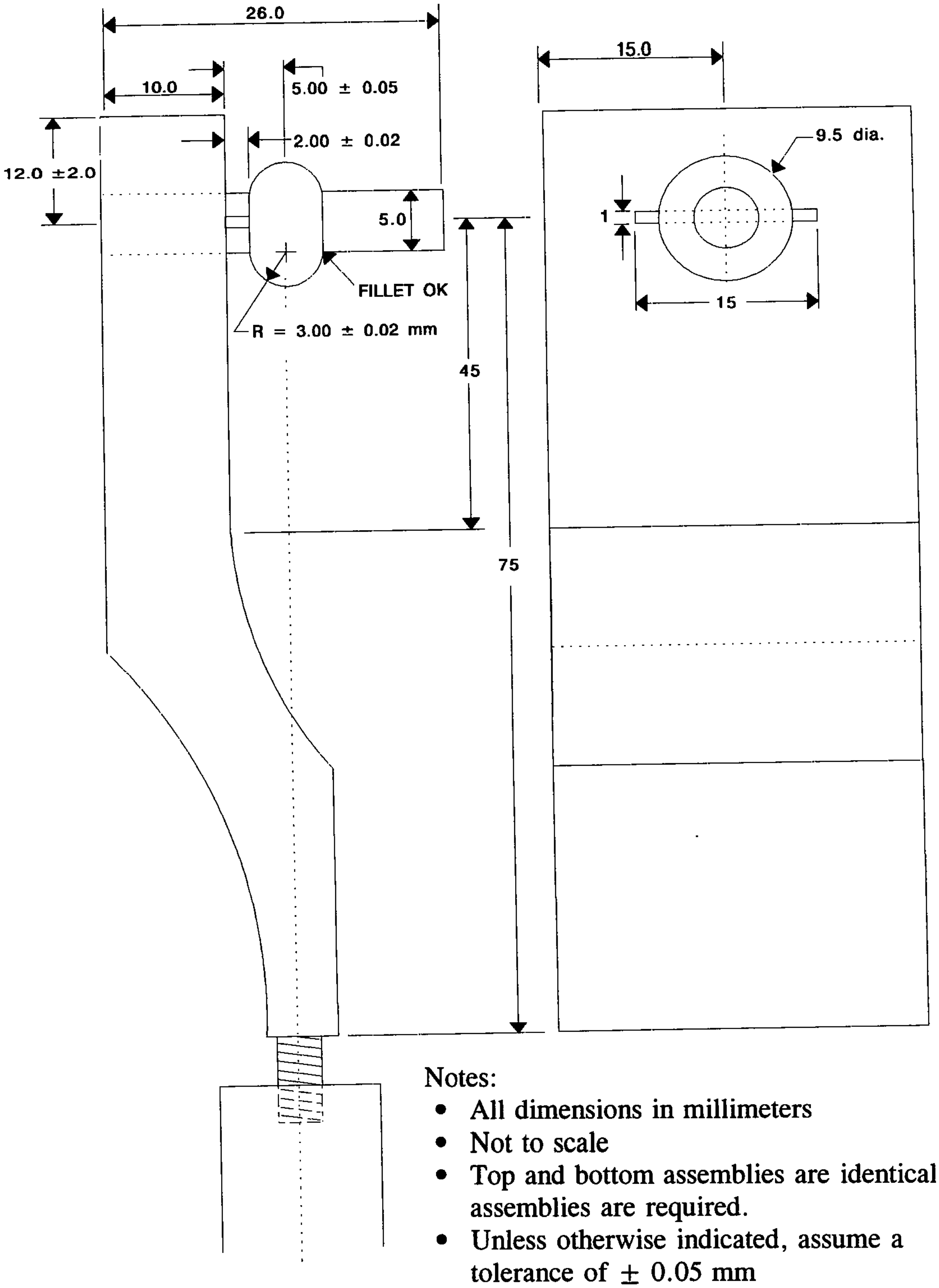
14. PRECISION AND BIAS

14.1 *Precision*—The research required to develop precision estimates for this test method has not been conducted.

14.2 *Bias*—The research required to establish the bias of this method has not been conducted.

15. KEY WORDS

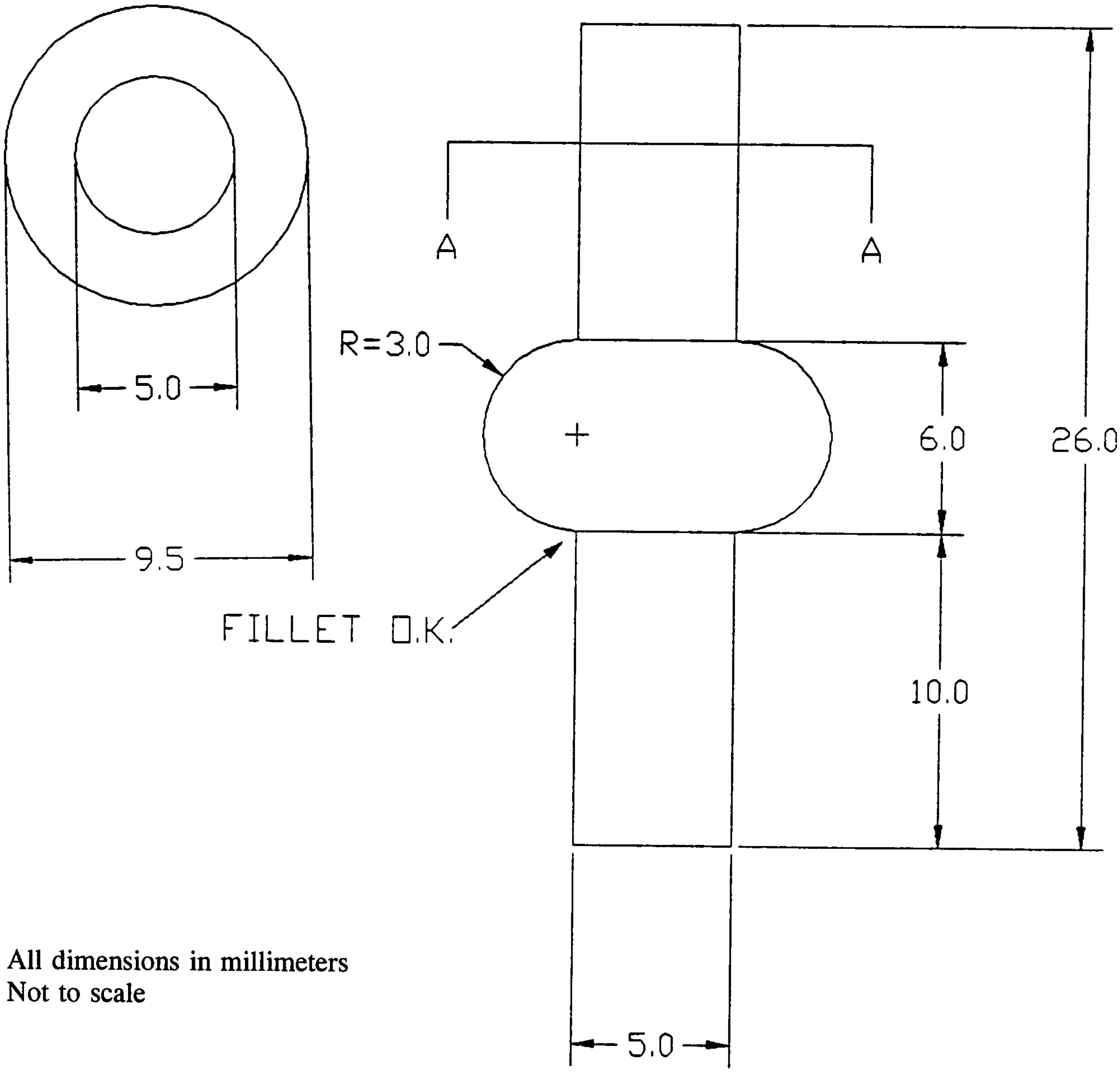
Asphalt binder, direct tension, failure, failure strain, fracture, thermal cracking.



Notes:

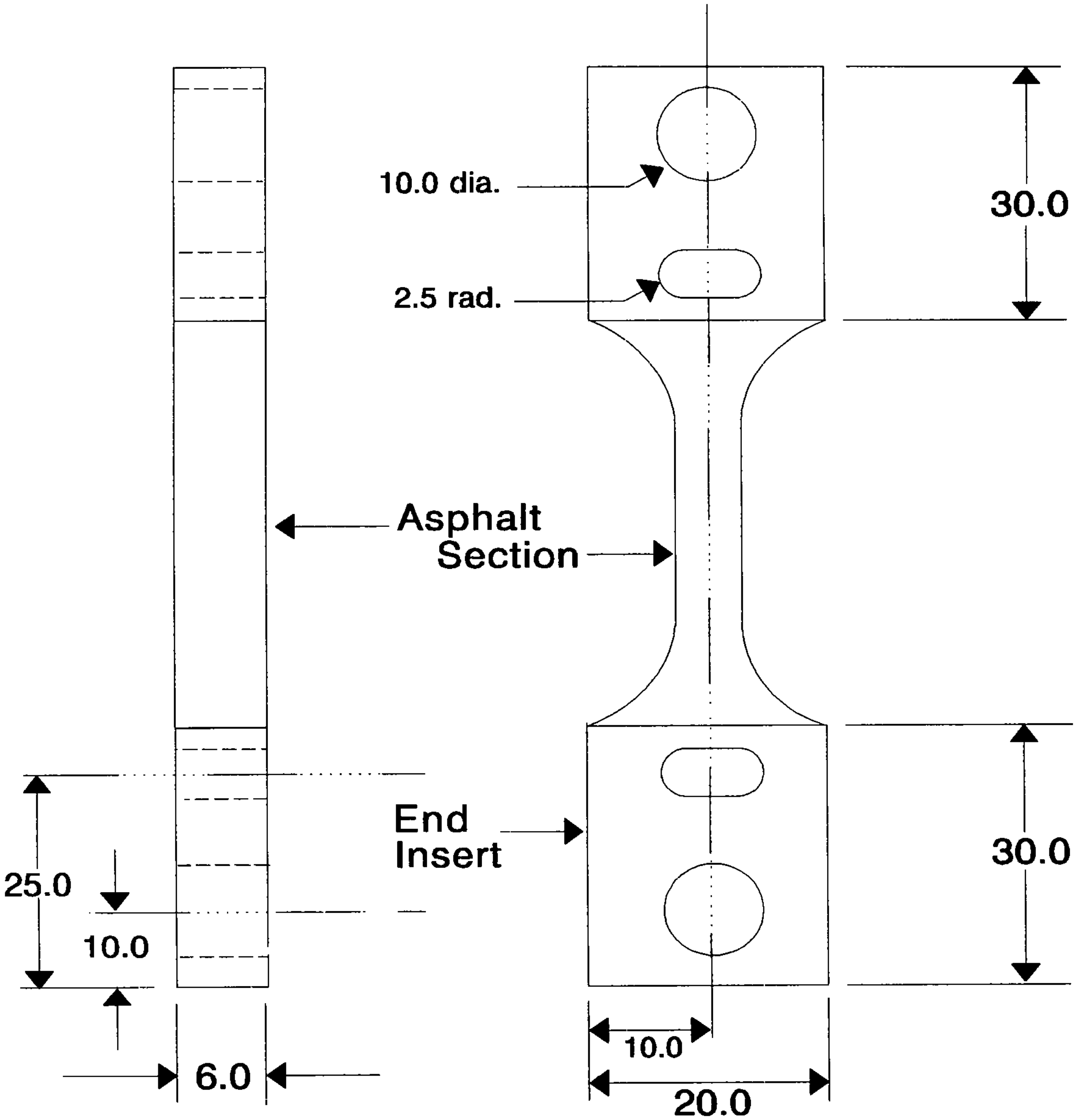
- All dimensions in millimeters
- Not to scale
- Top and bottom assemblies are identical. Two assemblies are required.
- Unless otherwise indicated, assume a tolerance of ± 0.05 mm

