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| 16. Abstract<br>In this work asphalt air blowing has been studied from two perspectives. First, the process itself was investigated in terms of the effect of air-blowing conditions on the properties of the asphalts obtained. It was found that according to the Superpave specification, very good grade asphalts can be produced by air blowing, and the blowing temperature does not seriously impact the grade span. Asphalt composition has a significant effect on the grade span. The materials with a higher concentration of asphaltenes and saturates have a higher performance grade span. In this work it is shown that the subsequent 88 °C hardening and oxidation rates are higher for materials blown at higher temperature, and this is not detected by Superpave specifications. Blowing fluxes with a high saturate content may result in a higher grade but can cause subsequent susceptibility to oxidative hardening. The mechanism by which air blowing can affect the 88 °C hardening rate is related to oxidation kinetics and the tendency of oxidation products to form asphaltenes, causing hardening. For some materials air blown at higher temperatures, the subsequent accelerated hardening rate results from an increase in the oxidation rate, while the hardening susceptibility may decrease. The second part of this work deals with the development of a new procedure for simulation of asphalt short-term aging that occurs at a hot mix asphalt cement plant. The standard tests for simulation of asphalt hot-mix aging are the RTFOT (ASTM D 2872) and the TFOT (ASTM D 1754). They have a number of deficiencies when used for viscous or modified asphalts, such as uneven aging, film formation, and difficulty cleaning laboratory equipment. The Stirred Air-Flow Test (SAFT) employs a stirred, thermally controlled vessel with an attached condenser. The proposed test eliminates the shortcomings of standard methods. It provides the same aging in a shorter amount of time at lower equipment cost with simplified handling. |  |                                                     |                                                                                                                                                                                                        |                                                                                    |           |
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**DEVELOPMENT OF STIRRED AIR-FLOW TEST (SAFT) FOR  
IMPROVED HMAC PLANT BINDER AGING SIMULATION AND  
STUDIES OF ASPHALT AIR BLOWING**

by

Charles J. Glover  
Richard R. Davison  
Research Engineers  
Chemical Engineering/Texas Transportation Institute

Nikolai Vassiliev  
Graduate Student  
Chemical Engineering/Texas Transportation Institute

Todd Hausman  
Shelly A. Williamson  
Research Associates  
Chemical Engineering/Texas Transportation Institute

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and Chemical Engineering Department  
The Texas A&M University System  
College Station, Texas 77843-3135



## **DISCLAIMER**

This research was performed in cooperation with the Texas Department of Transportation (TxDOT) and the U.S. Department of Transportation, Federal Highway Administration (FHWA). The contents of this report reflect the views of the authors, who are responsible for the facts and accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the FHWA or TxDOT. This report does not constitute a standard, specification, or regulation, nor is it intended for construction, bidding, or permit purposes. Trade names are used solely for information and not for product endorsement. The engineer in charge of this project was Charles James Glover, Ph.D., P.E. (Texas, 48732).

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## CHAPTER 1. INTRODUCTION AND BACKGROUND

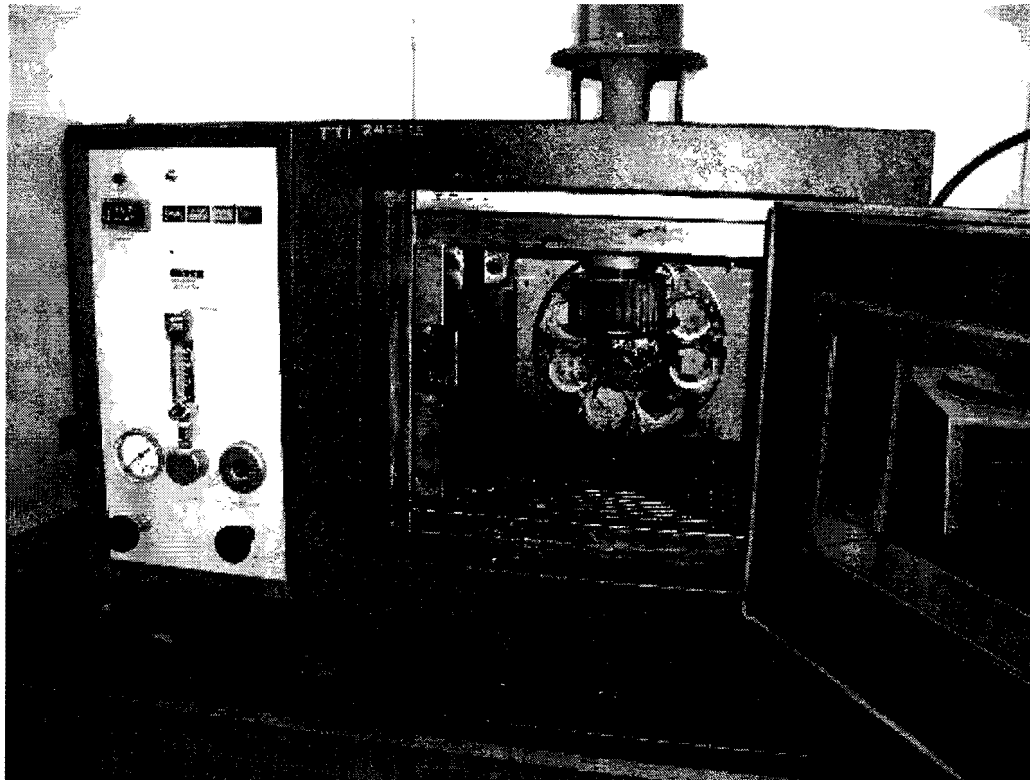
Historically, the variety of asphalt binder tests has included a simulation of hot mix asphalt concrete (HMAC) plant aging to predict the change in material properties during conventional hot mixing at approximately 302 °F (150 °C). These tests yield a residue that simulates the asphalt in terms of viscosity and other rheological measurements after HMAC production. Under the latest two grading systems, AC and PG, the aging simulations used are the Thin Film Oven Test (TFOT) (ASTM D1754, AASHTO T179) and the Rolling Thin Film Oven Test (RTFOT) (ASTM D2872, AASHTO T240), respectively. When used for unmodified asphalts, these methods are essentially identical in simulating asphalt short-term aging. However, when applied to modified binders, practitioners have encountered a number of problems with both RTFOT and TFOT procedures (Sirin et al., 1998). These problems are discussed later in this chapter.

According to the TFOT procedure, a film of asphaltic material is heated in an electrical oven for 5 hours at 163 °C (325 °F). Cylindrical pans containing 50 grams of material are placed onto a horizontally rotating shelf (Figure 1-1). After completion of the test, the selected asphalt properties such as mass loss, viscosity, penetration and ductility of aged material, are determined and compared with those of unaged material.



**Figure 1-1. Thin Film Oven.**

A moving film of asphalt is heated in the RTFOT oven for 85 minutes at 163 °C (325 °F). The oven is equipped with a vertical circular carriage that has 8 openings and clips to firmly hold glass containers each with 35 grams of material in a horizontal position (Figure 1-2). The carriage is rotated at a rate of 15 revolutions per minute. The oven also has an air jet positioned to blow heated air at a rate of 4000 mL/min into each bottle as they rotate. The RTFOT allows determination of the same properties as the TFOT, and both tests are practically interchangeable in this respect.



**Figure 1-2. Rolling Thin Film Oven.**

## **PROBLEM STATEMENT AND RESEARCH OBJECTIVES**

The TFOT is a static test, which works well with most unmodified binders. However, it may not adequately simulate aging of some polymer-modified binders, which form a film on the surface. These binders have a tendency to separate or stratify. Oxygen penetrates the sample through the surface exposed to the atmosphere. Anything that impedes mass transfer will change and generally reduce the aging of the binder.

The RTFOT is a test that was designed to overcome some of the shortcomings of the TFOT. The sample is rolled in a glass container to facilitate exposure of the asphalt to oxygen. Thus, the RTFOT is faster and prevents skin formation, but there are some heavily modified or gelled binders, which are not fluid enough at the aging temperature to facilitate “rolling” of the binder around the surface of the RTFOT bottle. These materials are not exposed to the air as the

test intended and consequently are not aged sufficiently in the laboratory process. Furthermore, modified materials adhere more strongly to the bottle than unmodified materials, making it necessary to scrape the material from the container. This requires prolonged handling of hot materials and equipment. This not only makes the test more difficult to perform, but also can lead to inconsistencies in results and exposes the technicians to a safety risk. Finally, the design of the containers for the RTFOT makes cleanup after the test a large and time-consuming task when a large number of tests are performed.

The objective of this research was to develop an improved test procedure and a new apparatus to address the shortcomings of the existing aging techniques. Development requirements included:

- similar testing time and aging effect to RTFOT,
- non-prohibitive cost,
- capable of producing up to 200 grams (0.44 lbm) of aged material per test,
- no prolonged handling of hot equipment or materials, and
- simplified cleanup.

This report presents both fundamental and development studies leading to a new Stirred Air-Flow Test (SAFT).

## **LITERATURE REVIEW**

### **Review of Hot-mix Aging Simulation Development**

The history of accelerated asphalt aging dates back to 1897 when Dow proposed two tests to analyze this material (Welborn, 1984; Lewis and Welborn, 1940). One of the tests involved heating 20 grams of asphalt at 204 °C (400 °F) for 30 hours, then weighing the residue to determine mass loss. The other test required mixing asphalt and sand at 149 °C (300 °F) and sampling before and after heating for 30 minutes. The residue was extracted and recovered and the penetration determined. These tests served as the basis for current asphalt aging tests.

The American Society for Testing and Materials (ASTM) Committee on Road and Paving Materials was formed to design appropriate test methods for asphalts (Welborn, 1984). By 1911 the test developed by the Office of Public Roads and Rural Engineering of the Department of Agriculture had been adopted. This test required that 20 grams of asphalt be placed in a shallow tin and heated at 163 °C (325 °F) for 5 hours. The amount of volatilization and retained penetration were checked. A 1916 revision of this test included a larger sample of 50 grams.

Shattuck (1940) developed a test that simulated the actual conditions in the batch plant: 1880 grams of sand were heated to 204 °C (400 °F) and mixed with 20 grams of asphalt heated to 149 °C (300 °F). The mixing took place in a small pugmill-type laboratory mixer for one minute. The mixture was then placed in a pan and heated at 177 °C (350 °F) for 30 minutes. Extraction and recovery were performed after cooling the sample to room temperature. This test

resulted in slightly more hardening than was present in actual hot-mix plants but provided a good indication of asphalt behavior under these severe conditions.

Lewis and Welborn (1940) designed a test consisting of shallow pans with asphalt 0.125 inch (3.2 mm) thick. These pans were placed on a rotating shelf in an oven maintained at 163 °C (325 °F) for 5 hours. Tests were also performed at a thickness of 0.0625 inch (1.6 mm) and 0.0313 inch (0.8 mm) and at times of 5 and 7 hours. The penetration, ductility and softening point resulting from the hot-mix conditions were most closely duplicated by the test conducted at 163 °C (325 °F) for 5 hours and the 0.125 inch (3.2 mm) films. This test is still widely used and referred to as the Thin Film Oven Test.

The recognition that thinner films may be desired to simulate hot-mix aging led to the development of microfilm tests (Fink, 1958; Traxler, 1967). Thinner films correspond better to actual pavement mixtures, harden faster, and decrease any diffusion effects that may be present in thicker films. The Microfilm Durability Test involves placing a 5-micron film on glass slides before subjecting the sample to aging in an oven (Griffin et al., 1955). This test was designed to simulate road aging, but has been correlated with hot-mix as well (Heithaus and Johnson, 1958; Simpson et al., 1959). Only small amounts of asphalt can be aged with this method, and special devices for measuring viscosity are required. Other literature sources (Lewis and Welborn, 1940) indicate that 1 mm films are thin enough to eliminate the diffusion effects with modified and unmodified asphalts.

Hveem et al. (1963) designed the RTFOT to age large amounts of asphalt uniformly in thin films. This test uses 35 grams of asphalt in special rotating glass bottles in an oven maintained at 163 °C (325 °F). Rotation of these bottles constantly produces new films 5 to 10 micron thick. Air is blown into the bottles to remove volatile compounds and promote oxidation. The RTFOT, run for 75 minutes after reaching 163 °C (325 °F) (85 minutes including warm-up), simulates the physical properties of hot-mix samples.

Numerous variations have been made on the TFOT and RTFOT methods with many intended to simulate road aging as well. Vallerga et al. (1957) proposed tilting the oven used for the TFOT and provided an effect similar to that of the RTFOT. Schmidt and Santucci (1969) developed a rolling microfilm test in which benzene-dissolved asphalt was cast in bottles and aged in a manner similar to that used in the RTFOT. The modification of adding a circulating fan as suggested by Schmidt (1973b) has been maintained. Schmidt (1973a) has also used several modifications to the rolling microfilm test at various temperatures and rates of air circulation, as well as in the presence of aggregate, in an effort to simulate hot-mix and road aging.

Drum mixers may require slightly different laboratory simulations than batch mixers. The presence of a fair amount of moisture in some plants initiated the theory that something similar to steam distillation may be occurring in drum plants. A Small Steam Distillation (SSD) technique involving steam bubbling through an asphalt sample was found not to represent drum hot-mix plants (Chollar et al., 1989). Two other methods, Forced Air Distillation (FAD) and Revolving Forced Air Distillation (RFAD), were found to closely resemble drum mixers. These methods involve blowing air over asphalt samples and collecting the volatile matter removed. The FAD and RFAD are similar in operation to the TFOT and RTFOT methods, respectively, but the FAD method is performed at a temperature of 328 °C (622 °F). The FAD and RFAD



tests are reportedly better than the TFOT and RTFOT methods in representing the aging that takes place in drum mixers (Chollar et al., 1989).

The TFOT results have been well correlated with extracted hot-mix samples based mostly on viscosity and penetration data (Chipperfield et al., 1970; Page et al., 1985; Chollar et al., 1989; Epps and Kari, 1983; Lewis and Welborn, 1940; Button et al., 1983; Lee, 1973; Hveem et al., 1959; Bright and Reynolds, 1962; Sisko and Brunstrum, 1968; Adam, 1988). The RTFOT results have also been shown to match extracted hot-mix samples (Chipperfield and Welch, 1967; Hveem et al., 1963; Chollar et al., 1989; Epps and Kari, 1983; Button et al., 1983; Kim et al., 1987; Thenoux et al., 1988) as well as TFOT results (Schmidt, 1973a; Schmidt, 1973b). The RTFOT is considered to be the better of the two methods. The RTFOT requires a shorter aging time, is easier to perform, and gives more precise results than the TFOT (Schmidt, 1973b; discussion by Schmidt in Skog, 1967). This added precision is attributed to the fact that the RTFOT ages more uniformly than the TFOT (Chipperfield et al., 1970). Both methods are considered interchangeable, however, to predict hot-mix aging.

Several properties and tools can verify these tests. The most common method of evaluation is the comparison of the physical properties of the test samples and the extracted asphalt. These properties include the penetration and viscosity values at various temperatures, ductility, softening point and viscoelastic properties. The chemical composition as indicated by either Corbett or Rostler fractions has also been used (Chipperfield et al., 1970; Thenoux et al., 1988; Brule et al., 1986). Chipperfield et al. (1970) conclude that the chemical changes that occur in the hot mix are greater than those produced in the TFOT or RTFOT tests. Recently, more sophisticated tools have been used to evaluate the validity of hot-mix simulations. These include the use of Gel Permeation Chromatography (GPC) to provide a molecular size distribution of the asphalt molecules before and after hot mixing and the aging test procedures (Chollar et al., 1989; Edler et al., 1985; Sisko and Brunstrum, 1968; Jennings et al., 1982; Brule et al., 1986; Glover et al., 1989). Chemical functional group analysis using infrared spectroscopy has also been used effectively for this purpose (Chollar et al., 1989; Glover et al., 1989; Dickinson, 1980). These various methods do not necessarily support one another, however. For example, different infrared absorbance does not necessarily indicate different physical properties (Dickinson, 1980; discussion by Plancher in Dickinson, 1980). An ideal test would duplicate the changes that occur in the hot-mix plant as detected by all of these techniques.

Jeminson et al. (1991) performed an extensive comparison of TFOT, RTFOT and the aging of asphalts extracted from hot mix. Asphalt was extracted from hot-mix samples, and the properties were compared to the same asphalts following TFOT and RTFOT aging. The results showed TFOT and RTFOT to be essentially identical but the extracted hot-mix materials were usually more aged as indicated by a variety of physical and chemical tests: complex viscosity at 60 °C (140 °F) and 135 °C (275 °F), penetration at 25 °C (77 °F), infrared analyses of carbonyl formation and the percent large molecular size as indicated by GPC analyses.

TFOT and RTFOT showed corresponding results for all of these tests, and the GPC chromatographs of the aged materials were identical. Others have reported that RTFOT is generally more severe than TFOT and may change the relative rankings (Zupanick, 1994; Bishara and McReynolds, 1995; Phromsorn and Kennedy, 1995; Huang et al., 1996). Agreement was not so good between the oven-aged materials and the extracted hot-mix material. There was considerable scatter among several asphalts, but every test showed the majority of the extracted

asphalts to be more aged than the oven-aged materials. The best agreement was obtained for the 135 °C (275 °F) viscosity. Percent Large Molecular Size (LMS) showed all extracted hot-mix samples to be higher than the oven-aged materials. Additionally, the shape of the chromatograph was different for the extracted asphalt. These differences likely result from the different mechanisms of oxidation that occur in the hot-mix plant where oxidation is very rapid as the asphalt is exposed to the large surface area of hot aggregate.

A number of comparative studies have been conducted to evaluate the compatibility of different aging methods. Shiau et al. (1992) compared TFOT and RTFOT at different temperatures. They report that the rolling thin film oven (RTFO) method is more severe than the thin film oven (TFO) method at 141 °C (285 °F) and 163 °C (325°F), but at 185 °C (365 °F) the aging effect is approximately the same. Kandhal and Chakraborty (1996) report results from an aging procedure identified as SHRP N-1025 in which loose mix is aged in a forced draft oven for 4 hours at 135 °C (275 °F). The materials were extracted by the Abson method for analysis. The asphalt-to-aggregate ratio was varied to study the effect of film thickness. Aging was greater at low film thickness.

Bishara and McReynolds (1995, 1996) compared aging by microwave to TFOT and RTFOT aging in terms of the Superpave specification, finding in general a fairly good agreement with 18 asphalts. Dunning and Meeks (1968) compared the air-blown asphalt with material obtained after the RTFOT. Comparisons were made only on the basis of softening point but the agreement was very good. According to this study, the oxidation mechanism of a thin film of asphalt at elevated temperatures is essentially the same for RTFOT and air blowing.

### **Simulation of Modified Asphalts**

Sirin et al. (1998) have developed a rotovapor procedure to simulate short-term aging of modified and unmodified asphalts, replacing the usual vacuum connection by airflow. They compared results with TFOT and RTFOT for an AC-30 and an AC-30 with 10 percent, 80-mesh crumb rubber. Fifty grams of sample were aged for 85 minutes at 163 °C (325 °F) and 185 °C (365 °F). The degree of aging at 163 °C (325 °F) was between those caused by TFOT and RTFOT. The rate of aging decreased with increasing sample size.

Later, the procedure was modified using a Morton flask (Sirin et al., 2000). This achieved lower temperature variation in the oil bath and better film agitation in the flask. At 163 °C (325 °F) for a sample weight of 200 grams it takes 160 minutes to achieve the aging effect closest to that of the TFOT and 210 minutes to compare with that of the RTFOT.

Another approach to address the problems encountered with modified viscous materials was suggested by Bahia et al. (1998), who placed 127 mm by 6.4 mm diameter steel rods within the RTFOT bottles. This allowed the creation of shearing forces to improve the spreading of thin films that in turn accelerated aging of modified binders. No negative effect was attributed to the rods. In addition, the spillage problems were eliminated.

### **FURTHER FACTORS AND CONSIDERATIONS FOR TEST DEVELOPMENT**

It is logical to assume that a realistic simulation of hot-mix aging would require the use of some solid phase with a large area comparable to the aggregate. While technically this may be true, there are several reasons for rejecting it. In the first place, it would considerably increase

the time required to run the test, but a greater problem is the complexity introduced by the necessity of extracting the asphalt from the solid phase for the subsequent analysis. The fact that one of the objectives of this study was to develop a method that can be used with modified asphalt ruled out such a technique. It is nearly impossible to extract a complex composition from a solid phase without changing its molecular microstructure. For many additives, it is nearly impossible to recover the entire modifier with the asphalt. Moreover, the extraction process changes the dispersion of the modifier and, thus, the properties of the recovered material.

Even with unmodified asphalts, extraction and recovery can introduce a significant error. Experience with extraction and recovery of asphalts shows it to be much more complex and subject to more problems than is generally realized (Burr et al., 1990; Burr et al., 1991; Cipione et al., 1991; Burr et al., 1993; Burr et al., 1994).

Judging by the greater aging that typically occurs in the hot-mix plant than in the RTFOT, it might be desirable to make the test somewhat more severe. This severity could likely be accomplished by a small increase in temperature, and the change could be justified by the fact that the rapid aging that occurs in the hot-mix plant might actually be better simulated by a higher temperature without aggregate. On the other hand, as long as Superpave specifications are based on RTFOT results, any new test must be able to duplicate the RTFOT aging.

