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16. Abstract

This report presents issues associated with long-term aging of polymer modified asphalt cements (PMACs) as reflected by dynamic mechanical analysis (DMA) data. In this study a standard SBS (styrene-butadiene-styrene block copolymer) polymer modified asphalt cement containing 3% copolymer (PMAC) meeting LADOTD specifications for PAC-40HG and PG 76-22M was selected and subjected to accelerated laboratory aging. Procedures were developed for simulation of long term aging of asphalt binders using multiple pressure aging vessel (PAV) operations in the absence and in the presence of water. Three, five and seven year old field aged asphalt samples originally of similar PMAC composition as that of PG 76-22 listed above were recovered from a wearing course mixture located on interstate I-55 near Granada, MS. All binders were characterized with respect to their composition and rheological properties. The extent of oxidation of both laboratory- and field-aged aged samples was estimated from Fourier transform infrared (FTIR) spectroscopy analysis and non-aqueous potentiometric titration data.. Changes in the molecular mass of the asphalt cement components were estimated from gel permeation chromatography (GPC) measurements. Aging determined a drastic reduction of molecular mass of SBS species and an increase in the content of large molecular species (LMS) asphalt components. Dynamic viscoelastic properties were determined using a high torque instrument. The asphalt architecture has been simulated with that of a gel. The cross-over temperature at which G” equals G’ at a frequency of 10rad/s as temperature increases was considered as the critical temperature, T_c, and chosen as a criterion to assess the advancement of hardening (aging). Oxidative aging in the presence of water promoted an increase in the carbonyl content of aged samples, primarily as acid groups, but the high humidity aging reduced the extent of asphalt hardening. Critical temperature of the field 3 year old I-55 paving sample correlated better with the laboratory wet 0.5xPAV aged PMAC sample, T_c of the field 5 year sample was intermediate between T_c of the dry 0.5xPAV and that of the dry 1.0xPAV laboratory aged PMAC samples and T_c of the field 7 year old sample correlated better with the laboratory dry 1.0xPAV aged PMAC sample. This type of correlation was used to determine if a binder extracted from the damaged LA 3234 Hwy road pavement was excessively aged after three years of service.

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Polymer Modified Asphalt Cement, Dry Aging, Wet Aging, Field Aging, FTIR, GPC, Rheology, Dynamic Mechanical Analysis

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The Use of DMA to Characterize the Aging of Asphalt Binders

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ABSTRACT

This report presents issues associated with long-term aging of polymer modified asphalt cements (PMACs) as reflected by dynamic mechanical analysis (DMA) data. In this study, a standard styrene-butadiene-styrene block copolymer (SBS) modified asphalt cement containing 3 percent copolymer (PMAC) meeting LADOTD specifications for PAC-40HG and PG 76-22M was selected and subjected to accelerated laboratory aging. Procedures were developed for simulation of long-term aging of asphalt binders using multiple passes through a pressure aging vessel (PAV) both in the absence and in the presence of water. Three-, five-, and seven-year old field aged asphalt samples originally of similar PMAC composition as that of PG 76-22 listed above were recovered from a wearing course mixture located on Interstate I-55 near Granada, MS. All binders were characterized with respect to their composition and rheological properties.

The extent of oxidation of both laboratory- and field-aged aged samples was estimated from Fourier transform infrared (FTIR) spectroscopy analysis and non-aqueous potentiometric titration data. Oxidative aging in the presence of water promoted an increase in the carbonyl content of aged samples, primarily as acid groups. Changes in the molecular mass of the asphalt cement components were estimated from gel permeation chromatography (GPC) measurements.

Aging determined a drastic reduction of molecular mass of SBS species and an increase in the content of low molecular species (LMS) asphalt components.

Dynamic viscoelastic properties were determined using a high torque instrument. The asphalt architecture has been simulated with that of a gel. The cross-over temperature at which loss modulus of rigidity, G”, equals the storage modulus of rigidity, G’, as temperature increases was considered as the critical temperature, T_c, and chosen as a criterion to assess the advancement of hardening (aging). Critical temperature is dependent on frequency and, therefore, data have been compared at a frequency of 10 rad/s. Water had a retarding effect on hardening. Critical temperatures of asphalts aged in the presence of water were inferior to that of dry-aged PAV samples.

Critical temperature of the field 3-year-old I-55 paving sample correlated better with the laboratory wet 0.5xPAV aged PMAC sample; T_c of the field 5-year-old sample was intermediate between T_c of the dry 0.5xPAV and that of the dry 1.0xPAV laboratory aged

PMAC samples, and T_c of the field 7-year-old sample correlated better with the laboratory dry 1.0xPAV aged PMAC sample. This type of correlation was used to determine if a binder extracted from the damaged LA 3234 Highway road pavement was excessively aged after 3 years of service.

ACKNOWLEDGMENTS

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IMPLEMENTATION STATEMENT

This forensic analysis evaluated the oxidative aging of asphalt cements modified with an elastomeric styrene-butadiene-styrene block copolymer. The long term oxidation was mimicked in the laboratory by repeated PAV operations in dry and wet atmospheres. Field-aged binders of similar composition were recovered from pavements after 3, 5, and 7 years of service. The extent of oxidation of both laboratory- and field-aged aged samples was estimated from FTIR spectroscopy analysis and non-aqueous potentiometric titration data. Changes in the molecular mass of the asphalt cement components were estimated from GPC measurements. Dynamic viscoelastic properties were determined using a high torque instrument working both as a DMA and dynamic shear rheometer (DSR). Based on the findings of this research the following is recommended for implementation:

- FTIR procedure was developed for detection and quantification of oxidized species in aged binders. This procedure is described in Appendix A.
- A potentiometric titration method was used for determination of acidity of asphalt binders. The procedure is useful for quantification of both carboxylic and other types of acids developed during binder oxidation. This procedure is described in Appendix B.

The developed procedures are recommended for use in forensic analysis of existing pavements to determine levels of oxidation and polymer presence. With further study, these procedures may be used in specifications.

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INTRODUCTION

The role played by time and environmental factors on aging of asphalt cements within the pavement applications is a subject of continuous interest *[1-12]*. Earlier studies carried out on the effect of temperature and relative humidity on the oxidation of airblown asphalts as a function of exposure time showed that the rate of oxidation is dependent on both of these environmental factors *[1-3]*. The behavior of bitumens was studied in hot mix wearing courses subjected to climates ranging from hot and dry summers to continental cold winter with much heavier rainfall *[2]* and *[3]*. The environmental temperature effect on the age hardening characteristics of asphalt binders is rather well documented. Hardening is due to chemical reactions, including oxidation, polymerization, and condensation, and/or due to physical processes, including loss of volatiles and structural morphological change. However, reaction with oxygen has been shown to be the principal factor responsible for hardening of asphalt in the road *[4-8]*. It has been concluded that the high average air temperature (thermal oxidation) is the most significant factor affecting the rate and amount of asphalt hardening in hot climates *[4], [9],* and *[10]*. To mimic road aging of asphalt pavements, testing at increased temperature has been widely used since the rate of most oxidation reactions approximately doubles for each 10°C increase *[4]*. Diffusion of oxygen has been shown to control aging *[5], [11],* and *[12]*. Therefore, aging was considered as a chemical as well as a physical problem *[5]*. Voids and aggregate porosity were also found to be contributing factors but were dependent upon the type of asphalt and average temperature *[7]*.

Laboratory protocols were recently developed under the Strategic Highway Research Program (SHRP) to simulate the field hardening of asphalt binder and mixes in which the mean annual air temperatures prevalent during field aging have been taken into account. The influence of atmospheric humidity has not been considered *[13]*. Dynamic Shear Rheometry (DSR) testing conducted both on laboratory aged and field aged binders, was used to correlate changes in physical properties upon aging. However, only a recommended provisional protocol applicable for non-modified binder was presented.

The climate of the continental United States is diverse. Most of U.S. Southeast states experience both hot and wet summer weather. While the July mean temperature and mean precipitation for Louisiana and Mississippi are the same (32.2/34.4°C and 1,220-1,625 mm), some states might experience a higher temperature (e.g., 37.8°C for Texas and Oklahoma) or more rain (e.g., 1,980-2,030 mm for Carolinas) *[14]*. Extremely high relative humidity and a low dew point maintain more often than not a continuous film of water on the Gulf Coast roads during the night and early morning hours. One might wonder, therefore, if the laboratory protocols for aging asphalt binders should not consider the vapors of water as components of the aging atmosphere as well as air (oxygen) exposure. Aging in the presence of water of several Strategic Highway Research Program (SHRP) core asphalts and two polymer modified asphalt cements has been investigated recently at the Western Research Institute from Laramie, Wyoming *[15]*. Analytical methods have been developed to assess the chemical composition of asphalts before and after aging *[15-17]*. However, while very interesting data have been reported, no real connection has been made with data on similar asphalts extracted from long term aged asphalt pavements.

It was the goal of the present investigation to address the potential influence of water on the aging of road pavements containing polymer modified asphalt cements.

OBJECTIVE

The objectives of this research were (1) to analyze the properties of an SBS copolymer modified asphalt cement (PMAC) aged in the laboratory in dry and wet atmospheres and of a similar PMAC field age on the road for several years and (2) to develop a criterion for assessing the extent of aging based on laboratory fundamental engineering tests.