Figure 1. Top and Bottom Grip and Loading Pin Assembly



All dimensions in millimeters
Not to scale

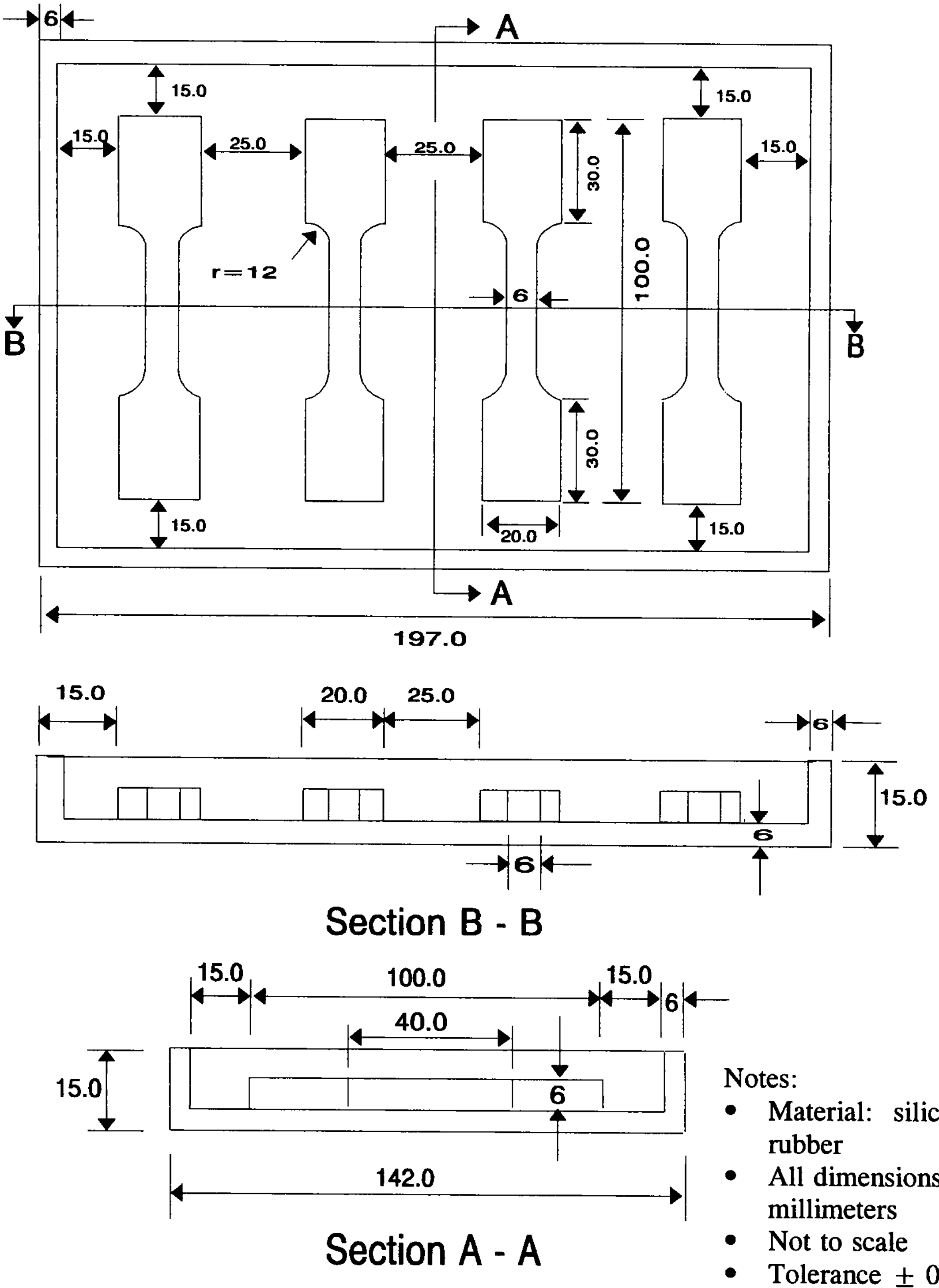
Figure 2. Loading Pins Used to Mount the Direct Tension Specimen



Notes:

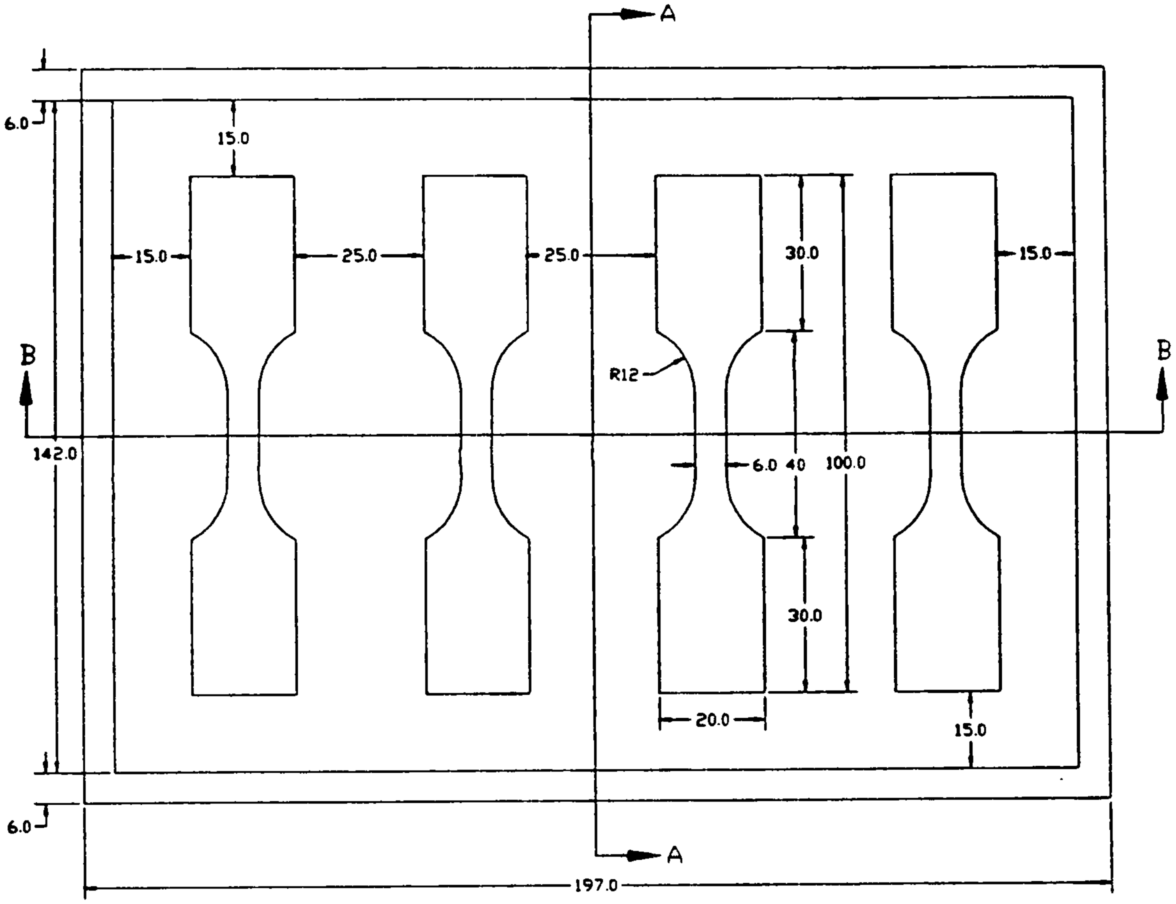
- All dimensions in millimeters
- Not to scale
- Unless otherwise indicated, assume a tolerance of ± 0.05 mm

Figure 3. Plastic End Inserts

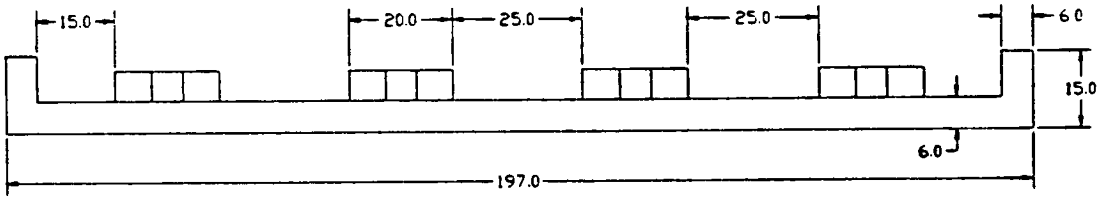


Notes:
- Material: silicone rubber
- All dimensions in millimeters
- Not to scale
- Tolerance ± 0.03 mm

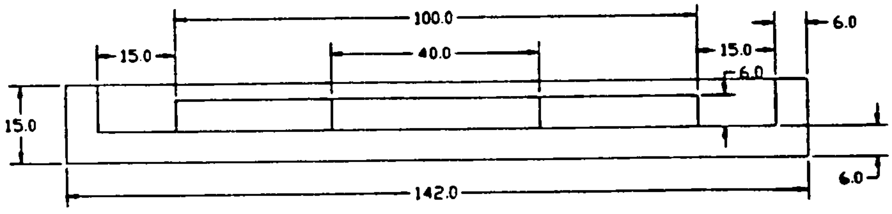
Figure 4. Direct Tension Specimen Mold



DIRECT TENSION TYPE I MOLD



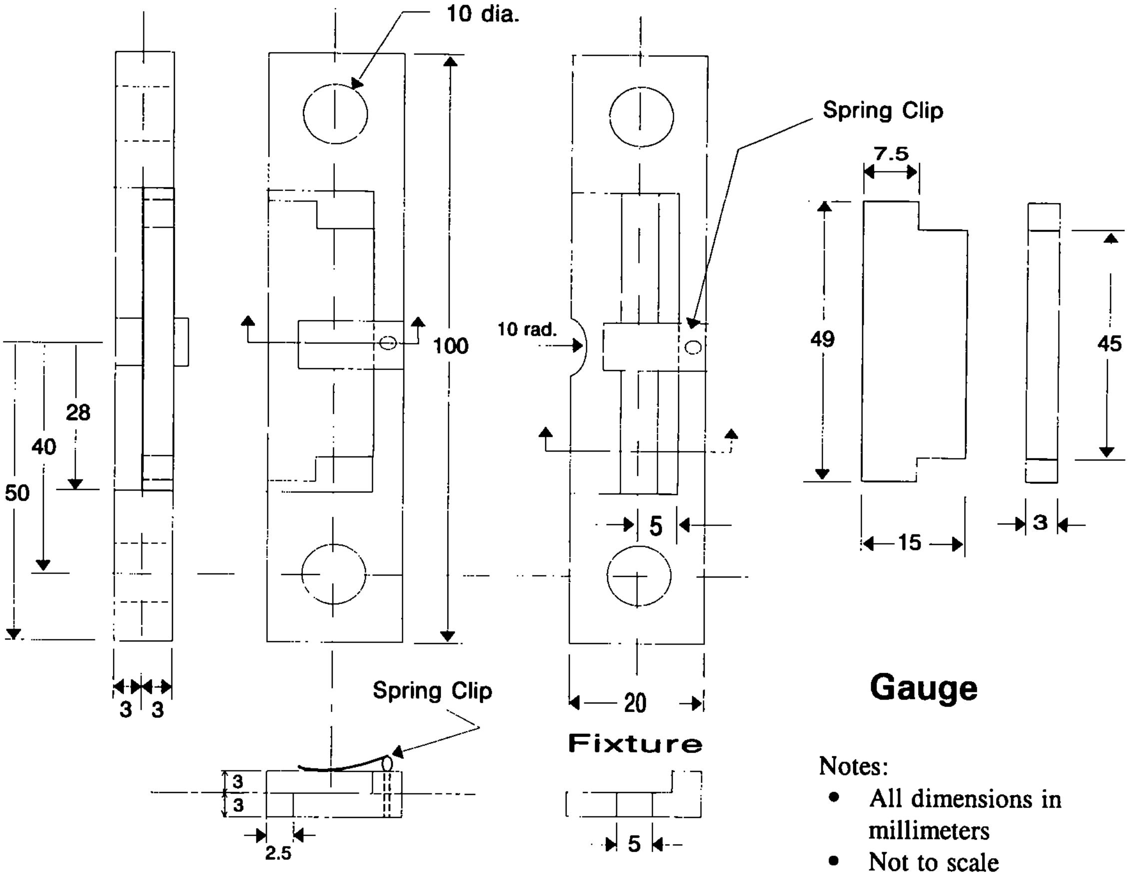
SECTION B-B



SECTION A-A

B1-CO No.: 1992-12
Material: aluminum
All dimensions in
millimeters
Tolerance: ± 0.03 mm

