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Oxidative Aging of Asphalt Cements from an Ontario Pavement Trial

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Abstract: This paper documents and discusses a rheological and spectroscopic investigation of the oxidative aging in asphalt cements from a 2003 northern Ontario pavement trial. Seven asphalt cements were aged according to standard methodology (rolling thin film oven test (RTFOT) and pressure aging vessel test (PAV)), as thin films at temperatures of 45, 65, and 85 °C and standard pressure (thin film oven test (TFOT)), and under modified PAV conditions (extended time of 40 hours). It was found that the current RTFOT/PAV protocol provided insufficient aging for the poor performing asphalt cements. Infrared analysis of the TFOT-aged samples for the formation of carbonyl groups could largely explain the performance ranking in service. The only significant outlier was modified with polymer and waste engine oil residue. Rheological investigations of the recovered and the TFOT-aged residues were able to show that such materials likely suffer from early gel formation. These findings illustrate the need for improved asphalt cement aging protocols. A preliminary example is provided that shows how simply doubling the PAV aging time to 40 hours can produce materials that more closely replicate those aged for 5-6 years in a northern Ontario climate. It was further confirmed that both chemical and physical hardening tendencies are closely correlated, likely because they involve similar asphalt constituents.

Key words*: Asphalt cement; Cracking; Specification grading; Oxidative and physical hardening.*

Introduction

Low temperature cracking in adjacent asphalt paving contracts or trial sections for identical AASHTO M320 grades can range from best-case to worst-case scenarios [1, 2]. The ubiquitous nature of such cracks can largely be attributed to the use of inappropriate test protocols for material selection. The currently used asphalt cement specification, as embodied in the AASHTO M320 standard, regularly fails to prevent premature and excessive cracking for the following reasons:

1. Bending beam rheometer (BBR) samples are conditioned for only one hour prior to testing and therefore fail to capture the physical hardening phenomenon [1-3];
2. Measurements are made in the linear viscoelastic regime and largely ignore variations in high strain (failure) properties [1, 2]; and
3. Oxidative aging in the RTFOT/PAV fails to replicate hardening in service [2, 4-6].

These insufficiencies promote the use of undesirable asphalt sources and modification technologies (air blowing; use of waxes, polyphosphoric acid, waste engine oils, “gelling agents”; blending of incompatible asphalts, etc.) to reach a given grade, often causing premature and excessive hardening and consequent thermal cracking [1-3].

The first two issues have received our attention over the past ten years. The reader is referred to earlier publications to learn more about how physical hardening tendencies and variations in asphalt cement toughness help to explain performance variability [1-3, and references therein].

The third issue has been considered by a significant number of research programs over the years, but an improved and practical oxidative aging method has yet to be adopted. Hence, we have undertaken to develop an improved version of the RTFOT/PAV protocol. This investigation started with a look at the premature hardening that has occurred in several Ontario pavement trial sections constructed in support of a comprehensive undertaking to develop better asphalt cement specifications.

The objective of the research described herein was to obtain a better understanding of the fundamental oxidative aging processes that cause the performance to vary enormously between seven test sections constructed with asphalt cements of identical AASHTO M320 grades. The trial area is located on Highway 655 just north of Timmins, Ontario, in a climatic zone that regularly experiences extremely low temperatures. All seven side-by-side test sections were designed with identical thickness, asphalt cement contents, air void contents and other variables that are known to affect cracking distress.

Background

Historical Development of the RTFOT/PAV Protocol

Early asphalt cement aging tests focused on replicating the aging that occurs during production and compaction of the hot mix asphalt. Volatility loss during heating of a relatively thick film of material in a flat dish was standardized in the ASTM D6 Loss on Heat test over 100 years ago. This test is generally no longer used since the thick film is not representative of the way that aging occurs during the production of hot mix asphalt [7].

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The thin film oven test (TFOT, 1940) and later the rolling thin film oven test (RTFOT, 1963) were developed to increase the degree of aging. The RTFOT test was generally considered to be an improvement over the TFOT as it prevents an oxidized skin from forming on the surface of the asphalt cement, although a high correlation between the two methods has since been recognized [7-9].

In the late 1980s, with the start of the U.S. Strategic Highway Research Program (SHRP), an asphalt cement aging method was sought that would not suffer from the phase separation problems associated with both the TFOT and RTFOT in situations where highly polymer-modified materials were processed [10]. Both the TFOT and RTFOT are conducted at high temperatures that can cause rapid phase separation in many polymer-modified materials. Hence, a test at lower temperatures and higher pressures would allow for sufficient aging while avoiding phase separation. The pressure aging vessel (PAV) was adopted based on an oxygen pressure vessel developed at Iowa State University [11]. The oxygen was replaced by compressed air early during the SHRP, for safety reasons, and the temperature was increased from 60ºC to 90-110ºC to conduct the test within a 20 hour period rather than the 144 hours in the original work [12]. The RTFOT/PAV protocol was never validated with sufficient field data, and the original researchers cautioned that some accuracy was sacrificed by switching from 60ºC to higher temperatures. Since the development of the current PAV protocol, there have been a number of field validation attempts, which are discussed in the following section.

