

## Physical Hardening of Paving Grade Asphalts as Related to Compositional Characteristics

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### Introduction

In a recent investigation of the rheological properties of paving grade asphalts a new hardening phenomenon was observed. The phenomenon, called "physical hardening" by the authors was observed to cause significant isothermal changes in the creep compliance and was shown to relate to the glass transition phenomenon of the asphalts (1). Physical hardening is similar to what is known as physical aging for many amorphous solids such as polymers and plastics. To explain physical hardening, creep compliance, glass transition, and isothermal volume measurements were made on a number of selected asphalts. The isothermal changes in creep compliance were related to volume measurements and a hypothesis was introduced to explain the hardening mechanism. Being a newly discovered phenomenon, there has been speculation regarding the mechanism responsible for the hardening. Crystallization of waxes and internal structuring of highly polar fractions have been offered as possible mechanisms. Data collected by the authors, however, indicates that the hardening is simply a collapse of free volume as the asphalt passes through the glass transition region. The different measurements obtained by the authors clearly proves that physical hardening of paving grade asphalts is no different than physical aging of other amorphous solids that are free of waxes or any crystallizable fractions.

The purpose of this paper is to give a brief review of the physical hardening behavior of selected asphalts and to present creep compliance and volume measurements that support the authors' hypothesis that physical hardening is the result of free volume collapse. Data collected by others for wax contents and melting points of waxes separated from the same asphalts are used to discuss relations between hardening and crystallized fractions. The work reported here is part of the Strategic Highway Research Program (SHRP) project A-002A, Bituminous Characterization and Evaluation.

### Effect of Hardening on Creep Response

Using the bending beam rheometer (2) beam specimens of asphalt were tested for creep compliance in three point bending after storage for different times at several isothermal temperatures. Testing was done at four temperatures below  $-5^{\circ}\text{C}$  ( $23^{\circ}\text{F}$ ) and for isothermal storage times ranging between 30 minutes and four months. The effect of isothermal storage

was consistently observed to decrease the creep compliance (increased stiffness). An example of the effect for one of the SHRP asphalts is shown in figure 1. The test results indicate that the creep compliance is affected by the isothermal storage temperature (T), isothermal storage time ( $t_i$ ), and asphalt source (3). The lower the temperature, the higher the hardening level and rate. As a function of  $t_i$ , the hardening rate was observed to be very rapid at initial  $t_i$ , decreases rapidly with  $t_i$ , and not reach equilibrium within the time limits of experiment (four months).

### Hardening and Resemblance to Temperature Effect

One of the basic characteristics of physical aging of many amorphous materials is that its effect on the viscoelastic properties is similar to the effect of temperature (4). For thermo-rheologically simple materials, the effect of temperature is reflected by a shift in the relaxation spectrum to longer times as the temperature is reduced without changing the shape of the master curve. The same behavior was observed for the asphalt cements that were tested. Figure 2 depicts creep compliance curves for asphalt AAM-1 measured after 30 minutes and 60 days of isothermal storage at  $-15^\circ\text{C}$ . When plotted on logarithmic scale, the compliance versus loading time curves can be perfectly superimposed by a one dimensional shift along the loading time scale. The simplicity of the hardening effect was confirmed for many different asphalts at all testing temperatures at which physical hardening was observed (3). Therefore the effect of physical hardening on the creep compliance can be defined by a single parameter called the hardening shift factor,  $a_i$ , in which the shape of the relaxation spectra is unchanged by physical hardening.

Similar to other thermo-rheologically simple materials, asphalts are believed to change their properties with temperature mainly due to changes in free volume which decreases when the temperature is decreased (5,6). The decrease in free volume results in more closely packed molecular arrangement and reduced molecular mobility. During physical hardening, time dependent collapse of free volume is hypothesized to result in volumetric creep that continuously increases the degree of packing, thus producing hardening.

### Isothermal Volume Measurements

To verify the free volume collapse hypothesis, isothermal volume measurements were obtained for eight asphalts at selected temperatures. A specially designed dilatometer equipped with precise capillary tubes was used to measure the volume changes for a period of 24 hours. The dilatometers were kept in a liquid bath controlled to within  $\pm 0.1^\circ\text{C}$  and volume changes were measured to within 0.0002 ml. Figure 3 is an example of the measurements for three of the asphalts at the temperature of  $-15^\circ\text{C}$ . Curves shown in the figure represent best fit curves for three independent replicates per asphalt. Using the isothermal-isobaric volume measurements, the reduction in volume relative to an initial volume (initial equals 30 minutes after quenching) were correlated to the hardening shift factors,  $a_i$ , obtained from the creep compliance measurements. Isothermal ages of 2, 6, and 24 hours were used and the correlations were very high ( $R^2=92\%$ ) as shown in figure 4 for all asphalts. Each asphalt shows its own relation which, if the free volume hypothesis is true should have a slope that is equivalent to the thermal coefficient of contraction at sub- $T_g$  temperatures ( $\alpha_c$ ). The slopes have an average slope of  $0.45 \log(s)/\text{mm}^3/\text{g}$ , which can be