Figure 5. Specimen Mold Dimensions



Notes:

- All dimensions in millimeters
- Not to scale
- Unless otherwise indicated, assume a tolerance of ± 0.05 mm

Figure 6. Extensometer Verification Device

Appendix D

Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel

AASHTO Designation: PP1

Standard Practice for

Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel

AASHTO Designation: PP1[1]

1. SCOPE

1.1 This practice covers the accelerated aging (oxidation) of asphalt binders by means of pressurized air and elevated temperature in a pressurized aging vessel (PAV). The test method is intended to simulate in-service oxidative aging of asphalt binders and is intended for use with residue from T240 (Rolling Thin Film Oven Test (RTFOT)) or T179 (Thin Film Oven Test (TFOT)).

NOTE 1.—T240 is the recommended procedure. Modified asphalt binders may phase separate or form skins during conditioning with T179 (TFOT); the results from subsequent testing of this residue in TP5, TP1, and TP3 may be distorted.

1.2 The aging of asphalt binders during service is affected by mixture-associated variables such as the volumetric proportions of the mix, the permeability of the mix, properties of the aggregates, and possibly other factors. This test is intended to provide an evaluation of the relative resistance of different asphalt binders to oxidative aging at selected temperatures and cannot account for mixture variables.

1.3 The values stated in SI units are to be regarded as the standard.

1.4 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this procedure to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.*

2. REFERENCE DOCUMENTS

2.1 *AASHTO Standards:*

M231	Standard Specification for Standard Masses and Balances Used in the Testing of Highway Materials
MP1	Proposed Standard Specification for Performance-Graded Asphalt Binder

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[1] This standard is based on SHRP Product 1003.

T179 Test Method for Effect of Heat and Air on Asphalt Materials (Thin-Film Oven Test)

T240 Test Method for the Effect of Heat and Air on a Moving Film of Asphalt (Rolling Thin Film Oven Test)

2.2 *ASTM Standards:*

E220 Method for Calibration of Thermocouples by Comparison Techniques

2.3 *DIN Standards:*

43760

3. TERMINOLOGY

3.1 *Definitions*

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

3.1.2 in-service, *adj*—refers to aging of the asphalt binder that occurs in the pavement as a result of the combined effects of time, traffic and the environment.

4. SUMMARY OF TEST METHOD

4.1 Asphalt binder is first aged using T240 (RTFOT) or T179 (TFOT). A specified thickness of residue, from the RTFOT or TFOT, is then placed (or left) in standard TFOT (T179) stainless steel pans and aged at the specified aging temperature for 20 hours in a vessel pressurized with air to 2.10 MPa. Aging temperature is selected according to the grade of the asphalt binder.

5. SIGNIFICANCE AND USE

5.1 This method is designed to simulate the oxidative aging that occurs in asphalt binders during pavement service. Residue from this test may be used to estimate the physical or chemical properties of an asphalt binder after five to ten years of aging in the field.

5.2 Asphalt binders aged using PP1 are used to determine specification properties in accordance with MP1. The asphalt binder is aged with the RTFOT or TFOT prior to this conditioning step. Tank asphalt binders, as well as RTFOT or TFOT, and residue from this test are used to determine specification properties in accordance with MP1.

5.3 For asphalt binders of different grades or from different sources, there is no unique correlation between the aging time and temperature in this test and in-service pavement age and temperature. Therefore, for a given set of in-service climatic conditions, it is not possible to select a single PAV aging time and temperature that will predict the properties of all asphalt binders after a specific set of in-service exposure conditions.

5.4 The relative degree of hardening of different asphalt binders varies at different temperatures in the PAV. Therefore, two asphalt binders may age similarly at one temperature, but age differently at another temperature.

6. APPARATUS

6.1 The test system consists of a pressurized aging vessel (PAV), pressure controlling devices, temperature controlling devices, pressure and temperature measuring devices, and a temperature recording device (figure 1).

6.1.1 *Pressure Vessel*—A stainless steel pressure vessel designed to operate at 2.1 ± 0.1 MPa between 90 and 110°C with interior dimensions no greater than 200 mm in diameter and 215 mm in height (adequate to hold 10 TFOT pans and pan holder). The pressure vessel shall contain a pan holder capable of holding 10 TFOT stainless steel pans in a horizontal (level) position such that the asphalt binder film thickness in the bottom of the pans does not vary by more than 0.1 mm across any diameter of the pan. The holder shall be designed for easy insertion and removal from the vessel when the holder, pans, and asphalt binder are at the test temperature. A schematic that shows the vessel, pan holder and pans, and the specific dimensional requirements is shown in figure 2.

NOTE 2.—The vessel may be a separate unit to be placed in a forced draft oven for conditioning the asphalt binders or an integral part of the temperature control system (for example, by direct heating of the vessel or by surrounding the vessel with a permanently affixed heating unit, forced air oven, or liquid bath).

6.1.2 *Pressure Controlling Devices*

6.1.2.1 A pressure release valve that prevents pressure in the vessel from exceeding 2.2 MPa during the aging procedure

6.1.2.2 A pressure regulator capable of controlling the pressure within the vessel to ± 1 percent of the desired pressure, and with a capacity adequate to reduce the pressure from the source of compressed air so that the pressure within the loaded PAV is maintained at 2.1 ± 0.1 MPa during the test

6.1.2.3 A slow-release bleed valve that allows the pressure in the vessel at the completion of the conditioning procedure to be reduced at an approximately linear rate from 2.1 MPa to local atmospheric pressure within 9 ± 1 minutes

6.1.3 *Temperature Controlling Devices*—A temperature control device as described in section 6.1.3.1 or 6.1.3.2 for maintaining the temperature during the aging procedure at all points within the pressure vessel at the aging temperature ± 0.5°C and a digital proportional controller for maintaining the specified temperature control.

6.1.3.1 A forced-draft oven or fluid bath capable of (1) bringing the loaded unpressurized vessel to the desired conditioning temperature ± 0.5°C, as recorded by the resistance thermal detector (RTD) inside the vessel, within 2 hours, and (2) maintaining the temperature at all points within the pressure vessel at the aging temperature ± 0.5°C. The oven shall have sufficiently large interior dimensions to allow forced air to freely circulate within the oven and around the pressure vessel when the vessel is placed in the oven. The oven shall contain a stand or shelf which supports the loaded pressure vessel in a level position above the lower surface of the oven (i.e., maintains the film thickness in the aging pans within the specified tolerance).

6.1.3.2 A PAV with integral temperature control system that is capable of (1) bringing the loaded vessel to the desired conditioning temperature ± 0.5°C within 2 hours, as recorded by the RTD inside the PAV, and (2) maintaining the temperature at all points within the pressure vessel at the aging temperature ± 0.5°C.

6.1.4 *Temperature and Pressure Measuring Devices*

6.1.4.1 A platinum RTD accurate to the nearest 0.1°C and meeting DIN Standard 43760 (Class A), or equal, for measuring the temperature inside the PAV. The RTD shall be calibrated as an integral unit with its respective meter or electronic circuitry.

NOTE 3.—The RTD or thermistor and its meter may be calibrated by the manufacturer or a commercial vendor. Verification can be obtained by comparing the output from the RTD with a NIST-traceable ASTM 94C mercury-in-glass thermometer in accordance with ASTM E220. A stirred fluid bath is suitable for calibrating the thermal detector. Select a partial immersion mercury-in-glass thermometer with an appropriate range and place the thermal detector and the thermometer in the stirred water bath. Fasten the detector to the glass thermometer with a rubber band or rubber O-ring. Allow the bath, detector, and thermometer to come to thermal equilibrium and record the temperature of the glass thermometer and the readout from the thermal detector. The temperature in the bath shall not change by more than 0.1°C per minute during the calibration process.

6.1.4.2 *Temperature Recording Device*—A strip chart recorder or other data acquisition system capable of recording temperature throughout the test to 0.1°C. As an alternative, an electronic device capable of reporting maximum and minimum temperatures (accurate to ± 0.1°C) may be used. In this case if the test temperature varies by more than ± 0.5°C of the conditioning temperature during the 20-hour period, the test shall be declared invalid.

6.1.4.3 A pressure gauge capable of measuring the pressure in the PAV to ± 1% of the desired pressure during the test.

6.2 *Stainless Steel Pans*—Ten standard stainless steel TFOT pans meeting the requirements of T179.

6.3 *Balance*—A balance conforming to the requirements of M231, Class G2.

7. MATERIALS—Commercial bottled air or equivalent.

8. HAZARDS—Use standard laboratory safety procedures in handling the hot asphalt binder when preparing test specimens and removing the residue from the PAV. Use special precaution when lifting the vessel.

9. CALIBRATION AND STANDARDIZATION

9.1 *Temperature Detector*—Verify the calibration of the RTD to 0.1°C at least every 6 months using a calibrated thermometer.

9.2 *Pressure gauge*—Calibrate the pressure gauge to an accuracy of 1% of the desired pressure at least every 6 months.

NOTE 4.—The pressure gauge is usually calibrated by the manufacturer or a commercial calibration service. Verification of the continued stability of the pressure gauge within the specified requirements should be done periodically by checking against another certified pressure measurement device.

10. PROCEDURE

10.1 Condition the asphalt binder and determine the mass change during conditioning in accordance with T240 (RTFOT) or T179 (TFOT).

10.2 Combine the hot residue from the RTFOT into a single container, stir to blend, then transfer into (or leave in) TFOT pans for PAV conditioning or allow the hot residue in the container to cool to room temperature and cover and store at room temperature for PAV conditioning at a later date. If conditioned asphalt binder is allowed to cool to room temperature, heat it until it is sufficiently fluid to pour and stir it before pouring it into the TFOT pans. To remove asphalt binder from RTFOT bottles, scraping of the bottles is allowed, to assure sufficient material is obtained for later testing. Scraping is not currently allowed in T240. If scraping is used, report with the test results.

10.3 Place the pan holder inside the PAV. If an oven is used, place the pressure vessel inside the oven. If an integrated temperature control pressurized aging vessel is used, turn on the heater. Select an aging temperature and preheat the vessel to the aging temperature selected.