Validation Studies for Oxidative Aging Protocols

The validation efforts of the RTFOT/PAV protocol for asphalt cement aging have provided mixed messages, with some supporting studies and others raising doubts about its validity. The original SHRP researchers developed the PAV method and tested the rheological properties of 12 asphalt cements for which test sections were available. Unaged, TFOT-aged, PAV-aged, and field-aged asphalt cements were tested at 25ºC for their complex loss modulus (G''); based on these findings, the researchers stated that "the PAV appears to highly resemble the changes in rheological properties that asphalts are undergoing due to aging in the field" [12]. However, limited validation tests were done on asphalt cements from test sections of five different trials (from as far south as Florida and California to as far north as Pennsylvania, Washington, and Wyoming). These materials were recovered after 4 to 19 years of service, and low temperature properties were not examined. Hence, the positive conclusions may have been premature, given the limited data and the qualitative nature of the study.

A subsequent validation attempt by Galal and White [13], which looked at a large number of contracts and studied six in more detail, contradicted the findings of the SHRP. The authors stated in their conclusions that "neither the short term aging procedure (RTFO test) nor the long term aging procedure (PAV test) succeeded in accurately simulating field aging in Indiana pavements." They went on to say that a realistic aging protocol must be developed to avoid premature pavement deterioration due to thermal cracking. Since these early efforts, a large number of studies have supported the RTFOT/PAV aging approach either in part or in full [8, 14, 15, and others] or considered it to be inadequate [4-6, and others]. However, these studies looked at a wide range of temperatures and pressures in the PAV method, and none of them considered low temperature performance of aged asphalt cement in detail. In view of these contradictions, and since low temperature properties are most important to control thermal and fatigue cracking, the issue of which oxidative aging method is best used for northern climatic conditions merits further study.

Table 1. Asphalt Cements Details.

Section	Modification	AASHTO M320 Grade, °C
655-1	RET + PPA	64-34
655-2	Ox + SBS	64-34
655-3	SBS	64-34
655-4	SBS + WEO	64-34
655-5	SBS	64-34
655-6	Ox	58-34
655-7	WEO	52-34

Note: All asphalt cements were modified. Modifiers for this trial included reactive elastomeric terpolymer (RET) with polyphosphoric acid (PPA), and styrene-butadiene-styrene (SBS). Undisclosed additives such as PPA and/or regular phosphoric acid (H_3PO_4) in Section 655-6 were likely used as a catalyst for the production of air oxidized asphalt (Ox), and waste engine oil (WEO) residue in Sections 655-4 and 655-7 was likely used to boost the grade span and/or dilute the straight asphalt cement [2, 14]. Grades were determined from pass/fail tests after one hour of conditioning at the test temperature and are rounded to the nearest 6°C. The required Superpave^{TM} grade for the trial area is PG 52-34.

Materials and Methods

Materials

The seven asphalt cements investigated in this study were used for the construction of seven side-by-side test sections on Highway 655 just north of Timmins, Ontario. The location is regularly exposed to extremely low temperatures.

Asphalt cements were obtained from the sampling valve on the pipeline feeding directly into the hot mix plant during the construction of each individual test section. Materials aged in service were obtained by extracting core samples with tetrahydrofuran (THF). Details of the extraction procedure can be found elsewhere [2]. However, it should be mentioned that extra care was exercised so that the extraction and recovery procedure did not alter the asphalt cement properties. In particular, infrared spectra were taken before and after recovery to make sure that the solvent removal from the extract did not significantly alter the oxidation state of the binders. The pertinent compositional and grading data for materials as sampled during construction are provided in Table 1 [2].

The trial was designed so that all seven asphalt cements graded in the bending beam rheometer (BBR) at between -35°C and -36°C. This is just above the -37°C needed to obtain a 98% confidence level to ensure that no damage will occur in any given winter for the Timmins, Ontario, area [2].

The construction of the trial sections was governed by the end result specification system (ERS) of the Ministry of Transportation of Ontario (MTO). The contractor obtained a bonus for the quality obtained and no notable issues arose regarding any of the measured variables under the ERS system (voids, VMA, VFA, lift thickness, fines, and asphalt cement content all fell within the narrow range of acceptable limits). Further details about the construction of the test sections and site characteristics can be found in our previous publication [2].

Methods

The trial sections have been surveyed at regular intervals following their construction in late 2003 [2]. The cracking distress and ride comfort indices were measured in detail during a survey conducted by MTO staff in 2008 and in a more cursory inspection by one of the authors in the summer of 2010 [2].

The temperature history for this trial has previously been discussed in Hesp *et al.* [2]. In brief, the temperature is monitored with two thermocouples placed in trees alongside the road and eight thermocouples glued into the pavement surface. The loggers are battery operated and record a temperature reading every 30 minutes over an entire year. In the spring of each year, batteries are replaced and the data is downloaded. The air temperature reached a record low of approximately -48ºC on January 9, 2004. The pavement temperature reached the design value of -34ºC on two occasions on January 9 and January 15, and fell below -30ºC on eight separate occasions during the first winter. In early 2005, the air temperatures reached around -40ºC on six occasions, while the pavement at 5 mm below the surface reached -30ºC or slightly lower on five occasions. In early 2006 the two lowest air temperatures recorded were around -39ºC with what would have been corresponding surface temperatures of around -30ºC or slightly lower. Air temperatures for 2007 reached between -35ºC and -40ºC on 16 occasions, with corresponding pavement temperatures in the -25ºC to -30ºC range. For 2008, the lowest air temperature of approximately -35ºC was reached on January 20, with corresponding pavement surface temperatures of approximately -24ºC. It is clear that this pavement trial is located in an ideal area where pavement surface temperatures reach close to the design value on regular occasions.