converted to an  $\alpha_g$  of  $4.03 \cdot 10^{-4}/^{\circ}\text{C}$  using the average temperature shift function of  $0.183 \log(\text{s})/^{\circ}\text{C}$  calculated for these asphalts (3). The value of  $\alpha_g$  is within the range of values reported by others (7) and measured in this study. The correlation found between the isothermal volume changes and the isothermal hardening shift factor confirms the analogy between temperature and isothermal storage time and gives strong evidence that favors the free volume collapse hypothesis.

### **$T_g$ and the Physical Hardening**

Physical aging of amorphous solids is known to be predominant below  $T_g$  (6,8). In fact, the results of isothermal volume measurements suggest that physical hardening is essentially a continuation of the glass transition phenomenon. When the asphalt is cooled from high temperature its volume shrinkage, which is mainly a reduction in free volume, reaches equilibrium almost immediately. When the glass transition region is approached, the transport mobility of molecules is reduced and, at some point, results in non-equilibrium volumes. At this point the asphalt is in a metastable state causing the material to continuously shrink isothermally. Asphalts, however, have a wide glass transition region that reflects the complexity of their composition and a multiplicity of transition temperatures.

To investigate the relation of the glass transition phenomenon to physical hardening, dilatometric glass transition measurements were made for the asphalts using the same dilatometers used in the isothermal measurements but equipped with larger capillary tubes and a well-controlled ramping thermal bath. At the rate of  $1^{\circ}\text{C}/\text{min}$ , the volume change in a 10 ml specimen was measured in a cooling and heating mode to an accuracy of 0.002 ml over a temperature range of  $-60^{\circ}\text{C}$  to  $40^{\circ}\text{C}$ . The measurement clearly reflected a wide transition that for some asphalts extend to temperatures well above  $0.0^{\circ}\text{C}$ . Following the concept of free volume, the deviation of measured volume from the hypothetical thermodynamic equilibrium was used as an indicator of free volume that needs to be recovered (or collapsed) during isothermal storage (1). Figure 5 depicts the relation between isothermal hardening shift factors ( $a_i$ ) and the estimated deviation from thermodynamic equilibrium volume line. The correlation shown ( $R^2=85\%$ ) reinforces the finding that free volume entrapped at the onset of the glass transition region is the cause of the meta-stable state that leads to the time dependent physical hardening.

### **Crystallizable Fraction (Wax) and Hardening**

Being observed at low temperatures, and being completely reversible, has lead several researchers to propose to the authors that physical hardening is related to crystallization of waxes in the asphalts. Using a modified Shell method (SMS-1769) (9) the wax contents of SHRP asphalts were measured for SHRP by researchers of INTEVEP-Venezuela (10). The wax contents and the melting points are listed in table 1 for 16 of SHRP asphalts that have different chemical composition and different low temperature creep compliance properties. Figure 6 was prepared to show the correlation of the wax content and the hardening shift factor at  $-15^{\circ}\text{C}$ . The shift factors were obtained for each asphalt by measuring the isothermal shift factor needed to superimpose creep response measured after 30 minutes at  $-15^{\circ}\text{C}$  on the creep response after 24 hours at  $-15^{\circ}\text{C}$  (see figure 2 for shift explanation).

There is a definitive relation between the wax content determined by the Shell method

and the physical hardening,  $R^2 > 70\%$ . What is surprising, however, is that the melting points of these asphalts are all above  $30^\circ\text{C}$  while the hardening is observed only at temperatures below  $-5^\circ\text{C}$ .

### Hardening Potential and Endothermic Peaks in DSC Thermograms

Differential scanning calorimetry has been used by several asphalt researchers to determine glass and melting transition. In the early 1970's Noel and Corbett (11) compared wax determinations by several traditional methods and indicated that variations as high as 5 fold can be observed when these methods are used for the same asphalts. The authors stated that "the traditional concept of asphalt wax content is of questionable significance." The authors, however, presented DSC thermograms that show clear endothermic peaks at moderate temperatures. The peaks were typical of crystallite melting transitions and therefore led the authors to conclude that asphalts contain some kind of waxes that are not completely crystalline nor completely amorphous. They called the material crystallized fractions and offered a method for calculating them from DSC thermograms. Recently this concept was used by other researchers in the US and in Europe and relations between the crystallized fractions and physical properties were reported (12).