Whether the RTFOT can be made to work with modified asphalts is problematic. As noted above, putting steel rods in the bottles solves the problem. Even if this is generally true, which is questioned, the RTFOT has other problems. It is hard to clean and remove the asphalt from the bottles, a difficulty complicated by rods. The problems of handling hot equipment, as well as the high cost of equipment, are also important issues. It would be desirable to have equipment that is easier and safer to use as well as less expensive to build and maintain.

The rotovapor design has positive features. In particular, conducting the aging in a rotating flask prevents spillage and film formation problems. This method also allows a variety of operating conditions, such as airflow rate, speed of rotation, and sample weight. However, these possible advantages can pose additional problems in terms of selecting optimal values of multiple variables and ensuring test reproducibility. For instance, the airflow rate, sample size, even the angle of the rotating flask and the depth of its submergence into the heating bath can potentially affect the test results. Moreover, heat transfer is not uniform in the system that creates a varying temperature distribution and makes the sample temperature difficult to control.

Decreasing film thickness in the TFOT to avoid the diffusion limitation might seem like a reasonable solution. The test time will also decrease. However, in order to age the necessary amount of material, a large sample area is required.

The microwave idea is appealing in that it is rather simple and fast. However, the mechanism of hardening might be different, and non-oxidative reactions might be occurring. These can be verified by infrared (IR) and gel permeation chromatography (GPC). Applying microwave radiation to simulate a process that does not involve any source of microwaves would seem to be questionable.

The air-blowing procedure appears to be particularly interesting. The equipment is easy to assemble, operate and clean. The entire sample is placed in a single, easily emptied container

that could handle a sample of any desired mass. Some previous studies of asphalt air blowing have been carried out, particularly at temperatures below 232 °C (450 °F) (Vassiliev et al., 2001). The results indicate that good material can be produced without undergoing any harmful or undesirable changes. Therefore, the effect identical to RTFOT aging can be achieved by asphalt air blowing under conditions similar to those of the oven test. On the other hand, the effect of air blowing could depend on material viscosity and concentration of volatiles. Hypothetically, better contact with air can be obtained for less viscous material. Air blowing can also enhance the evaporation of volatile compounds. Thus, the process can be sensitive to the airflow and air distribution, asphalt viscosity and volatile loss.

For modified asphalts, several serious problems need to be recognized in the simulation of either hot-mix or road aging when modifiers are present. In the first place, both are difficult to verify due to the complexity of asphalt recovery from the hot-mix without serious changes in its composition and properties. Secondly, oxidation of modified asphalt is much more complicated if the modifier reacts with the asphalt or aggregate. Reaction rates of modifier and asphalt may respond differently to changing conditions of time and temperature. The presence of modifiers introduces very time- dependent diffusion effects that may be quite different in the rapid oxidation of a hot-mix plant and the slower oxidation of a laboratory test simulation.

## **REPORT OUTLINE**

This report is a combination of fundamental studies, test development, and test procedures. Chapter 2 presents fundamental studies of air blowing and very thin film aging. Chapter 3 describes methods and materials used in these research and reports fundamental studies of air blowing and the changes that occur to asphalts as a result. This is important for understanding the air-blowing SAFT process for short-term aging and also for understanding the achievement of asphalt grade by air-blowing methods. This chapter also includes studies of very thin films of asphalt aging as an alternate method for achieving short-term aging. Chapter 4 presents studies that were directed specifically at the development of the SAFT apparatus and procedure. Chapter 5 presents the recommended apparatus and test procedure. Finally, Chapter 6 presents a summary, conclusions, and recommendations.

## CHAPTER 2. FUNDAMENTAL STUDIES OF AIR BLOWING AND VERY THIN FILM AGING

(Pages 2-1 to 2-17 reprinted, with permission, from Vassiliev N. Y., S. A. Williamson, R. R. Davison, and C. J. Glover. (2001) Air Blowing of Supercritical Asphalt Fractions. *Ind. Eng. Chem. Res.*, Vol. 40, 1773-1780, Copyright 2001 American Chemical Society.)

### ABSTRACT

Air blowing of asphalt at higher temperature does not greatly impact such parameters as the softening point-penetration relationship. With new Superpave specification, very good grade asphalts can be produced by air blowing, and the blowing temperature does not seriously impact the grade span. It is shown, however, that the subsequent 88 °C hardening and oxidation rates are higher for materials blown at higher temperature, and this is not detected by Superpave specifications. Blowing fluxes with high saturate content may result in higher grade but can cause subsequent susceptibility to oxidative hardening. The mechanism by which air blowing can affect the 88 °C hardening rate is related to oxidation kinetics and the tendency of oxidation products to form asphaltenes, causing hardening. For some materials air blown at higher temperature, the subsequent accelerated hardening rate results from an increase in the oxidation rate, while the hardening susceptibility may actually decrease.

### INTRODUCTION

It is widely believed that pavement asphalts produced by air blowing are inferior to straight run asphalts, and indeed their properties may depend strongly on the starting material and blowing conditions. Because the time to reach the desired consistency is greatly reduced by elevated temperature, there is an incentive to operate this way. One can find a wide range of temperatures reported in the literature (Corbett, 1975; Gallagher et al., 1996; Bahl and Singh, 1983) even up to 320-325 °C, with 230-275 °C common. While air blowing is commonly employed in the production of roofing asphalts, it is also possible to produce good pavement grade asphalt by this method if the proper starting material is blown at the right conditions.

It is well known that blowing can improve temperature susceptibility by giving a higher penetration for a given softening point temperature with a lower glass transition temperature (Poirier and Sawatzky, 1992), and this can be improved by catalyst addition (Corbett, 1975; Bahl and Singh, 1983). With the introduction of Superpave specifications it is important to determine if air blowing can produce materials of high grade. Gallagher et al. (1996) air blew four asphalts, AC-2.5 and AC-5 from two crude oil sources, to make AC-10 and AC-30 asphalts. AC-2.5 was used to produce 60 and 93 °C softening point materials and these were backblended with the AC-2.5 asphalt to produce AC-10 and AC-30 materials. They were compared to straight run asphalts from the same crude oils on the basis of their grades. There was little difference in the upper grade, determined by the temperature at which the permanent deformation governed by the value of  $G^*/\sin \delta$  meets a required value before and after the rolling thin film oven test (RTFOT) (ASTM D2872). However, this would be expected because all materials were designed to meet a specific viscosity grade. On the other hand, following further aging in the pressure aging vessel (PAV), every air-blown material demonstrated better lower temperature characteristics than the straight run material.

There are a number of older studies of the effect of blowing temperature and composition on properties. These include a variety of variables such as softening point versus penetration, heat of reaction, size of asphaltenes, etc. Smith and Schweyer (1967) showed that the heat of reaction varied with blowing temperature indicating a probable change in the predominant reactions. Girdler (1965) reported that blowing at 232 °C produced larger asphaltenes than those originally present, while blowing at 316 °C produced asphaltenes similar in size to those originally present. Corbett (1975) blew softer and harder fluxes from three separate asphalts to softening points of 54, 88, and 104 °C at 232 and 260 °C. There was little difference in the penetration obtained by blowing at the two temperatures, though they tended to be slightly lower at 260 °C. There was a large effect of composition, however, with the penetration improving as the sum of the saturates and naphthene aromatics percentages increased.

Dunning and Meeks (1968) report little difference in softening point-penetration relations when the blowing temperature is increased from 177 to 232 °C. He also reported that while increasing the blowing temperature generally improves the softening point-penetration relation, it lowers the ductility. This is interesting in view of the results of Gallagher et al. (1996), who pointed out that blowing improved low-temperature Superpave properties. Chaffin et al. (1997) air blew SHRP asphalts at 93, 121 and 149 °C. They observed that the hardening susceptibility, the viscosity increase per growth in carbonyl content, increased with the blowing temperature.

Dickinson (1974) used two light materials air blown at 200 and 245 °C to produce paving-grade material. He also air blew them further to produce material with a penetration of 25 that was fluxed back to material with a penetration of 80. Then he aged these materials, first in the RTFO and then in an oven at 90 °C. The material blown at 200 °C aged more slowly than that that blown at 245 °C. He also compared refinery material blown at 265 °C with the one blown at 320 °C. High blowing temperature had a very deleterious effect on the subsequent aging of the asphalt.

These results indicate that the effect of blowing temperature depends on the property measured and on the composition of the blown material. In this study we examine blowing temperature and the composition effect on the resulting asphalt Superpave specification properties as well as on the hardening properties when subsequently aged at lower temperatures. It is generally believed that the PAV aging specified in the Superpave specification simulates road aging; however, it has been demonstrated (Domke et al., 1999) that it is possible to produce a good Superpave performance grade (PG) material which has poor pavement-temperature aging properties.

In previous work it was shown (Lin et al., 1996) that the rate of asphalt hardening as measured by the change in its limiting complex viscosity could be expressed as the product of three independent functions:

$$\frac{\partial \ln \eta_0^*}{\partial t} = \frac{\partial \ln \eta_0^*}{\partial AS} \cdot \frac{\partial AS}{\partial CA} \cdot \frac{\partial CA}{\partial t} \quad (1)$$

or

$$\frac{\partial \ln \eta_0^*}{\partial t} = HS \cdot r_{CA} \quad (2)$$

where  $AS$  is weight percent asphaltene,  $t$  is aging time in days,  $CA$  is the area of the carbonyl peak in arbitrary units,  $HS$  is the hardening susceptibility,  $\eta_0^*$  is the complex low shear rate limiting viscosity, and  $r_{CA}$  is the rate of carbonyl formation.

The hardening that occurs in asphalt is almost entirely caused by the growth in asphaltenes and increased interaction between them (Lin et al., 1995a; Lin et al., 1995b). This is represented in equation 2 by the  $HS$ , which, by comparison with equation 1, is represented by two terms. The first term in the expression for  $HS$ ,  $\partial \ln(\eta_0^*) / \partial AS$ , is well represented by a modified Pal Rhodes suspension viscosity model (Lin et al., 1998).

$$\frac{\eta}{\eta_m} = (1 - K \cdot AS)^{-\nu} \quad (3)$$

where  $\eta_m$  is maltene viscosity,  $K$  is an association constant, which is a function of the solvent power of the maltene fractions for the asphaltene fraction, and  $\nu$  is the particle shape factor. The solubility power is adversely affected by saturates, so even though saturates do not oxidize and tend to soften asphalt, they can lead to increased hardening rates (HRs) as asphaltenes accumulate during oxidation.

The second term in equation 1 is the degree to which the newly formed carbonyl bonds produce asphaltenes. This term in equation 1 is increased by the presence of heavy polar aromatics (Liu et al., 1998a).

It may be surprising that changes in physical properties as an asphalt oxidizes correlate so well with only the change in the carbonyl peak area as measured by infrared spectroscopy. It turns out that, for every asphaltic material, this change is proportional to the oxygen uptake (Liu et al., 1998b).

Asphalt oxidation occurs in two stages: first there is a rapid step or initial jump region during which both the carbonyl area and the viscosity increase rapidly, and this is followed by a prolonged oxidation that occurs at a constant rate. Equations 1 and 2 are only strictly accurate during this constant rate period. During the constant oxidation period, the  $HS$  remains constant and is a property of each asphalt that is independent of oxidation temperature below 100 °C. Within the initial jump region the  $HS$  may change as shown by the fact that linear plots of  $\ln \eta_0^*$  vs  $CA$  do not usually intercept the value for the unaged asphalt. This is not of great significance because the initial jump is largely eliminated during the hot-mix operation before the material goes on the road. To move past the initial jump region, all materials were subjected to short-term aging according to the RTFOT procedure.

## EXPERIMENTAL DESIGN AND METHODS

Seven fractions of SHRP AAA-1, AAF-1, and ABM-1 as well as of other asphalts were obtained using a supercritical extraction unit as described by Chaffin et al. (1997). Asphalt supercritical fractions 2 and 3 were used for the subsequent air-blowing and aging experiments together with blends of commercially available materials. Fraction 1 is not suitable for air-blowing experiments because of its composition. Fraction 1 contains mostly saturates and naphthene aromatics and has very low viscosity. Other fractions, from 4 through 7, were either

too viscous or not available in sufficient quantity for air blowing. Table 2-1 lists the materials and some of their initial properties such as the complex low shear rate limiting viscosity  $\eta^*_0$  and composition as determined by Corbett's method (ASTM D4124-97) and an HPLC method (Chaffin et al., 1996). The blends were not air-blown. These materials were mixtures of flux I and resin, or flux I and highly blown flux I and, as such were suitable asphalt materials for further study. Fluxes I - III are commercial materials used in air blowing, and resin is a commercial blending stock. The highly blown flux I is a commercially air-blown material.

Asphalt fractions were air-blown at the conditions specified in Table 2-2 using the laboratory unit depicted in Figure 2-1. The same airflow rate of 4323 cm<sup>3</sup>/min was used to air blow asphalt fractions at two or three temperature levels. Blowing of most of the materials was targeted to a low shear rate limiting dynamic viscosity level of 2000 ± 400 P in order to make possible the comparison of their subsequent oxidation and hardening properties. However, the materials with higher resulting viscosity were also obtained and studied. The time of air blowing depended on the operating temperature and was less at higher temperatures. A total of 300 grams of heated material was placed in a 1 qt (0.946 L) can and air-blown with constant agitation by a mixer attached to a motor. An insulated heating tape was used to heat the can. A thermocouple and a temperature controller maintained the operating temperature at the desired level.

The blending was performed using the same laboratory unit as that used for the air blowing. Two components were mixed in a proportion necessary to obtain a material with specified viscosity. The fractions were blended for 1 hour at 177 °C using nitrogen instead of air in order to avoid oxidation of the mixed materials.

**Table 2-1. Materials Used for Air Blowing and Aging Experiments.**

| Material/Blend                      | Viscosity at 60 °C, $\eta^*_0$ , Poise | Composition as determined by Corbett analysis, wt % |                     |                 |             |
|-------------------------------------|----------------------------------------|-----------------------------------------------------|---------------------|-----------------|-------------|
|                                     |                                        | Saturates                                           | Naphthene Aromatics | Polar Aromatics | Asphaltenes |
| 35% Flux I-65% Resin                | 2361.0                                 | 9.75                                                | 47.65               | 32.05           | 10.55       |
| 45% Flux I-55% Highly Blown Flux I  | 2394.0                                 | 20.57                                               | 31.68               | 28.08           | 19.67       |
| Flux I                              | 72.7                                   | 21.72                                               | 46.83               | 26.48           | 4.97        |
| Flux II                             | 72.0                                   | 20.80                                               | 50.20               | 25.70           | 3.30        |
| Flux III                            | 72.0                                   | 18.37                                               | 55.38               | 22.18           | 4.07        |
| YB/F Supercritical Fraction 3       | 137.4                                  | 16.11                                               | 60.97               | 22.66           | 0.26        |
| YB/F Supercritical Fraction 2       | 29.2                                   | 18.20                                               | 81.70*              |                 | 0.20        |
| SHRP AAA-1                          | 14.5                                   | 20.00                                               | 79.80*              |                 | 0.20        |
| Supercritical Fraction 2 SHRP AAF-1 | 11.7                                   | 23.50                                               | 76.20*              |                 | 0.40        |
| Supercritical Fraction 2 SHRP AAF-1 | 67.1                                   | 14.30                                               | 85.40*              |                 | 0.40        |
| Supercritical Fraction 3 SHRP ABM-1 | 91.1                                   | 12.90                                               | 87.10*              |                 | 0.0         |
| Supercritical Fraction 2            |                                        |                                                     |                     |                 |             |

\* determined by difference as a total sum of aromatic compounds for YB Fina and SHRP asphalt fractions by HPLC method developed by Chaffin et al. (1997).

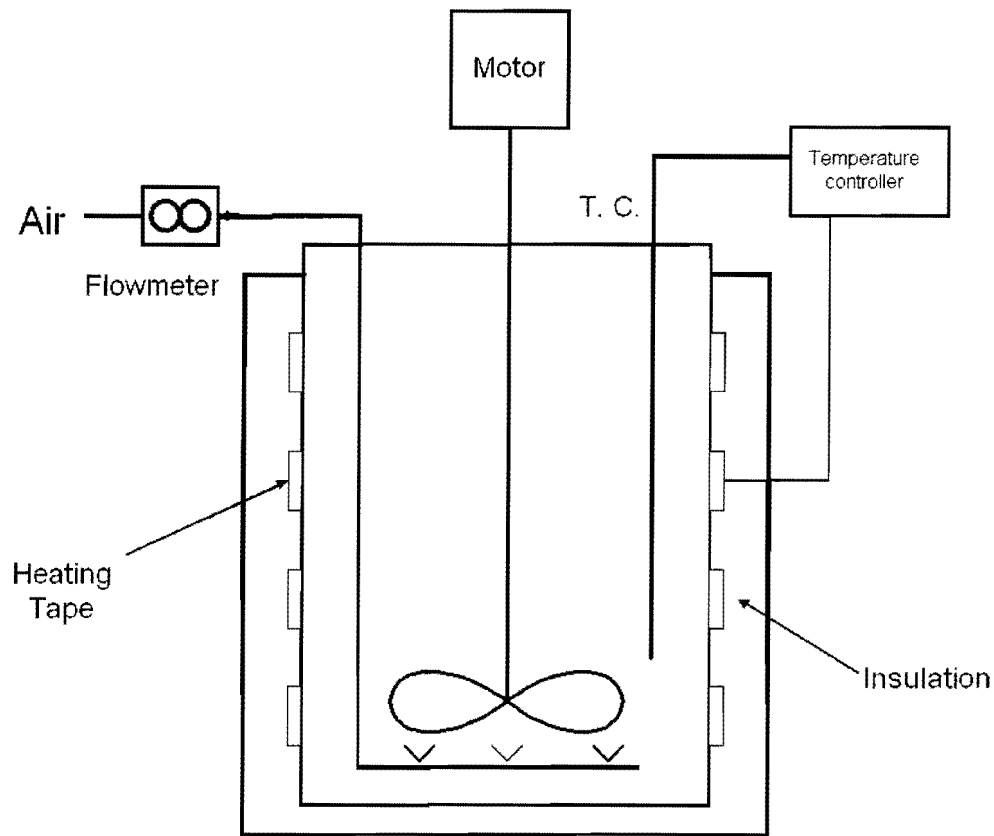


After blending or air blowing, Superpave performance grading (PG) (SHRP, 1994) was conducted according to standard procedures, with continuous grading done by linear interpolation between two temperatures. According to Superpave binder specification, the material is tested in conditions that simulate three stages of the binder's life. These include testing the original binder, material aged in a rolling film oven that is intended to simulate changes that occur during mix production and construction, and material aged in a pressure aging vessel simulating in-service aging in a pavement. A dynamic shear rheometer, a bending beam rheometer, and a direct tension tester are used to determine the temperature at which the physical properties of asphalt meet required values.

The aging studies were performed first according to the standard RTFOT procedure followed by aging in a pressure oxidation vessel (POV) (Liu et al., 1996) at 88 °C and atmospheric pressure. The samples were removed periodically and analyzed for their physical and chemical property changes. From infrared absorbance spectra and rheological measurements, several parameters were obtained.

**Table 2-2. Air-Blowing Conditions and Superpave PGs.**

| Material                               | Temperature<br>°C | Time,<br>hours | Limiting<br>viscosity at<br>60 °C,<br>Poise | Superpave<br>Performance<br>Grade | Continuous<br>Performance<br>Grade |
|----------------------------------------|-------------------|----------------|---------------------------------------------|-----------------------------------|------------------------------------|
| 35% Flux I-65% Resin                   | blended           | blended        | 2361                                        | 64-16                             | 65-20                              |
| 45% Flux I-55% Highly<br>Blown Flux I  | blended           | blended        | 2394                                        | 64-34                             | 65-35                              |
| Flux I                                 | 177               | 8.00           | 1798                                        | 58-34                             | 60-39                              |
|                                        | 204               | 3.75           | 2661                                        | 64-34                             | 64-35                              |
|                                        | 232               | 8.00           | 2228                                        | 64-28                             | 65-28                              |
| Flux II                                | 177               | 6.75           | 1803                                        | 58-34                             | 60-37                              |
|                                        | 204               | 4.50           | 1994                                        | 58-28                             | 62-31                              |
|                                        | 232               | 3.50           | 2308                                        | 64-28                             | 65-28                              |
| Flux III                               | 177               | 8.00           | 3732                                        | 64-22                             | 64-22                              |
|                                        | 204               | 4.00           | 3318                                        | 64-22                             | 64-22                              |
| YB/F Supercritical<br>Fraction 3       | 204               | 7.00           | 1628                                        | 58-22                             | 59-27                              |
|                                        | 232               | 5.00           | 1949                                        | 58-22                             | 61-25                              |
| YB/F Supercritical<br>Fraction 2       | 204               | 12.00          | 2108                                        | 58-28                             | 63-29                              |
|                                        | 232               | 8.00           | 2883                                        | 64-28                             | 64-29                              |
|                                        | 246               | 6.50           | 3500                                        | 64-22                             | 68-27                              |
| SHRP AAA-1<br>Supercritical Fraction 2 | 204               | 11.00          | 1719                                        | 58-28                             | 61-29                              |
|                                        | 232               | 6.50           | 2241                                        | 64-28                             | 64-28                              |
|                                        | 246               | 5.50           | 2715                                        | 64-22                             | 67-26                              |
| SHRP AAF-1<br>Supercritical Fraction 2 | 204               | 11.00          | 2881                                        | 58-22                             | 63-24                              |
|                                        | 260               | 5.00           | 2425                                        | 64-22                             | 64-23                              |
| SHRP AAF-1<br>Supercritical Fraction 3 | 204               | 7.50           | 2317                                        | 58-22                             | 61-24                              |
|                                        | 232               | 5.00           | 2169                                        | 58-22                             | 62-22                              |
|                                        | 260               | 4.50           | 3202                                        | 64-22                             | 67-24                              |
| SHRP ABM-1<br>Supercritical Fraction 2 | 204               | 8.00           | 2112                                        | 58-22                             | 62-27                              |
|                                        | 232               | 4.50           | 2674                                        | 58-16                             | 63-20                              |
|                                        | 260               | 2.25           | 2778                                        | 64-16                             | 64-16                              |



**Figure 2-1. Laboratory Unit Used for Air-Blowing Experiments.**

## **RESULTS AND ANALYSIS**

### **Superpave Specification Analysis**

The air blown asphalts were analyzed and characterized in terms of Superpave specifications and Corbett composition. Table 2-2 gives the Superpave and continuous PG and Table 2-3 shows the continuous PG span of the blends and air-blown materials, along with their Corbett compositions. One problem encountered with data analysis was that the materials obtained by air blowing at different temperature levels had varying viscosities at 60 °C even though the air-blowing end-point objective was to obtain materials of the same complex viscosity. This is a result of a tendency to overshoot the target viscosity. Any delay in stopping the air blowing results in overshooting of the viscosity, and the higher air-blowing rates at higher temperature produce a correspondingly greater overshoot. Therefore, the 60 °C viscosities tend to be higher at the higher air-blowing temperatures. However, as can be seen, for the most part, very satisfactory grades have been obtained with little effect of the blowing temperature.