SCOPE

This project was sub-divided into two phases, including (I) laboratory binder aging and characterization and (II) field binder extraction and characterization. During Phase I a protocol for long-term laboratory aging was developed. Binder tests were based on chemical component analysis and Superpave binder characterization that included (1) FTIR (Fourier transform infrared) spectroscopy measurements, (2) GPC (gel permeation chromatography) measurements, (3) DSR (dynamic shear modulus) and phase angle measurements, and (4) dynamic mechanical analysis (DMA) and phase angle measurements. During Phase II, road samples were taken from a highway paved 7 years ago for which asphalt cores sampled after 3 and 5 years and a sample of the original PMAC aged in the PAV (pressure aging vessel) were available. The binder of the 3-, 5-, and 7-year-old road samples was extracted and analyzed together with the original PAV PMAC road sample using the same suite of tests for Phase I. GPC chromatograms used in a forensic evaluation of a distressed highway are also discussed.

METHODOLOGY

Materials

Asphalt Binder

In this study, a standard SBS (styrene-butadiene-styrene block copolymer) elastomer polymer modified asphalt cement containing 3% copolymer (PMAC) meeting LADOTD specifications for PAC-40HG and PG 76-22M was selected. It was obtained from Paragon Technical Service, Jackson, MS. This PMAC met LADOTD specification for PG 76-22M. To prepare the PMAC composition, an asphalt cement PG 64-22 was blended with SBS dissolved in lower performance grade asphalt in order to enhance the efficiency of polymer dispersion. Three-, five-, and seven-year-old field aged asphalt samples originally of similar PMAC composition as that of PG 76-22 listed above were recovered from a wearing course mixture located on Interstate I-55 near Granada, MS. The binder was extracted from pavements with hot toluene as described before *[18, 19]*. An original road PMAC sample PAV-aged at the time of the road paving accompanied the field aged pavement samples and was characterized as received.

Binder Aging

Representative asphalts and modified asphalts were selected for thin film oven testing (TFOT), (Thin-Film Oven Test AASHTO T179-93 or ASTM D1754-97), which is to simulate the aging of the asphalt binder during mixing and construction operations (short term). The RTFO (rolling thin-film oven test), (AASHTO T240-97 or ASTM D2872-97) was not used because of foaming. A PAV (Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel, PAV, AASHTO Standard PP1-98) was used to simulate binder aging during the service life (long term) [*20, 21]*. All samples for the PAV were prepared using 50±0.5 g material and were aged in the TFOT oven @ 163°C for 5 hours under a continuous air flow. The TFOT aged samples were submitted to dry aging step in the PAV at 100°C and 300 psi (1 psi = 6.9 kPa) for 10, 20, 30, and 40 hours. For the wet aging of asphalts, the only difference was that water (50 g) was placed in one pan instead of asphalt inside the pressure vessel.

Material Characterization

A suite of binder composition and rheology characterization tests was performed in this study. The section below briefly describes the tests conducted.

FTIR Spectroscopy

The functional group composition of the binders was examined by FTIR spectroscopy using a Perkin Elmer 1700 FTIR instrument. Films of asphalts and rubber were cast from toluene on a NaCl plate and analyzed taking the blank plate as background. The concentration of toluene solutions (5 wt %) and the solution amounts pipetted on plates were kept the same. Background information on FTIR method can be found elsewhere *[19]*.

Potentiometric Titration

Determination of acid groups in asphalts was made by non-aqueous potentiometric titration as described earlier by Buell, Dutta, and Holland and recently adapted by investigators at the Western Research Institute in Laramie, WY *[15], [16]*, and *[17]*. According to the WRI method, asphalt samples were dissolved in chlorobenzene/ethyl alcohol mixture (9/1, v/v), and the solution was titrated with 0.1 M tetrabutylammonium hydroxide in toluene/isopropyl alcohol (43/7, v/v). The endpoint was determined using a KCl, liquid junction membrane, working electrode. Benzoic acid was used for calibration.

GPC Characterization

The molecular weight distribution of the asphalt components was estimated by using a gel permeation chromatograph equipped with a Waters 590 pump and a Waters model 410 differential refractive index detector. The separation of the polymer from the asphalt components was affected with two Phenogel 10 μ, 300 x 7.8-mm columns (Phenomenex, Torrance, CA), connected in series (1) 10-5 Å (10-1,000 K) and (2) MXM (5-500 K). The column set was calibrated with narrow molecular weight polystyrene standards. All samples were prepared at a concentration of 2 percent in tetrahydrofuran (THF) and 100 μL samples were injected at room temperature. Samples were eluted with THF at 0.8 mL/min., and the polymer concentration in the eluent was recorded using a differential refractometer. The change in the differential refractive index (DRI) was plotted versus THF elution time (min.) or eluted volume (mL). The method has been described recently in introductory terms in one of the investigator's reports *[19]*.

Rheological Measurements

A high torque controlled stress AR2000 rheometer specially designed for characterization of soft materials (TA Instruments Inc Waters Corp., New Castle, DE) was used to determine the complex viscoelastic modulus G* (describing rigidity) of asphalt binders.

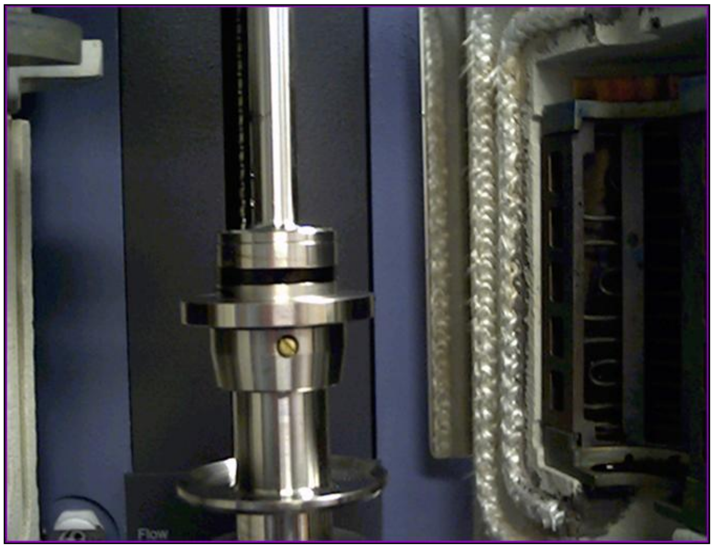

Figure 1
Setting of the instrument in DSR mode
[environmental temperature control (ETC) oven open]

The geometry included a set of 5- and 25-mm steel parallel plates (h = 1-3 mm) for the instrument working as a DSR (Figure 3) and asphalt torsion bars (3 x 6 x 40 mm) for working as a DMA (Figure 4). An environmental temperature control (ETC) oven allowed a precise control of temperature within 0.1°C (Figures 1 and 2). While both DSR and DMA modes provided similar results around room temperature, i.e. 20°C, the torsion bars were used at negative temperatures, while the DSR mode was preferred at higher temperatures (above 50°C). Test procedures included dynamic temperature ramp determinations using low heating or cooling rates (0.25 to 1°C/min.) and a sweep of frequencies covering two decades (0.5-50 rad/s; 5 points/decade).

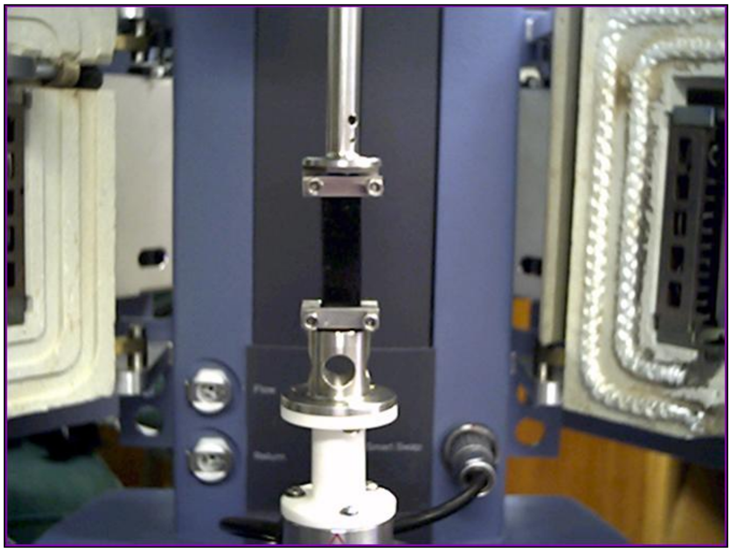

Figure 2
Setting of the instrument in DMA mode (ETC open)

DISCUSSION OF RESULTS

Characterization of Binder by Chemical Analysis

Performances of asphalt pavements are directly related to the chemical composition of asphalt binders the roads are made of *[22-24]*. Chemical composition of asphalts, however, changes during both long term and short term aging. Different asphalts age differently. As mentioned previously, a major factor leading to the hardening and embrittlement of asphalt pavements is the reaction of asphalt with atmospheric oxygen. As proposed by Petersen, the hardening phenomenon is primarily a result of the formation in asphalt of polar oxygen containing functional groups that increase asphalt consistency through strong molecular interaction forces *[8]*. Quantification of the oxygen uptake during aging is, therefore, a direct measure of the advancement of the aging process. Spectroscopic determinations (FTIR) and "wet chemistry" analysis (direct titration of functional groups) are the most used methods to this aim *[20]*.

FTIR

Aging was reflected in the infrared spectra of asphalts by multiple peaks centered around 1695 cm^{-1}, which correspond to carbonyl (C=O) absorptions of oxidized species, such as ketones or carboxylic acids *[8]*. By comparing the intensity of the 1695 cm^{-1} region to that of 1455 cm^{-1}, which is attributed to saturated C-C vibrations, the relative degree of oxidation of the samples can be estimated.