NOTE 5.—If conditioning asphalt binders for conformance to MP1, select the appropriate aging temperature from table 1 of MP1.

NOTE 6.—Preheating the vessel 10 to 15°C above the conditioning temperature can be used to reduce the drop in PAV temperature during the loading process and minimize the time required to stabilize the system, after loading, to attain the required temperature.

NOTE 7.—Aging temperature in the PAV is selected to account for different climatic regions. Temperatures in excess of approximately 115°C can change the chemistry of asphalt binders aged in accelerated tests and should be avoided.

10.4 Place the TFOT pan on a balance and add 50 ± 0.5 gram mass of asphalt binder to the pan. This will yield approximately a 3.2-mm-thick film of asphalt binder.

NOTE 8.—The mass change is not measured as part of this procedure. Mass change is not meaningful because the asphalt binder absorbs air as a result of pressurization. Any gain in mass as a result of oxidation is masked by air absorbed by the asphalt binder as a result of the pressurization.

10.5 If the vessel is preheated to other than the desired aging temperature, reset the temperature control on the heating device to the aging temperature.

10.6 Place the filled pans in the pan holder. Pans containing asphalt binders from different sources and grades may be placed in the pressure vessel during a single test. Place the panholder with filled pans inside the vessel and close the vessel.

10.7 If an oven is used, place the loaded and closed vessel in the oven.

10.8 Connect the temperature transducer line and the air pressure supply line to the loaded vessel's external connections.

10.9 Perform the operations described in sections 10.5 to 10.8 as quickly as possible to avoid cooling of the vessel and pan holder.

10.10 Wait until the temperature inside the pressure vessel is within 2°C of the aging temperature. Apply an air pressure of 2.1 ± 0.1 MPa and then start timing the test. If the temperature inside the pressure vessel is not attained within two hours of loading, discontinue the test.

NOTE 9.—Pressures in excess of 2.1 MPa do not substantially increase the rate of aging. Therefore, higher pressures are not warranted.

NOTE 10.—Once pressurized, the temperature inside the pressure vessel will equilibrate rapidly. The time under pressure, not to include any preheating time at ambient pressure, is the aging time. Relatively little aging occurs at ambient pressure during the time that the vessel is being reheated to the test temperature, given that asphalt binder residue under test has been exposed to 163°C in the RTFOT.

10.11 Maintain the temperature and air pressure inside the pressure vessel for 20 hours ± 10 minutes.

10.12 At the end of the 20-hour test period, slowly begin reducing the internal pressure of the PAV, using the air pressure bleed valve. Adjust the bleed valve to an opening that requires 9 ± 1 minutes to equalize the internal and external pressures on the PAV, thus avoiding excessive bubbling and foaming of the asphalt binder. During this process it may be necessary to adjust the setting of the needle valve as the pressure drops in order to maintain an approximate linear rate of pressure decrease. Do not include the pressure release and equalization time as part of the 20-hour aging period.

10.13 If the temperature indicated by the temperature recording device falls above or below the target aging temperature ± 0.5°C for more than 10 minutes during the 20-hour aging period, declare the test invalid and discard the material.

10.14 Remove the pan holder and pans from the PAV, and place in an oven set at 163°C. Heat until sufficiently fluid to pour. Stir gently to assist in the removal of air bubbles

NOTE 11.—Minimum pouring temperatures that produce a consistency equivalent to that of SAE 10W30 motor oil (readily pours but not overly fluid) at room temperature are recommended. Heating unaged asphalt binders to temperatures above 135°C should be avoided. Some modified asphalts or heavily aged binders, however, may require pouring temperatures above 135°C. PAV residue may be heated in the TFOT pans to 163°C and stirred to remove air bubbles. In all cases heating time should be minimized. These precautions will help avoid oxidative hardening and volatile loss that will harden the sample. During the heating process the sample should be covered and stirred occasionally to ensure homogeneity.

10.15 Remove pans from oven and pour the hot residue from the pans into a single container. If tests to determine the properties of the PAV residue are not performed immediately, cover the container and store it at room temperature for future testing.

11. REPORT

11.1 Report the following information:

11.1.1 sample identification;

11.1.2 aging test temperature, to the nearest 0.5°C;

11.1.3 maximum and minimum aging temperature recorded, to the nearest 0.1°C;

11.1.4 total time during aging that temperature was outside the specified range, to the nearest minute;

11.1.5 total aging time, in hours and minutes.

11.1.6 Report the heating temperature and heating time if temperatures greater than 163°C are required at any time during the handling of the material.

12. PRECISION AND BIAS

12.1 *Precision*—The research required to develop precision estimates for tests performed on PAV residue has not been conducted.

12.2 *Bias*—The research required to establish the bias of tests performed on PAV residue has not been conducted.

13. KEY WORDS

Accelerated aging, elevated temperature, in-service aging, PAV, pressure aging, pressure aging vessel.

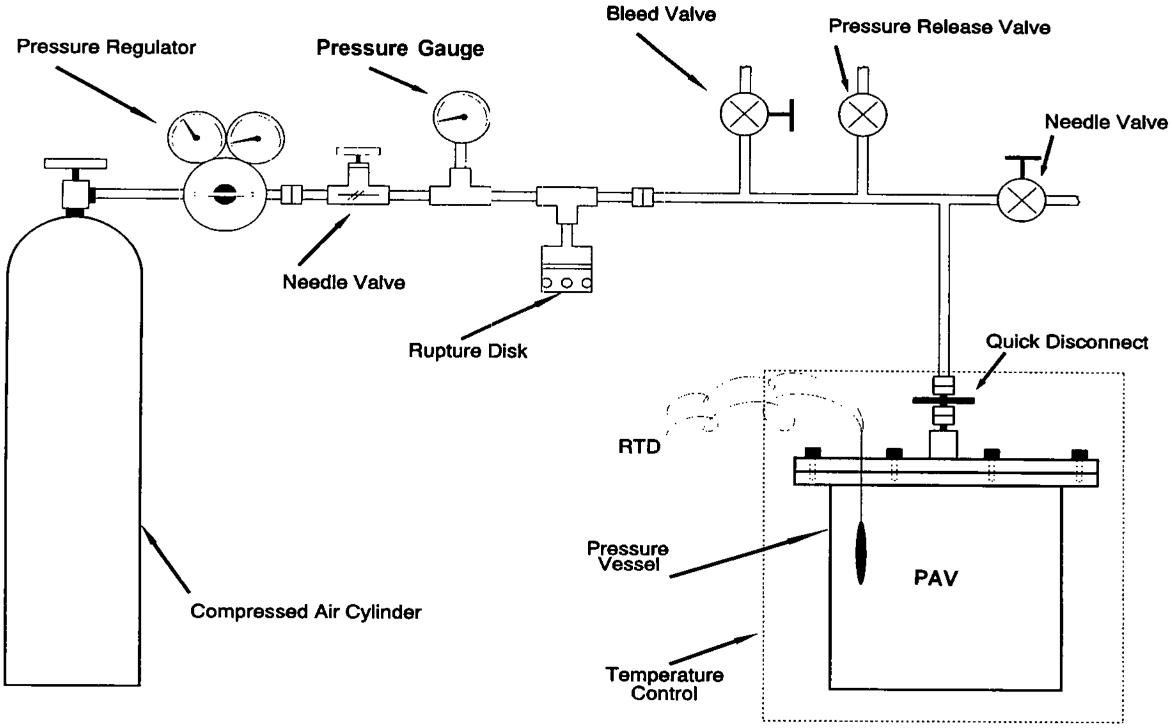
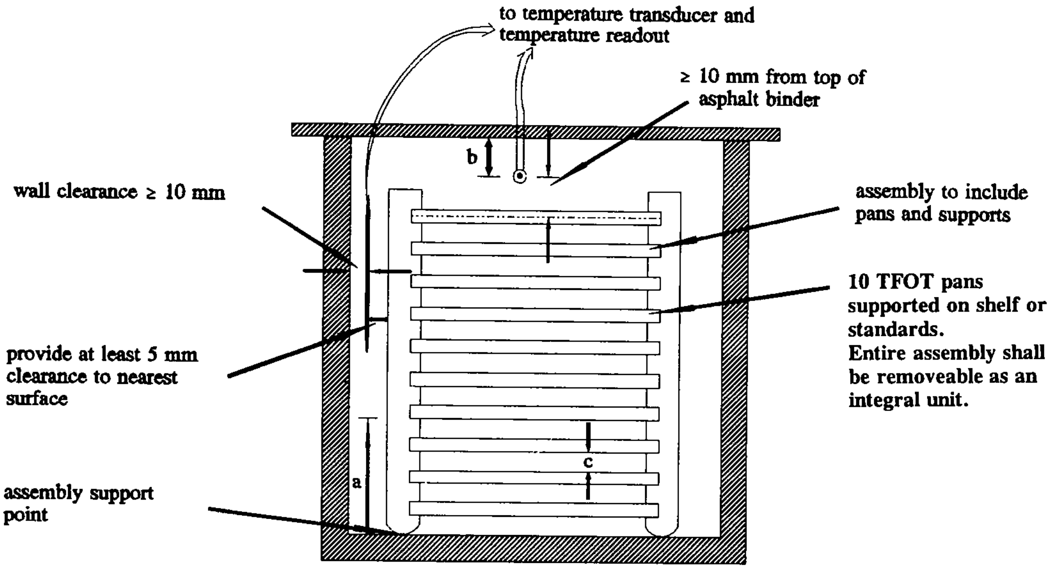


Figure 1. Schematic of Typical PAV Test System



Note 1: Distance *a* controls the levelness of the pans. The assembly shall be supported at three or more support points. The distance *a*, measured from each assembly support point to the bottom of the pan (top of shelf or pan support point), shall be controlled to ± 0.05 mm. Provision shall be made to ensure that the bottom of the vessel is leveled so that the thickness of the binder in the pans varies by no more than ± 0.05 mm across the diameter of any pan.

Note 2: Distance *b* shall be such that any active portion of the temperature transducer is ≥ 10 mm from the top surface of the vessel.

Note 3: Distance *c* shall be ≥ 12 mm.

Figure 2. Location of Pans and Resistance Thermal Detector within Representative PAV

Appendix E

Extraction and Recovery of Asphalt Cement for Rheological Testing

SHRP Designation: B-006

Standard Practice for

Extraction and Recovery of Asphalt Cement for Rheological Testing

SHRP Designation: B-006[1]

1. SCOPE

1.1 This test method describes the extraction and recovery of asphalt from bituminous concrete samples. It is to be used to determine the physical or chemical properties of an asphalt binder. It is *not* recommended for use in determining aggregate gradations.

1.2 *This procedure may involve hazardous materials, operations and equipment. This procedure does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this procedure to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

1.3 The values stated in SI units are to be regarded as the standard.

2. APPLICABLE DOCUMENTS

2.1 *AASHTO Documents:*

T44	Solubility of Bituminous Materials in Organic Solvents

2.2 *ASTM Standards:*

D979	Standard Practice for Sampling Bituminous Paving Mixtures
D1856	Recovery of Asphalt from Solution by Abson Method
D2172	Test Methods for Quantitative Extraction of Bitumen from Bituminous Paving Mixtures

2.3 *Other Documents:*

TRB papers 890445, 910350, 910352

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[1] This standard is based on SHRP Product 1004.

3. SUMMARY OF METHOD

3.1 The paving mixture is repeatedly washed and filtered with solvents in the extraction/filtration apparatus shown in figure 1. Each filtrate is distilled under vacuum in a rotary evaporator with the asphalt remaining in the flask. After recovery of the final filtrate, the solution is concentrated and centrifuged to remove aggregate fines. The decanted solution is distilled under vacuum to remove the extraction solvents. Nitrogen gas is introduced during the final phase of distillation to drive off any remaining traces of solvents. The recovered asphalt (distillation residue) may then be subjected to further testing as required.