Asphalt cements were aged according to standard RTFOT (AASHTO T240) and PAV (AASHTO R28) methods and graded according to the regular AASHTO M320 specification [16] as well as Ontario's extended BBR standard test method, LS-308 [17], and double-edge-notched tension (DENT) test method, LS-299 [18]. The LS-308 method conditions the asphalt cement for periods of one, 24, and 72 hours at both 10°C and 20°C above the pavement design temperature and calculates the limiting temperatures according to regular AASHTO M320 criteria where the stiffness at 60 seconds reaches 300 MPa or the m-value at 60 seconds reaches 0.3. In addition to using the warmest limiting temperature to set the low temperature grade, the specification also places a maximum at the three day grade loss [1, 2]. The LS-299 DENT test sets a limit on the strain tolerance as given by an approximate critical crack tip opening displacement (CTOD) in order to avoid overly gelled binders. It is expected that this specification provides a significant incentive for asphalt cement suppliers to use better quality asphalt cement sources and production techniques.

Additional oxidative aging protocols investigated for this study included the following:

1. Thin film oven (TFO) aging at 45°C, 65°C, and 85°C to study chemical and rheological changes under more moderate conditions compared to those for the RTFOT/PAV;
2. Extended PAV aging for 40 hours rather than the normal 20 hours.

The TFO aging experiments were conducted to investigate the effect of thinner films and extended times on the chemical and rheological changes that occur in these asphalt cements of different origin and composition. The TFOT-aged materials were investigated with infrared spectroscopy (IR) to monitor changes in carbonyl, sulfoxide, aromatic, and butadiene concentrations, and dynamic shear rheometry (DSR) to monitor changes in rheological performance.

Infrared spectral ranges were integrated to determine carbonyl, sulfoxide, aromatics, and butadiene indices using the CH_3 methyl peak as an internal standard. A Bomem model 120 infrared spectrometer was used to take 32 scans, over the range of 4000-400 cm^{-1}, for each specimen. The spectrum was integrated from 1400 to 1330 cm^{-1} to determine the absolute CH_3 concentration (this signal is known to be relatively inert to oxidative changes). The peaks for carbonyl, aromatics, and sulfoxide were located at 1700 cm^{-1}, 1600 cm^{-1} and 1030 cm^{-1}, respectively. Hence, the integral bounds used were from 1760 to 1655 cm^{-1}, 1650 to 1535 cm^{-1}, and 1070 to 985 cm^{-1}, respectively.

The change in the PAV protocol of doubling the aging time from 20 hours to 40 hours was investigated to explore a simple modification to improve the current AASHTO PAV approach [19].

Results and Discussion

Distress Surveys

The distress surveys were conducted by staff of the Northeastern Regional Office of MTO in summer 2008 and in a more cursory fashion by one of the authors in summer 2010. The detailed 2008 findings are provided in Fig. 1 [2], while representative images for several sections are provided in Fig. 2.

The data show three categories of materials. Sections 655-1 and 655-5 have remained largely free of distress. Sections 655-2, 655-3, 655-6, and 655-7 have cracked prematurely and severely. Finally, Section 655-4 has cracked prematurely, severely and excessively. At various times over the last eight years, and depending on how the distress is expressed (e.g., transverse versus total cracking), these trial sections have shown slightly different rankings. Hence, we have considered it prudent to group these materials in this more general way rather than to focus on what can only be considered as minor differences [2].

The more cursory survey in 2010 by one of the authors has shown that Section 655-1 has remained largely free of distress and that Section 655-5 has started to show mild transverse cracking as well as more regular cracking along the centerline joint. Furthermore, the distress in Sections 655-6 and 655-7 has increased relative to the others so that both are now approaching that of Section 655-4.

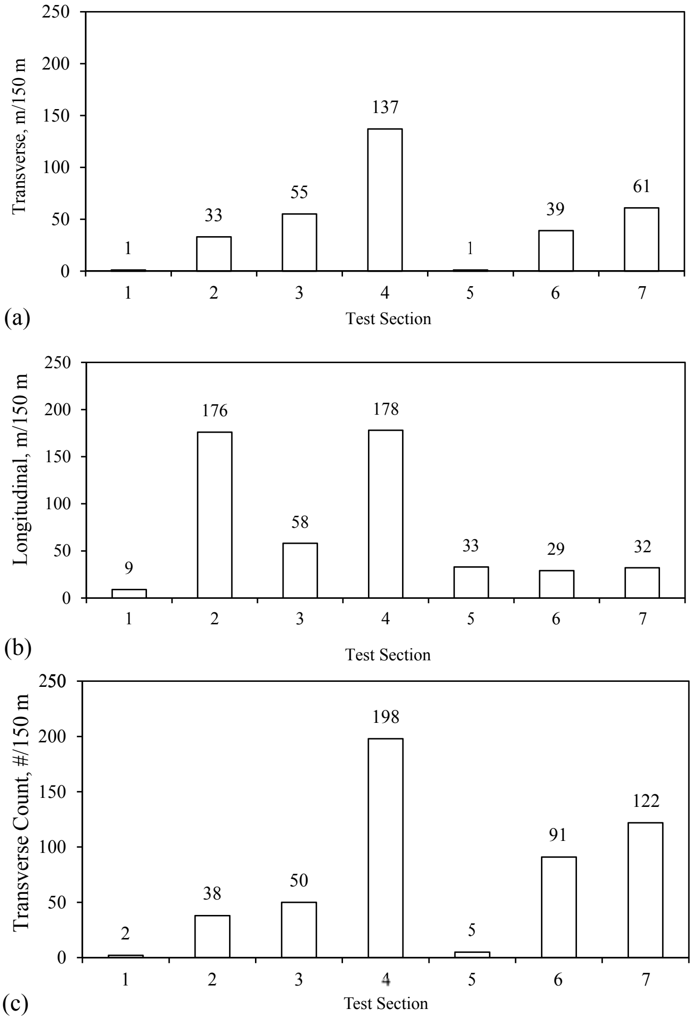

Fig. 1. (a) Transverse Distress; (b) Longitudinal Distress; and (c) Transverse Crack Counts [2].