The more oxidized the asphalt (e.g., PAV aged), the more intense the 1695 cm^{-1} peak becomes, and the corresponding 1698/1455 cm^{-1} ratio increases. Figure 3 presents the FTIR spectra of un-aged and PAV-aged asphalt samples. Carbonyl species are present also in the asphalt, but their concentration is very small. The 1695/1455 cm^{-1} ratio calculated from the spectrum is not relevant due to the lack of oxidized species. After PAV aging, the sample was clearly oxidized; the 1695/1455 cm^{-1} ratio is 0.53 (Figure 4). The higher auto-oxidative sensitivity of PMAC suggests that the polymer additive is behaving as a sacrificial antioxidant. The allylic positions adjacent to the C=C double bonds within polybutadiene blocks can readily react with oxygen, particularly at elevated temperatures (t >100°C), bringing about a significant increase of carbonyl species and a concomitant cleavage of the polymer backbone. The reduction in molecular weight can be detected using gel permeation chromatography (vide infra).

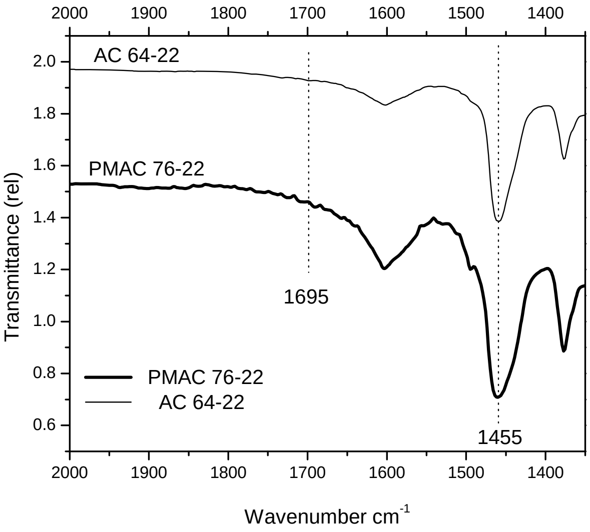

Figure 3
FTIR spectra of asphalts before dry PAV aging

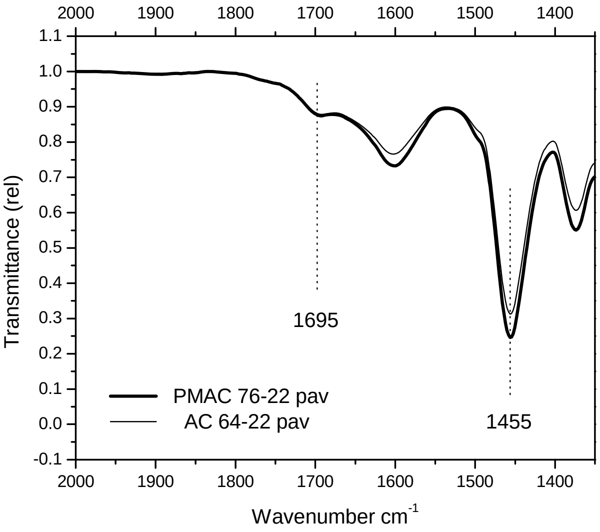

Figure 4
FTIR spectra of asphalts after dry PAV aging

The uptake of oxygen became more relevant after extensive PAV aging, with a 1695/1455 cm^{-1} peak ratio of 2.5 after 2 x PAV operations (40 hrs.) in the presence of water (Figure 5).

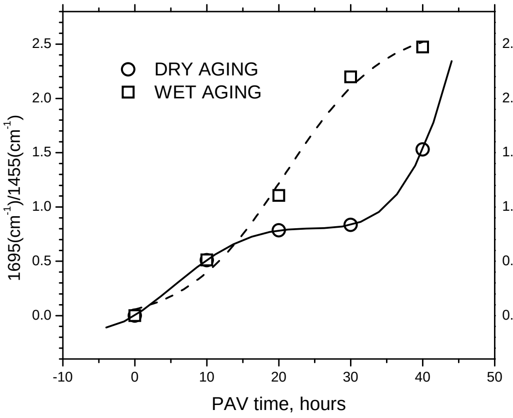

Figure 5
Increasing of carbonyl species of asphalts samples after dry and wet PAV aging as indicated by the ratio of peak absorption

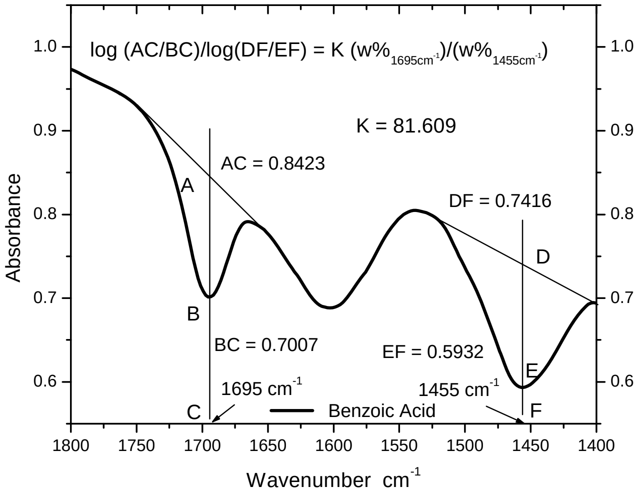

Figure 6
Illustration of method for quantifying carboxylic acid content using benzoic acid

Table 1
Results of non-aqueous potentiometric titration of acid groups in asphalts

Asphalt Sample	Aging Time	Acid Groups Content (meq/g)
0.5 x PAV Dry	Lab 10 hrs.	0.01543
0.5 x PAV Wet	Lab 10 hrs.	0.03253
1.0 x PAV Dry	Lab 20 hrs.	0.02953
1.5 x PAV Dry	Lab 30 hrs.	0.03060
1.5 x PAV Wet	Lab 30 hrs.	0.03663
I-55 Extract	Field 3 yrs.	-
I-55 Extract	Field 5 yrs.	0.02293
I-55 Extract	Field 7 yrs.	0.02450

The water interferes with the oxidation process perhaps by forming an asphalt-oxygen-water complex *[1]*. An attempt was made to quantify the carboxylic acid groups after aging using solutions of benzoic acid in asphalt of known concentration to build a calibration curve (Figure 6). A linear correlation between the absorbance ratios and carboxylic acid content was observed.

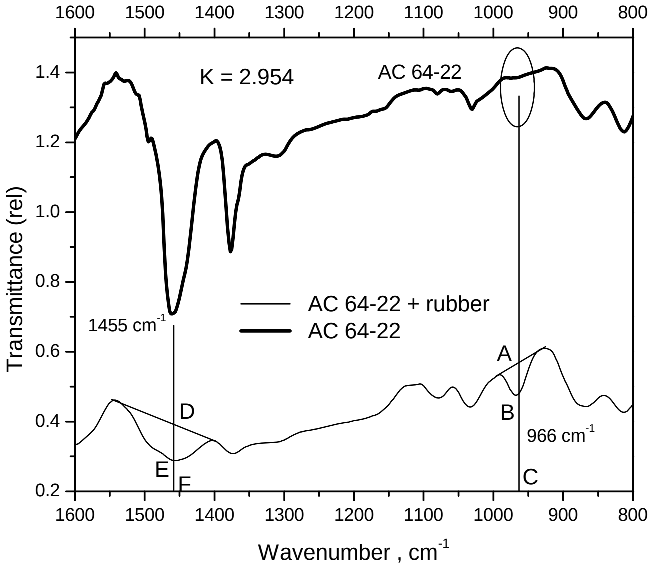

Figure 7
Illustration of method for quantification of double bonds using the 966 cm^{-1} peak absorption of SBS rubber dissolved in AC 64-22 asphalt cement

While the same trend was observed as that indicated by the ratio of 1695/1455 cm^{-1} absorption peaks, the results were somewhat different from that obtained by potentiometric titration (Table 1).

One reason might be the presence of other carbonyl species in FTIR spectra that were not accounted by titration. As shown by data listed in Table 1, the content of carboxyl groups of field-aged asphalt samples after 5 and 7 years on the road were close but less than that of the 1.0 x PAV sample aged in the absence of water. Data for I-55 extracted samples aged for 3 years were not reproducible because of technical problems encountered. The laboratory results of PAV samples that aged in the presence of water did not match the data of asphalts extracted from aged pavements; after only 10 hrs. of treatment (0.5 x PAV), the carboxylic acid content exceeded that of the longest field aged asphalt.

A similar FTIR analysis was made to quantify double bond content of polybutadiene blocks in PMAC samples before and after aging. The building of the calibration curve was based on the vibrations of unsaturated carbon bonds at 966 cm^{-1} relative to the same 1455 cm^{-1} peak (Figure 7). Analysis of data obtained for PAV aged samples indicated a rapid decrease of unsaturation both for dry- and wet-aged asphalt samples (Figure 8). These results correlated well with GPC data reported previously, which indicated a severe diminution of molecular weight of polymeric species after aging *[18]*. However, it seems that for a reduced aging time (10 hrs.) the water retarded the oxidation of the SBS double bonds (Figure 5).

Gel Permeation Chromatography

As shown previously, the polymer and asphalt components of polymer modified asphalt cements could be separated using gel permeation chromatography *[18]* and *[19]*. The large differences in the molecular weights between the asphalt and polymer components allowed baseline separation of the two components in the GPC chromatogram of the laboratory PMAC sample prepared from AC 64-22 and 3 percent SBS (Figure 9).

Short term aging (TFOT) did not visibly affect the dissolved polymer that eluted at the same time as the original SBS sample, corresponding to a molecular weight MW of 120.000 Daltons in the calibration diagram (Figure 10). However, the long term PAV aging drastically reduced the molecular weight of polymeric SBS species towards lower molecular weights (Figure 9).