4. SIGNIFICANCE AND USE

4.1 The method can be used both for obtaining asphalt for further analyses and for calculation of asphalt content in pavement samples. **Warning: The aggregate should not be used for sieve analysis because it undergoes prolonged grinding in the extraction device.**

5. APPARATUS AND MATERIALS

5.1 Oven, capable of maintaining the temperature at 110°C ± 5°C

5.2 *Utilities*—Vacuum source, nitrogen gas source, and cooling water source

5.3 Balance, having an accuracy of at least .01% of the sample mass

5.4 Extraction vessel (figures 2, 3, 4), a piece of aluminum pipe with removable upstream and downstream plates. The upstream plate (figure 5) has a mixing motor mount and a ¾ in addition port. The downstream plate (figure 6) is equipped with a ¼" in NDT quick connect fitting. Four 4 × 1 in baffles (figure 7) are mounted in the extraction vessel, followed by a 10-mesh screen, a glass wool plug, an 8-micron filter, and a 10-mesh backup screen.

5.5 A fine filter (figure 8), consisting of a top (figure 9) and bottom (figure 10), each fabricated from ½ in aluminum plate, which hold a 1-micron woven polypropylene filter and a 10-mesh stainless steel backup screen.

5.6 Flask, suction, 500 mL

5.7 Round bottom flasks, 1000 mL and cork stands

5.8 Gas flowmeter, capable of indicating a gas flow up to 1000 mL/min

5.9 Buchi Rotavapor RE-111A (or equivalent) with transfer and purge tubes

5.9.1 Transfer tube, ¼ in polypropylene tubing 17 in long

5.9.2 Purge tube, ¼ in polypropylene tubing 23 in long

5.10 Hot oil bath, capable of heating oil to 177°C

5.11 Copper tubing (note 1), amount adequate to connect apparatus as shown in figure 1

NOTE 1.—The quantity of copper tubing needed will be dependent upon the space utilized in setting up the apparatus.

5.12 Single Speed Mixing Motor, 150 W, 30 rpm

5.13 Polypropylene Tubing (note 2), ¼ in for transferring solution throughout the procedure

NOTE 2.—To avoid contamination of the sample due to solvent degradation of the tubing, do not substitute Nalgene or rubber tubing for the polypropylene tubing specified.

5.14 *Woven polypropylene filter cloths*—Coarse filter made from 2 × 2 twill weave, monofilament, 8 micron or 5 CFM rating, and fine filter made from oxford weave multifilament, 1-2 micron or .5 CFM rating

5.15 Centrifuge, batch unit capable of exerting a minimum centrifugal force of 770 times gravity

5.16 Wide-mouth centrifuge bottles, 250 mL

5.17 Thermometer, having a range of -2 to 300°C

5.18 Glass wool, borosilicate

5.19 Six 3-mm glass boiling beads

6. REAGENTS

6.1 Toluene, reagent grade

6.2 Ethanol, absolute

6.3 Nitrogen gas, at least 99.95% pure, in a pressurized tank, with pressure-reducing valve.

6.4 Argon gas, at least 99.99% pure, in a pressurized tank.

7. PRECAUTIONS

7.1 Solvents should be used only under a hood or with an effective surface exhaust system in a well-ventilated area.

8. SAMPLING AND SAMPLE PREPARATION

8.1 Obtain samples in accordance with ASTM D 979.

8.2 If the mixture is not sufficiently soft to separate with a spatula or trowel, place it in a large, flat pan and warm to 110 ± 5°C only until it can be handled or mixed. Split or quarter the material until 1000 g or the mass of material (note 3) required for the test is obtained.

NOTE 3.—This procedure works best for quantities of asphalt less than 60 g. Therefore, if the asphalt content of the mix is known, then the mass of sample required is that which yields about 50 to 60 g of asphalt.

9. PROCEDURE

9.1 *Equipment Setup*

9.1.1 Prepare the extraction vessel by first installing the baffle pieces. Place the metal screen downstream of the baffle. Cut several pieces of glass wool and pack them in the space between the screen and the downstream end of the extraction vessel. Place gaskets, filter and aluminum end piece on extraction vessel, as shown in figure 3. Tightly and evenly fasten the end piece with wing nuts.

9.1.2 Weigh an amount of pavement sample that will yield approximately 50 to 60 g of extracted asphalt. Place sample in extraction vessel. Put gasket and upstream end piece on the vessel and tightly and evenly fasten the wing nuts, creating a secure seal.

9.1.3 Prepare the rotary evaporator. Turn on the cooling water. Turn on the oil bath and set the temperature to 100 ± 2.5°C. Place six 3-mm glass boiling beads in a 1000-mL round bottom flask. Attach the recovery flask to the rotary evaporator and immerse 1½ in of the flask into the oil bath. Set the recovery flask at a 15° angle from the horizontal to the bath. Set the flask rotation at 40 rpm. Clamp the empty condensate flask onto the condenser. Attach transfer tube inside neck of rotary evaporator. Apply vacuum of 700 ± 5-mm Hg to the rotary evaporator. Attach the filtrate transfer line to the external fitting on the neck of the rotary evaporator.

9.2 *Extraction and Filtration*

9.2.1 Charge 600 mL of toluene through the ¾-in port on the upstream end of the extractor. To purge the interior of the extraction vessel, inject nitrogen through the upstream port at 1000 mL/min for 1 minute. Close the port with a threaded plug. Attach the extractor to the motor. Start the motor and mix for 5 ± 1 minutes at 30 rpm. Shut off the motor.

9.2.2 Remove the extractor, place it on a stand and attach the quick connect fitting to the filtrate receiving flask. Make sure the filtrate transfer line is closed. Remove the upstream port and blanket the extractor with 400 mL/min of nitrogen while filtering. Apply 700 ± 5 mm Hg vacuum to the filtrate receiving flask. Filter until the filtrate flow rate is below 10 mL/min. Shut off the vacuum.

9.2.2.1 If using the fine filter, switch vacuum to a second filtrate receiving flask and apply 700 ± 5 mm Hg vacuum. Filter until filtrate flow rate is below 10 mL/min. Shut off vacuum.

9.2.3 Disconnect the extractor from the quick connect fitting. Repeat the extraction procedure. For the second and third washes, use 400 ± 10 mL of toluene. For subsequent washes (note 4), use 400 ± 10 mL of toluene with 15 volume % ethanol. In addition, mix the second wash for ten minutes and all subsequent washes for 30 minutes or more.

NOTE 4.—It is suggested that after the third wash, the condensate from the primary distillation step be used for extraction solvent. Recycling solvent in this manner allows the entire procedure to use approximately 1500 mL toluene.

9.3 *Primary Distillation*

9.3.1 After filtration, open the filtrate transfer valve and allow the solution to flow from the filtrate receiving flask to the recovery flask. Continue the transfer until the filtrate receiving flask is empty or the recovery flask is about ⅔ full.

9.3.2 Close the filtrate transfer valve line and distill solvent at 100 ± 2.5°C (oil bath temperature) and 700 ± 5 mm Hg vacuum.

9.3.3 If the condensate flask is over half full after the primary distillation step, empty the flask. Save this solvent for use in subsequent washes (note 4). After primary distillation of each filtrate, maintain vacuum, temperature, flask rotation, and cooling water. Repeat the primary distillation after each filtration (note 5).

NOTE 5.—It is important to concentrate the asphalt in the recovery flask after each wash at a low temperature. This minimizes the time and temperature spent in dilute solution and therefore minimizes asphalt hardening in solvent.

9.3.4 After primary distillation of the first three filtrates, remove the recovery flask (which should contain only small amounts of solvent) and set it aside. Replace it with another 1000 mL roundbottom flask containing six 3-mm glass boiling beads.

9.3.5 Carry out the remaining primary distillations using the new recovery flask.

9.4 *Final Extraction and Recovery*

9.4.1 If the filtrate flowing through the transfer tube is a light brown color after a 30-minute wash, proceed to the final recovery step.

9.4.2 Pour contents of the current recovery flask into the original recovery flask. Attach the original recovery flask to the Rotavapor.

9.4.3 Distill the contents of the recovery flask until it is about ⅓ full.

9.4.4 Disconnect the recovery flask and pour the contents into the centrifuge bottles. Fill the bottles so that their weights are equal. Wash any residue from the recovery flask into the centrifuge bottles. Raise the oil bath temperature to 177 ± 2.5°C. Centrifuge the bottles at 3600 rpm for 25 minutes.

9.4.5 Decant the asphalt-solvent solution into the recovery flask and add six 3-mm glass boiling beads. Attach the flask to the rotary evaporator. Disconnect the transfer tube from the rotary evaporator and replace it with the gas purge tube. Disconnect the filtrate transfer line from the external rotary evaporator neck fitting and replace it with the nitrogen gas line. Apply 700 mm Hg vacuum. Lower the flask 1½ in into the oil bath.

9.4.6 Distill the solvent.

9.4.7 When the condensation rate falls below 1 drop every 30 seconds, introduce nitrogen gas at 1000 mL/min. Maintain the gas flow, vacuum and bath temperature for 30 ± 1 minutes to reduce the residual solvent concentration to near zero. **Complete removal of residual solvent is very important for obtaining accurate asphalt properties.**

9.4.8 Shut down the oil bath, flask rotation, vacuum, gas flow, and cooling water. Remove the evaporating flask and pour the asphalt into a sample tin.

NOTE 6.—A high temperature annealing step is recommended as a finishing step. This enables the asphalt molecules to "realign" themselves and promotes the attainment of an equilibrium state. Flood the asphalt container with argon and cover. Heat container to 163°C and maintain temperature for 2 hours. Place container in a paint shaker for 5 minutes, and then allow to cool to room temperature.