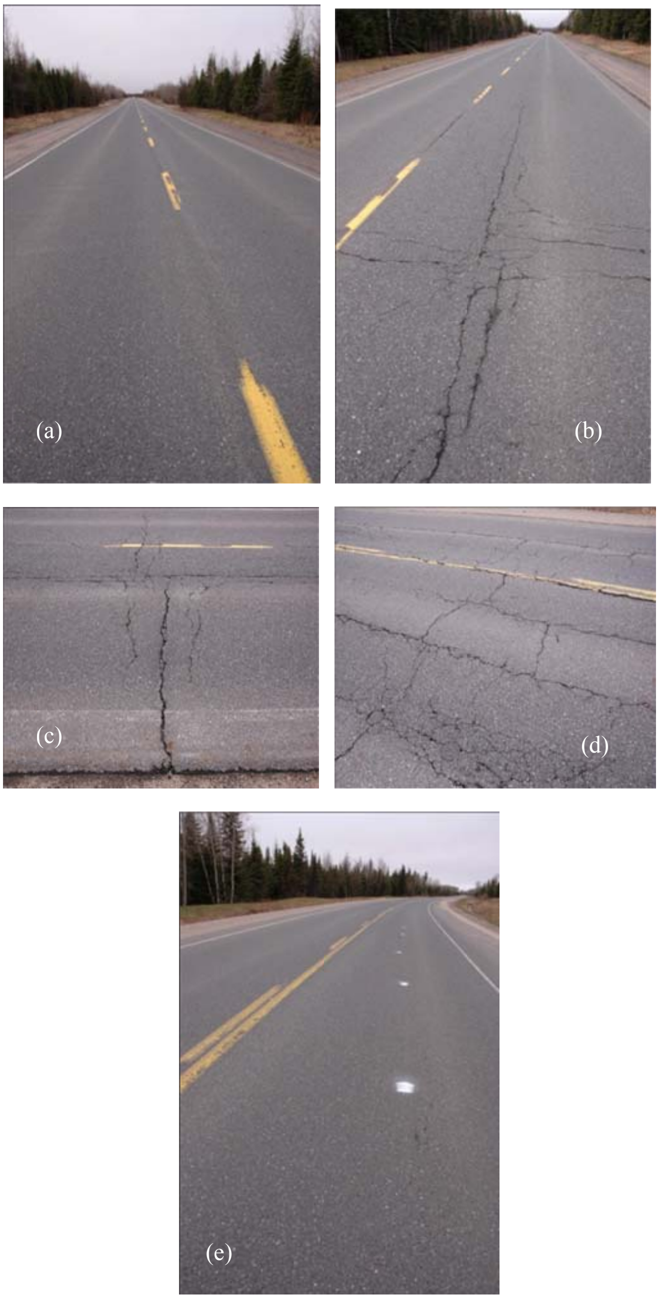

Fig. 2. Representative Photographs for Trial Sections: (a) 655-1, (b) 655-2, (c) 655-3, (d) 655-4, and (e) 655-5. *Note*: No photographs were taken for Sections 655-6 and 655-7 in 2008 but these appeared similar to Sections 655-2 and 655-3.

AASHTO M320, LS-308, and LS-299 Grading

Figs. 3 and 4 provide the AASHTO M320 (regular BBR) and LS-308 (extended BBR) findings for the RTFOT/PAV residues as well as the materials recovered from 2008 and 2009 core samples [2]. The regular AASHTO M320 grades for the RTFOT/PAV residues, as provided in Fig. 3, suggest that all these binders should have survived the cold spell in early 2004 when the pavement surface temperature dropped to -34°C on two occasions (they all grade between -35°C and -36°C). This has obviously not happened as most of the sections are now badly damaged after only seven years of service. Hence, in light of the absence of any other causes [2], excessive binder stiffening is likely to blame for the poor performance in five of the sections. The LS-308 grades for the RTFOT/PAV materials, as given in Fig. 3, provide a slightly improved picture, with the Section 655-1 material losing little when conditioned at -12°C and several others losing close to a full grade (6°C) over the three day conditioning period. The fact that Section 655-5 has yet to show significant thermal cracking distress is likely due to its high polymer content providing a significant strain tolerance in the ductile state as measured according to the LS-299 protocol and shown in Fig. 5 [2]. However, as mentioned previously, this section has started to show significant centerline cracking since the last winter and this will likely lead to additional transverse cracking distress over the next few years.