It is difficult to find an apparent trend in these data in the dependence of the continuous performance grade span on the air-blowing temperature; for some of the materials the PG span increased with temperature, for some it decreased, and for some it remained constant. Nevertheless, there has been observed an overall slight decrease of the span with increasing

blowing temperatures, because of the influence of the air-blowing temperature on the top and bottom PGs separately (Figure 2-2). While the increase of the top PG with temperature can be explained by a generally higher viscosity of the material due to overshooting of the target viscosity, the air-blowing temperature appears to be responsible for the change in the bottom PG value. Figure 2-2 shows the relationship between PG and the air-blowing temperature. The bottom temperature grade of all studied materials becomes higher (or, in the case of flux III, stays the same) as the air-blowing temperature increases.

According to the Superpave specification, the low-temperature PG indicates the temperature at which an asphalt material possesses the specified values of creep stiffness  $S(t)$  and creep rate ( $m$ -value) or direct tension failure. Creep stiffness represents the response of asphalt binder to creep loading, and the  $m$ -value is the creep stiffness time rate of change determined at 60 seconds. Figures 2-3 and 2-4 show the relationship between the air-blowing temperature and asphalt  $S(t)$  and  $m$ -values determined at  $-18\text{ }^{\circ}\text{C}$ . As the air-blowing temperature increases, asphalts become stiffer with an even more significant deterioration in  $m$ -value. In fact, most air-blown asphalt fractions failed the bending beam rheometer test at the test temperature because of an  $m$ -value deficiency rather than  $S(t)$ . Also, this was typical for fractions air blown at higher temperatures, meaning that the increasing temperature of air blowing worsens the relaxation properties of materials relative to their stiffness. This might be explained by the growing importance of condensation reactions taking place during air blowing together with oxidation reactions. This would seem to be confirmed, as discussed later, by the changes in HS, resulting from a higher asphaltene formation rate for a given carbonyl formation rate. In addition to formation of secondary bonds, the number of primary bonds formed among asphalt constituents is likely to increase with temperature. This can lead to formation of asphaltene aggregates that are not only bigger in size but also stronger. This type of molecule and their aggregates would be less able to relax the stress. From Table 2-3 it is obvious that the amount of asphaltenes formed during air blowing is not responsible for this effect.

A similar effect was noticed when several air-blown asphalt fractions were subjected to the direct tension test. Figure 2-5 shows that the failure strain decreases with the air-blowing temperature for flux I and II asphalts. This behavior is typical for asphalts; normally the stiffer materials are more brittle. Although the stiffness of both flux I and II is not a strong function of the air-blowing temperature, the failure percent strain decreases significantly as their temperature increases. It shows an increased susceptibility of the material to thermal cracking with the air-blowing temperature. Thus, the direct tension test may be a more sensitive indicator of low-temperature asphalt performance properties than the bending beam rheometer test.

Table 2-3 shows the composition of air blown and blended asphalts in terms of Corbett fractions, PG span and HR. It should be pointed out that the higher PG span is typical for asphalts with higher saturate and asphaltene contents. In general, an increase in the asphaltene content raises the top grade more than the bottom grade. Saturates lower both top and bottom grades, but the effect is smaller. The net result is that increasing saturate and asphaltene contents will increase the PG span. For instance, a grade may be gained at the top while the bottom grade is maintained in this manner.

**Table 2-3. Effect of Composition of Air-Blown Asphalts and Blends on Superpave PG and Lower Temperature Hardening.**

| Material/Blend                     | Air blowing Temperature, °C | Composition as determined by Corbett analysis, wt % |                     |                 |             | PG Span | HR x10 <sup>2</sup> |
|------------------------------------|-----------------------------|-----------------------------------------------------|---------------------|-----------------|-------------|---------|---------------------|
|                                    |                             | Saturates                                           | Naphthene Aromatics | Polar Aromatics | Asphaltenes |         |                     |
| 35% Flux I-65% Resin               | Blended                     | 9.75                                                | 47.65               | 32.05           | 10.55       | 85      | 6.70                |
| 45% Flux I-55% Highly Blown Flux I | Blended                     | 20.57                                               | 31.68               | 28.08           | 19.67       | 100     | 13.50               |
| Flux I                             | 177                         | 21.50                                               | 37.30               | 22.50           | 18.70       | 99      | 9.40                |
|                                    | 204                         | 21.76                                               | 34.46               | 23.95           | 19.82       | 99      | 13.50               |
|                                    | 232                         | 21.60                                               | 36.10               | 23.78           | 18.52       | 93      | 16.10               |
| Flux II                            | 177                         | 25.31                                               | 33.17               | 23.16           | 18.34       | 97      | 11.96               |
|                                    | 204                         | 20.99                                               | 34.54               | 26.67           | 17.83       | 93      | 12.60               |
|                                    | 232                         | 19.24                                               | 34.60               | 26.22           | 19.91       | 93      | 18.88               |
| Flux III                           | 177                         | 11.70                                               | 32.80               | 43.50           | 12.00       | 86      | 3.10                |
|                                    | 204                         | 12.56                                               | 38.53               | 39.10           | 9.74        | 86      | 4.70                |
| YB/F Fraction 3                    | 204                         | 16.33                                               | 35.03               | 37.43           | 11.23       | 86      | 3.20                |
|                                    | 232                         | 14.50                                               | 34.90               | 39.30           | 11.30       | 86      | 5.31                |
| YB/F Fraction 2                    | 204                         | 15.15                                               | 34.25               | 31.55           | 19.05       | 92      | 7.30                |
|                                    | 232                         | 17.38                                               | 30.98               | 33.88           | 17.78       | 93      | 6.64                |
|                                    | 246                         | 16.33                                               | 30.63               | 33.93           | 19.13       | 95      | 8.58                |
| SHRP AAA-1 Fraction 2              | 204                         | 30.18                                               | 33.78               | 15.08           | 20.98       | 90      | 7.90                |
|                                    | 232                         | 29.40                                               | 32.00               | 16.20           | 22.40       | 92      | 10.30               |
|                                    | 246                         | 28.65                                               | 33.85               | 16.75           | 20.75       | 93      | 13.30               |
| SHRP AAF-1 Fraction 2              | 204                         | 21.10                                               | 27.30               | 29.50           | 22.10       | 87      | 7.30                |
|                                    | 260                         | 21.40                                               | 27.80               | 31.00           | 19.80       | 87      | 19.90               |
| SHRP AAF-1 Fraction 3              | 204                         | 16.03                                               | 33.23               | 34.73           | 16.03       | 85      | 5.63                |
|                                    | 232                         | 14.65                                               | 32.65               | 41.45           | 11.25       | 84      | 8.05                |
|                                    | 260                         | 13.50                                               | 35.70               | 36.20           | 14.60       | 91      | 12.10               |
| SHRP ABM-1 Fraction 2              | 204                         | 16.33                                               | 35.03               | 37.43           | 11.23       | 89      | 3.90                |
|                                    | 232                         | 14.50                                               | 34.90               | 39.30           | 11.30       | 83      | 5.13                |
|                                    | 260                         | 13.65                                               | 33.15               | 41.75           | 11.45       | 80      | 7.00                |

### 88 °C Aging Studies

In addition to the physical properties of air-blown asphalt materials, how these properties change with time due to in-service conditions is also very important because it determines the material's long-term serviceability. Because asphalts' physical properties are closely related to their chemical composition, the analysis of hardening and oxidation rates can give extremely useful information for predicting the change of material service properties.

An example of how asphalt infrared absorbance spectra change as an asphalt ages is shown in Figure 2-6. The rate of oxidation is defined to be the rate of increase of the carbonyl peak area (CA) between wavenumbers of 1820 and 1650 cm<sup>-1</sup>. The area is reported in arbitrary units. Figure 2-7 shows a plot of CA versus aging time for air blown fraction 3 of SHRP AAF-1 asphalt as an example. The oxidation rate is determined as the slope of the linear region of the plot.

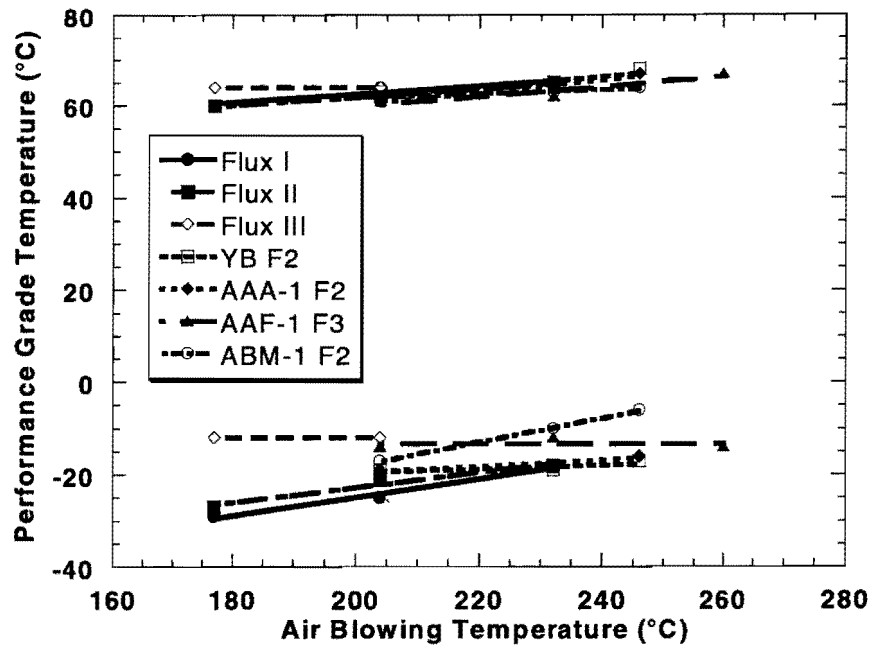


Figure 2-2. Relationship Between the Air-Blowing Temperature and PG.

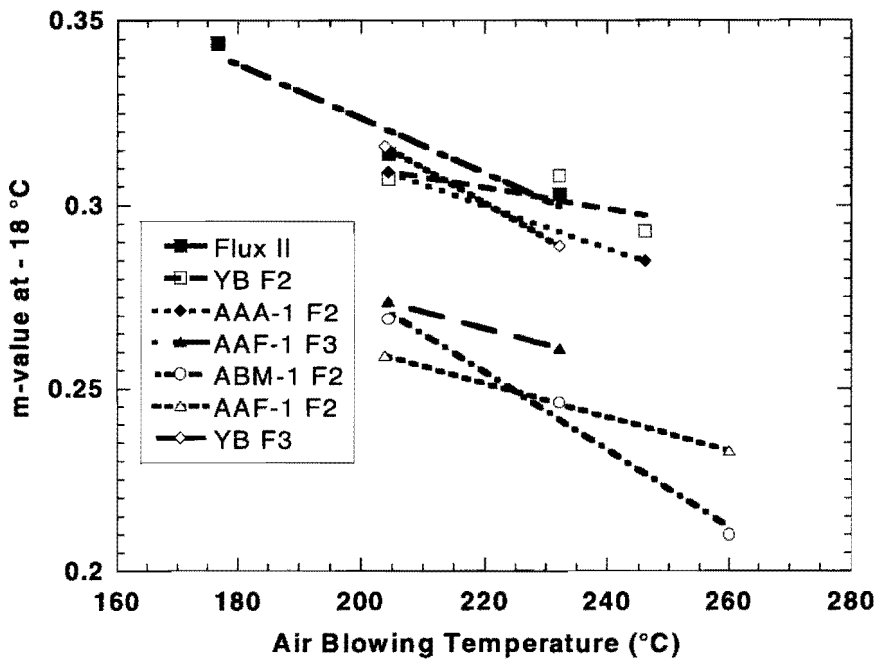


Figure 2-3. Air-Blowing Temperature Effect on *m*-value.

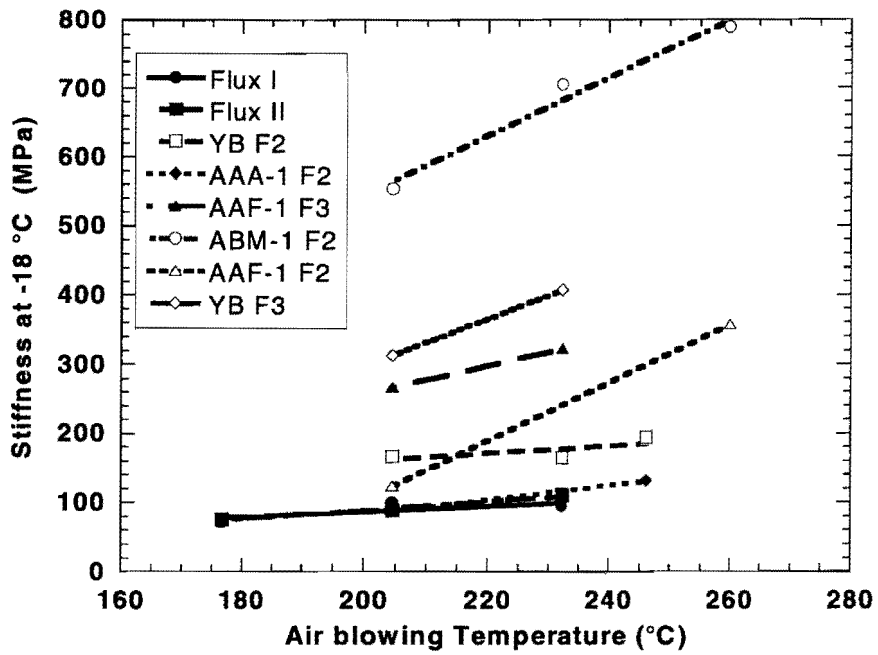


Figure 2-4. Air-Blowing Temperature Effect on Stiffness.

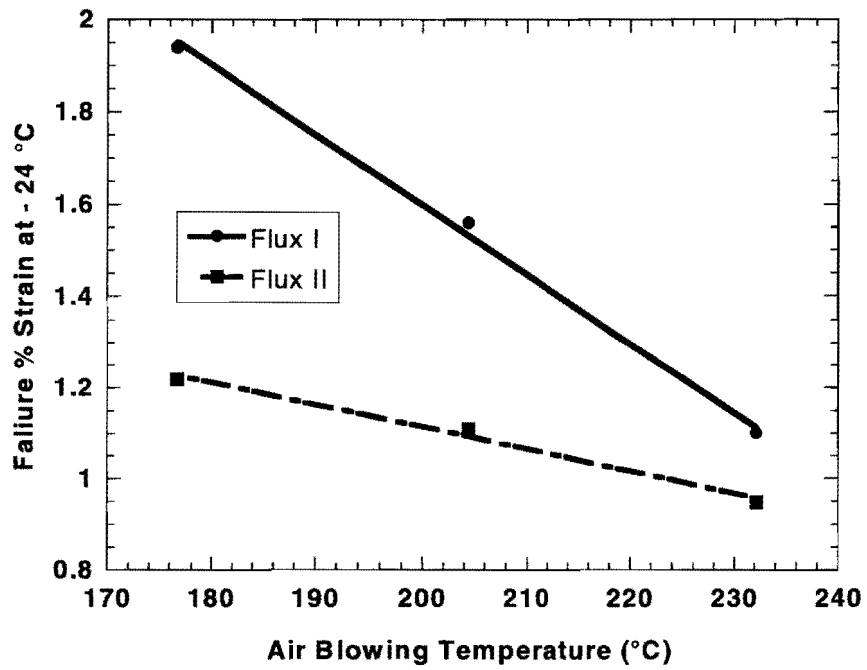


Figure 2-5. Air-Blowing Temperature Effect on Failure Strain.

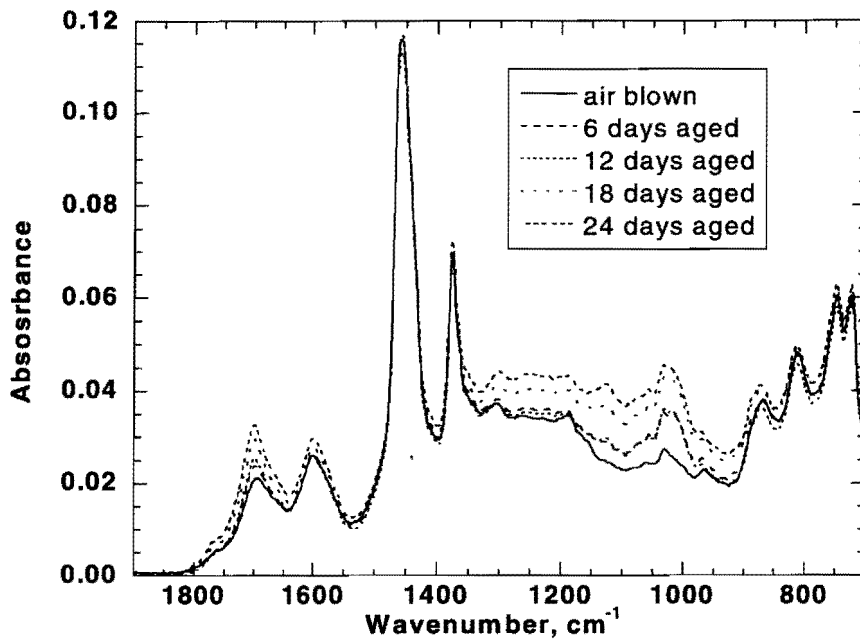


Figure 2-6. IR Spectra of Aged SHRP AAF-1 Fraction 3 Air Blown at 260 °C for 4.5 hours.

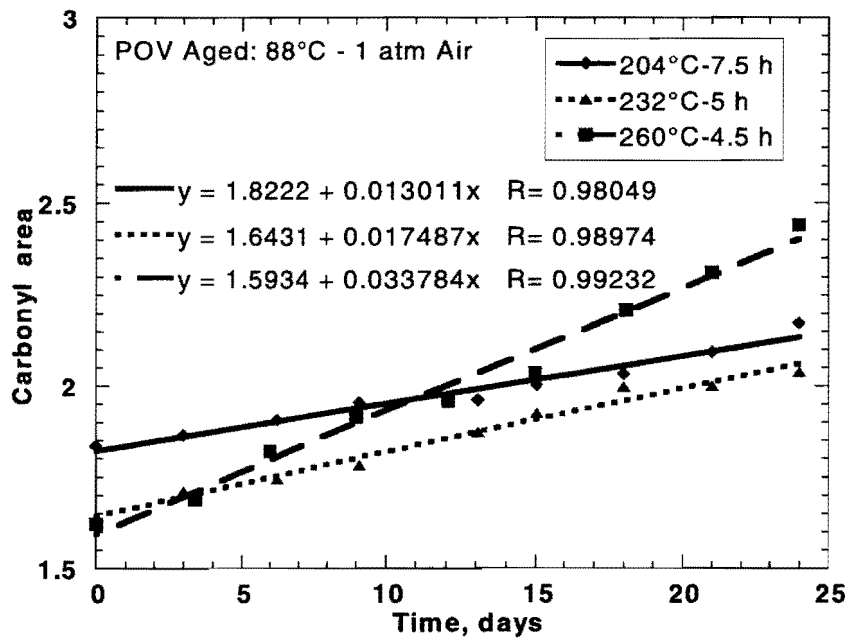


Figure 2-7. Oxidation Rate of SHRP AAF-1 Fraction 3 at 88 °C After Air Blowing at Different Temperatures.