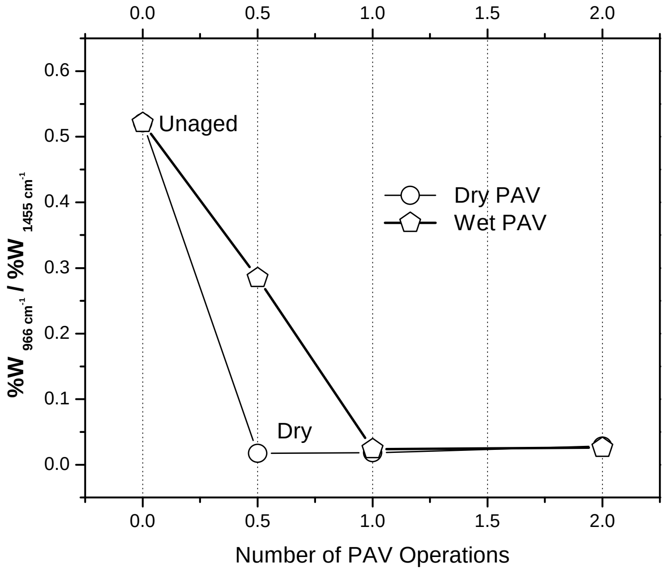

Figure 8
Diminution of PMAC unsaturation after dry and wet PAV aging

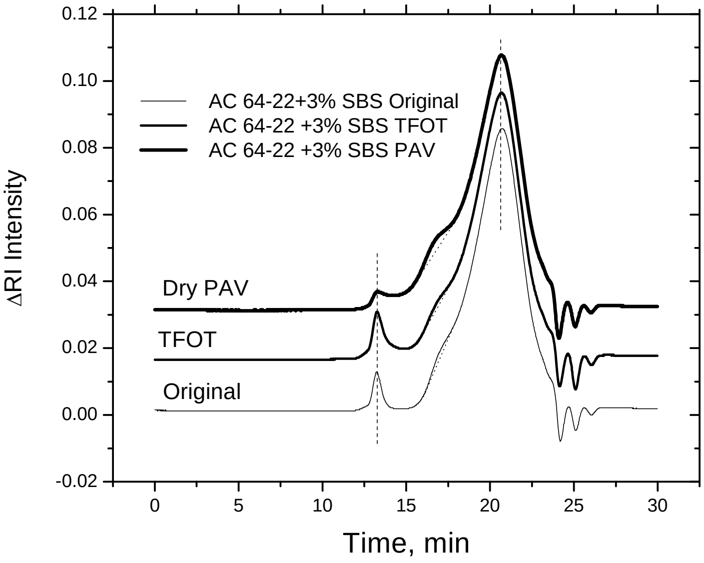

Figure 9
GPC traces of AC 64-22 + 3% SBS sample after short and long term aging

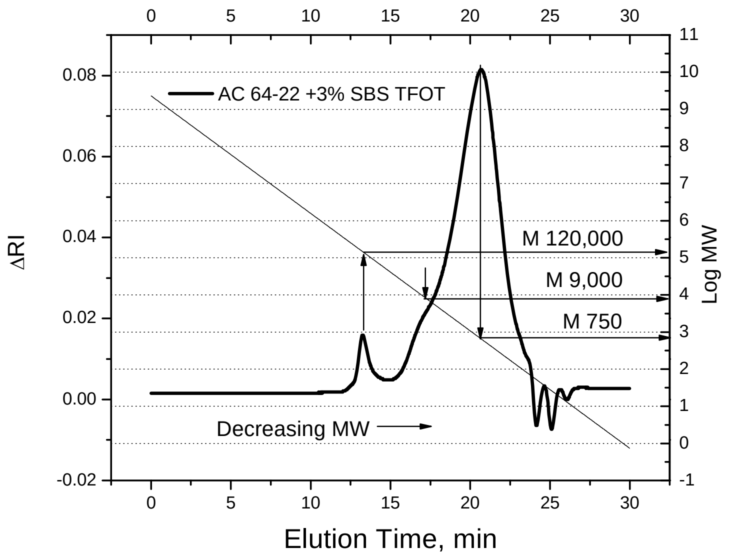

Figure 10
Annotated GPC trace of AC 64-22 + 3% SBS sample after short term aging

Thermo-oxidative degradation of an SBS elastomer occurs within the polybutadiene segment only; no oxidation of the polystyrene segments is expected *[24]*. After extensive oxidation, the polymer is effectively degraded and can be hardly detected in the aged binder *[25]*. Although oxidation of the asphalt components may be retarded by the presence of the polymer; age hardening continues to occur *[26]*. As shown schematically in Figure 11 polar groups created by aging may stabilize aggregation. Asphalt aggregates reinforce the binder matrix and may enhance its adhesion to mineral aggregate surfaces.

When the PMAC sample subjected to TFOT and dry PAV aging was analyzed in similar conditions, the large differences in the molecular weights between the asphalt and polymer components allowed another baseline separation of the two species in the GPC chromatogram (Figure 12). The polymer species from PMAC eluted at a time that corresponded to a molecular weight of 120,000 Daltons. However, the PAV aging process caused a severe oxidation of the PMAC polymer molecules, broadening the polymer peak towards higher elution times, or lower molecular weights. Besides the degradation of polymeric species to lower molecular weight (MW), weathering of the base asphalt cements resulted in a significant increase of large molecular size (LMS) species seen at around 10^4 Dalton in Figure 9 and a significant decrease of medium and small molecular size species *[27]*.

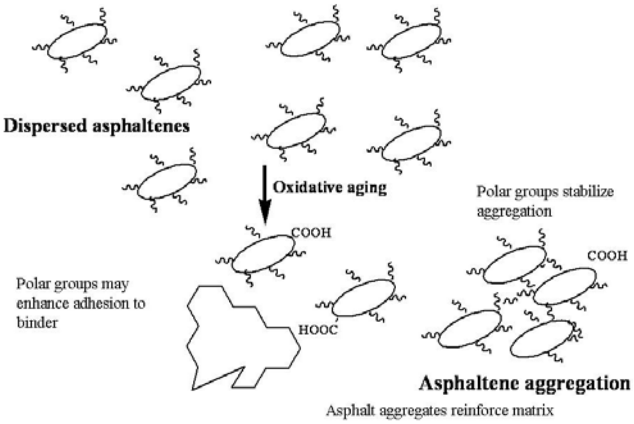

Figure 11
Stabilization of asphalt aggregation by polar groups created by oxidation

This shift is clearly represented by the results of the GPC analysis of asphalts extracted from core samples taken after years of aging on the road (Figure 13). A PAV aged sample from the time of the road paving was available for comparison (RTFO was specified on the container as short term aging before PAV aging). Polymeric SBS species, clearly still present after PAV aging at MW of the order of 10^5 Daltons (a polystyrene standard with molecular weight of 2.18×10^5 Daltons shown for comparison), diminished drastically after years of service on the road, while the large molecular weight components (asphaltenes) of the binder itself increased the intensity of LMS species of 10^4 Daltons. The longer the aging time, the higher the concentration of LMS components observed.

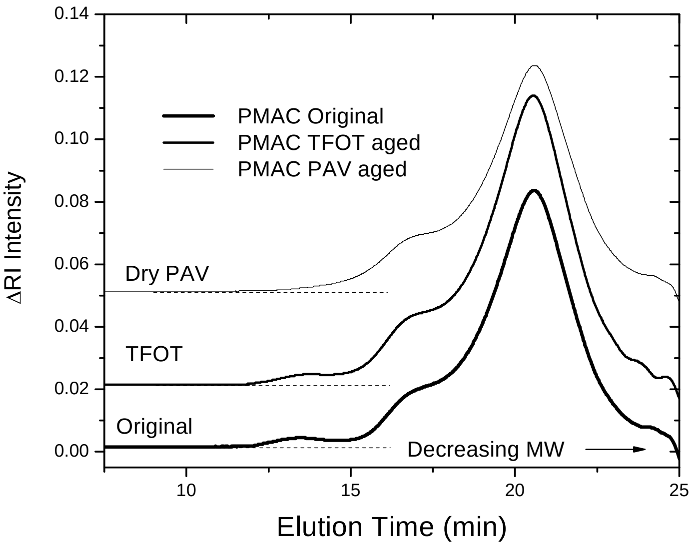

Figure 12
GPC traces of PMAC sample after short and long term aging

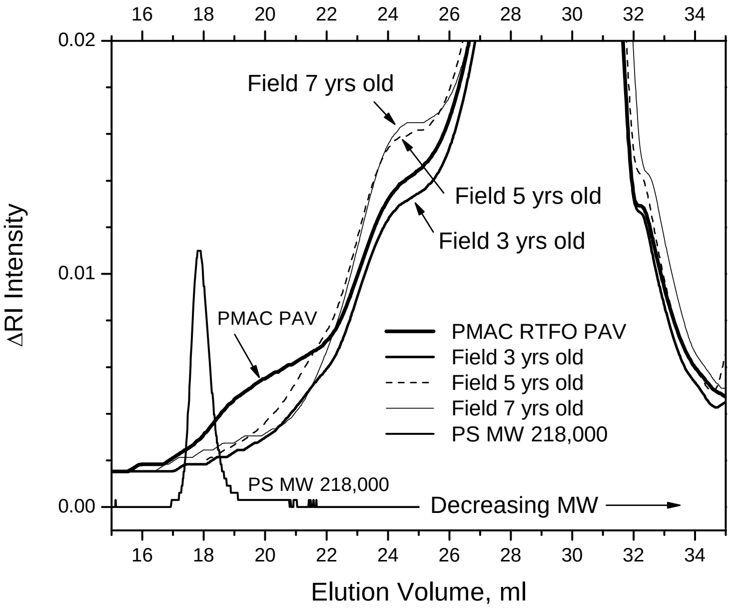

Figure 13
GPC traces of asphalt samples extensively aged on the road

This gradual increase of LMS species over the years indicates that after 7 years of service the asphalt hardening (not necessarily only through oxidation processes as mentioned above) might not be over. Asphaltene aggregation suggested in Figure 11 might continue at a slower pace as aging advances.