10. PRECISION AND BIAS

10.1 Repeatability and reproducibility tests have not been established in accordance with standard AASHTO practice.

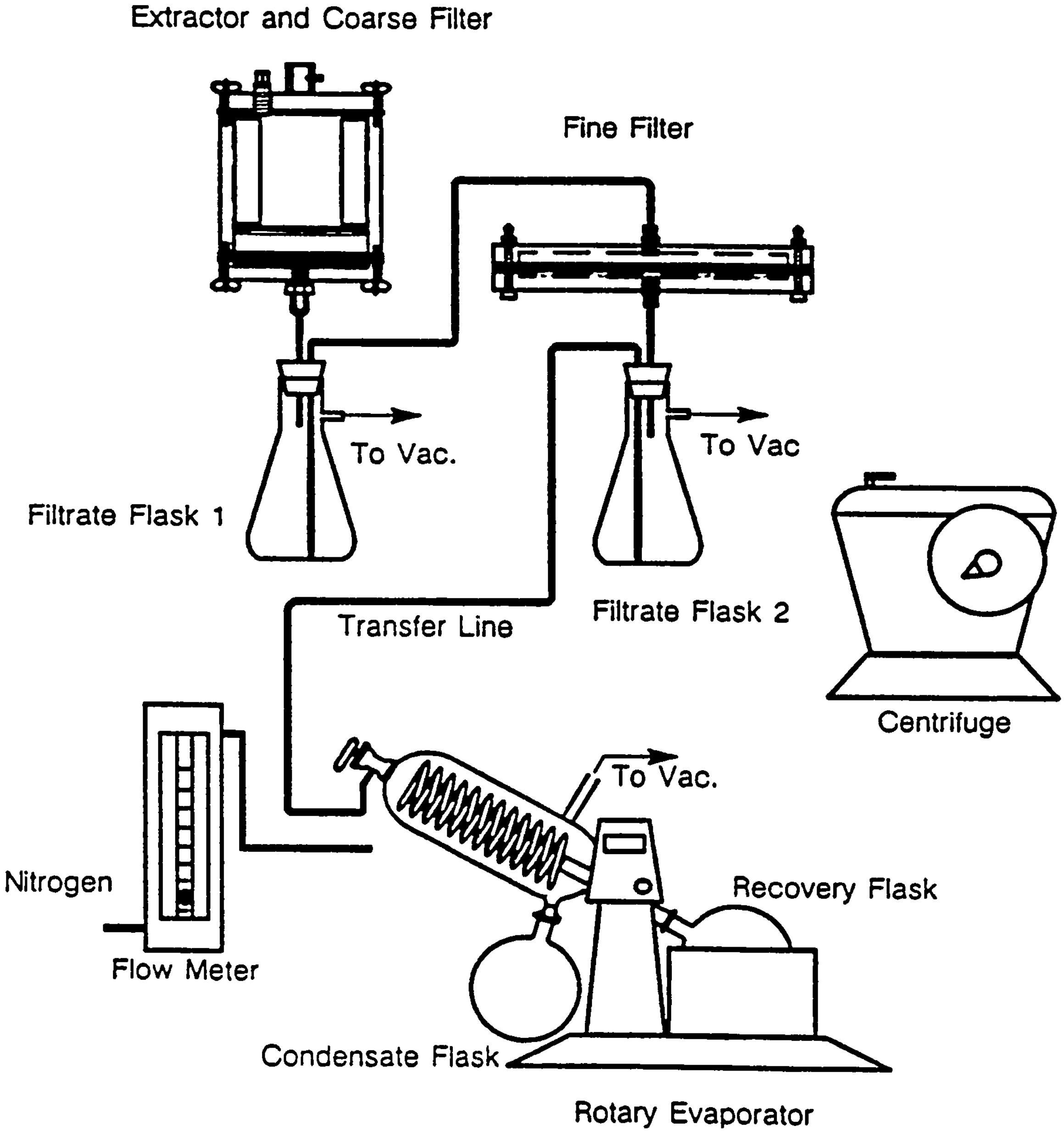


Figure 1. Asphalt Extraction and Recovery Apparatus

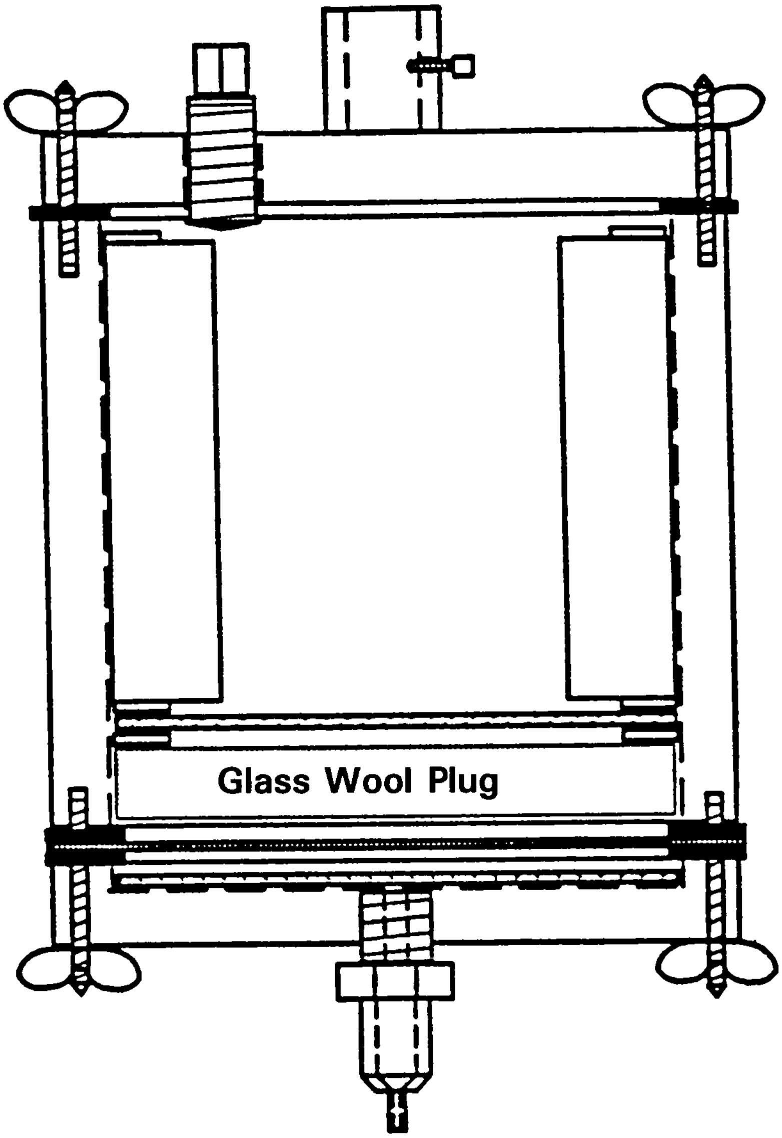
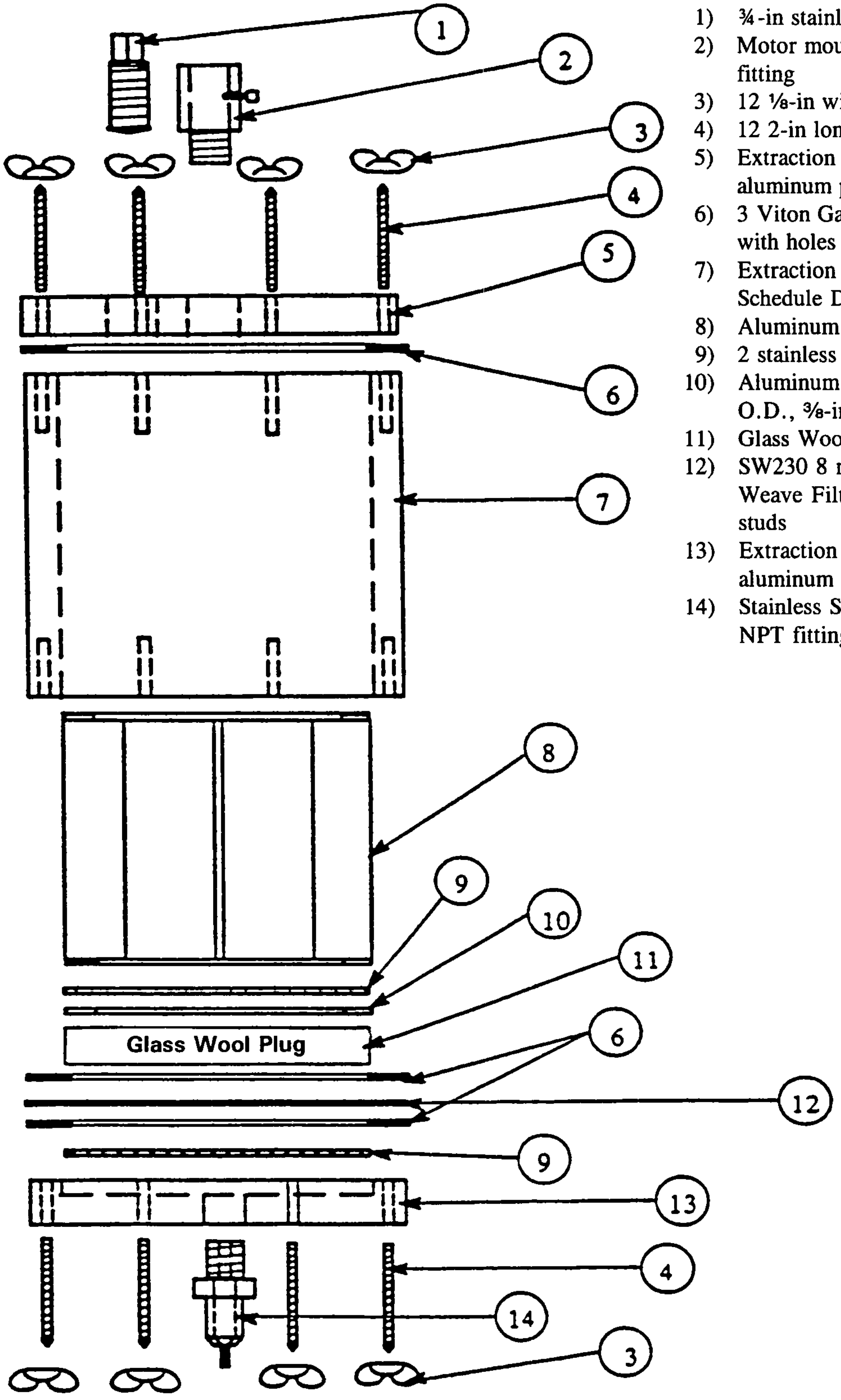


Figure 2. Extraction and Filtration Vessel



1) ¾-in stainless steel NPT plug
2) Motor mount ⅝ in I.D. ½-in NPT fitting
3) 12 ⅛-in wing nuts
4) 12 2-in long ⅛-in screws
5) Extraction Vessel Top (½-in thick aluminum plate)
6) 3 Viton Gaskets ⅛-in thick, ⅝-in width with holes to fit over studs
7) Extraction Vessel (5-in long, 6-in ϕ, Schedule D aluminum pipe)
8) Aluminum Baffle Housing
9) 2 stainless steel screens 10 mesh
10) Aluminum ring ⅛-in thick, 5.75-in O.D., ⅜-in width
11) Glass Wool
12) SW230 8 micron Polypropylene Twill Weave Filter with holes to fit over studs
13) Extraction Vessel Bottom (½-in thick aluminum plate)
14) Stainless Steel Quick Connect ¼-in NPT fitting