Hardening is reported in terms of the low shear rate limiting complex viscosity  $\eta_o^*$ , measured at 60 °C with a dynamic shear rheometer. The slope of  $\ln(\eta_o^*)$  plotted versus aging time is termed the HR and the relationship (Figure 2-8) is linear, also after an initial jump region, as is the oxidation rate. It has been shown previously that  $\ln(\eta_o^*)$  has a linear relation with CA that is independent of an oxidation temperature of below about 100 °C (Lau et al., 1992). The line characterizing the relationship between these two parameters can be determined for each asphalt. The slope of the line is designated as HS and it denotes the increase of an asphalt's viscosity in response to oxidation. Figure 2-9 shows the HS relations determined by 88 °C aging for three asphalt materials, produced by air blowing flux I at three different temperatures.

HR data and the values obtained for terms in equation 1, namely, HS and the oxidation rate ( $r_{CA}$ ), are summarized in Table 2-4. It was observed that all of the materials blown at a higher temperature subsequently hardened faster when aged at 88 °C in the POV and also have higher oxidation rates. However, the HS actually decreased for many fluxes. This happened primarily because of increased rates of carbonyl formation relative to the degree of hardening. This indicates that higher blowing temperatures produce asphalts that subsequently oxidize faster at the lower temperature, but the oxidation has a reduced tendency to produce the asphaltenes that increase viscosity. This may mean that higher blowing temperatures activate smaller molecules that oxidize without producing asphaltenes, causing an increase in the concentration of the carbonyl functional groups without a commensurate increase in viscosity. However, the net effect is still an increased rate of hardening.

To analyze further the effect of the blowing temperature, it is informative to assess the effect of the RTFOT (used to simulate hot mix aging, and performed at 163 °C) on subsequent oxidation conducted at a lower temperature. In the context of this discussion, the RTFOT plays the role of the air-blowing process but at a lower temperature than the typical 230-275 °C. Liu et al. (1996) measured the carbonyl formation rates for 14 asphalts at a variety of temperatures below 100 °C and at 0.2 and 20 atm of oxygen and found that prior exposure to the RTFOT at 163 °C had no effect on the subsequent carbonyl formation rates. However, there was an effect on HS and the resulting HR. Table 2-5 shows HSs for 10 of these asphalts. In every case but two at 20 atm, HS increased, though for some insignificantly. Thus, there is a slight increase in HR following the RTFOT, and this will be entirely due to increase in HS. These data of Liu, together with the results reported herein, suggest a change in the hardening mechanism between 163 and 204 °C. There are other data in the literature that support this. The difference in the mechanism is even more significant at higher air-blowing temperatures.

It is also interesting to compare the low-temperature hardening properties of air-blown asphalt fractions with those of their unblown sources. Liu et al. (1997) ran HS for a variety of light unblown fluxes similar to the ones studied in this work and obtained much lower values (Table 2-5) for the HS than those reported in Table 2-4. For instance, for AAF-1 fraction 3 they reported a value of HS of 2.0 versus 3.55 - 4.55 for the air-blown material. Thus, the exposure of asphalt fractions to high-temperature oxidation caused HS to increase twofold. Normally these fractions contain materials that do not readily oxidize at low temperatures (Liu et al., 1997; Liu et al., 1998) and therefore do not form asphaltenes. Thus, they have excellent HRs until activated by high blowing temperatures.



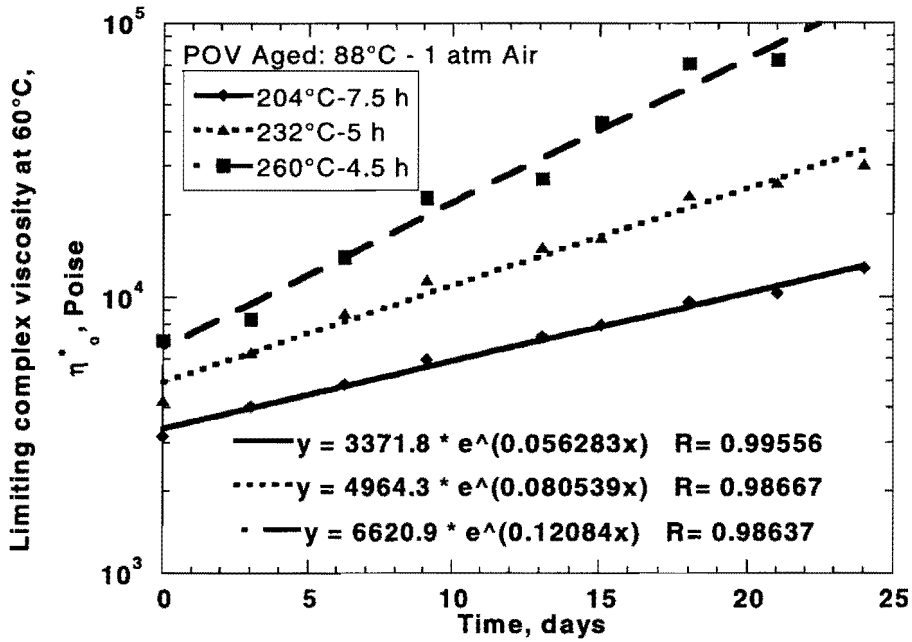


Figure 2-8. HR of SHRP AAF-1 Fraction 3 at 88 °C After Air Blowing at Different Temperatures.

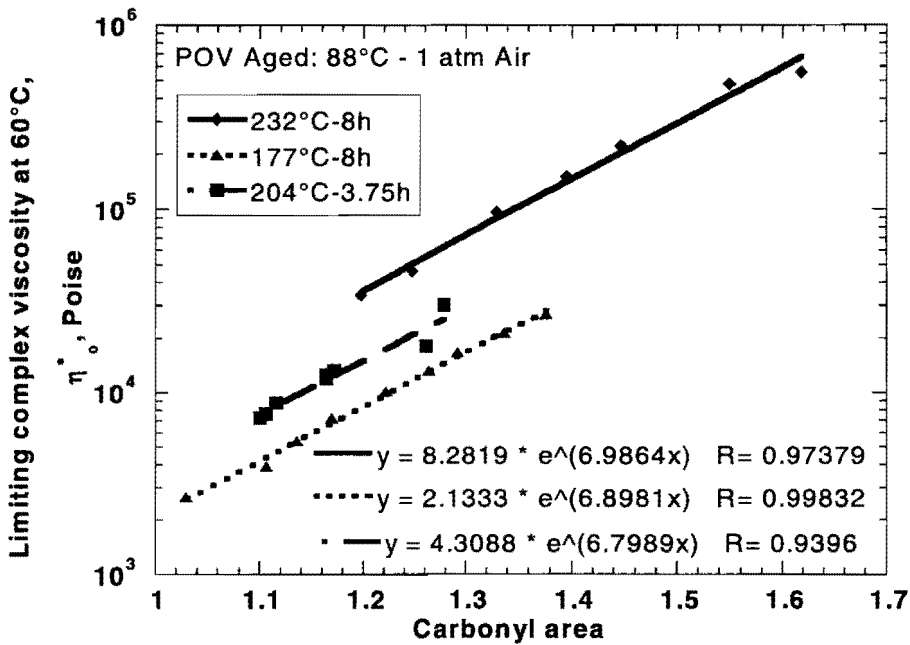


Figure 2-9. HS of Flux I at 88 °C After Air Blowing at Different Temperatures.

**Table 2-4. Low Temperature Hardening Properties  
of Air-Blown Asphalt Fractions and Blends.**

| Material/Blend                     | Air blowing Temperature, °C | Hardening Susceptibility at 1 atm | Oxidation Rate *10 <sup>2</sup> at 88 °C |
|------------------------------------|-----------------------------|-----------------------------------|------------------------------------------|
| 35% Flux I-65% Resin               | Blended                     | 1.73                              | 3.80                                     |
| 45% Flux I-55% Highly Blown Flux I | Blended                     | 6.70                              | 2.00                                     |
| Flux I                             | 177                         | 6.90                              | 1.40                                     |
|                                    | 204                         | 6.80                              | 2.00                                     |
|                                    | 232                         | 6.99                              | 2.30                                     |
| Flux II                            | 177                         | 9.06                              | 1.28                                     |
|                                    | 204                         | 7.04                              | 1.40                                     |
|                                    | 232                         | 7.38                              | 2.54                                     |
| Flux III                           | 177                         | 3.10                              | 0.90                                     |
|                                    | 204                         | 2.78                              | 1.60                                     |
| YB/F Fraction 3                    | 204                         | 3.60                              | 0.84                                     |
|                                    | 232                         | 3.49                              | 1.54                                     |
| YB/F Fraction 2                    | 204                         | 4.55                              | 1.50                                     |
|                                    | 232                         | 4.41                              | 1.48                                     |
|                                    | 246                         | 5.56                              | 1.54                                     |
| SHRP AAA-1 Fraction 2              | 204                         | 9.08                              | 0.80                                     |
|                                    | 232                         | 6.13                              | 1.66                                     |
|                                    | 246                         | 5.73                              | 2.31                                     |
| SHRP AAF-1 Fraction 2              | 204                         | 7.42                              | 1.00                                     |
|                                    | 260                         | 8.65                              | 2.30                                     |
| SHRP AAF-1 Fraction 3              | 204                         | 4.13                              | 1.30                                     |
|                                    | 232                         | 4.55                              | 1.75                                     |
|                                    | 260                         | 3.55                              | 3.40                                     |
| SHRP ABM-1 Fraction 2              | 204                         | 2.30                              | 1.70                                     |
|                                    | 232                         | 2.01                              | 2.50                                     |
|                                    | 260                         | 2.75                              | 2.52                                     |

A plausible explanation for the observed effects of blowing temperature on subsequent low-temperature hardening is as follows. At blowing temperatures somewhat above 100 °C, the reaction mechanism begins to change. As noted earlier, Chaffin et al. (1997) obtained higher HS values from blowing as the temperature increased. This is likely the result of dehydrogenation reactions that enable intermolecular reaction between heavy polar aromatics that produce asphaltenes but do not result in the formation of carbonyl groups. Following air blowing at intermediate temperatures such as during the RTFOT, these reaction sites are created in some abundance and they continue to react at lower oxidation temperatures. This increases the HS but not the oxidation rate and carbonyl formation.

As the air-blowing temperatures increase, the rate of dehydrogenation reactions would increase, but also reactive sites could be produced rapidly in smaller molecules that do not form asphaltenes but do form carbonyl groups during further low-temperature oxidation (Liu et al., 1998). These competing reactions produce erratic effects in the HS but a rapid increase in low-temperature oxidation and hardening with increasing blowing temperature.

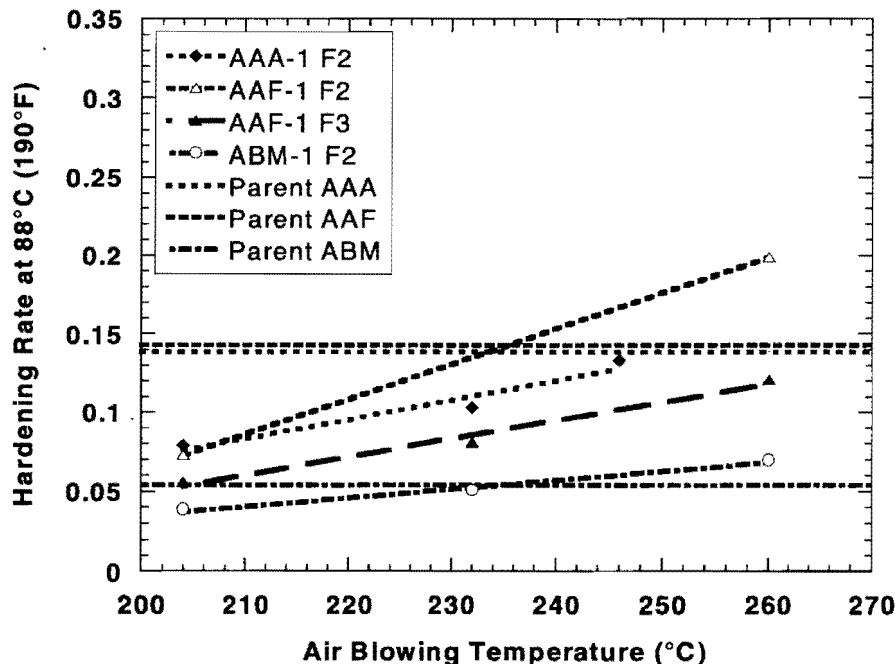
**Table 2-5. Parent Asphalt HS, Oxidation Rate, and HR.**

| Asphalt    | Hardening Susceptibility |        |             |        | $\Gamma_{CA}^*$ | HR at 88°C** |
|------------|--------------------------|--------|-------------|--------|-----------------|--------------|
|            | No RTFOT                 |        | After RTFOT |        |                 |              |
|            | 0.2 atm                  | 20 atm | 0.2 atm     | 20 atm |                 |              |
| SHRP AAA-1 | 6.926                    | 4.6055 | 7.2269      | 5.0641 | 0.02            | 0.139        |
| SHRP AAD-1 | 8.0016                   | 4.2939 | 8.8925      | 4.7224 |                 |              |
| SHRP AAF-1 | 4.4662                   | 3.4604 | 4.6222      | 3.564  | 0.032           | 0.143        |
| SHRP ABM-1 | 1.3523                   | 1.2181 | 1.4094      | 1.1644 | 0.04            | 0.054        |
| SHRP AAM-1 | 4.9115                   | 4.6226 | 5.3386      | 5.0136 |                 |              |
| SHRP AAB-1 | 5.8649                   | 4.1135 | 6.1799      | 4.2461 |                 |              |
| SHRP AAS-1 | 5.3069                   | 4.3839 | 5.4389      | 4.4707 |                 |              |
| TX1        | 5.4527                   | 4.5265 | 6.1436      | 4.1300 |                 |              |
| Lau 4      | 2.9755                   | 2.5083 | 2.9945      | 2.6445 |                 |              |
| TX2        | 7.2392                   | 5.6241 | 8.2966      | 5.7233 |                 |              |

\*Liu et al. (1996)

\*\* Calculated

Figure 2-10 shows how the HR of air-blown asphalt fractions increases with the air-blowing temperature and compares it with HR values obtained for parent materials. For all three materials, when blown at lower air-blowing temperatures, the fractions have a lower HR than the asphalts they were extracted from. As the air blowing temperature is increased, it is possible to produce a material with the same HR as the source material and the material blown at higher temperatures ages even faster than its source.



**Figure 2-10. Air-Blowing Temperature Effect on HR.**

A very interesting aspect of these experiments is a further composition effect, which goes beyond the bulk Corbett analyses. Fraction 2 for each of the three SHRP asphalts compares to each other in the same way as their whole asphalts with respect to HS, oxidation rate, and HR determined at 88 °C and atmospheric pressure:

|          |                   |
|----------|-------------------|
| HS       | AAA-1>AAF-1>ABM-1 |
| $r_{CA}$ | ABM-1>AAF-1>AAA-1 |
| HR       | AAF-1≈AAA-1>ABM-1 |

Thus, the source of the light fraction is a major factor affecting their properties.

Another very interesting comparison is between a 45 percent flux I – 55 percent highly blown flux I blend and flux I blown at 204 °C. The grade as well as HS,  $r_{CA}$  and HR values is almost identical. Blowing part of the light fraction to a high-end viscosity and then mixing back with more light feed produced the same results as blowing entirely light material to the desired viscosity.

The flux I – resin blend and flux III, being low in saturates and asphaltenes (Table 2-4), have good HRs but not good grade spans. There tends to be an inverse relation between good hardening susceptibility and good grade span because of the combined effect of asphaltenes and saturates. This relation is only approximate, however, because of the large variation in maltene properties that are not accounted for by the Corbett analysis. This is evident from the large differences in the effect of the blowing temperature shown in Figure 2-10.

Qualitatively, equation 3 predicts a higher increase in viscosity as more solid particles are added into the suspension. Thus, if the initial concentration of asphaltenes is high, the volume fraction of the solid phase will increase further because of condensation and association reactions. Consequently, there will be an increase in the viscosity, which will be higher for higher asphaltene concentrations. Saturates do not undergo chemical transformations, but they have low solubilizing power with respect to asphaltenes compared to naphthene and polar aromatics. This creates larger asphaltene conglomerates because of higher value of  $K$  in equation 3 and causes material to harden faster as the subsequent oxidation occurs. Thus, the materials with higher concentration of asphaltenes and saturates may have a higher HR.

## CONCLUSIONS –AIR BLOWING

Very good asphalts with respect to Superpave grade and 88 °C HR can be produced by the air-blowing technique. PG as such is not strongly affected by the air-blowing temperature, although there is some deterioration of the low temperature properties when a material is air blown to a constant high-temperature grade. Relaxation properties, represented by the  $m$ -value, tend to limit the low-temperature PG, and this becomes more pronounced for high air-blowing temperatures.

Subsequent HRs and oxidation rates are better for materials air blown at a lower temperature. HS, however, is a more complex function of temperature because it involves other factors whose dependence on process conditions is difficult to determine. The importance of different reaction pathways changes with the air-blowing temperature, and the trend in HS values is determined by the kinetics of several competing reactions. The HR and the oxidation rate at

low temperature increase rapidly with blowing temperature and can be affected by asphalt composition.

A flux having a higher saturate content, compared to one having a low saturate content when both are blown to the same high-temperature PG, generally will have a higher asphaltene concentration and a better Superpave PG span. However, these materials also have a higher HS, meaning that their physical properties may deteriorate faster with subsequent aging. Thus, the optimal combination of PG and hardening properties can be achieved by careful selection of both the flux composition and air-blowing conditions.

## THIN FILM AGING EXPERIMENTS

Samples of Exxon AC-10 asphalt were placed in standard TFOT pans and kept in the thin film oven for different amount of time at 163 °C (325 °F). The thickness of the samples was 0.5, 1, 1.5, 2, 2.5, 3 and 3.5 mm. The goal was to estimate the rate of oxidation (OR) and hardening (HR) as a function of film thickness and determine an approximate amount of time needed to reach the same amount of aging as achieved by the RTFOT procedure. The sample of thickness 3.2 mm takes 5.5 hours in the TFOT to achieve the same amount of aging compared to the RTFOT procedure. Thicker asphalt films present a diffusion barrier to oxygen to penetrate the material and partake in oxidation reactions. Thus, by decreasing the film thickness it is possible to increase the reaction rate and speed up the testing process. However, less material will be produced per test run, and this can make the test more laborious.

Figure 2-11 shows the plot of  $\ln \eta^*_0$  versus aging time. The rate of hardening expressed by the slope of the plot decreases from 0.55 to 0.087 as the film thickness increases. The same pattern is observed for the linear plot of carbonyl area versus aging time (Figure 2-12). The slope of this plot is the oxidation rate and as it can be seen, it is also a function of the film thickness. It is easier for oxygen molecules to diffuse into thin films and react with asphalt components. For thicker films oxidation reactions take place mostly on the surface, with highly reduced rates in the bulk of the material.

Since both  $\ln(\eta^*_0)$  and CA have linear relations with aging time, they are also linear with respect to each other. Figure 2-13 shows this relationship. It should be pointed out that the slopes of the curves defined as hardening susceptibility (HS) do not change significantly with respect to film thickness. Therefore the reaction mechanism does not change and the only contribution to increased oxidation and hardening rates is the improved oxygen diffusion through the bulk of the film.

From linear regression equations reported in Figure 2-11 the amount of time needed to obtain the same aging as in the RTFOT process can be estimated. The target limiting complex viscosity was 1665 P, as obtained after RTFOT. The required time for different thicknesses is summarized in Table 2-6. This is only an estimate that shows approximate times for a possible very thin film alternative to existing tests. As seen from the table, the time required to achieve the same aging as for RTFOT can be as short as 50 minutes.

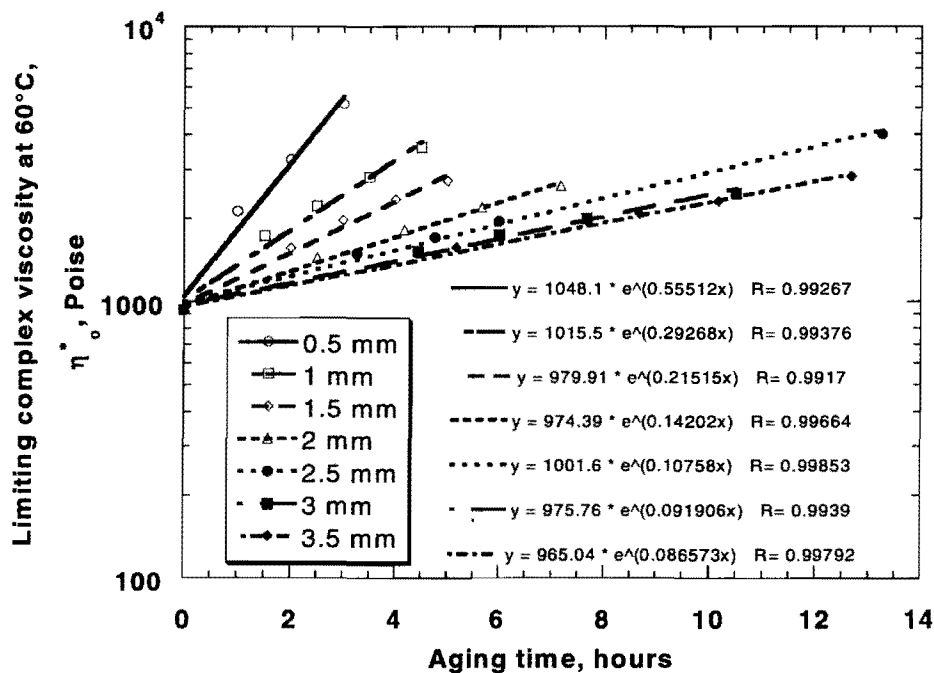


Figure 2-11. Hardening Rate of Exxon AC-10 Films Aged in TFOT Oven at 163 °C (325 °F).