Rheological Characterization

In addition to the polar chemical functional groups formed on oxidation, asphalt properties can also be significantly altered by molecular structuring, sometimes called steric hardening. This potentially reversible phenomenon may also be a major factor contributing to pavement embrittlement *[8]*. While difficult to quantify in asphalt pavement mixtures, it is highly dependent on temperature. Early on, the road of determination of the rheological properties of asphalts in relation to durability and pavement performance, Sisko and Brunstrum pointed out that aging produces changes in consistency that appeared to be due to the development of a gel structure *[28]*. Heteroatoms introduced by aging may have formed secondary valence bonds that were involved in the gel. Evidence for the gel structure came from a number of observations: the aged asphalt did not flow back into a crater cut into its surface; the penetration-softening point relation changed; the viscosity increased greatly with small increase in molecular weight; the WLF constants of time-temperature superposition relationship changed, and large changes of viscosity occurred without a significant change in temperature *[29]*.

By adding polymers, such as cross-linkable rubbers, the gel character of asphalt cements enhances. The three dimensional network resists deformation and recovers the initial shape at temperatures at which the storage modulus (G') is superior to the modulus describing the viscous character of the asphalt, i.e., the loss modulus (G"). The effectiveness of the network diminishes rapidly above the cross-over temperature at which these two moduli become equal ($G' = G''$ at $\delta = 45°$ for which $\tan\delta = 1$).

This cross-over temperature (to be called critical temperature, T_c, in the following) is proposed in the present work to discern the changes in rheological characteristics of polymer modified asphalts brought about by aging.

Applying a special high frequency torsional rheometer to study the impact of long term aging of asphalt joint materials, Swiss scientists proposed the unitary value of $\tan\delta$ as a distinctive threshold point for analyzing aging of bituminous binders *[30]*. Figures 14 and 15 exemplify the determination of T_c for laboratory aged AC 64-22 and PMAC binders, respectively. The cross-over temperature increased after adding polymer to the asphalt cement (Table 2).

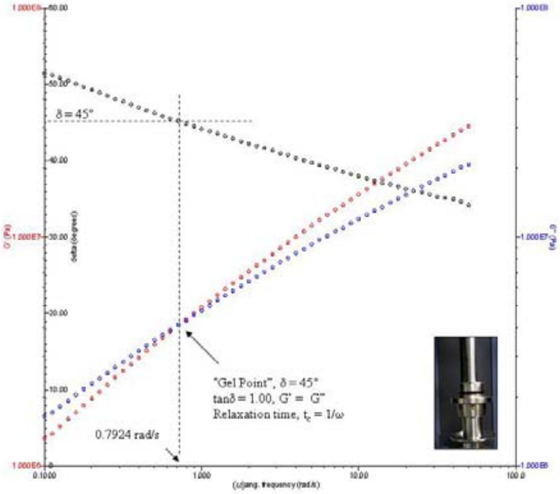

Figure 14
Plot of G’ and G” vs. frequency applied to the determination of the cross-over temperature of the AC 64-22 aged without water for 30 hrs. (1.5 x PAV)

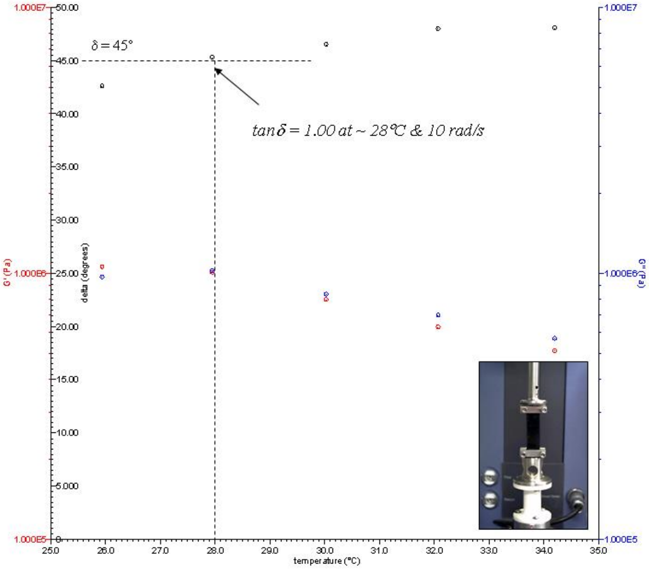

Figure 15
Plot of G’ and G” vs. frequency applied to the determination of the cross-over temperature of the PMAC 77-22 aged without water for 20 hrs. (1.0 x PAV)

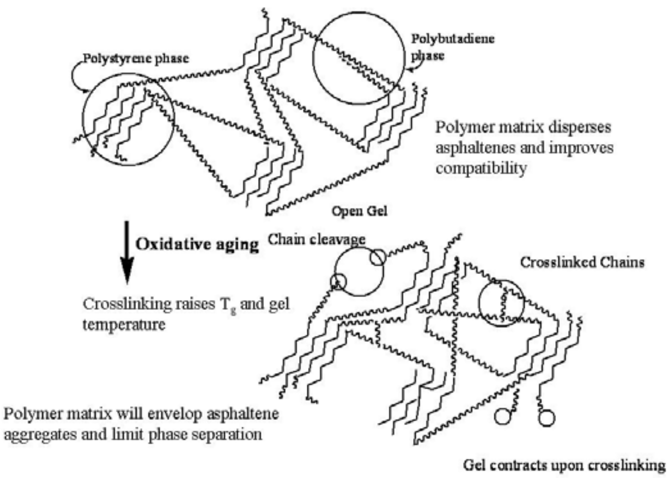

Figure 16
Oxidative aging of the SBS polymer matrix in PMAC asphalts

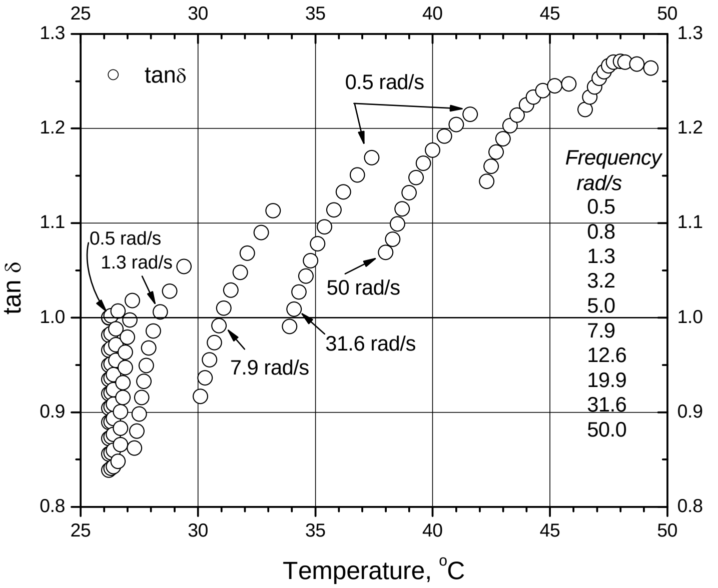

Figure 17
Variation of tanδ with temperature for dry-aged 1.0 x PAV PMAC sample

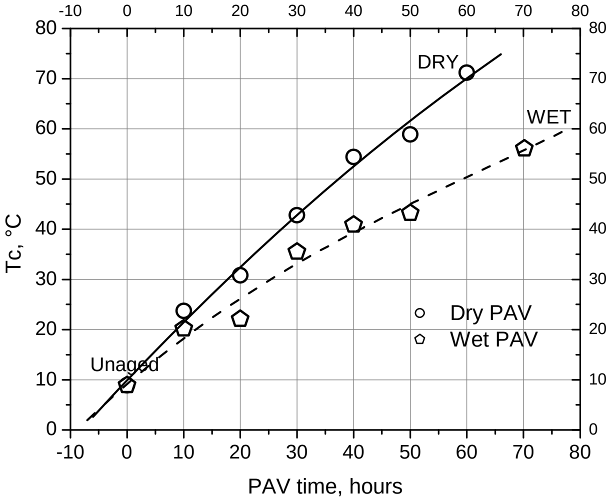

Figure 18
Variation of critical temperature of multiple PAV dry-aged and wet-aged PMAC samples

Table 2
Critical temperatures T_c (tanδ = 1, G' = G") of aged asphalt samples determined at a frequency of 10 rad/s

Asphalt Sample	Aging Time	T_c Dry Aged °C	T_c Wet Aged °C	T_c Road Aged °C
AC 64-22	Unaged	8.2		
PMAC 76-22	Unaged	9.5		
PMAC 0.5xPAV	10 hrs	23.8	20.3	
PMAC 1.0xPAV	20 hrs	30.6	22.1	
PMAC 1.5xPAV	30 hrs	42.0	36.0	
I-55 Extract	3 yrs			21.0
I-55 Extract	5 yrs			27.3
I-55 Extract	7 yrs			29.4

When SBS is used as an asphalt additive, the oxidative aging changes the polymeric matrix towards an open gel structure still capable of stabilizing asphaltene/maltene emulsion (Figure 16). The combined effects of oxidative aging of SBS and asphalt components (i.e., crosslinking of polymer and aggregation of asphaltenes) lead to higher gel points (T_c). The cross-over temperature depends, however, on the frequency at which the test is conducted (the higher the frequency, the higher the temperature). Therefore for each temperature, a relaxation time can be determined, corresponding to the frequency at which the moduli are the same (the higher the temperature, the shorter the time). An example is shown in Figure 17 that describes the variation of tanδ of the PAV dry-aged PMAC sample. There is a rather short temperature domain (less than 10°C) for which tanδ = 1 (G' = G") with the lower end concentrating to low frequency.