The regular AASHTO M320 grades for the recovered materials provided in Fig. 4 show a stronger correlation with the cracking distress in these test sections. This result suggests that the current RTFOT/PAV protocol is partly to blame for the differences in performance between the various sections of identical Superpave grades. However, a close look at these grades suggests that Section 655-2 should not have failed to the degree that it has, considering

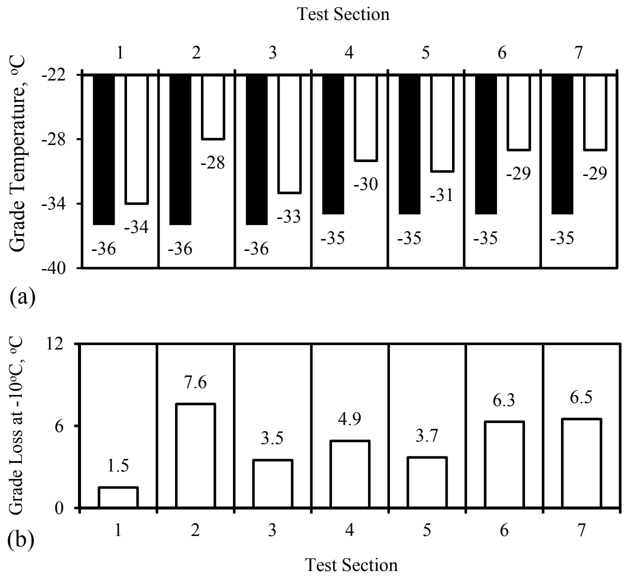

Fig. 3. (a) AASHTO M320 Grades (First Columns) and LS-308 Grades (Second Columns) and (b) LS-308 Grade Losses after Three Days of Condition at -10°C for the Laboratory-aged RTFOT/PAV Residues [2].

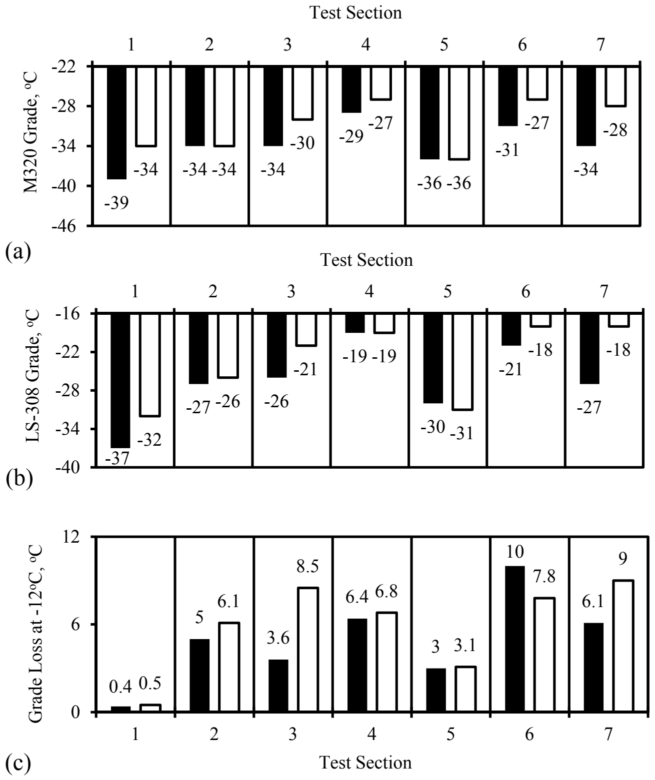

Fig. 4. Grading Results for Recovered Asphalt Cements: (a) AASHTO M320 (First Columns (2008 [2]) and Second Columns (2009)); (b) LS-308 (First Columns (2008 [2]) and Second Columns (2009)); and (c) LS-308 Grade Losses after Three Days Condition at -12°C (First Columns (2008 [2]) and Second Columns (2009)). *Note*: The 2008 and 2009 data are for the most part in good agreement. Significant changes in grades and grade losses for Sections 655-1, 655-3, and 655-7 may reflect errors in measurement or accelerated aging.

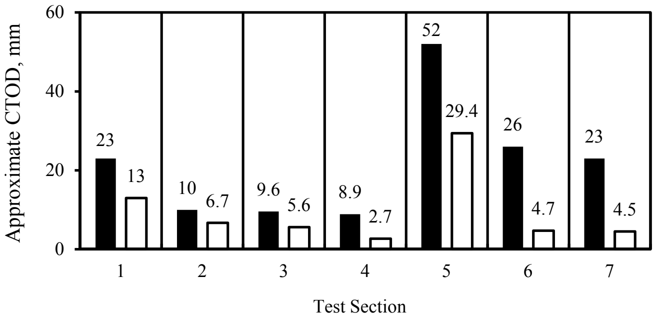

Fig. 5. Approximate Critical Crack Tip Opening Displacement (CTOD) as Measured in the Double-Edge-Notched Tension Test (DENT) for Recovered Asphalt Cements (First Column (2008 [2] and Second Column (2009)). *Note*: The LS-299 protocol was conducted at 50 mm/min and 15°C. Significant reductions in the approximate CTOD between 2008 and 2009 may reflect errors in measurement or accelerated aging.

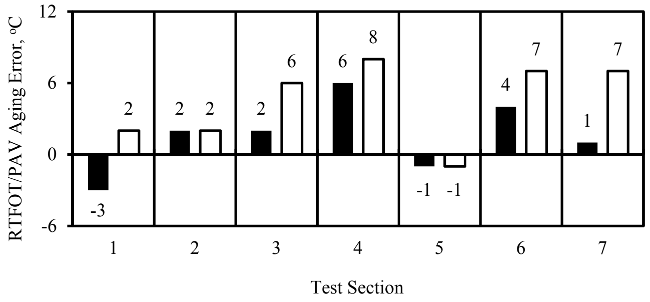

Fig. 6. Approximate RTFO/PAV Aging Errors for 2008 (First Column) and 2009 (Second Column). *Note*: Grading errors were determined as the difference between the RTFOT/PAV residue grade minus the recovered grade according to AASHTO M320 criteria.

that its 2009 recovered binder still graded at -34°C. Hence, it is clear that the problems with the current specification are related to both oxidative and physical hardening. The LS-308 grades for the recovered materials show that the poor performers are penalized more than the good performers, which is a beneficial outcome for any specification grading test.