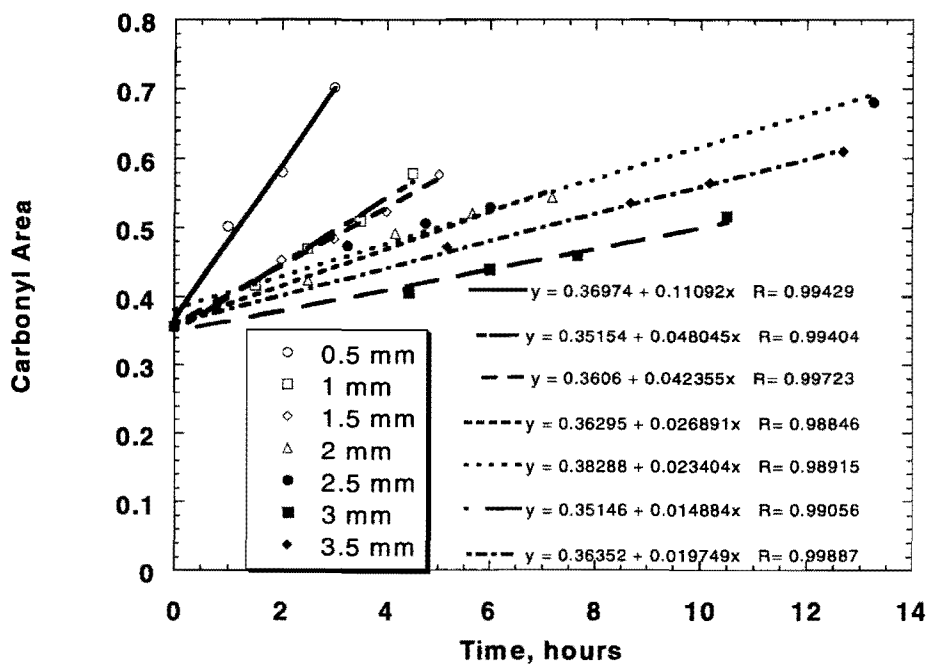
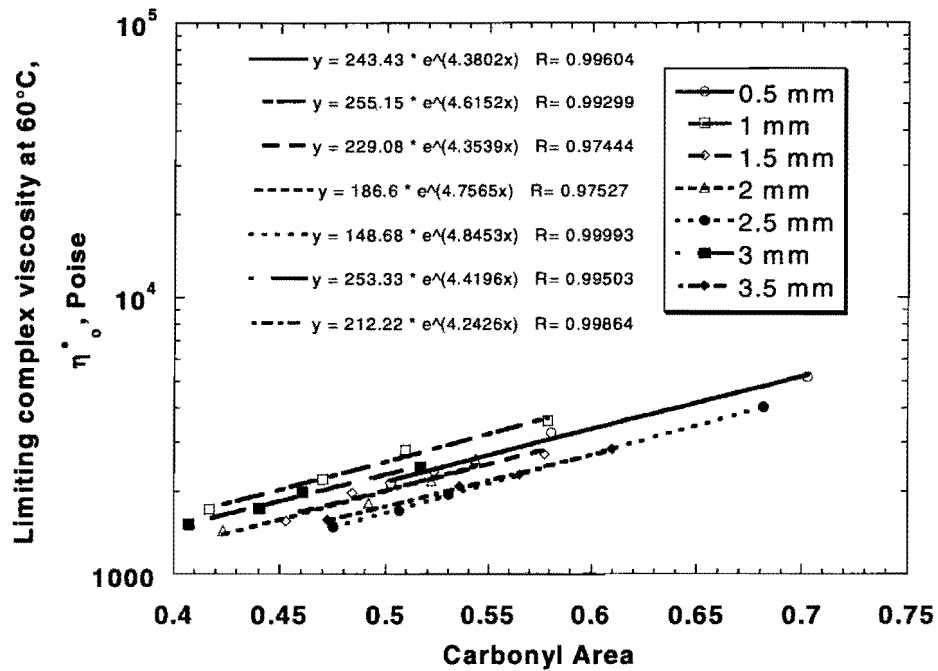


Figure 2-12. Oxidation Rate of Exxon AC-10 Films Aged in TFOT Oven at 163 °C (325 °F).



**Figure 2-13. Hardening Susceptibility of Exxon AC-10 Films Aged in TFOT Oven at 163 °C (325 °F).**

**Table 2-6. Estimated Time Required to Achieve the Same Degree of Aging as RTFOT for Exxon AC-10 Films of Varying Thickness.**

| Film Thickness, mm | Estimated aging time, minutes |
|--------------------|-------------------------------|
| 0.5                | 50                            |
| 1.0                | 100                           |
| 1.5                | 150                           |
| 2.0                | 225                           |
| 2.5                | 280                           |
| 3.0                | 350                           |
| 3.5                | 380                           |

## CONCLUSIONS –FILM AGING

Film thickness does not affect the mechanism of oxidation reactions. By decreasing the thickness of the film it is possible to reduce the diffusion barrier and speed up the reaction. The time necessary to obtain the same effect as the RTFOT aging by the thin film procedure can be reduced to approximately 50 minutes.





## **CHAPTER 3. DEVELOPMENT OF A NEW STIRRED AIR-FLOW TEST (SAFT) PROCEDURE FOR SHORT-TERM AGING OF ASPHALTIC MATERIALS**

### **ABSTRACT**

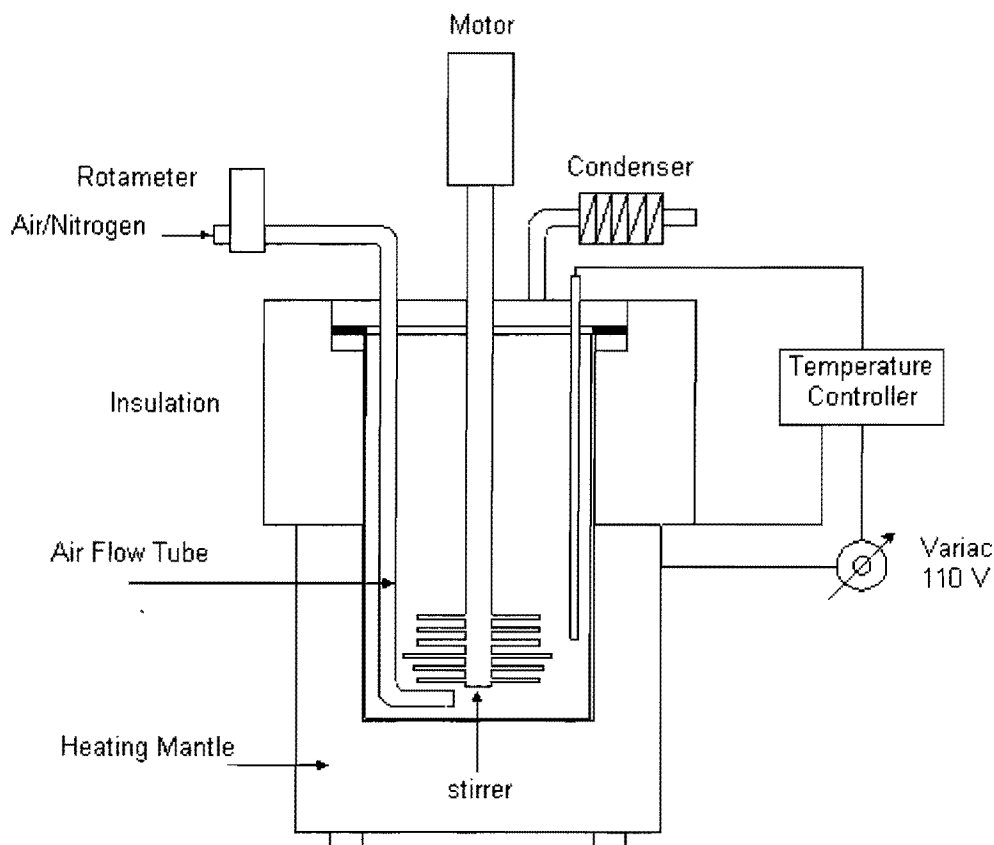
Short-term aging procedures, either the thin-film oven test (TFOT) or the rolling thin film oven test (RTFOT), are used to approximate the aging, which occurs by asphalt binders during the hot-mix process. For unmodified binders, both of these procedures do a reasonable job of duplicating this aging, both with respect to physical property changes in the binder but also with respect to oxidation, as measured by changes in the infrared absorption spectrum. For modified binders, however, significant difficulties exist, among them surface skin formation and poor flow in the bottles.

A new apparatus specifically designed to age modified binders as well as unmodified binders has been developed. This apparatus consists of a temperature-controlled vessel, a tube for introducing either nitrogen or air, a dispersing impeller for mixing the air and binder, and a condenser for collecting volatiles. Besides temperature, gas flow rate and mixing speed are controlled to desired values. The collection of volatiles allows a direct, rather than indirect, measure of volatiles loss. The required aging time of 30 minutes is less than the RTFOT's 85 minutes. Tests of the process with unmodified binders achieve excellent comparisons with RTFOT aging in both physical properties (DSR) and oxidative aging (FTIR). Trials with modified binders achieve uniform aging with no complications caused by the rheology of these materials. Modified binders studied included polymer modified SBR and SBS materials.

### **EXPERIMENTAL DESIGN, MATERIALS, AND METHODS**

The study used an array of modified and unmodified asphalts. Those included SHRP asphalts: AAA-1, AAD-1, AAF-1, AAG-1, AAM-1, AAS-1, ABM-1, and commercially available materials from five suppliers (A, B, C, D, E), A AC-10, A AC-20, B AC-20, C AC-20. Polymer modified materials included D AC-10 with 10 and 18 percent of Rouse ground fine 20 mesh (RSGF-20) tire rubber, 2 percent of styrene butadiene di-block co-polymer (SBR), 3 percent of styrene butadiene tri-block co-polymer (SBS). Another base material was E AC-20 modified with 1 and 3.5 percent of SBR.

Preliminary evaluation of the air-flow technique as a short-term aging method was conducted using the laboratory unit described in Chapter 2. A total of 300 grams of heated material was placed in a 0.946 L (1 qt) can and air-blown with constant agitation by a mixer at 1550 RPM. The air blowing was conducted at 163 °C (325 °F) for 65-80 minutes and air flow rate of 2800 mL/min. TFOT and RTFOT aging procedures were performed on the same array of asphalts and a number of parameters were obtained to characterize the aging effect. A prototype air-blowing apparatus and test procedure were developed based on the results of preliminary studies, which, with minor changes, became the current apparatus shown in Figure 3-1.



**Figure 3-1. SAFT Apparatus.**

This stirred air-flow test (SAFT) aging vessel is constructed from a stainless steel section of pipe 17.8 cm (7 in) long and 9 cm (3.55 in) in diameter. The total capacity of the vessel far exceeds the sample volume in order to avoid the accumulation of sample droplets on the lid of the vessel. The bottom, welded to the column, is made of stainless steel. One neck flange is welded to the upper end of the section of pipe. A stainless steel lid is secured to the flange by three screws. There is a rubber gasket between the vessel and the lid.

A thermocouple and air tube are attached to the lid using the Swagelok fittings. The stirrer is inserted in the vessel through the bronze bushing in the lid. The contact is lubricated periodically to avoid excessive friction. The stirrer is made of a rigid stainless steel rod with 24 rigid pins attached at four angles and six levels from the bottom. This design of the impeller allows good dispersion of air into and mixing with the asphaltic material. The lengths of the pins from the bottom up are different to allow clearance with the thermocouple and air tube. Gas enters the vessel in the center through a single tube below the impeller. A single tube rather than a multiport sparger was chosen to eliminate variability in the process that would be introduced if some sparger ports became plugged while total airflow remained constant.

The prototype and SAFT vessels were equipped with a variable speed 0.1 hp motor capable of 0 to 1000 RPM. An air supply tube was positioned at the bottom of the vessel so that the air enters below the impeller. The apparatus was provided with a flow rate controller capable of accurately supplying the gas flow at a rate of 2000 mL/min at the outlet. The gas was filtered prior to being supplied to the vessel and did not contain water, dust and particulate matter. For determining the amount of hydrocarbon volatiles, an air-cooled condenser was used.

A 500 mL cylindrical heating mantle was used to heat the lower portion of the vessel with insulation covering the upper part. A good fit of the vessel in the heating mantle is required for effective heating and temperature control. In the SAFT apparatus, this was achieved with a removable cylindrical sleeve over the bottom portion of the vessel. A variable transformer supplied power to the heating element.

The vessel was equipped with a proportional control thermostat capable of maintaining 163 °C (325 °F) temperature within  $\pm 0.5$  °C ( $\pm 1.0$  °F). The temperature control sensor was placed 0.76 cm (0.3 in) from the vessel's wall and the end of the thermocouple was submerged 1.27 cm (0.5 in) into the sample. The heating control was capable of bringing the air-flow vessel to the test temperature within 15 minutes of charging the vessel with preheated material at 93.3 °C (200 °F). Nitrogen was admitted during the heating period to prevent oxidation. Temperature control is performed by a thermocouple attached to OMEGA CN9000A Series Miniature Autotune Microprocessor Controller, connected to a variable transformer and heating mantle.

To determine the level of oxidation and aging properties of asphalt binders, several analytical techniques were used. A Mattson 5000 Galaxy Series FT-IR spectrometer was used to collect infrared spectra of asphalt binders. Of particular interest was the change in the absorbance in the region from 1650 to 1820  $\text{cm}^{-1}$ , referred to as the carbonyl band. The concentration of the carbonyl group in asphalt tends to increase proportionally with oxidative aging. The carbonyl area is linearly related to the oxygen content in asphalt binder (Liu et al., 1998). The low shear rate limiting complex viscosity was approximated by measurements at 0.1 rad/s frequency and 60 °C by Carri-Med CSL 500 Controlled Stress Rheometer. Also,  $G''$  at 10 rad/s was measured at 60 °C. Both  $\eta^*_0$  and  $G''$  are quite sensitive to oxidative aging.

To analyze the change in molecular size distribution, a Waters Gel Permeation Chromatography (GPC) system was employed. The system includes a Waters 600E controller/solvent delivery system, a Waters Satellite Autosampler, and a Waters 410 Differential Refractometer. An asphalt sample of approximately 0.2 grams was dissolved in 10 mL of tetrahydrofuran (THF), filtered and placed in a sample vial. THF served as the mobile phase at a flow rate of 1.0 mL/min. A 100- $\mu\text{L}$  sample was injected, separated in accordance to molecular size by flowing through a column packed with 7 mm styrene-divinylbenzene copolymer particles. A plot of refractive index versus retention time provides a molecular size distribution and its change as asphalt is oxidized.

Two traditional test methods besides the chromatography and viscosity measurements were used to compare the materials produced by the air-flow technique with those produced by the standard oven procedures, namely penetration (ASTM D 5-97) and softening point by ring and ball apparatus (ASTM D 36-95).

## **DEVELOPMENT OF IMPROVED HMAC PLANT BINDER AGING SIMULATION**

The process of developing a new aging technique included three main stages: preliminary air-flow testing of the concept using the equipment described in Chapter 2, development of prototype equipment, and equipment evaluation.

### **Stage 1: Preliminary Testing**

The infrared spectra obtained for A AC-10 are shown in Figure 3-2. No significant amount of chemical change is seen by the IR spectra during short-term oxidation. Only a slight

difference was observed in the carbonyl and sulfoxide regions ( $1100\text{ cm}^{-1}$ ). The carbonyl area of the aged materials is slightly bigger than the one of unaged asphalt, though the difference is not very significant. The same was observed for other asphalts tested. Therefore, IR measurement is not a very sensitive test of short-term aging. The comparison of carbonyl areas determined for different asphalts is given in Figure 3-3. The data show that the amount of change in the carbonyl area is similar for the thin film aging methods and the preliminary technique, indicating similar asphalt oxidation mechanisms.

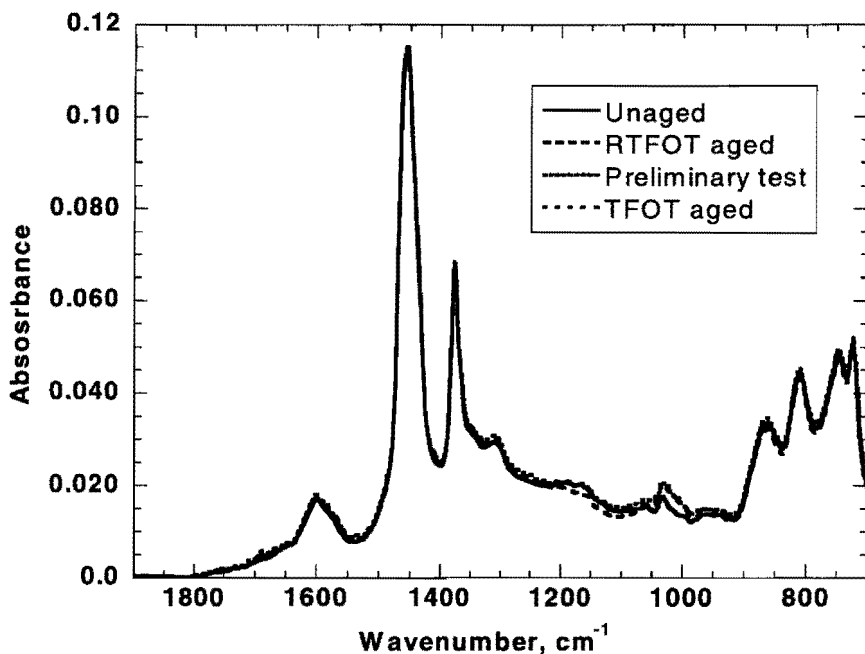


Figure 3-2. IR Spectra of Unaged and Aged A AC-10.

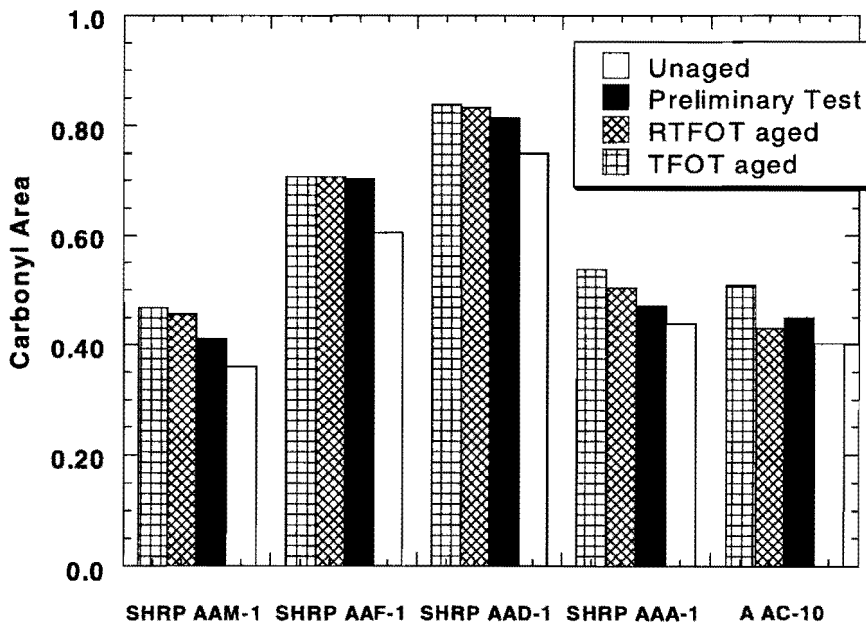


Figure 3-3. Carbonyl Area of Unaged and Aged Asphalts.

Figures 3-4 through 3-7 also summarize the rheological properties, penetration, and softening point ( $T_{R\&B}$ ) results. It demonstrates good agreement of these properties for the different aging techniques. Similar to the carbonyl area, the softening point is not very sensitive to the differences in aging. Rheological data show some difference among the procedures. The biggest difference in the limiting complex viscosity of samples aged by the different methods was observed for SHRP AAF-1 asphalt. However, it should be noted that the viscosity of this unaged asphalt is almost twice as great as the viscosity of other materials. This leads to higher values of viscosity of aged asphalt and its higher sensitivity to aging conditions.

Figure 3-8 shows the GPC chromatogram obtained for aged and unaged A AC-10. The asphalts aged by preliminary method, TFOT, and RTFOT appear to be identical in terms of molecular size distribution. The chromatograms obtained for other asphalts demonstrated similar results. Thus, based on the similar properties of the materials aged by different methods, it is concluded that the oxidation mechanism is essentially the same for each of the aging methods, and it is possible to obtain materials with essentially the same physical and chemical properties using the air-flow technique.