As part of another SHRP project, DSC measurements were conducted on eight of the asphalts used in this study (13). Very distinct endothermic peaks were observed for several of the asphalts in the temperature region of  $0.0^\circ\text{C}$  and  $90^\circ\text{C}$ , and the enthalpies of these peaks were reported to an accuracy of  $\pm 10\%$ . Asphalts showing the most hardening and the most isothermal volume change also showed the largest endothermic peaks, Figure 7. Although the temperatures at which these endothermic peaks occur do not correlate well with the melting point temperatures of the waxes extracted from the corresponding asphalt, the peaks are within the same temperature range as the melting points,  $30^\circ\text{C}$  to  $90^\circ\text{C}$ . In contrast, physical hardening is observed some  $30^\circ\text{C}$  below the melting point temperatures and becomes more pronounced as the isothermal temperature is decreased (3). Further, the physical hardening is completely destroyed by heating the asphalt to  $25^\circ\text{C}$ , well below the melting point of the wax.

### Discussion

The above results leave no doubt that there is some connection between physical hardening at low-temperatures and the amount of crystallizable or wax fractions in an asphalt. The isothermal volume measurements and the dilatometric  $T_g$  measurements, on the other hand, also suggest that the hardening is caused by the time-dependent collapse of free volume below the glass transition temperature. Further, the creep compliance master curves (not shown here) do not reveal the presence of a crystallizable phase at low temperatures (14). The master curves and the relaxation spectra are smooth and without the shape that would suggest a second low-temperature phase. The only irregularity in the master curve is in the region of the melting point temperatures where a vertical shift in the data is required to produce smooth master curves (15).

Ignoring the temperatures at which these two phenomena--physical hardening and crystallization--occur, the answer could be that volume change is merely caused by the crystallization. The maximum volume change measured for an isothermal time of 23.5 hours

is 0.0025 ml/g for asphalt AAM-1. Considering the wax content of this asphalt, 4.21 percent, a 6 percent volume change in the wax would be sufficient to account for the 0.0025 ml/g volume change. Other studies indicate that a that wax changes volume by 4 to 10 percent upon crystallization. Therefore, it is plausible that crystallization of wax is the source of the low-temperature volume change. There are however a number of points that stands against this hypothesis:

**First**, the large difference between the melting points of the waxes and the temperature at which the isothermal volume change is being observed cannot be ignored. If dissolution of wax, and the endothermic peaks are observed at high temperatures, why is the hardening observed at much lower temperatures.

**Second**, physical hardening and isothermal volume change continue for very long times (hardening measured after 4 months for some asphalts). It is highly unlikely that crystallization continues for such long times and continues to effect the creep compliance in such significant way.

**Third**, the effect of physical hardening on the viscoelastic properties is analogous to the effect of temperature reduction of a thermo-rheological simple material. The rheological properties show no evidence of a second phase at the low temperatures but do seem to account for some orientation of the wax molecules in the region of the melting point temperatures.

**Fourth**, the rheological behavior of all SHRP asphalts is simple in that creep compliance master curves and the relaxation spectra show no sign of crystallization in the temperature region between -35°C and 60°C.

## Conclusions

Circumstantial evidence suggests a link between the wax content and low-temperature physical hardening. A closer examination of the evidence suggests that this link is probably not a cause and effect link but that some third factor is the link between the wax content and physical hardening. Interestingly, both the wax content and the degree of physical hardening appear to increase with the molecular weight of the neutral fraction. Could it be that the molecular weight distribution affects both the percent of wax-like molecules present as well as affecting the low-temperature physical hardening? Most likely this is the case. Therefore, although there is a statistical correlation between measured wax content, DSC properties, and physical hardening it is unlikely that there is a cause and effect relationship between these variables. More research is needed to answer this question.