An approximate error for the current RTFOT/PAV aging protocol is provided in Fig. 6, which gives the difference in AASHTO M320 grades for RTFOT/PAV-aged and recovered materials. These findings, together with the physical hardening losses as provided in Figs. 3(b) and 4(c), show that both oxidative and physical hardening processes can provide equally plausible explanations for the premature and excessive cracking observed in the trial. However, as recognized many years ago by Petersen [20], these processes go hand in hand, so it is not meaningful to enter into a discussion as to whether one is more important than the other.

Thin Film Oven Aging

Thin asphalt cement films of 700 μm thickness were aged in a convection oven at moderate temperatures for a total of 5,000 hours

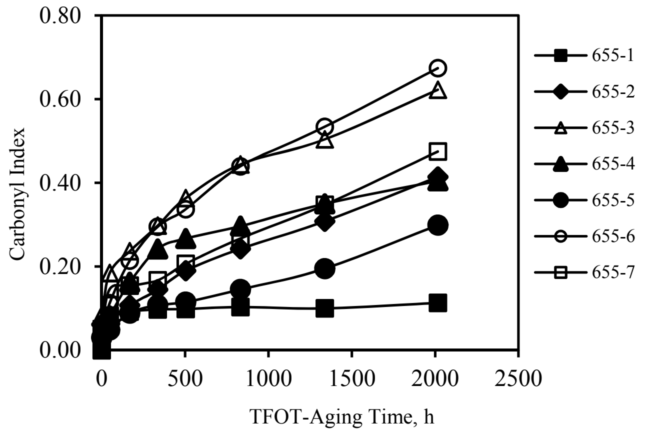

Fig. 7. Carbonyl Indices as a Function of Time for TFOT-aged Asphalt Cement Film. *Note*: Film thickness was 700 μm and temperature was 65°C. Carbonyl index for Section 655-1 was corrected for the initial carbonyl absorbance of the Elvaloy® RET polymer. Carbonyl indices were determined by dividing the carbonyl peak areas between 1760 and 1655 cm^{-1} by the CH_3 methyl peak areas between 1400 to 1330 cm^{-1}. The spurt is defined by the initial period of distinctively rapid carbonyl formation whereas the steady state is defined by the subsequent period of relatively steady carbonyl formation.

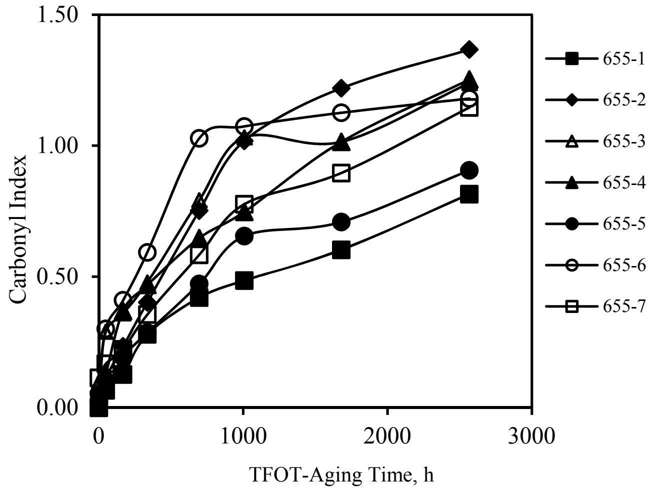

Fig. 8. Carbonyl Indices as a Function of Time for TFOT-aged Asphalt Cement Films. *Note*: Film thickness was 700 μm and temperature was 85°C. Carbonyl index for Section 655-1 was corrected for the initial carbonyl absorbance of the Elvaloy® RET polymer. Carbonyl indices were determined by dividing the carbonyl peak areas between 1760 and 1655 cm^{-1} by the CH_3 methyl peak areas between 1400 to 1330 cm^{-1}. The spurt is defined by the initial period of distinctively rapid carbonyl formation whereas the steady state is defined by the subsequent period of relatively steady carbonyl formation.

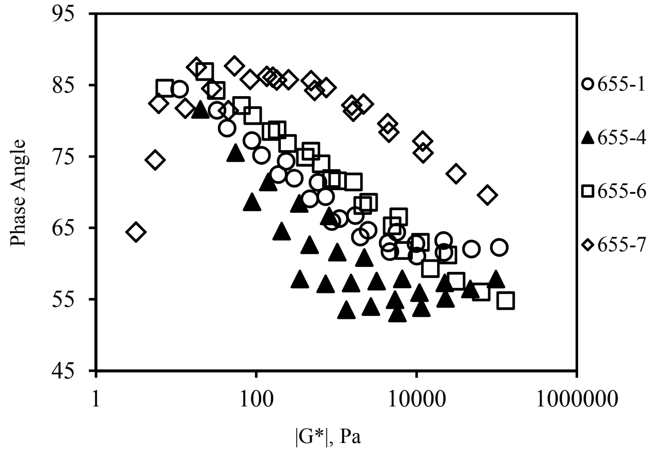

Fig. 9. Black Space Diagram for TFOT-aged Asphalt Cements. *Note*: Temperatures used for measurements included 34, 46, 58, 70, and 82°C. Findings for Sections 2, 3 and 5 were similar to those for Sections 1 and 6 but are left out for clarity. Materials were aged as 700 μm films at a temperature of 45°C for 1,000 hours. Results for Section 655-4 show the lowest phase angles and a large degree of discontinuity, which is indicative of phase separation.