In order to compare the results, all determinations were made using a frequency of 10 rad/s. The results are presented in Figure 18. Extremely high critical temperatures have been recorded after only three to four full PAV aging cycles. Surprisingly, wet aging produced much softer materials with a T_c of samples aged for 70 hrs. equivalent to that of dry PAV samples aged for only 30-40 hrs.

Critical temperatures of PMAC laboratory aged samples are compared with that of asphalt samples extracted from I-55 aged pavements in Table 2. Perusing data listed in this table, one might conclude that the maximum critical temperature exhibited by the sample aged for 7 years is more similar to that of the PMAC sample aged for 20 hrs. in the absence of water (one dry PAV cycle), while shorter periods of aging on the road (3-5 yrs.) produced samples with a cross-over temperature somewhat closer to that of PMAC samples aged in a wet atmosphere for 10-20 hrs.

As it has been previously mentioned, the oxidation process is controlled at a given temperature by the reactivity of the binder and the rate of diffusion of oxygen into the binder. As the viscosity of asphalt increases, the coefficient of diffusion of oxygen decreases. The coefficient of diffusion was found also dependent on the concentration of chemically bound oxygen, i.e., as the later increases, the coefficient decreases *[11]*. The concentration of chemically bound oxygen was found to be higher in asphalt samples aged in the presence of water both in this work and in other investigations *[15]*. Water might, therefore, moderate the aging process towards a more open gel structure that, at its turn, translates in a "softer" material with a corresponding lower T_c. The chemistry of the water effect on PMAC aging is under investigation.

The diagram developed in Figure 18 can be calibrated with data presented In Table 2 for field-aged I-55 Hwy samples. The cross-over temperature can be used then as a criterion to build a nomogram for assessing the aging of SBS PMAC binders. (Other polymeric additives might behave differently on aging because of the lack of double bonds.)

The cross-over temperature criterion was applied for checking the binder characteristics extracted from a distressed LA 3234 Hwy with 3 years of service. SBS was also the polymer additive used by contractors for the preparation of the PMAC composition. The cores from which the binder was extracted are shown in Figure 19. The presence of the polymer was clearly identified by GPC measurements that produced diagrams similar to that of I-55 Hwy binder extracts previously presented. GPC chromatograms of LA 3234 Hwy binder extracts are shown in Figure 20. Polystyrene standards mark the domain of interest of polymeric and asphaltene species. The content of LMS suggested that the aging degree of the wear course was less advanced than that of the binder course (compare MW traces around 10^5 Daltons).

Figure 19
Cores taken from LA 3234 Hwy

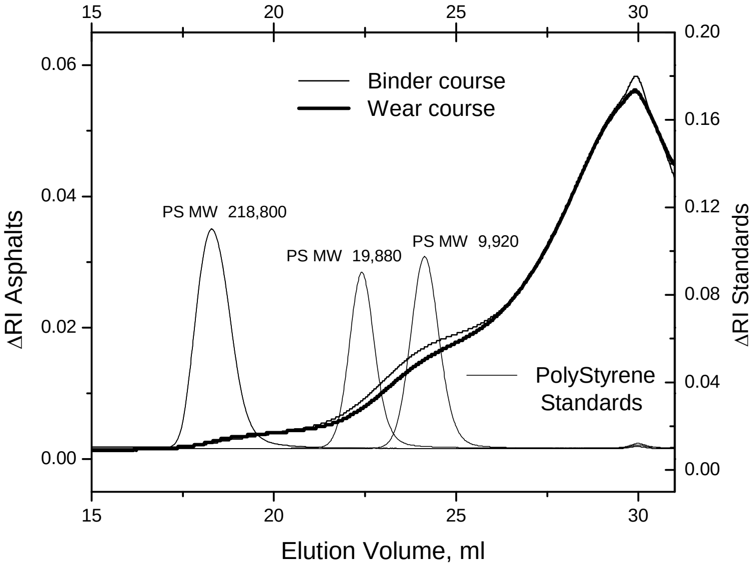

Figure 20
GPC traces of asphalts extracted from LA 3234 Hwy paving samples

Rheological measurements at 10 rad/s resulted in a crossover T_c of 25.2°C for the wear course and 26.4°C for the binder course. The wearing course extract also had a lower complex viscosity at 25°C (4.4 x 10^5 Pa.s) than the binder course (5.5 x 10^5 Pa.s), agreeing with GPC and T_c data. Critical temperatures of 25-26°C are experienced for pavements 3-5 yrs. old (dry aging) or 5+ yrs. for wet conditions. The fact that data for the wearing course point to a less advanced degree of aging than that of the binder course might be related to the moderation effect of water. At any rate, the T_c values listed above (less than 30°C) do not suggest that the LA 3234 Hwy extracts are over-aged binders, and other reasons should be considered for the rather rapid degradation of this road.

CONCLUSIONS

Processes Occurring During Laboratory Aging of PMAC Samples

When discussing aging of binder when polymer is present and its long term effect on pavements, one must understand the chemistry of the polymer and asphalt. It seems that polymers do not reduce aging. FTIR data have shown that multiple PAV aging introduced polar carboxylic acid oxygen species. The concentration of acid groups increased with the aging time. It was higher when the aging operation was carried out in the presence of water. Generation of acid carboxylic groups may improve the adhesion to aggregates from asphalt pavement. At the same time, the acid polar groups could lead to aggregation of asphaltene components from base AC. Aging drastically reduced the molecular mass of SBS species and increased the content of LMS asphalt components. The relative condition of the remaining asphalt without polymer cannot be deduced at this point.

Rheological Investigations

The asphalt architecture has been simulated with that of a gel. The cross-over temperature at which G" equals G' as temperature increases was considered as the critical temperature and chosen as a criterion to assess the advancement of hardening (aging). Critical temperature is dependent on frequency and, therefore, data have been compared at a frequency of 10 rad/s. Initially the SBS copolymer additive helped to disperse the asphaltenes. Breaking of C=C bonds shortened the B blocks and encouraged formation of an open gel structure. Upon aging, the copolymer crosslinked and contracted around the asphaltene aggregates. The combination of these effects with aggregation of asphaltenes led to an increase of the PMAC critical temperature. Critical temperatures of asphalts aged in the presence of water were inferior to that of dry-aged PAV samples. Further research on the chemistry of this effect is recommended.

Field Data Evaluation

Critical temperature of the field 3-year-old I-55 paving sample correlated better with the laboratory wet 0.5xPAV aged PMAC sample. Critical temperature of the field 5-year-old I-55 sample was intermediate between T_c of the dry 0.5xPAV and that of the dry 1.0 x PAV laboratory aged PMAC samples. Critical temperature of the field 7-year-old I-55 sample correlated better with the laboratory dry 1.0 x PAV aged PMAC sample. By calibrating the laboratory aging results with field data, a nomogram can be obtained for assessing the aging of SBS PMAC binders. This type of correlation was used to determine if a binder extracted from a damaged road pavement was excessively aged after 3 years of service.

RECOMMENDATIONS

The procedures used in the present project are recommended for forensic analysis of existing pavements to determine levels of oxidation and polymer presence. Louisiana is in a unique situation in the US with roads paved with polymers containing asphalts in use for 5-10 years and with well documented characterization of binders used. Forensic analysis of asphalts extracted from these pavements and the correlations of results obtained with the condition of roads will build a data bank based on which new specifications can be developed

ACRONYMS, ABBREVIATIONS, AND SYMBOLS

AASHTO	American Association of State Highway and Transportation Officials
C_s	solution concentration
DMA	dynamic mechanical analysis
DRI	differential refractive index
DSR	dynamic shear rheometer
ETC	environmental temperature control
FHWA	Federal Highway Administration
FTIR	Fourier transform infrared
G’	storage modulus of rigidity
G”	loss modulus of rigidity
GPC	gel permeation chromatography
K_i	infrared factor
LADOTD	Louisiana Department of Transportation and Development
LMS	large molecular species
LTRC	Louisiana Transportation Research Center
meq	10^{-3} equivalents
MW	molecular weight
PAV	pressure aging vessel
PG	performance grade
pH	the $-\log_{10}$ of the concentration of protons $[H^+]$ in solution
PMACs	polymer modified asphalt cements
rad/s	unit for angular frequency expresses in radian/second
RTFO	Rolling Thin-Film Oven Test
SBS	styrene-butadiene-styrene
SHRP	Strategic Highway Research Program
tanδ	tangent of loss angle with the value of G”/G’
T_c	critical temperature or cross-over temperature at which G” equals G’
TFOT	Thin-Film Oven Test
THF	tetrahydrofuran
WLF	Williams Landel Ferry
WRI	Western Research Institute

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APPENDIX A

FTIR Procedure for Detection and Quantification of Oxidized Species in Aged Binders

Films of asphalts and rubber are cast from toluene on a NaCl plate and analyzed taking the blank plate as background. The concentration of toluene solutions (5-10 wt %) and the solution amounts pipetted on plates (0.5-1.0 ml) are kept the same. Aging is reflected in the infrared spectra of asphalts by multiple peaks centered around 1695 cm^{-1}, which correspond to carbonyl (C=O) absorptions of oxidized species, such as ketones or carboxylic acids. The relative degree of oxidation of the samples is estimated by comparing the intensity of the 1695 cm^{-1} region to that of 1455 cm^{-1}, which is attributed to C-C vibrations. Benzoic acid (C_6H_5-COOH) is used for making a calibration curve and the results are expressed in equivalents of benzoic acid/g sample. Since benzoic acid has only one carboxylic group, the number of equivalents of benzoic acid equals the equivalence number of carboxylic groups.