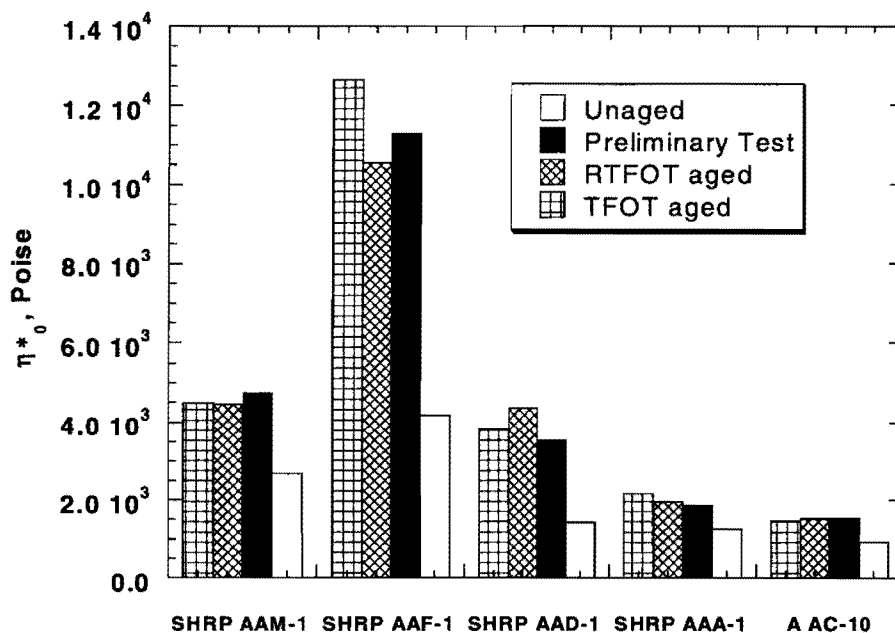


Figure 3-4. Limiting Complex Viscosity at 60 °C and 0.1 rad/sec of Aged and Unaged Asphalts.

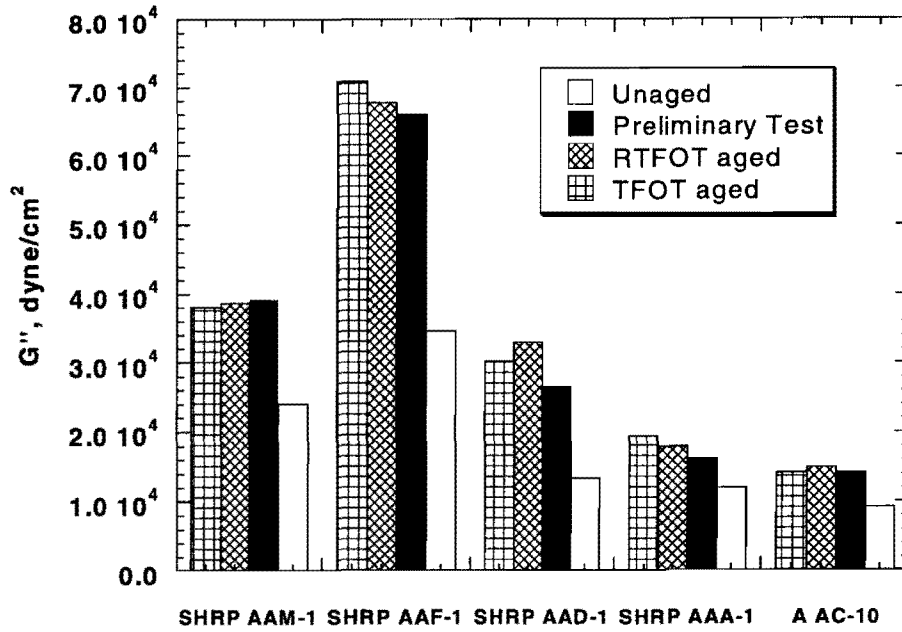


Figure 3-5. Loss Modulus  $G''$  at 60 °C and 10 rad/sec of Aged and Unaged Asphalts.

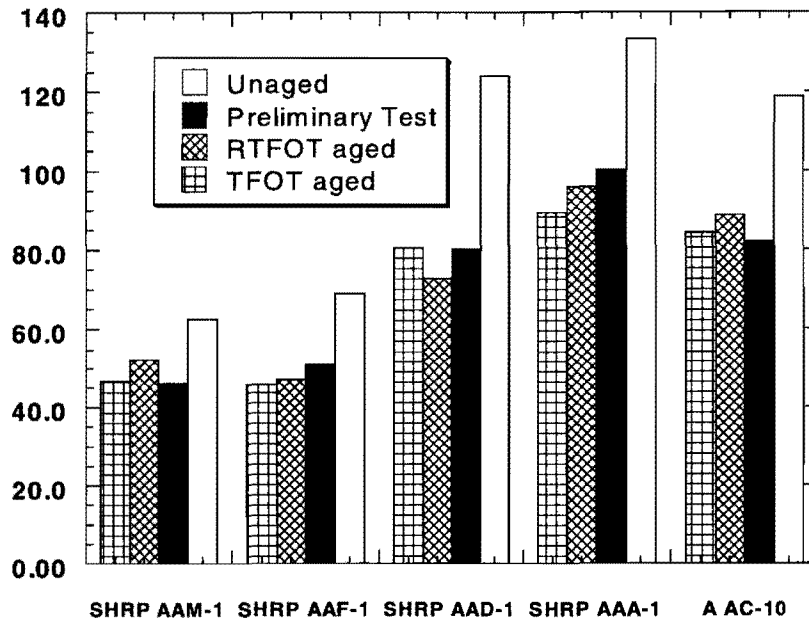


Figure 3-6. Penetration at 25 °C of Aged and Unaged Asphalts.

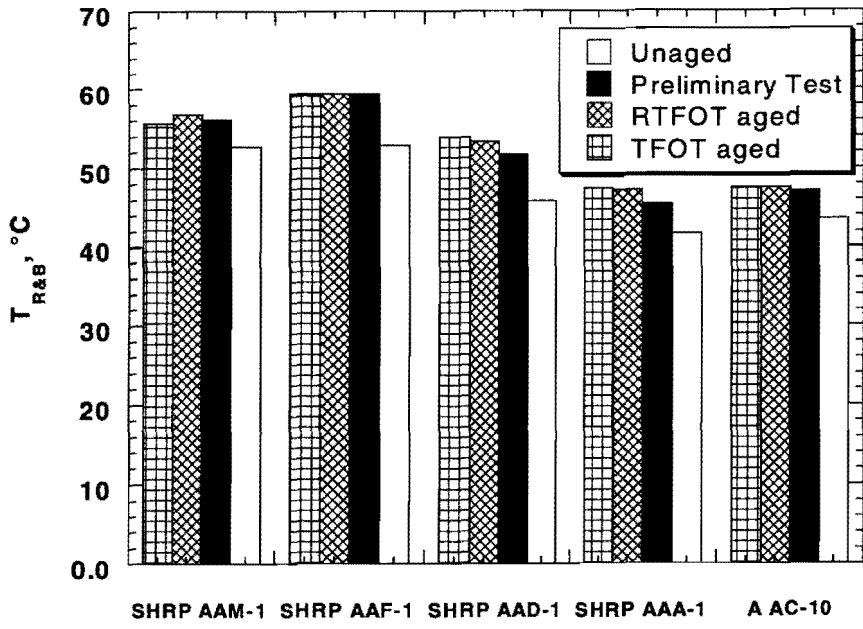


Figure 3-7. Softening Point ( $T_{R\&B}$ ) of Aged and Unaged Asphalts.

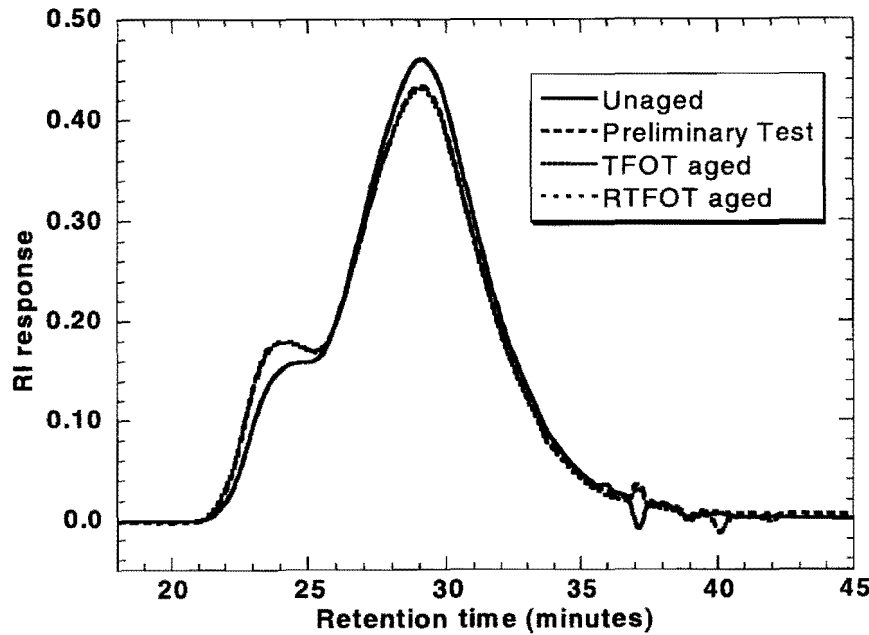


Figure 3-8. GPC Spectra of Unaged and Aged A AC-10.

## Stage 2: Development of Prototype Test Equipment

In the next stage of this project, the prototype testing equipment was built according to a design shown in Figure 3-9. The apparatus included a vessel holding the entire sample of asphalt with a place for air introduction and dispersion. The vessel was covered by a lid with a thermocouple and a condenser attached. It was possible to collect the volatiles, determine their mass, and analyze their GPC chromatogram. The sample mass was chosen to be 250 grams so that the air tube, impeller and thermocouple were covered with asphalt. It was found by experiments that aging was not significantly affected by sample mass in the range of  $\pm 50$  grams. The mixer was used to enhance oxygen-asphalt contact to speed up the oxygen diffusion and, thus, asphalt oxidation rates and also to make the test less sensitive to asphalt viscosity.

The effect of such parameters as air flow rate, speed of the mixer rotation, type of air tube, and type of impeller was investigated in order to select test parameters that optimally represent standard short-term aging procedure and also simulate hot-mix aging. Such factors as equipment maintenance, and cleaning and handling were also taken into consideration.



**Figure 3-9. Assembled SAFT Apparatus (Insulation is not Shown).**



Experiments with various materials were conducted in order to determine the optimal testing conditions (time, airflow rate, temperature control, sample mass and RPM of mixer) and to make possible design corrections. The properties of aged asphalts were evaluated by available analytical techniques such as rheological measurements, GPC, and IR.

### *Design Aspects*

The main design aspects considered while building the prototype apparatus were the type and geometry of air sparger, impeller, condenser, type of insulation, and apparatus height.

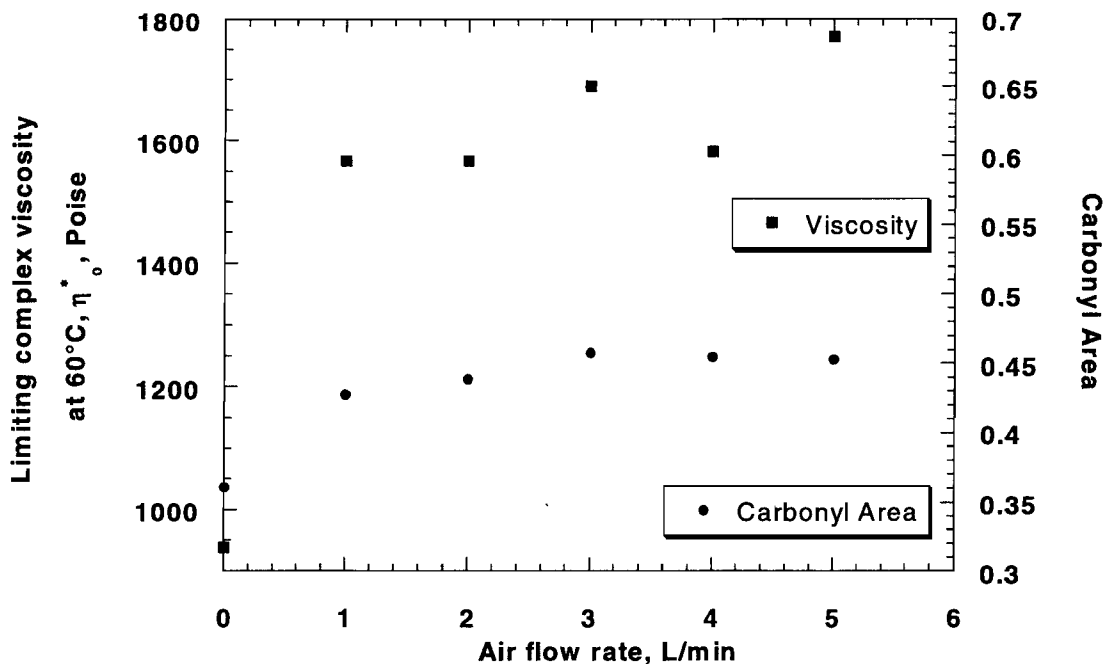
Two types of air spargers were considered. A circular multi-port sparger provided distribution of air across the vessel's perimeter. However, cleaning of this type of sparger was more complicated as clogging with asphalt material during or after the test was a significant probability. Thus, a single-port air tube was chosen with its simple cleaning and fixed position of air entry that allowed better reproducibility of aging results. For the prototype apparatus, the exit of the single-port tube was exactly in the center of the vessel; for the final design, this was moved back as in Figure 3-1 to achieve more efficient air mixing.

Additionally two types of impeller were tested. An impeller that provides both axial and radial flow was rejected in favor of one that acts primarily to disperse the air into the asphalt. The reason for that was to eliminate formation of a film of various thicknesses at the wall that might cause uneven oxidation and, perhaps, temperature distribution in the sample. The impeller had three blades and was supplied with the mixer. The disperser, which has six rows of pins welded to the stainless steel rod, was constructed specifically for this apparatus. The length of pins varied in order to allow enough room for air tube and thermocouple to be inserted into the vessel. Figure 3-1 shows the air tube and disperser final design.

The height of the vessel was chosen to be 17.8 cm (7 in). Only a small part of the container is occupied by the sample during the test so as to avoid the accumulation of asphalt droplets on the lid of the container. This enabled uniform oxidation of the sample and better reproducibility.

### *Effect of Airflow Rate*

Samples of 250 grams of A AC-10 asphalt were aged in the prototype apparatus for 70 minutes with 500 RPM and airflow rate ranging from 1 to 5 L/min using the single port air tube and dispensing impeller. Figure 3-10 shows that both CA and viscosity do not change significantly with airflow rate over this range. An airflow rate of 1 L/min achieved approximately the same level of oxidation as the RTFOT. Standard RTFOT specifies an airflow rate of 4 L/min. However, only a fraction of this air is used for asphalt oxidation, as it flows into the RTFOT bottle only when it passes the air jet, and the air is not blended with the asphalt. An airflow rate of 2 L/min was selected to provide a level that is above a low-level threshold for reliable oxidation and below the level at which asphalt splattering and droplet accumulation occur on the container lid.



**Figure 3-10. Effect of Air Flow Rate on Limiting Complex Viscosity and Carbonyl Area, Prototype Apparatus.**

### *Effect of RPM*

A sample of 250 grams of A AC-10 was used to study the effects of speed of mixer rotation on asphalt short-term aging. The mixer's RPM was varied from 100 to 1000 RPM. The airflow rate was controlled to 3 L/min, and the other test parameters were the same as in previous experiments. Figure 3-11 shows how the final limiting complex viscosity and carbonyl area change with increasing RPM. In the interval from 300 to 800 RPM, neither viscosity nor carbonyl area of the aged asphalt changed significantly. However, at an RPM of 900 and higher, an increase in viscosity and carbonyl area of aged materials was observed.

Table 3-1 summarizes the results of experiments conducted with different sparger types, sample mass, flow rates, and RPM. When needed, a different motor, capable of higher RPM, was used. From this table, it can be inferred that RPM has the strongest effect on aging. For example, increasing the RPM from 880 to 1600 led to an increase of viscosity of aged A AC-10 from 1650 to 3379 P indicating that the asphalt oxidation was a mass-transfer limited process.

Other process parameters have less impact on the oxidation process. These are the types of impeller, air sparger, and the amount of asphalt charge. They produced small effects on asphalt aging. Increasing the airflow rate from 5 to 10 L/min and sample mass from 250 to 350 grams did not produce any significant effect on properties of aged asphalts.

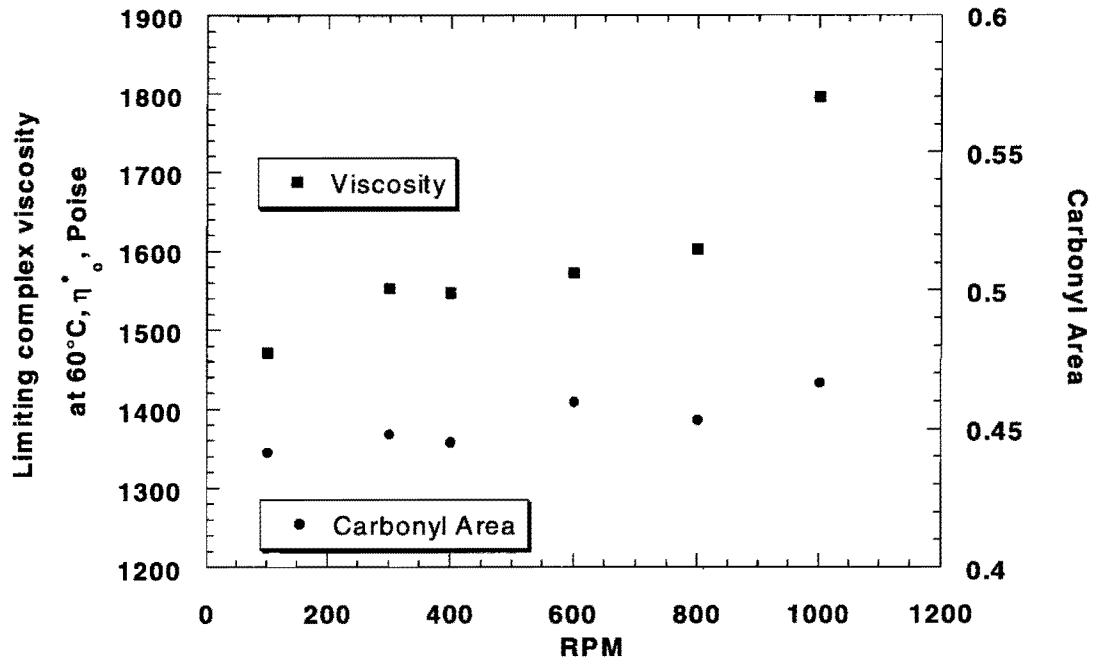


Figure 3-11. Effect of RPM on Limiting Complex Viscosity and Carbonyl Area, Prototype Apparatus.

Table 3-1. Effect of Prototype Apparatus Conditions for A AC-10, 163 °C (325 °F), 70 Minutes Aging.

| Sample mass, g | Sparger type          | Impeller type | Airflow rate, L/min | RPM  | Viscosity, Poise | Carbonyl Area |
|----------------|-----------------------|---------------|---------------------|------|------------------|---------------|
| 250            | Circular, multi-entry | Axial flow    | 3                   | 300  | 1442             | 0.42          |
| 250            | Pipe, single entry    | Axial flow    | 3                   | 700  | 1744             | 0.46          |
| 250            | Pipe, single entry    | Dispenser     | 3                   | 700  | 1685             | 0.45          |
| 410            | Pipe, single entry    | Dispenser     | 5                   | 1000 | 1735             | 0.47          |
| 350            | Pipe, single entry    | Dispenser     | 5                   | 880  | 1650             | 0.44          |
| 350            | Circular, multi-entry | Dispenser     | 5                   | 880  | 2039             | 0.47          |
| 350            | Pipe, single entry    | Dispenser     | 5                   | 1600 | 3379             | 0.63          |
| 350            | Pipe, single entry    | Dispenser     | 10                  | 1600 | 3379             | 0.60          |
| 250            | Pipe, single entry    | Dispenser     | 10                  | 1600 | 3340             | 0.66          |

As a result of these experiments, test parameters were established. The test temperature was kept at 163 °C (325 °F), the same as for thin film tests. The airflow rate was selected as 2 L/min, necessary to provide enough oxygen for asphalt oxidation, but not too high to cause splattering and accumulation of asphalt droplets on the lid of the air-blowing vessel. Mixing at 700 RPM was selected as sufficient to ensure good air dispersion and provide enough agitation for uniform oxidation and temperature distribution while staying in the region of low sensitivity to RPM variation. The single port air tube was selected and slightly redesigned so that air enters the sample not exactly in the middle of container but slightly displaced in a radial direction (SAFT apparatus, Figure 3-1). This enabled better air entrapment by the dispersing impeller and led to better surface contact. This redesign allowed reducing the time of oxidation to 30 minutes to provide the same degree of aging as RTFOT.