Figure 3. Exploded Diagram of Extraction and Filtration Vessel

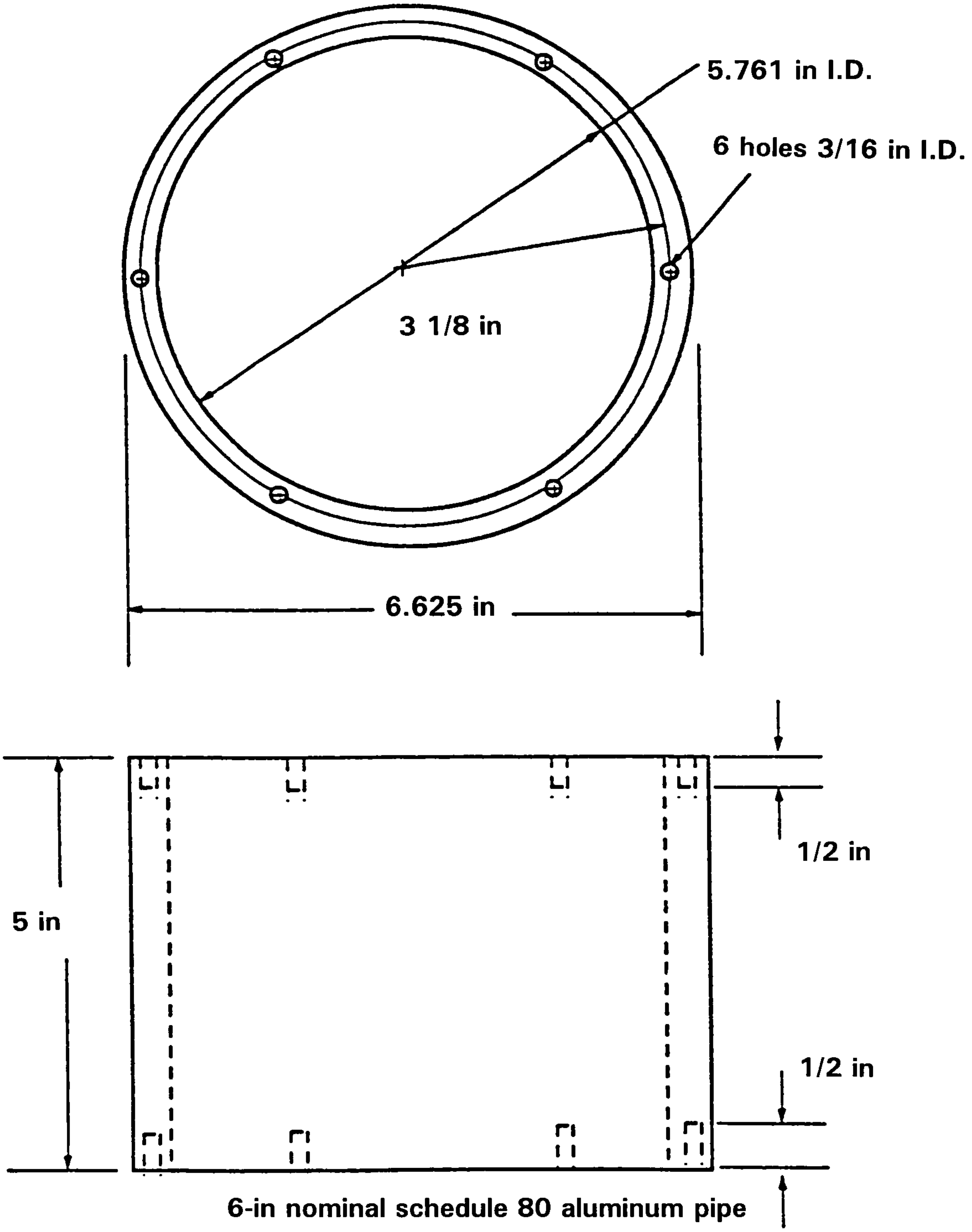


Figure 4. Dimensions for the Extraction Vessel

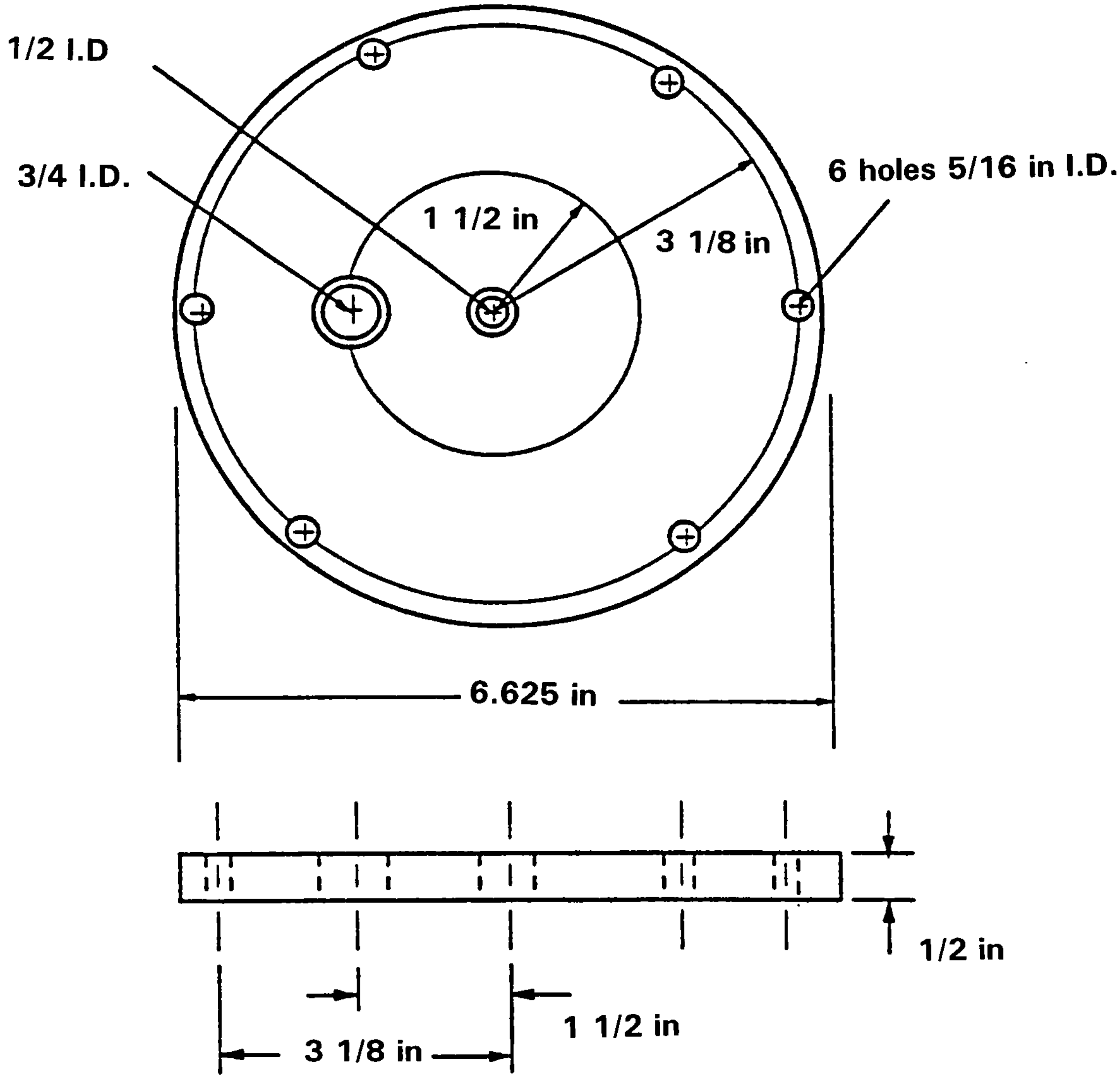


Figure 5. Extraction Vessel Top

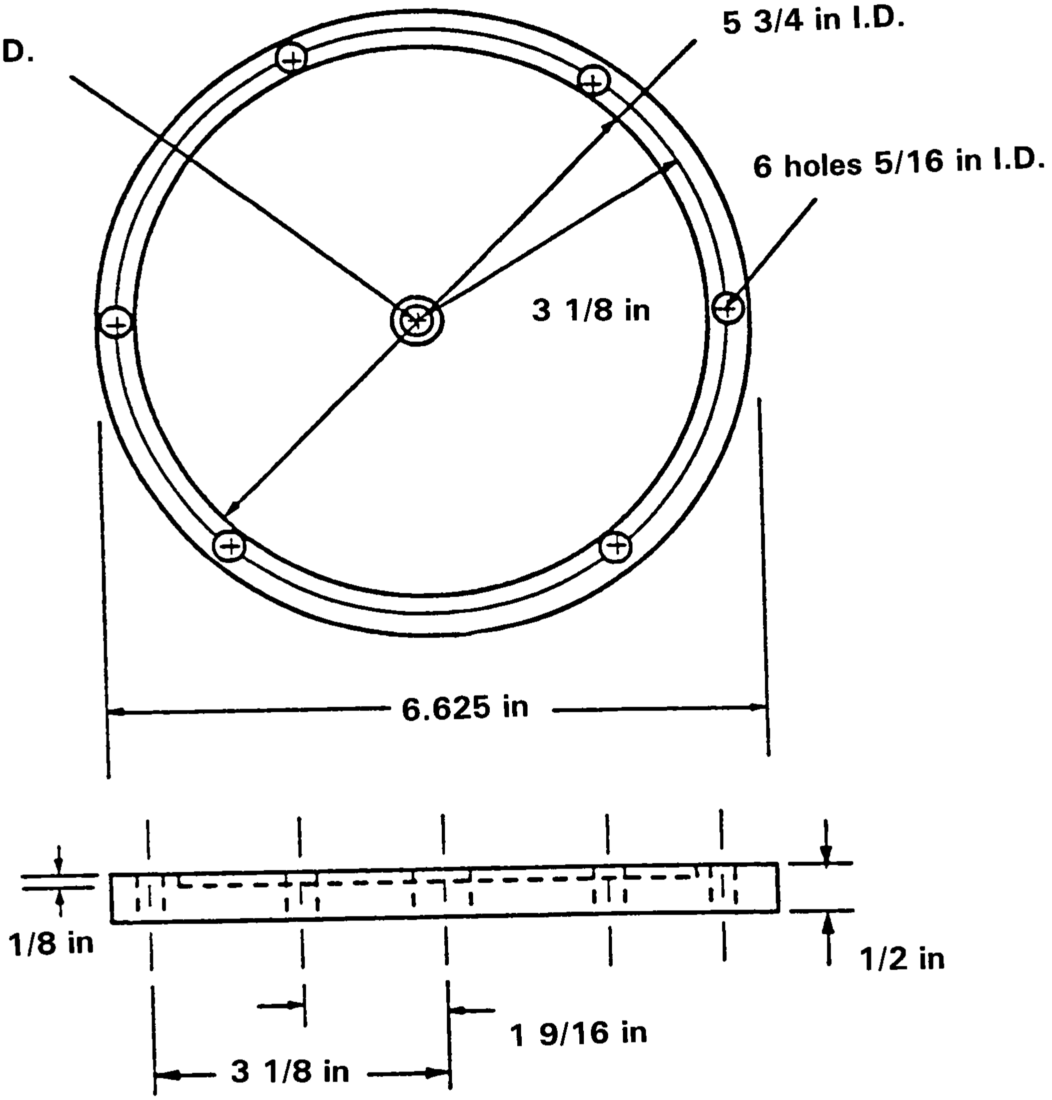
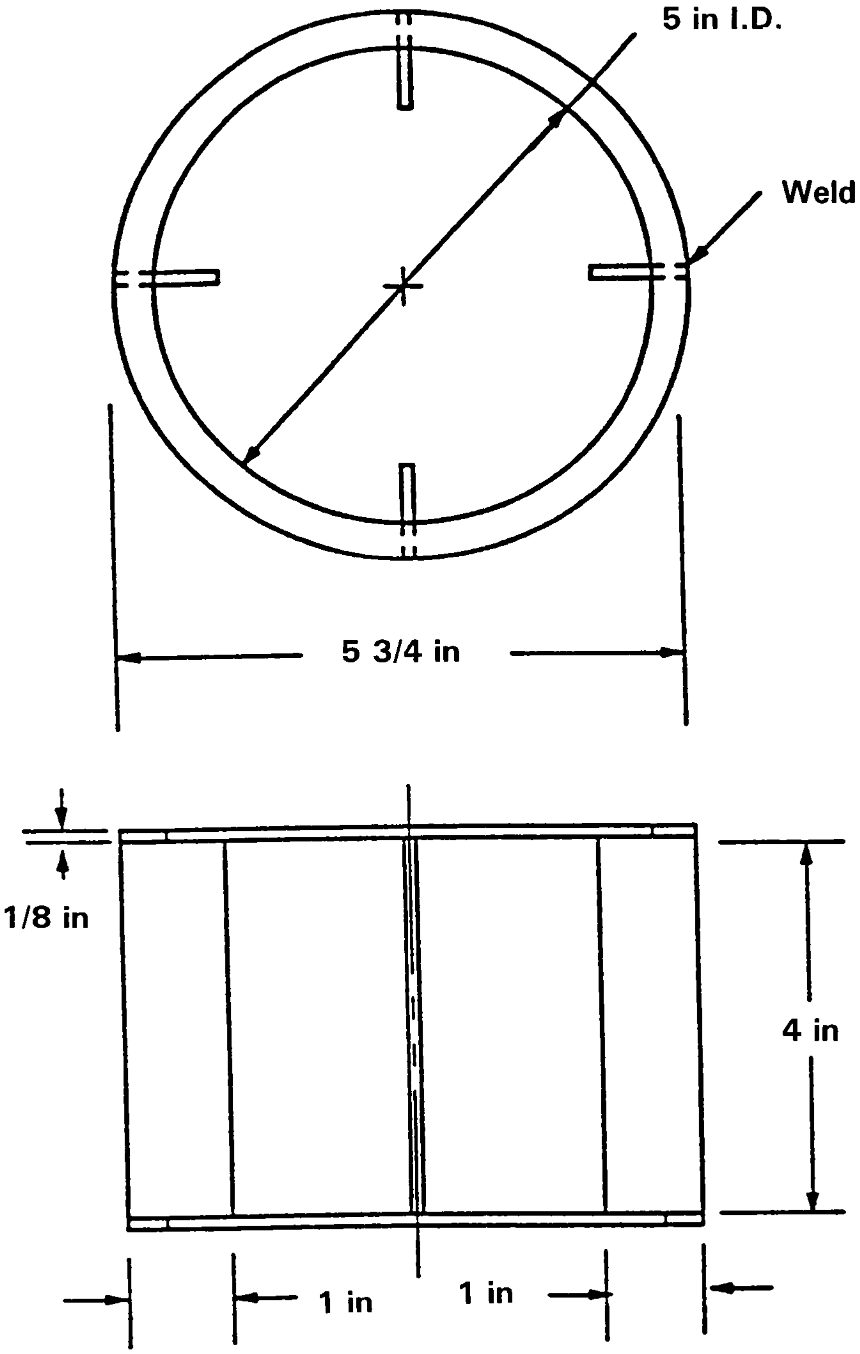