Table 2. Spurt and Steady State Oxidation Rates for TFOT-Aged Asphalt Cements.

Section	Spurt Rates × 10^4 (h^{-1})		Steady State Rates × 10^4 (h^{-1})	
	65°C	85°C	65°C	85°C
1	3.0	8.3	0.1	2.3
2	2.4	13	1.5	9.4
3	5.6	40	1.7	7.9
4	5.7	19	1.0	4.3
5	2.4	9.5	1.2	5.5
6	5.8	52	2.2	11
7	3.2	13	1.8	6.5

Note: All rates were calculated as the change in carbonyl index divided by time in hours. The spurt is defined by the initial period of distinctively rapid carbonyl formation whereas the steady state is defined by the subsequent period of relatively steady carbonyl formation (see Figs. 7 and 8). The relatively high spurt rates for Section 655-4 are followed by relatively low steady state rates due to early gel formation. Both spurt and steady state rates are relatively low for Sections 655-1 and 655-5.

in an effort to understand which aspects of the RTFOT/PAV protocol could be improved. Chemical changes were followed by IR spectroscopy while rheological changes were monitored by DSR. The findings are presented in Figs. 7-9 and Table 2. The carbonyl indices as a function of time at both 65°C and 85°C (Figs. 7 and 8), the spurt and steady state carbonyl formation rates (Table 2), and the complex modulus, G^*, and phase angle, δ, after aging at 45°C (Fig. 9) provide the greatest insights and will be discussed next. This data are compared with the carbonyl indices as determined for RTFOT and PAV residues as well as recovered asphalt cement samples from 2008 cores (Table 3).

The IR data shows that the carbonyl content ranks the sections in a reasonably accurate fashion, but the analysis is not entirely straightforward. Sections 655-1 and 655-5 possess low spurts and steady state oxidation rates (Table 2) and low carbonyl indices in service (Table 3), which is the likely reason for their superior performance [21]. Sections 655-2, 655-3, 655-6, and 655-7 possess intermediate spurts and rates (Table 2) and intermediate to high carbonyl indices in service (Table 3), which largely explains their poor performance in service.

Table 3. Carbonyl Indices for RTFOT-, PAV-, and Field-Aged Materials.

Section	Lab Aging Method			Recovered
	RTFOT	PAV (20 h)	PAV (40 h)	(2008)
1	0.00	0.12	0.28	0.20
2	0.10	0.28	0.52	0.41
3	0.19	0.42	0.67	0.52
4	0.12	0.33	0.54	0.60
5	0.07	0.18	0.31	0.35
6	0.11	0.30	0.53	0.59
7	0.13	0.30	0.47	0.50

Note: The carbonyl index for Section 655-1 is corrected for the initial carbonyl index (0.22) to account for the presence of Elvaloy® RET polymer. The PAV samples were first aged in the RTFOT for 85 minutes at 163°C, followed by PAV aging for either 20 or 40 hours at 2.1 MPa of air pressure at a temperature of 100°C. Carbonyl indices were determined by dividing the carbonyl peak areas between 1760 and 1655 cm^{-1} by the CH_3 methyl peak areas between 1400 to 1330 cm^{-1}.

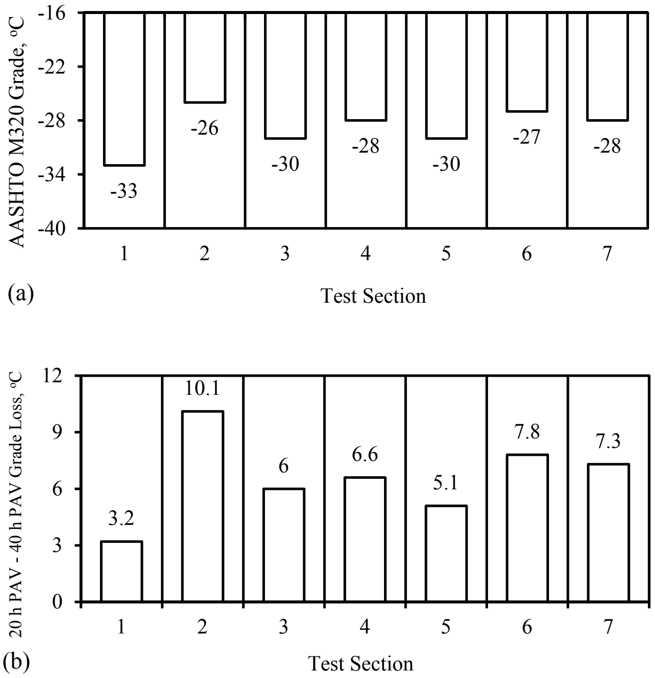

Fig. 10. AASHTO M320 Grades and Grade Losses after 40 hours of PAV Aging Relative to the Standard 20 hours of Aging.