*Condensation of Volatile Compounds*

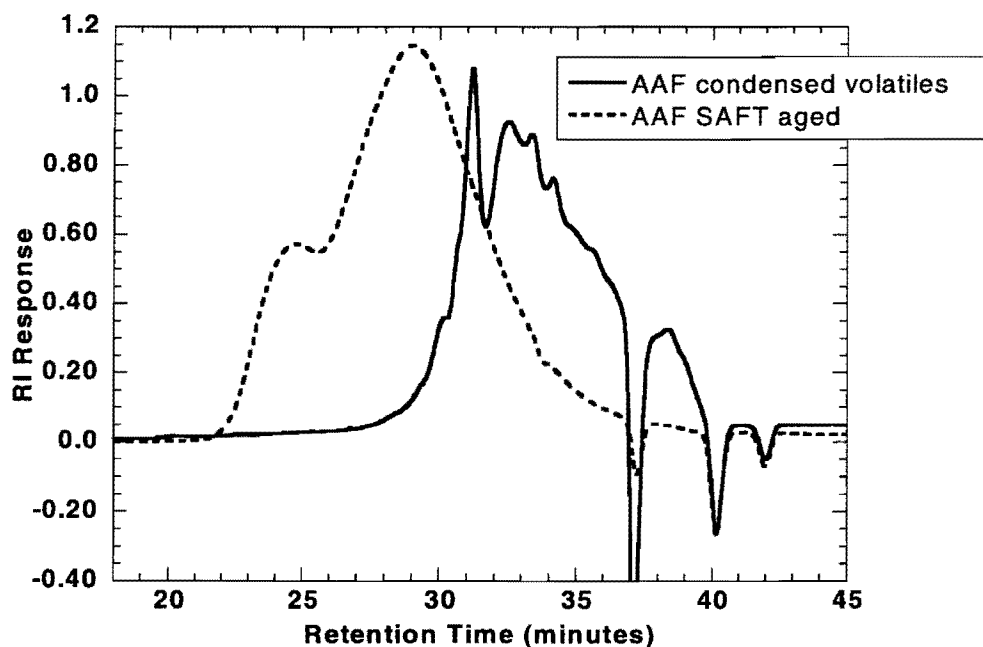
While conducting the experiments, the volatiles were condensed by a copper coil attached to the vessel. The percent of volatiles was measured, and their chemical composition was analyzed by the GPC method. Table 3-2 shows the comparison between the amount of volatiles condensed while air-blowing various asphalts and their RTFOT mass change as determined from running the standard or taken from SHRP Materials Reference Library (1993). Obviously, there is no agreement between the two aging methods. The reason is that RTFOT mass change indicates the mass loss of volatiles and the increase due to oxidation. Thus, the RTFOT mass change can be positive or negative depending on which phenomenon dominates for each particular asphalt. In contrast, volatiles condensation is a direct measurement, and the result is independent of mass increase. Additionally, the mass change measurement is subject to high experimental error as the difference between two large numbers is required.

**Table 3-2. Condensed Volatiles and RTFOT Mass Change, Prototype Apparatus.**

| Asphalt    | Condensed volatiles, wt. % | RTFO/Reference Library, wt. % |
|------------|----------------------------|-------------------------------|
| A AC-10    | 0.013                      | +0.057                        |
| A AC-20    | 0.043                      | N/A                           |
| SHRP AAA-1 | 0.027                      | -0.312                        |
| SHRP AAF-1 | 0.045                      | -0.092                        |
| SHRP AAM-1 | 0.014                      | +0.052                        |
| SHRP AAS-1 | 0.031                      | -0.039                        |
| SHRP AAD-1 | 0.051                      | -0.810                        |
| SHRP ABM-1 | 0.035                      | -0.248                        |
| SHRP AAG-1 | 0.051                      | -0.180                        |
| C AC-20    | 0.032                      | -0.400                        |
| B AC-20    | 0.018                      | +0.057                        |

Although the results of this experiment do not agree with the RTFOT mass loss, it is believed that this test adequately represents the amount of light material that asphalts may contain and is not sensitive to the ability of the material to react with oxygen.

GPC studies were performed on condensed volatile compounds. Figure 3-12 shows an example of a chromatogram of SHRP AAF-1 asphalt aged by the prototype technique and its volatiles condensed in a copper coil. Obviously, the condensed matter has a much lower average molecular weight, as indicated by a longer retention time. It consists mostly of aliphatic hydrocarbons. All condensed volatiles are light brown in color, which indicates light naphthene aromatics.



**Figure 3-12. GPC Spectra of Aged SHRP AAF-1 and Condensed Volatiles, Prototype Apparatus.**

### Stage 3: Test Verification

The SAFT apparatus (Figure 3-1) using the parameters discussed in previous sections (2 L/min airflow, 700 RPM, 30 minutes aging, 250 grams sample) was repeated on nine unmodified and six polymer modified asphalts. The results presented in Figures 3-13 and 3-14 indicate that the new method can well represent the RTFOT in terms of  $\eta^*_0$  for unmodified asphalt and  $\eta^*$  determined at 1 rad/s for modified materials. There is no perfect reproduction of asphalt properties for both tests. However, there is no indication that one test is more severe than the other. Jemison et al. (1991) obtained a similar degree of scatter while comparing TFOT and RTFOT techniques.

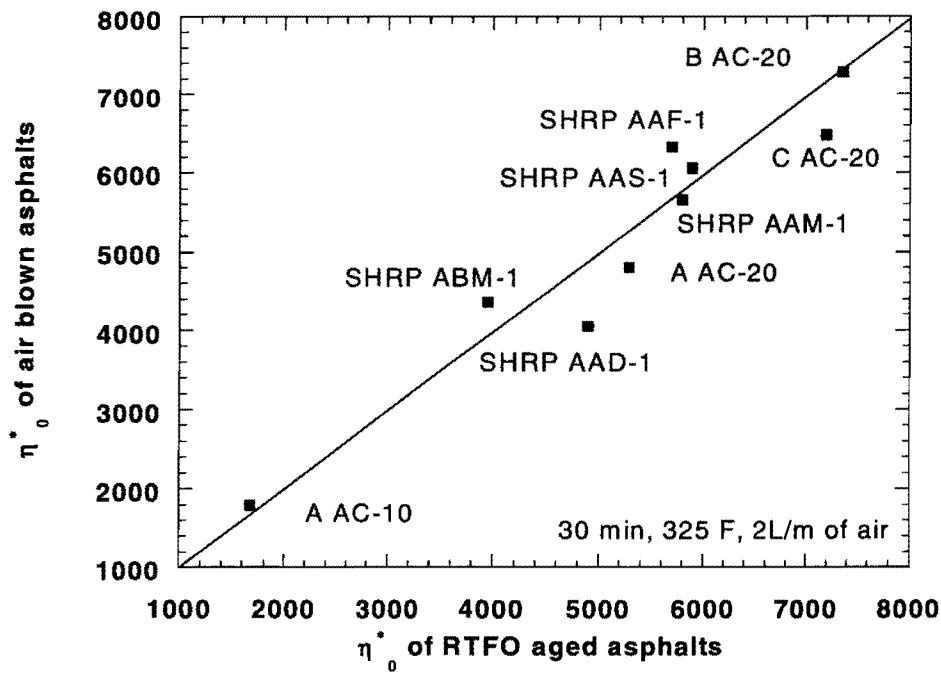


Figure 3-13. Comparison of Viscosity of RTFOT and SAFT Aged Unmodified Asphalts, SAFT Procedure.

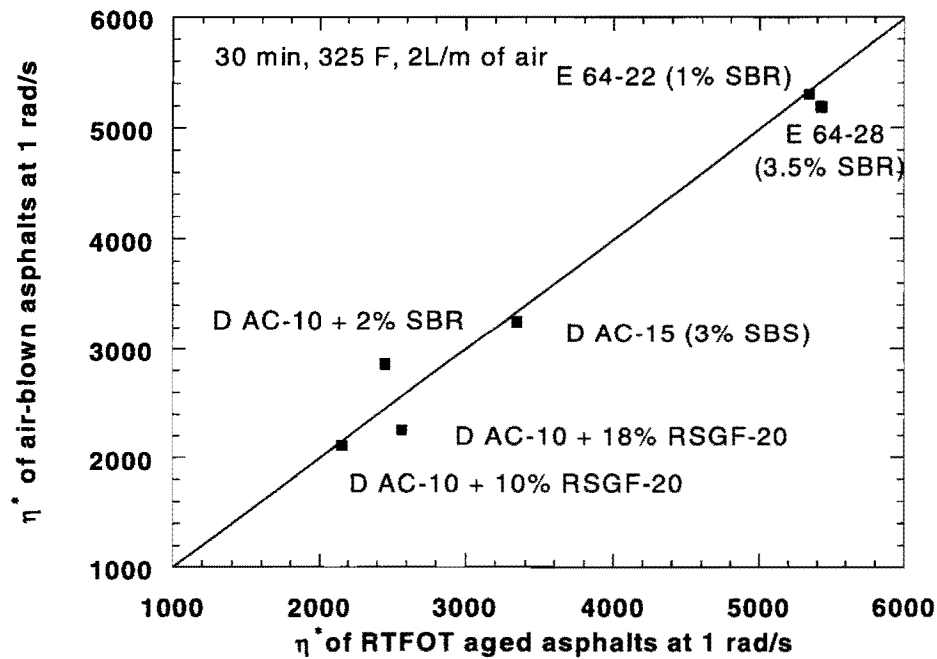


Figure 3-14. Comparison of Viscosity of RTFOT and SAFT Aged Modified Asphalts, SAFT Procedure.

Two asphalts were tested 10 times each on 5 SAFT units to evaluate test reproducibility. The results are summarized in Table 3-3. Overall, they show good reproducibility for the viscosity, but worse results for the amount of condensed volatiles. The reason for that might be the uneven heating across the height of the vessel. This leads to possible condensation of volatiles on the lid, which is colder than the temperature of the asphalt inside the vessel (163 °C). The solution for that would be to use the heating mantle that repeats the shape of the vessel and allows heating of its upper portion. Also, several tests were conducted using water-cooled condenser and liquid N<sub>2</sub> trap to be sure of condensing all volatiles. The results did not demonstrate a difference in the amount of volatiles condensed by those methods and by air-cooled coil.

**Table 3-3. Reproducibility Analysis, SAFT Apparatus.**

|                                        | A AC-10        |                          | SHRP AAF-1     |                          |
|----------------------------------------|----------------|--------------------------|----------------|--------------------------|
|                                        | Viscosity, P/% | Condensed Volatiles, g/% | Viscosity, P/% | Condensed Volatiles, g/% |
| Mean                                   | 4880           | 0.033                    | 5340           | 0.023                    |
| Standard Deviation                     | 195.3/4.0      | 0.013/39                 | 317.2/5.9      | 0.0072/31                |
| Difference between maximum and minimum | 560/11.5       | 0.0431/131               | 1170/21.9      | 0.0242/105               |

## CONCLUSIONS

The main conclusion that can be deduced from these results is that the SAFT technique duplicates the material produced by the RTFOT. Very good agreement between several aging techniques was obtained in terms of penetration, softening point, visco-elastic properties, and chemical composition as determined by FTIR and GPC. The SAFT was verified on a number of unmodified and modified asphalts, and it was found to reproduce RTFOT aging quite well. Therefore, the new test is recommended as a new procedure to simulate hot-mix asphalt aging.

Constant agitation of the material by the mixer prevents film formation and enhances air diffusion through the bulk of asphalt. The time required to achieve the same extent of aging as the RTFOT is 30 minutes. Together with the 15 minutes necessary for the vessel's warm-up, it is 40 minutes shorter than the total time specified by the RTFOT. In addition to these advantages, the suggested method controls the sample temperature directly, provides for collecting volatile compounds, and uses a single, easy to clean reusable container. Potentially lower equipment costs and decreased handling of hot equipment also should be noted.





## **CHAPTER 4. STIRRED AIR-FLOW TEST INSTALLATION PROCEDURE AND DRAFT ASTM AND TXDOT TEST STANDARD PROCEDURES**

This chapter contains test installation procedure and draft specifications written in both ASTM and TxDOT format.

### **STIRRED AIR-FLOW TEST APPARATUS INSTALLATION PROCEDURE**

#### **Purpose of the Test**

The purpose of this test is to measure the effect of heat and air on a bulk of semi-solid asphaltic material. The effects of this treatment are determined from measurements of the selected properties of the asphalt before and after the test. This method indicates approximate change in properties of asphalt during conventional hot-mixing at about 150 °C (302 °F) as indicated by viscosity measurements. Penetration, or ductility measurements may also be made if desired. It yields a residue, which approximates the asphalt condition as incorporated in the pavement. If the mixing temperature differs appreciably from the 150 °C (302 °F) level, more or less effect on properties will occur.

#### **Summary of Test Method**

Air is bubbled through a sample of asphaltic material, which is heated in a cylinder for 75 minutes at 163 °C (325 °F). The mixing of air and asphaltic material is provided by agitation with an inserted impeller. The effect of heat and air are determined from changes in physical test values as measured before and after the air-blowing treatment. An optional procedure is provided for determining the change in sample mass.

#### **Apparatus**

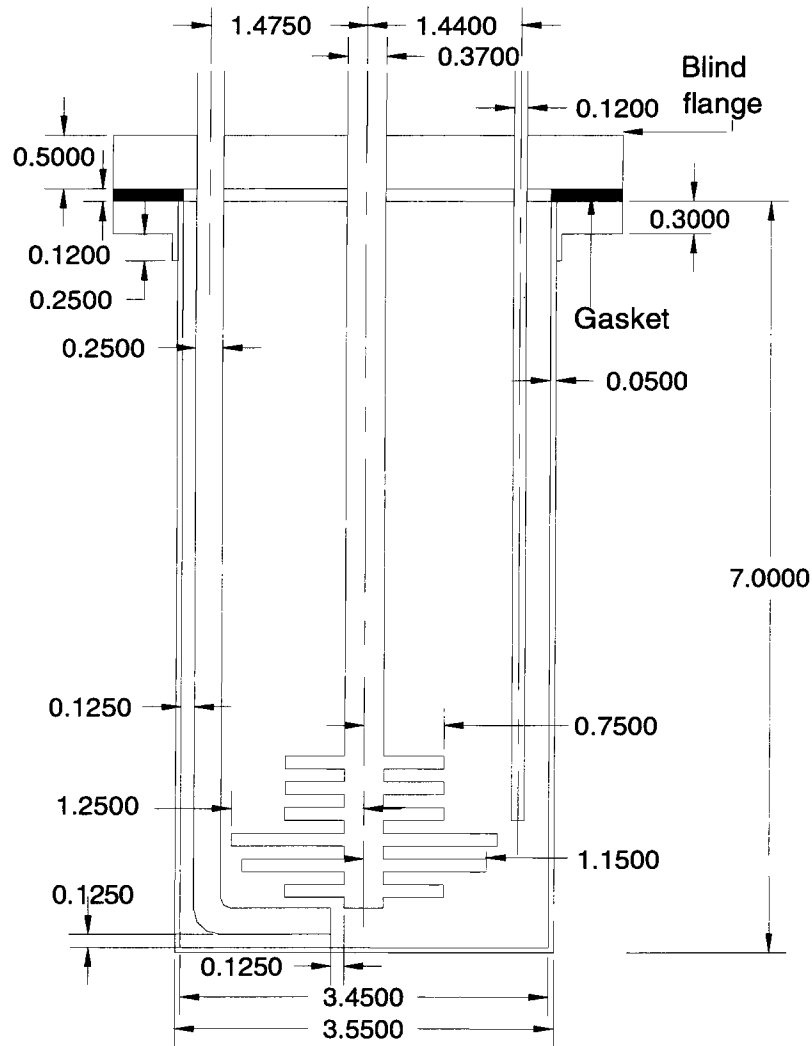
##### *SAFT Vessel*

The SAFT vessel is shown in Figure 4-1. It is constructed from a stainless steel section of pipe 7 inches (17.8 cm) long and 3.55 inches (9 cm) in diameter. The total capacity of the vessel far exceeds the sample volume in order to avoid the accumulation of sample droplets on the lid of the vessel. The bottom, welded to the column is made of stainless steel. One neck flange is welded to the upper end of the section of pipe. A stainless steel lid is secured to the flange by three screws. There is a rubber gasket between the vessel and the lid.

The lid is shown in Figure 4-2. A thermocouple and air tube pass through and are attached to the lid using the Swagelok fittings. The stirrer is inserted into the vessel through the bronze bushing in the lid. The contact should be lubricated periodically to avoid excessive friction. The stirrer is made of rigid stainless steel rod with six pins attached at the bottom. This design of the impeller allows good dispersion of air into and mixing with the asphaltic material. The length of pins varies to allow the optimal placement of the thermocouple and air tube. Gas enters the vessel in the center below the impeller.

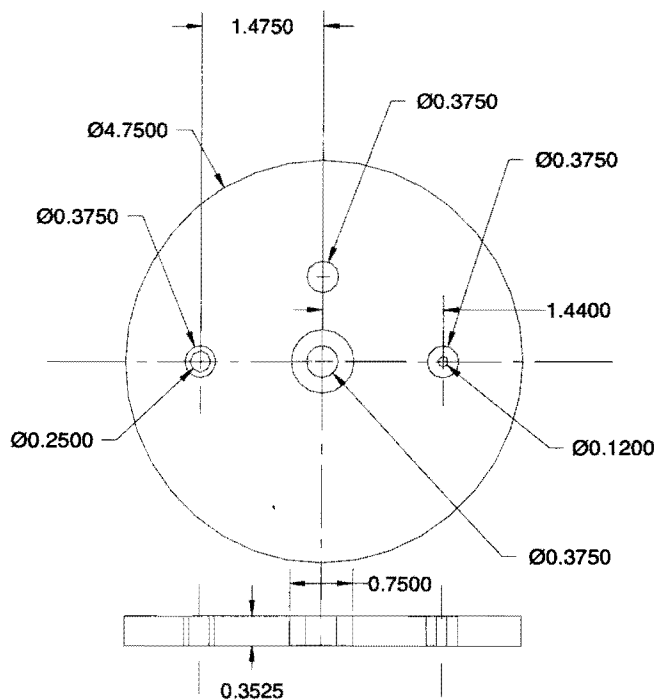
The heating of the sample is done by placing the vessel in a heating mantle. A 500 mL cylindrical heating mantle is used to heat the lower portion of the vessel with insulation covering the upper part. A good fit of the vessel in the heating mantle is required for effective heating and

temperature control. In the prototype apparatus, this is achieved with a removable cylindrical sleeve over the bottom portion of the vessel. A variable transformer supplies power to the heating element.



**Figure 4-1. SAFT Vessel.**

The vessel is equipped with a proportional control thermostat capable of maintaining 163 °C (325 °F) temperature within  $\pm 0.5$  °C ( $\pm 1.0$  °F). The temperature control sensor is placed 0.76 cm (0.3 inch) from the vessel's wall and the end of the thermocouple is submerged 1.27 cm (0.5 inch) into the sample. The heating control is capable of bringing the fully charged air-flow vessel to the test temperature within a 15-minute period after inserting the vessel containing the sample preheated up to 93.3 °C (200 °F). Nitrogen shall be admitted during the heating period.



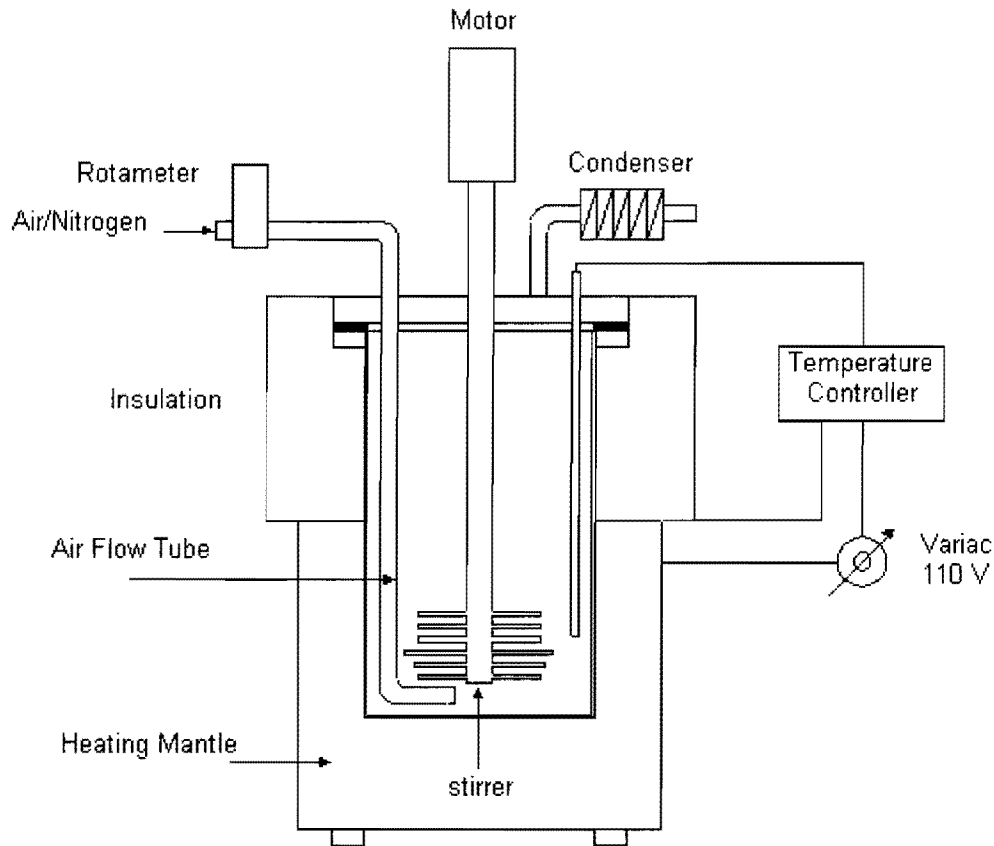
**Figure 4-2. Lid.**

The vessel is equipped with a variable speed 0.1 hp motor capable of 0 to 1000 RPM. The air supply tube is positioned at the bottom of the vessel so that the air enters below the impeller. The apparatus is provided with a flow-rate controller capable of accurately measuring the gas flow at a rate of 2000 mL/min at the outlet. The gas shall be filtered prior to being supplied to the vessel to remove water, dust and particulate matter. For determining the amount of hydrocarbon volatiles, the air-cooled condenser can be used. It is a copper coil 0.635 cm (1/4 inches) in diameter.