Figure 6. Extraction Vessel Bottom



4 aluminum plates 1/8 in thick

2 Aluminum rings 5 3/4 in O.D., 5 in I.D.

Figure 7. Baffle Housing

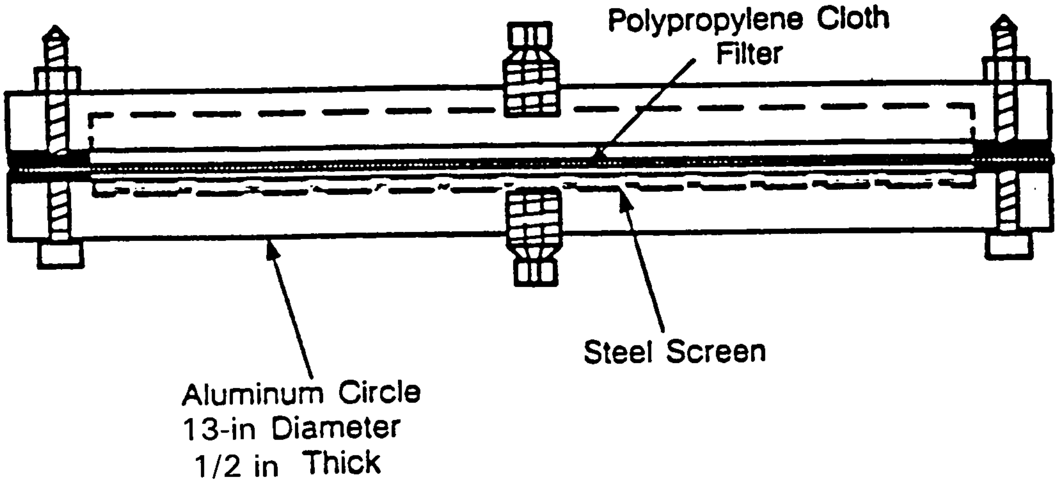


Figure 8. Fine Filter (1 to 2 microns)

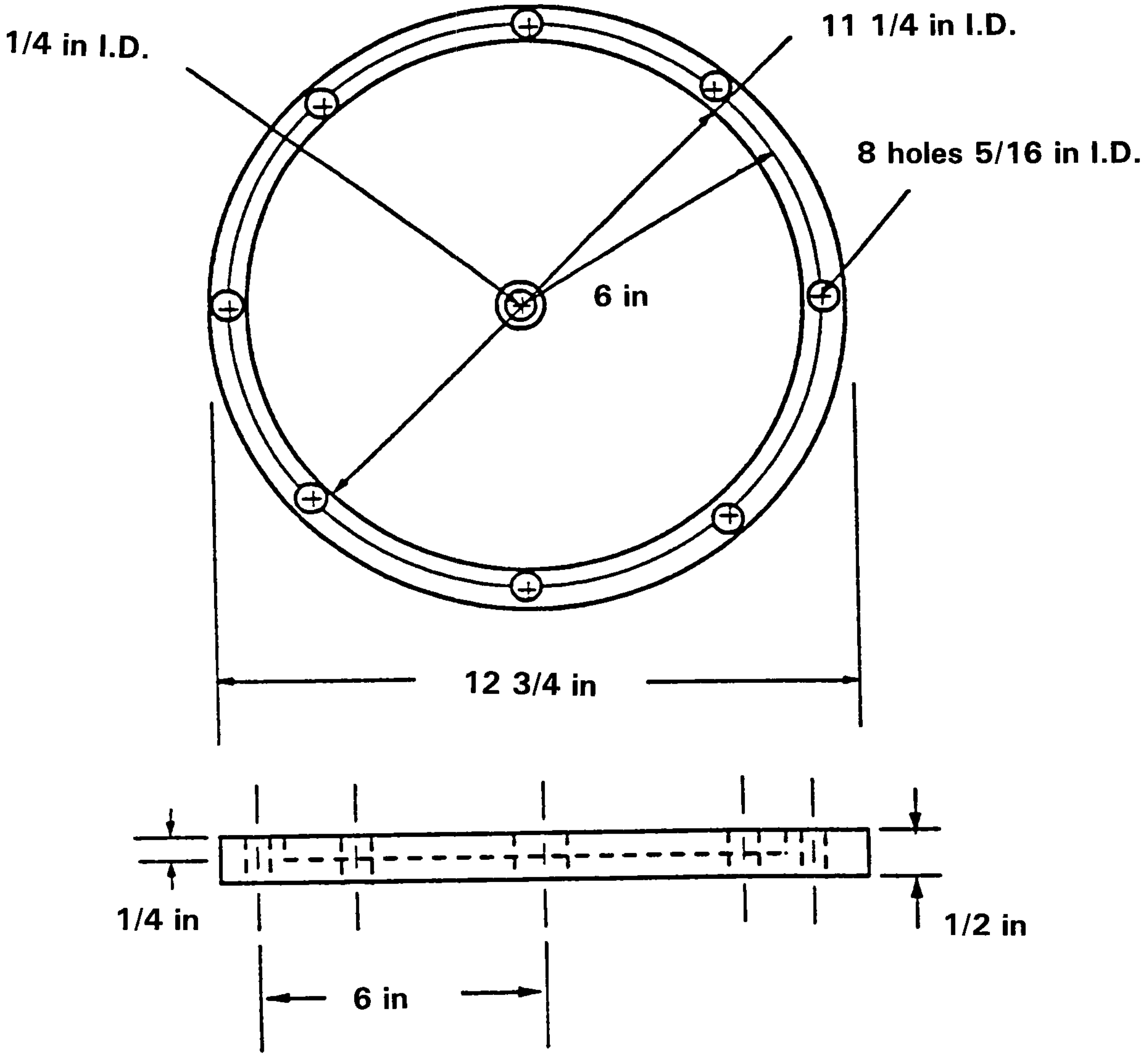


Figure 9. Top of the Fine Filter Housing

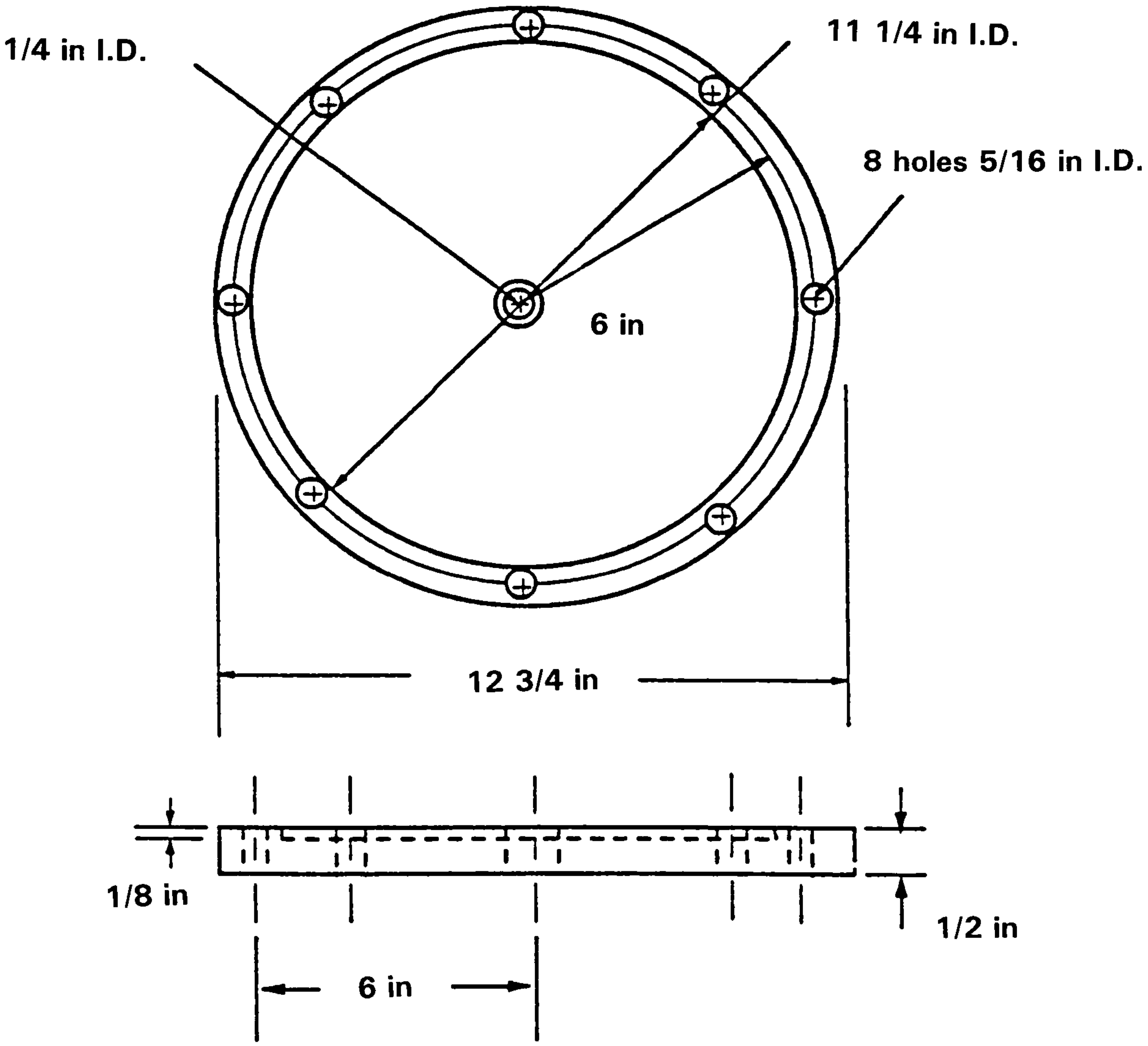


Figure 10. Bottom of the Fine Filter Housing

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