Section 655-4 provides somewhat of an anomaly in that it possesses an intermediate spurt severity at 85°C, a high spurt severity at 65°C, but relatively low steady state rates and therefore rather moderate carbonyl indices at both temperatures. The recovered binder for this section showed a carbonyl index that is high but comparable to those for the other poor performing sections (Table 3). In contrast, its performance in service has consistently been much worse than that of the other sections. The low linear phase slopes likely indicate early gelation as revealed by DSR analysis of thin films aged at 45°C for 1,000 hours (Fig. 9). This suggests that the maltene phase in the 655-4 material is less able to accommodate (peptize) the additional asphaltenes formed during the oxidation process [21-25]. Hence, the 655-4 binder entered the gel phase at an earlier point in time, likely due to its modification with largely paraffinic, waste engine oil residues [25]. The Black space diagram for the Section 655-4 material after 1,000 hours of TFO-aging at 45°C shows a discontinuous pattern that indicates thermorheologically complex behavior (i.e., phase separation), especially at low stiffness (high temperatures). Sections 655-1 and 655-5 oxidize the most slowly, and their rheological properties remained good even after 5,000 hours of thin film aging, which is largely due to their compatible phase structure. This result agrees well with their relatively superior field performance.

An analysis of the carbonyl indices in Table 3 shows that the recovered materials were oxidized almost twice as much as the PAV residues. Hence, it appeared sensible to investigate if a simple doubling of the PAV aging time could bring the low temperature grades of such residues closer to their corresponding recovered binders. The rheological results for this investigation are presented next.

Modification of Pressure Aging Vessel Protocol

A doubling of the PAV aging time to 40 hours was expected to increase the carbonyl formation for all the materials and thus deteriorate their limiting BBR grades. The carbonyl indices provided in Table 3 confirm that such a simple change in the PAV protocol provides a closer chemical match. The BBR findings for this experiment are provided in Fig. 10. As is apparent from the limiting temperatures, there is a benefit to the extended PAV aging in that during the course of the ageing, the grades deteriorate anywhere from 3.3°C to 10.1°C. Furthermore, the results show that the superior performing asphalt cements (665-1 and 655-5) lose less due to extended PAV aging, while the inferior materials lose more. While the agreement between the low temperature grades from this experiment and those for the recovered materials (Fig. 4) is not perfect in that Sections 655-2 and 655-5 appear to age excessively in the extended PAV treatment, this simple change appears to provide a net benefit.

Fig. 11 compares the grade losses in Fig. 10 with those provided in Fig. 3 showing that physical and oxidative hardening are highly correlated. This evidence is supportive of the proposition by Petersen [20, 21] that these processes involve the same asphalt components. Asphalt cements with a good phase compatibility (low Gaestel index [22], low lyophobicity index [23, 24], low penetration index or high penetration-viscosity number [26], low asphaltenes [3, 27], etc.) are able to endure low temperatures without physical hardening, and/or the formation of additional asphaltenes due to oxidation without hardening. As a result, such materials are unlikely to suffer from early and excessive thermal distress.

Conclusions

Given the results presented in this paper, the following summary and conclusions are provided:

- The currently used laboratory oxidative aging protocol of 85 minutes of rolling thin film oven aging at 163°C (AASHTO T240) followed by 20 hours of pressure aging vessel aging at

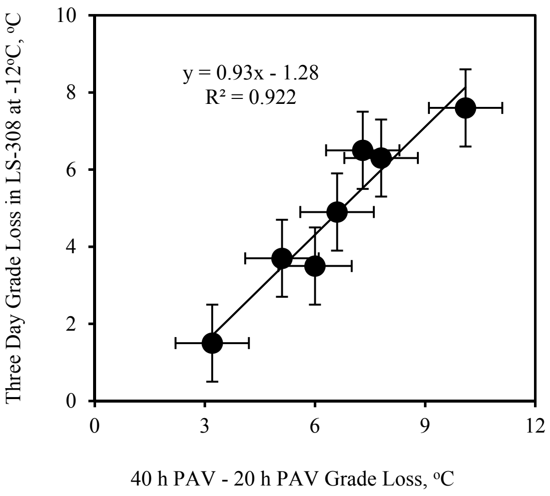

Fig. 11. Correlation between Grade Losses Due to Physical Hardening in RTFO/PAV Residues (LS-308 at -12°C) and Chemical Hardening (40 h PAV – 20 h PAV). *Note*: Error bars of ± 1°C represent approximate errors in the measurements according to round robin testing.

100 °C (AASHTO R28) does not provide sufficient oxidative hardening for poor performing asphalt cements to replicate properties from five- to six-year-old pavement trial sections.

- Thin film oven aging tests show that the carbonyl formation rate provides a reasonable prediction for performance. However, early formation of a gel is important in explaining the observed embrittlement for some materials. Those binders modified with waste engine oil residues of a paraffinic nature are especially prone to early gel formation and subsequent thermal cracking.
- A simple doubling of the PAV aging time to 40 hours appears to provide a significantly improved match between laboratory and recovered grades.

Given the encouraging findings of this study, further research on the development of improved thin film aging methods appears justified. A reduction of only 6°C in the grading error can improve the confidence level that no cracking is observed in a given year from approximately 50% to the 98% intended by the SHRP researchers [27]. Hence, an extended or modified PAV protocol could potentially eradicate a significant amount of the widespread thermal cracking distress in roads of northern Ontario and areas with similarly cold climates.

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Disclaimer

None of the sponsors necessarily concur with, endorse, or have adopted the findings, conclusions or recommendations either inferred or expressly stated in the subject data developed.

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