### **Apparatus Setup and Installation**

The overall test setup is shown in Figure 4-3. Filtered and dried air or a nitrogen supply is attached to the air tube through the rotameter. The tube, impeller, and thermocouple are attached to the lid and inserted into the vessel prior to beginning the test. The lid is attached to the vessel by three screws, and the impeller is attached to the mixer's shaft by two setscrews. The mixer is supported by the lab stand and is aligned vertically with the air-blowing vessel. Copper coil can be used for collecting the hydrocarbon volatiles; it is attached to the lid immediately before the beginning of the test.

Temperature control is performed by a thermocouple attached to OMEGA CN9000A Series Miniature Autotune Microprocessor Controller, connected to a variable transformer and heating mantle. The controller is designed for accurate, precise temperature control and is capable of PID (Proportional-Integral-Derivative) or Autotune PID with approach control (PDPI) for optimal control during start-up and steady-state operation. PDPI control enables the unit to suppress overshoot and allows the process warm-up to be tuned independently from the steady-state operating conditions.



**Figure 4-3. SAFT Apparatus.**

### *Installation*

Supply air must be filtered and dried for the air-flow aging test. A supply of nitrogen is also recommended. It can be connected to the same supply line and either air or nitrogen can be used when desired. Assembly is as follows:

1. Connect the rotameter to the air/nitrogen supply. Tygon tubing is recommended for connecting the air line to the sparger.
2. Attach the heating mantle to the lab stand using the screw on the mantle.
3. Connect the variac, controller and heating mantle according to the marks on the plugs. The variac and the controller are powered by 110 AC.
4. Attach the mixer to the lab stand using the clamps provided.
5. Check that the mixer, thermostat, and heating mantle are properly working.
6. Start the test as described in the test procedure.

# TEST METHOD FOR EFFECT OF HEAT AND AIR ON ASPHALTIC MATERIALS BY STIRRED AIR-FLOW TEST (SAFT)

## 1. Scope

- 1.1 The purpose of this test is to measure the effect of heat and air on a bulk of semi-solid asphaltic material. The effects of this treatment are determined from measurements of the selected properties of the asphalt before and after the test.
- 1.2 The values stated in inch-pound units are to be regarded as the standard.
- 1.3 *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 standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Reference Document

- 2.1 ASTM Standard:
  - D 113 Test Method for Ductility of Bituminous Materials.
  - D 2171 Test Method for Viscosity of Asphalts by Vacuum Capillary Viscometer.

## 3. Summary of Test Method

- 3.1 Air is bubbled through a sample of asphaltic material, which is heated in a cylinder for 30 minutes at 163 °C (325 °F). The mixing of air and asphaltic material is provided by agitation with an inserted impeller. The effect of heat and air are determined from changes in physical test values as measured before and after the air-blowing treatment. An optional procedure is provided for directly determining the mass of volatile loss.
- 3.2 Precision values for this test method have been adopted for dynamic low share rate limiting viscosity at 60 °C (140 °F).

## 4. Significance and Use

- 4.1 This method indicates approximate change in properties of asphalt during conventional hot-mixing at about 150 °C (302 °F) as indicated by viscosity measurements. Penetration, or ductility measurements, may also be made if desired. It yields a residue, which approximates the asphalt condition as incorporated in the pavement. If the mixing temperature differs appreciably from the 150 °C (302 °F) level, more or less effect on properties will occur.

## 5. Apparatus

- 5.1 *Aging vessel* - The air-flow aging vessel is constructed from a stainless steel section of pipe 17.8 cm (7 inches) long and 9 cm (3.55 inches) in diameter. The total capacity of the vessel far exceeds the sample volume in order to avoid the accumulation of sample droplets on the lid of the vessel. The bottom, welded to the column, is made of stainless steel. One neck flange is welded to the upper end of the section of pipe. A

stainless steel lid is secured to the flange by three screws. There is a rubber gasket between the vessel and the lid.

- 5.2 A thermocouple and air tube pass through and are attached to the lid using the Swagelok fittings. The stirrer is inserted in the vessel through the bronze bushing in the lid. The contact should be lubricated periodically to avoid the excessive friction. The stirrer is made of rigid stainless steel rod with six pins attached at the bottom. This design of the impeller allows good dispersion of air into and mixing with the asphaltic material. The length of pins varies to allow the optimal placement of the thermocouple and air tube. Gas enters the vessel in the center below the impeller.
- 5.3 The heating of the sample shall be done by placing the vessel in a heating mantle. A 500 mL cylindrical heating mantle shall be used to heat the lower portion of the vessel with insulation covering the upper part. A good fit of the vessel in the heating mantle is required for effective heating and temperature control. In the prototype apparatus, this is achieved with a removable cylindrical sleeve over the bottom portion of the vessel. A variable transformer supplies power to the heating element.
- 5.4 The vessel shall be equipped with a proportional control thermostat capable of maintaining 163 °C (325 °F) temperature within  $\pm 0.5$  °C ( $\pm 1.0$  °F). The temperature control sensor shall be placed 0.76 cm (0.3 inch) from the vessel's wall and the end of the thermocouple shall be submerged 1.27 cm (0.5 inch) into the sample. The heating controls shall be capable of bringing the fully charged air-blowing vessel to the test temperature within a 15-minute period after inserting the vessel containing the sample preheated up to 93.3 °C (200 °F). Nitrogen shall be admitted during the heating period.
- 5.5 The vessel shall be equipped with a variable speed 0.1 hp motor capable of 0 to 1000 RPM.
- 5.6 The air supply tube shall be positioned at the bottom of the vessel so that the air enters below the impeller. The apparatus shall be provided with a flow-rate controller capable of accurately measuring the gas flow at a rate of 2000 mL/min at the outlet. The gas shall be filtered prior to being supplied to the vessel to remove water, dust, and particulate matter.
- 5.7 For determining the amount of hydrocarbon volatiles, the air-cooled condenser shall be used. It is a copper coil 0.635 cm (0.25 inch) in diameter.

## **6. Preparation of the Vessel**

- 6.1 The vessel, the condenser, and the lid should be cleaned of any asphalt residues left from the previous test run and shall be carefully dried of the solvent used for cleaning.
- 6.2 The thermocouple, air tube, and impeller shall be attached to the lid. The tube is secured so that the air escapes at the center of the vessel.
- 6.3 Level the heating mantle and align the air-flow vessel to be upright in the mantle.

## 7. Procedure

- 7.1 The samples as received shall be free of water. Heat the sample in its container with a loosely fitted cover in an oven at a temperature not exceeding 150 °C (302 °F) for the minimum time necessary to ensure that the sample is completely fluid. The temperature of the sample should be approximately 93 °C (200 °F). It is suggested to supply nitrogen to the container to minimize the oxidation of the sample. After the sample is fluid, manually stir it, but avoid incorporating air bubbles.
- 7.2 Pour  $250 \pm 1.0$  grams of the sample into the air-flow vessel. It shall provide sufficient material for characterizing tests, which are to be run on the residue.
- 7.3 Place the gasket between the lid and the vessel; close the vessel by tightening the three screws, and insert the vessel into the heating mantle. Attach the impeller shaft to the mixer by tightening the two setscrews. Level the mixer so that there is a gap of 1-2 mm between the stop on the impeller's rod and the lid.
- 7.4 If the amount of volatiles is to be determined, attach the condenser to the Swagelok fitting in the lid.
- 7.5 Connect the thermocouple to the temperature controller and turn on the variac to 80 percent of its total output. Place fiberglass insulation around the top part of the vessel.
- 7.6 Start the mixer by increasing its RPM from 0 to 700.
- 7.7 Connect the air (nitrogen) line to the vessel. It is advisable to bubble nitrogen through the sample while the test temperature is being reached. By doing so, premature oxidation of material can be eliminated. This will provide better test reproducibility. Set the nitrogen flow rate to 4000 mL/min.
- 7.8 When the temperature reaches 160 °C (320°F), change from nitrogen to air or turn on the air if nitrogen is not used. The air flow rate shall be 2000 mL/min and the RPM shall be equal to 700. Start timing at this point. Maintain the process for 30 minutes. The test temperature  $163 \pm 0.5$  °C ( $325 \pm 1$  °F) shall be reached within the first 10 minutes; otherwise, discontinue the test. At the conclusion of the testing period, turn off the air; disconnect the air supply line, the condenser coil, and the impeller. Open the vessel, remove it from the mantle, and immediately pour all the residue, without scraping, into a container large enough that it is not over 75 percent full (e.g., a pint can). Do not let the container cool nor should the vessel be reheated to obtain more residue.
- 7.9 Test the residue within 72 hours of performing the air-flow aging test.
- 7.10 If the amount of volatile hydrocarbons is to be determined, pour 20-30 mL of heptane into the condenser coil using a squeeze bottle. Apply light pressure by attaching the air supply line to one end of the coil to remove the solvent. Collect the solution in a

pre-weighed 100 mL beaker. Repeat these steps until clean solvent starts flowing. If the solution is quite dark, it indicates that some asphalt material was trapped in the condenser. The test results should be disregarded in this case. After the bulk of solvent has evaporated, the beaker shall be placed on a warm hot plate for 20 minutes until the collected volatiles are free of the solvent. The beaker is weighed once again to determine the mass of the condensed volatiles. Other analytical tests (e.g., GPC) may be performed.

## **8. Report**

- 8.1 Report the results of the stirred air-flow test in terms of the physical changes in the asphalt brought about by the method. These values are obtained by performing appropriate ASTM tests to the asphalt before and after the air-flow oxidation procedure.



# TXDOT MANUAL OF STIRRED AIR-FLOW TEST (SAFT) PROCEDURE FOR ASPHALT BINDERS

## Overview

This procedure describes the Stirred Air-Flow Test (SAFT), which is used to simulate the short-term aging of asphalt binders that occurs during the hot-mix process. This test may be used to calculate the mass of evaporated volatiles, but its main function is to produce an aged material that may be analyzed by other suitable means.

## Apparatus

The following equipment is needed to perform this test:

- SAFT apparatus with the stirrer, mixer, air tube, aging vessel, thermocouple, heating mantle, temperature controller, variable transformer, and volatile condenser as specified in suggested ASTM test draft;
- supply of filtered, dry air, and nitrogen or other inert gas;
- balance;
- metal clamps to hold and carry hot aging vessel; and
- sample dishes, tins, or cups for collecting aged material at the end of the test.

## Preparation

The following preparations should be made to the SAFT in advance of any testing. Repeat this procedure as part of periodic calibration, or after any extended period of disuse.

| Preparing Stirred Air-Flow Test Apparatus |                                                                                                                                                                                                  |
|-------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Step                                      | Action                                                                                                                                                                                           |
| 1                                         | Ensure that the aging vessel in the heating mantle, the stirrer, and the motor are level.                                                                                                        |
| 2                                         | Position the air tube toward the center of the vessel so that there is less than a 0.125 inch gap between the tube and the bottom of the vessel when the vessel is closed.                       |
| 3                                         | Position the thermocouple so that it is slightly above the longest disperser pins. It will ensure that the thermocouple is submerged to the sample but is not touched by the rotating disperser. |
| 4                                         | Ensure that air and nitrogen supply tubes are connected to the calibrated rotameter.                                                                                                             |
| 5                                         | Ensure that the air tube, the vessel, the condenser, and the lid are cleaned of any asphalt residues left from the previous test run and are carefully dried of the solvent used for cleaning.   |

## Procedure

Follow this procedure to perform the SAFT:

| <b>Stirred Air-Flow Test</b> |                                                                                                                                                                                                                                                                                                                               |
|------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Step</b>                  | <b>Action</b>                                                                                                                                                                                                                                                                                                                 |
| 1                            | Verify that the air and nitrogen or other inert gas are available and the gas flow is set to $2 \pm 0.1$ L/min.                                                                                                                                                                                                               |
| 2                            | Verify that the temperature is set to the appropriate temperature (325 °F) and the variable transformer is set to appropriate power level (80 percent).                                                                                                                                                                       |
| 3                            | Heat the asphalt binder sample in a 163 °C (325 °F) oven until it is completely fluid and pourable.<br>NOTE: Other heating and/or pouring temperatures may be used if recommended by the material's manufacturer.                                                                                                             |
| 4                            | Remove the sample from the oven and stir the sample briefly with a clean spatula.                                                                                                                                                                                                                                             |
| 5                            | Pour $250 \pm 1.0$ grams of the sample into the air-flow vessel.                                                                                                                                                                                                                                                              |
| 6                            | Place the gasket between the lid and the vessel; close the vessel by tightening the three screws, and insert the vessel into the heating mantle. Attach the impeller shaft to the mixer by tightening the two setscrews. Level the mixer so that there is a gap of 1-2 mm between the stop on the impeller's rod and the lid. |
| 7                            | If the amount of volatiles is to be determined, attach the condenser to the Swagelok fitting in the lid.                                                                                                                                                                                                                      |
| 8                            | Connect the thermocouple to the temperature controller and turn on the variac to 80 percent of its total output. Place fiberglass insulation around the top part of the vessel.                                                                                                                                               |
| 9                            | Start the mixer by increasing its RPM from 0 to 700.                                                                                                                                                                                                                                                                          |
| 10                           | Connect the air (nitrogen) line to the vessel. It is advisable to bubble nitrogen through the sample while the test temperature is being reached. By doing so, premature oxidation of material can be eliminated. This will provide better test reproducibility. Set the nitrogen flow rate to 4000 mL/min.                   |
| 11                           | When the temperature reaches 160 °C (320°F), change from nitrogen to air or turn on the air if nitrogen is not used. The air flow rate shall be 2000 mL/min and the RPM shall be equal to 700.                                                                                                                                |
| 12                           | Start timing at this point. Maintain the process for 30 minutes. The test temperature $163 \pm 0.5$ °C ( $325 \pm 1$ °F) shall be reached within the first 10 minutes; otherwise, discontinue the test.                                                                                                                       |

|    |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |
|----|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 13 | At the conclusion of the testing period, turn off the air; disconnect the air supply line, the condenser coil, and the impeller. Open the vessel, remove it from the mantle, and immediately pour all the residue, without scraping, into a container large enough that it is not over 75 percent full (e.g., a pint can). Do not let the container cool nor should the vessel be reheated to obtain more residue.                                                                                                                                                                                                                                                                                                                                               |
| 14 | Allow residue samples to cool to room temperatures. Test the residue within 72 hours of performing the air-flow aging test. Samples should be preheated to temperatures not exceeding 163 °C (325 °F) and stirred thoroughly with a clean spatula.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |
| 15 | If the amount of volatile hydrocarbons is to be determined, pour 20-30 ml of heptane into the condenser coil using a squeeze bottle. Apply light pressure by attaching the air supply line to one end of the coil to remove the solvent. Collect the solution in a pre-weighed 100 mL beaker. Repeat these steps until clean solvent starts flowing. If the solution is quite dark, it indicates that some asphalt material was trapped in the condenser. The test results should be disregarded in this case. After the bulk of solvent has evaporated, the beaker shall be placed on a warm hot plate for 20 minutes until the collected volatiles are free of the solvent. The beaker is weighed once again to determine the mass of the condensed volatiles. |



## **CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS**

The standard tests for simulation of asphalt hot-mix aging are the Rolling Thin-Film Oven Test (RTFOT, ASTM D 2872) and the Thin-Film Oven Test (TFOT, ASTM D 1754). The RTFOT and TFOT have a number of deficiencies when used for viscous or modified asphalts, such as uneven aging, film formation, and difficulty with cleaning laboratory equipment. The purpose of this project was to develop a new procedure for simulating asphalt short-term aging that occurs at a hot-mix asphalt cement plant. This procedure overcomes the shortcomings of the existing procedures, while duplicating the changes that occur during RTFOT aging at improved cost and with more efficient operation.

The resulting Stirred Air-Flow Test (SAFT) is designed based on fundamental studies of the process of air-blowing asphalt materials. Asphalt air blowing is used commercially to produce roofing and paving asphalts by oxidizing the bottom crude oil products with air, thereby altering the asphalt chemical composition and physical properties. The process conditions and binder composition have a direct impact on the properties of the resulting materials.

### **STUDIES CONDUCTED**

Development of a replacement apparatus and procedure for the RTFOT occurred in several stages. After a literature review on short-term aging methods we conducted preliminary studies of the air-blowing technique. Next, we evaluated several designs of pilot test equipment and test operating parameters, such as air flow rate and rate of mixing, for their effectiveness at reproducing RTFOT aging. In the final development stage, we evaluated the apparatus by performing test trials.

Paralleling this development effort, we conducted fundamental studies of asphalt air blowing, as a basis for developing the SAFT aging procedure, but also to investigate the effect of air-blowing conditions and asphalt composition on Superpave performance grade properties and road-temperature aging properties. Several asphalt fractions were air blown at different temperatures. Their physical properties were analyzed with respect to Superpave performance grade and their composition was determined by the Corbett method. Such parameters as hardening susceptibility, hardening rate, and oxidation rate were determined for each air-blown asphalt.

### **CONCLUSIONS**

#### **Stirred Air-Flow Test (SAFT)**

- The proposed test reproduces the RTFOT and TFOT procedures with respect to changes in chemical and physical properties of asphalt materials.
- The SAFT eliminates the shortcomings of standard methods, including:
  - inconsistent or unreliable test results due to skin formation at the surface of the asphalt;
  - difficulties with removing the asphalt for testing, with cleaning the apparatus, and with handling the hot equipment and asphalt; and

- difficulties with processing polymer-modified materials.
- The SAFT procedure requires only 45 minutes to age an asphalt material, including 15 minutes required for pre-heating the sample in the apparatus. This total is about half the time required by the RTFOT.
- The proposed procedure achieves precise control of the oxidation time by using nitrogen or other inert gas during the warm-up stage, and by using the same inert gas to quench oxidation at the end of the aging process.
- The sample temperature in the SAFT is controlled directly and thus more precisely.
- The SAFT apparatus allows for directly collecting and weighing the mass loss of volatiles driven from the asphalt during the test. This is contrary to either the RTFOT or the TFOT which provide only a measure of mass change, which is a combination of mass loss by volatilization and mass gain by oxidation. The volatiles collected can be further analyzed for molecular size and composition.
- The SAFT apparatus costs significantly less and requires much less bench space than the RTFOT, and it can be manufactured from readily available materials and supplies.

### **Fundamental Studies of Air Blowing and Thin-Film Aging**

- As defined by Superpave specifications, very good grade asphalts can be produced by air blowing. The blowing temperature does not seriously affect the grade span although there is some deterioration of the low-temperature grade when a material is air blown to increase the high-temperature grade. Also, the low-temperature stiffness, stress relaxation (represented by m-value), and the failure strain tend to deteriorate with increasing air-blowing temperature. The low-temperature performance grade for air-blown materials tends to be limited by the m-value rather than by the stiffness.
- Asphalt composition has a significant effect on a material's grade span. Materials with a higher concentration of asphaltenes and saturates have a higher performance grade span.
- Air blowing an asphalt material tends to increase its subsequent aging and hardening rates at 88 °C. This increase is expected to have an adverse impact on long-term pavement performance but Superpave grading is not affected by this phenomenon.
- The subsequent 88 °C hardening and oxidation rates are higher for materials blown at higher temperatures. Hardening susceptibility is a more complex function determined by kinetics of several competing reactions.
- Blowing fluxes with a high saturate content may result in a higher grade but can cause subsequent susceptibility to oxidative hardening. Optimization of both chemical composition of air blown material and process parameters is required in order to produce binders of superior physical and aging properties.
- The oxidation mechanism is the same for asphalt films of varying thickness. Decreasing film thickness to 0.5 mm helps increase rate of oxidation and reduce aging time to 50 min to obtain degree of aging equal to the RTFOT.

## **RECOMMENDATIONS**

We make the following recommendations:

- Conduct testing of the SAFT apparatus to establish inter-laboratory precision and consistency statistics.
- Replace the RTFOT and TFOT test methods with the SAFT method for short-term (hot-mix plant simulation) asphalt binder aging.
- Consider adopting the SAFT apparatus and procedure as a nationwide standard.





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