Five solutions of benzoic acid in un-aged asphalt with concentrations 0.005, 0.010, 0.020, 0.040, 0.060, and 0.100 meq/g are required to be made in order to build a good calibration curve. Solutions (10 g) are made by dissolving the appropriate amount of benzoic acid in base asphalt (without polymer) at 100°C under inert atmosphere (nitrogen or argon). For example, by dissolving 0.0122 g benzoic acid in 9.9878g of base asphalt, one makes an asphalt blend containing 0.010 meq/g of carboxylic groups (assuming that initially there are no carboxylic groups in the base asphalt cement). The exact concentration of solutions, C_s, expressed in 10^{-3} equivalents (meq) of carboxylic acid groups/g of solution is determined as follows:

$$C_s \text{ (meq/g)} = W_{BA}/0.122\ (W_{BA} + W_{AC}) \qquad (1)$$

where,

W_{BA} is the weight of benzoic acid (g),

W_{AC} is the weight of base asphalt cement (g), and

0.122 represents the weight (g) of 1 meq of benzoic acid.

Solutions in toluene are made from each calibration sample and films on the NaCl plate are cast as described above. The FTIR absorbance is recorded for each calibration sample between 600 and 2000 cm^{-1}. A factor K_i is determined as exemplified in Figure 21 using the absorbance values for each solution at 1695 cm^{-1} and 1455 cm^{-1}:

$$\log (AC/BC)/\log(DF/EF) = K_i \qquad (2)$$

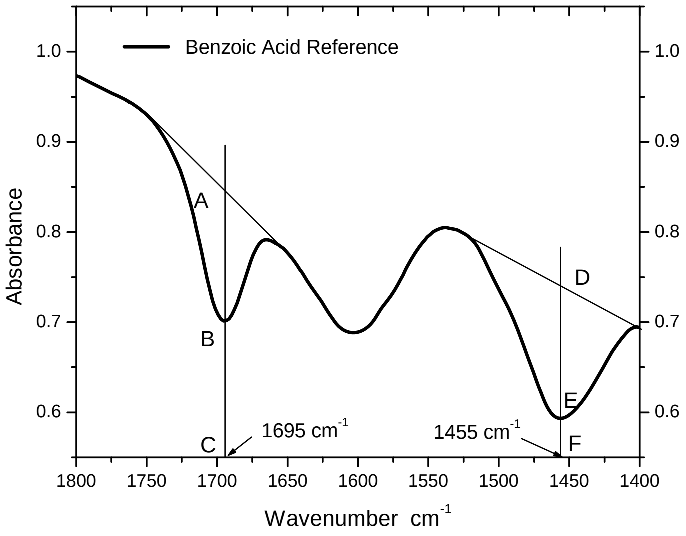

Figure 21
Illustration of method for quantifying carboxylic acid group content in asphalt binders using benzoic acid as reference monocarboxylic acid

APPENDIX B

Potentiometric Non-Aqueous Titration Method for Determination of Acidity of Asphalt Binders

Titration is a standard laboratory method of quantitative/*chemical analysis*, which can be used to determine the *concentration* of a known *reactant*. Because volume measurements play a key role in titration, it is also known as *volumetric analysis*. A *reagent*, called the *titrant*, of known concentration (a *standard solution*) and *volume* is used to react with a measured quantity of reactant (*analyte*). Using a calibrated *burette* to add the titrant, it is possible to determine the exact amount that has been consumed when the *endpoint* is reached. The endpoint is the point at which the titration is stopped.

This is classically a point at which the number of *moles* of titrant is equal to the number of moles of analyte. In the classic strong acid-strong base titration, the endpoint of a titration is when the pH (i.e., the $-\log_{10}$ of the concentration of the protons, $[H^+]$, liberated as shown in equation (3), with a scale from 1 for strong acids to 14 for strong bases; at pH = 7 the solution is neutral, viz., it is neither acidic nor basic) of the reactant is just about equal to 7 and often when the solution permanently changes color due to an *indicator*.

The term *back titration* is used when a titration is done "backwards": instead of titrating the riginal analyte, one adds a known excess of a standard reagent to the solution, then titrates the excess. A back titration is useful if the end point of the reverse titration is easier to identify than the end point of the normal titration. They are also useful if the reaction between the analyte and the titrant is very slow.

The normality of an acid solution is the number of equivalents per liter (moles per liter) of protons that it can dissociate. The normality of a solution of a base is equal to the number of equivalents of acid it can neutralize. The normality of a solution of a triprotic acid is three times its molarity (number of moles per liter). In discussing titrations of acid and base solutions, it is often convenient to think in terms of milliequivalents (meq).

Titrations are often recorded on titration curves, whose compositions are generally identical: the *independent variable* is the volume of the *titrant*, while the *dependent variable* is the pH of the solution (which changes depending on the composition of the two solutions). The *equivalence point* is a significant point on the graph (the point at which all of the starting solution, usually an acid, has been neutralized by the titrant, usually a base). In *monoprotic acids*, the point halfway between the beginning of the curve (before any titrant has been added) and the equivalence point is significant. At that point, the milliequivalent content of the two solutions (the titrant added and the original solution) is equal.

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Titrations can be classified by the type of reaction or by the method used to determine the endpoint. The *acid-base titration* represents the neutralization reaction between the analyte and an acidic or basic titrant. Strong acids, like hydrochloric acid, are completely dissociated in water, but weak acids, like carboxylic acids, are only partially dissociated. The extent of dissociation can be calculated from the value of the equilibrium constant and the amounts of weak acid and strong base added to the solution. The relative acidities of acids and bases are commonly expressed in terms of $pK_a = -\log_{10}K_a$

where, K_a is the dissociation constant for the reaction:

$$HA \rightarrow H^+ + A^- \qquad (3)$$

In the following derivation, a_{A^-}, $[A^-]$ and γ_{A^-} represent, respectively, the activity, the molar concentration, and the activity coefficient of the conjugate base, A^-.:

$$K_a = (a_H^+)(a_A^-)/(a_{HA}) = [H^+][A^-]/[HA] * (\gamma_{H^+})(\gamma_{A^-})/(\gamma_{HA}) \qquad (4)$$

Since

$$pK_a \equiv -\log K_a \qquad (5)$$

then

$$pK_a = -[\log (a_{H^+}) + \log (a_{A^-}) - \log (a_{HA})] \qquad (6)$$

Since

$$pH \equiv -\log (a_{H^+}) \qquad (7)$$

then

$$pK_a = pH + \log (a_{HA}) - \log (a_{A^-}) \qquad (8)$$

or

$$pK_a = pH - \log \{(a_{A^-})/(a_{HA})\} \qquad (9)$$

and

$$pK_a = pH - \log \{[A^-]/[HA] * (\gamma_{A^-})/(\gamma_{HA})\} \qquad (10)$$

Making the approximation that

$$(\gamma_{A^-})/(\gamma_{HA}) \cong 1 \qquad (11)$$

yields an apparent pH given by

$$pH = pK_a + \log ([A^-]/[HA]) \qquad (12)$$

This equation is referred to as the Henderson-Hasselbalch equation. It is very useful in the buffering region of the titration of a weak acid, such as carboxylic acid groups from asphalts. The pK_a is $-\log K_a$ at the ionic strength of the solution. Accordingly, the value of K_a obtained will deviate slightly from values listed in standard references since they report the thermodynamic value at zero ionic strength. Note that the pK_a is the pH at which the activities of the acid HA and its conjugate base A^- are equal.

The acid-base titrations most commonly use a pH color indicator, a pH meter, or a conductance meter to determine the endpoint. The pH meter is a potentiometer that uses an ion selective electrode whose potential depends on the amount of H+ ion present in the solution. It allows the pH of the solution to be measured throughout the titration. At the end point, there will be a sudden change in the the measured pH. It can be more accurate than the color indicator method and is very easily automated.

A *potentiometric titration* involves measuring, recording, or computing the first derivative of the potential of a single *indicator electrode* with respect to the volume or otherwise added amount of reagent (IUPAC Compendium of Chemical Terminology 2nd Edition, 1997). The *equivalence point* can be calculated precisely by finding the *second derivative* of the titration curve and computing the *points of inflection* (where the graph changes *concavity*). A typical potentiometric curve is presented in Figure 22.

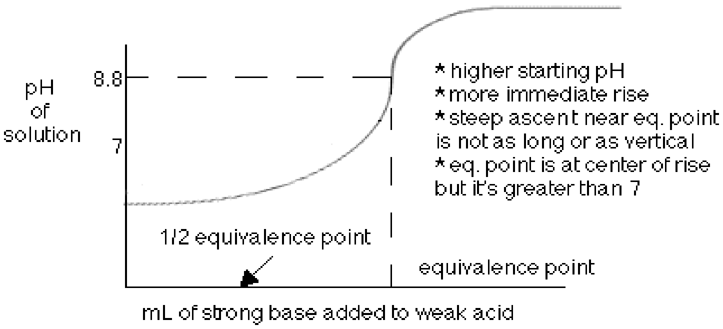

Figure 22
Equivalence point determination for potentiometric titration of acidity of asphalt samples

For the titration of weak acids, the equivalence point is reached when the pH is greater than seven [see equation (12)]. The half equivalence point is when half of the total amount of base needed to neutralize the acid has been added. Calculations are made and expressed as meq/g of acid groups in asphalt sample.

Ion-selective electrodes are used for detection of specific ions in a mixture of ions. The sensor element, an ion-selective membrane, has a construction similar to that of a glass electrode (Figure 23). It converts the *activity* of a sp specific *ion* dissolved in a solution into an electrical *potential* that can be measured by a *voltmeter* or *pH meter*.

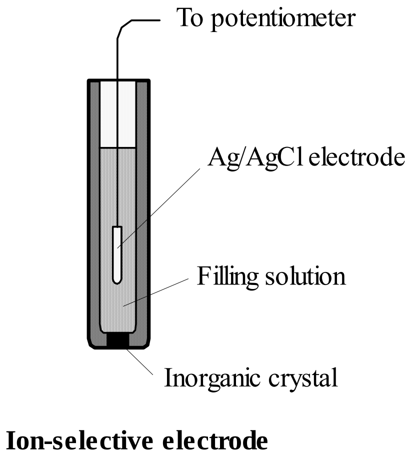

Figure 23
Construction of an ion selective electrode

Experimental

Burette Calibration. Use only deionized water that has been allowed to settle at room temperature for a few hours. Measure the temperature of the water and then record it in a notebook. Fill a 50 mL burette until it reads 0.00 mL. Confirm that neither trapped air nor a slow leak is present. Empty the burette into a small, tarred flask in 8.5 mL increments (so that a total of 6 measurements are taken). Note the volume to the nearest 0.01 mL, and measure the mass of each aliquot. Repeat this process trying to approximate similar aliquot volumes. Record the volume delivered versus individual differences at each aliquot. Repeat any measurements that differ by more than 0.04 mL; otherwise, average the values from each attempt. Produce a graph that plots cumulative delivered volume versus correction, which can be used to calculate the correct volume. Include this graph in the supplemental information section of the experiment. The information will be used to correct data later.

Instrument Calibration. Calibrate the pH meter according to the instrument instructions using buffers with pH 7, 4, and 10 (*vide infra* for the instructions listed for Orion 710Aplus pH meter used in the reported work). When finished, rinse and store pH electrodes in pH 7 buffer.

General Procedures. All glassware, chemicals, solutions, and titration set-up must be flushed with argon and sealed.. Argon is preferred to nitrogen because the gas density is higher than that of air and it is not easily replaced by it.

1. Flush the burette first with the solvent (titrant) and then with argon before use. Seal the burette if not used immediately.
2. Accurately measure the volume of the solvent into an Erlenmeyer flask under argon atmosphere.
3. Add a suitable volume of solvent to cover the electrode sensitive part and keep it constant for all the determinations.
4. Read the *start-point* of the liquid on the burette if different of 0.00 mL.
5. As is standard for measuring any liquids in the laboratory, measure from the bottom of the *meniscus* if it is concave and from the top if it is convex.
6. Turn the tap of the *burette* to allow the titrant to fall slowly into the reactant. Swirl the flask with a *magnetic stirring bar*.
7. As the end-point is approached, add the titrant more slowly at this point (one drop at a time).
8. When finished, rinse and store pH electrodes in pH 7 buffer.

Preparation of Solvents and Reagents. The follwing reagents are required:

1. Standard potassium hydrogen phthalate, KHP. Molecular weight, MW = 204.23 D (Dalton)
2. Benzoic acid, BA, MW = 122.12 D
3. Tetra butyl- ammonium hydroxide, TBAH, MW = 799.96 D
4. Solvents: toluene, isopropyl alcohol, chlorobenzene, and ethyl alcohol (ethanol).

Prepare the following solutions (in argon atmosphere to prevent the absorption of water from air by solvents; the thermostat controlling the temperature of the room should be set at standard 70°F). Crystalline KHP and BA must be dried for 2 hours at 105°C before use.

- Solution A: a mixture of chlorobenzene/ethanol (9 to 1 volumetric ratio)
- Solution B: a mixture of toluene/isopropyl alcohol (43 to 7 volumetric ratio)

Prepare 1L 0.05M KHP Using Solution A. Place the solid KHP (10.211g , 0.05 M) in a 1L volumetric flask and add 900 ml solution A. Dissolve of the salt by heating the solution under vigorous stirring almost to boiling until all the crystals dissolve (use an electric heating/magnetic stirring plate). Allow the solution to cool to room temperature, usually overnight; cap the flask under argon and adjust the solution volume to 1,000 mL by adding solution A.

Prepare 1L 0.05M BA Using Solution A. Dissolve BA (6.106 g, 0.05 M in 1000 mL solution A using the same procedure as described above for preparation of the 05M KPH solution.

Prepare 1L 0.05 MTBAH Using Solution B. Dissolve TBAH (39.998 g, 0.05 M in 1000 mL of solution B using the same procedure described above for the other two solutions.

Prepare the Asphalt Solution Using Solution A. Approximately 3 grams of asphalt (m_1) are weighed on a scale with sensitivity of no less than 0.001 g, and placed in a 250 mL Erlenmeyer flask (flushed with argon) containing 50 mL solution A, and stirred magnetically to allow complete dissolution.

Titration. The asphalt solution is titrated with 0.05 M TBAH in solvent B as follows: Place the Erlenmeyer flask containing the asphalt solution on a magnetic stirrer. On the top of the flask, place the argon tube and the burette with the titrating base (tetrabutyl-ammonium hydroxide solution). Dip the electrode into the solution. Be sure that the pH electrode is not in a position to be damaged by the magnetic stir bar. No air bubbles should be trapped under the polyethylene shield of the electrode. Also, make sure that no air bubble is trapped in the tip of the burette. Insulate the beaker from the magnetic stirrer with a layer of folded paper towel to prevent warming of the solution by the magnetic stirrer. Start stirring. Wait until the potential reading is stabilized and record the zero ml base point, and then start the actual titration using small amounts of base (0.5 ml/dose). With continuous stirring, add small increments of the 0.05 M standard solution of TBAH from the burette. Give the solution and instrument (pH meter) time to equilibrate. Read and record the potential of the solution after addition of each portion of the TBAH solution. Initially, the change of the potential upon the addition of titrant will be minimal. However, as the first equivalence point is approached, potential increments will increase more rapidly, and only drop wise increments of TBAH until it is apparent that the first equivalence point has been passed.

Separate titrations are made using 0.05 M solutions of KHP and BA dissolved in solution A. All titrations are made at room temperature set at 70°F. Collected data are recorded in Excel, and titration curves are developed and analyzed for the equivalence point. A typical potentiometric titration curve is presented in Figure 24.

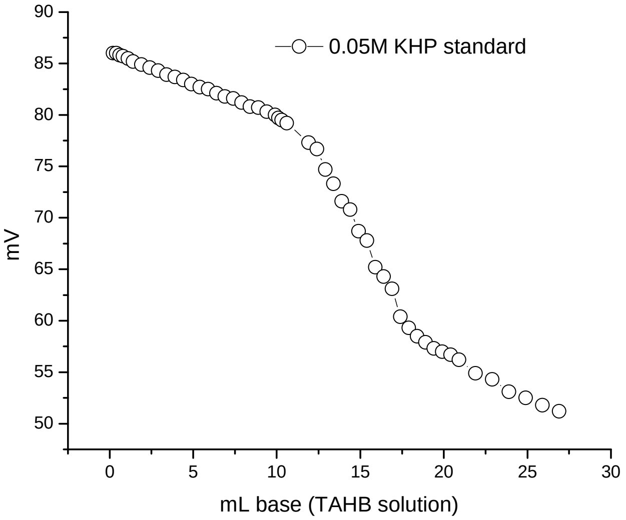

Figure 24
Non-aqueous potentiometric titration of KHP with TBAH solution

Treatment of Results

The concentration C_{acid} of acid groups in asphalt expressed in *meq/g* is given by:

$$C_{acid} = (0.05\ V_1/m_1)*(V_3/V_2) \qquad (13)$$

where,
m_1 is the amount of asphalt dissolved and analyzed,
V_1 is the volume (mL) corresponding to the equivalent point for the titration of the asphalt solution with 0.05 M TBAH base,
V_2 is the volume (mL) corresponding to the equivalent point for the titration of the 0.05M KHP solution with 0.05 M TBAH base, and
V_3 is the volume (mL) of 0.05 M KHP solution titrated with 0.05 M TBAH base.

A back titration is recommended if the concentration of acid groups in asphalt is low and the equivalence point is in doubt. To this aim, a known volume V_4 of 0.05 M BA solution is added in the Erlenmeyer flask containing the asphalt sample of mass m_1, and the titration is carried out as described previously. The concentration C_{acid} of acid groups in asphalt expressed in *meq/g* is given by:

$$C_{acid} = [0.05\ (V_1 - V_4)/m_1]*(V_3/V_2) \qquad (14)$$

Warning: Be sure no drops are left on the tip of the burette when reading the potential. The drop is part of the measured volume. There will not be good correlation between volume and potential if part of the volume measured is omitted. This is especially important in the regions of rapid potential change.

Orion 710Aplus pH Calibration. The pH meter should be calibrated prior to conducting a titration as follows:

1. Connect electrodes to meter. Choose buffers that will bracket the expected sample pH.
2. Press **mode** until the pH mode indicator is displayed.
3. Rinse electrode(s) and place into buffer.
4. Press **2nd** then **cal** to begin calibration. **CALIBRATE** is displayed above the main field. The date and time of the last calibration will be displayed.
5. When the electrode is stable, the **READY** prompt will be displayed and the

temperature correct value for the buffer is displayed. Press yes. If performing manual calibration, press **up** or **down** to change the values, then press **yes**. The buffer value is stored and meter display freezes for three seconds. The meter automatically switches to buffer two, indicated by the “P2” on the display in the lower field.

6. Repeat steps 3 and 5 for each buffer.

7. After the buffer value for the last buffer has been entered, the electrode slope will be displayed automatically. If doing a manual calibration or less than a 5 point autocalibration, press **measure**. SLP appears in the lower field while the actual electrode slope, in percentage, appears in the main field. The meter automatically advances to the measure mode. **MEASURE** is displayed above the main field.

8. Rinse electrode(s) and place into sample. Record pH directly from the main meter display when the **READY** prompt displays. Temperature is displayed in the lower field.