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**Table 1.** Properties measured in this study and previous studies of selected SHRP asphalts

Asphalt Source	Creep Compliance at -15 °C, 120s 1/GPa	Isothermal Shift, log (a <sub>t</sub> )	Wax Content% after (10)	Melting Point, °C after (10)	Total Enthalpy j/g after (13)	Temp. of 2nd Endothermic Peak, °C after (13)
AAA-1	43.48	0.42	1.62	35.8	0.27	83.5
AAB-1	14.29	0.67	3.85	62.1	9.94	41.9
AAC-1	7.67	0.93	5.06	65.7	4.00	53.9
AAD-1	35.71	0.57	1.94	50.6	3.48	46.1
AAE	20.80	0.32	1.23	42.5		
AAF-1	4.98	0.83	4.19	59.6	7.93	44.8
AAG-1	2.05	0.24	1.13	33.0	2.42	82.9
AAH	13.5	0.65	4.41	52.8		
AAJ	7.69	0.76	4.91	43.2		
AAK-1	13.89	0.52	1.17	56.1	1.83	47.2
AAL	40.32	0.21	1.23	43.9		
AAM-1	5.71	0.94	4.21	32.9	7.69	42.7
AAP	13.69	0.70	4.77	51.3		
AAU	3.52	0.60	2.35	58.6		
ABC	21.20	0.50	2.90	56.6		
ABD	1.58	0.45	0.81	38.2		

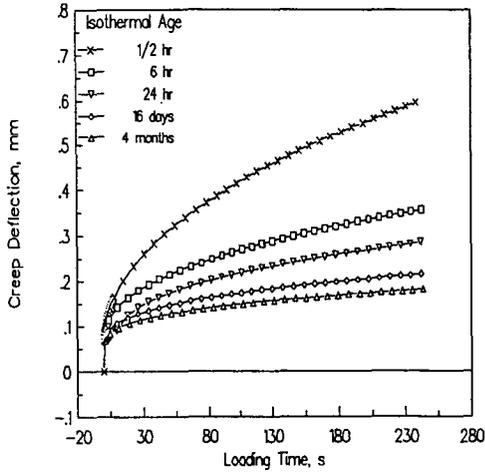


Figure 1. Reduction in creep deflection and rate due to physical hardening at  $-15^{\circ}\text{C}$  for asphalt AAF-1.

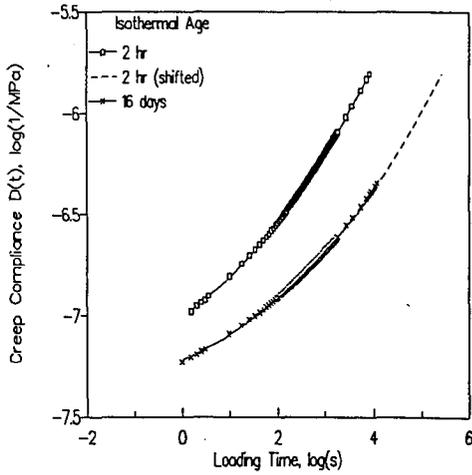


Figure 2. Superposition of creep curves of asphalt AAM-1 measured at isothermal ages of 1/2 hour and 16 days.

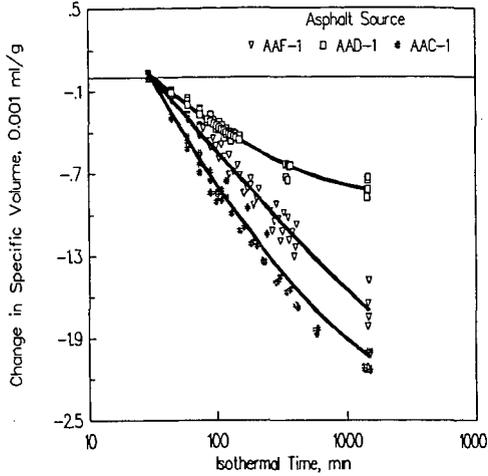


Figure 3. Isothermal Volume measurements for three asphalts at -15°C over a period of 24 hours.

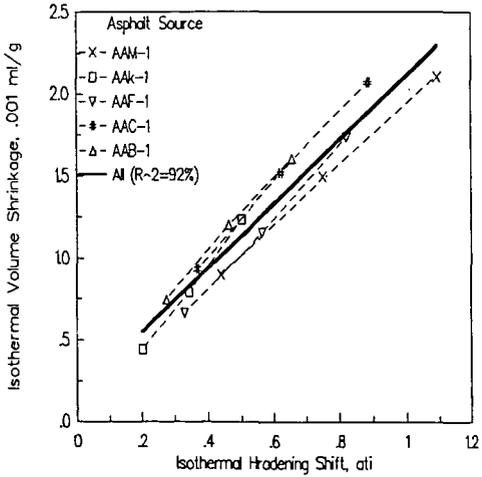


Figure 4. Correlation of volume change and hardening shift at equi-isothermal ages.

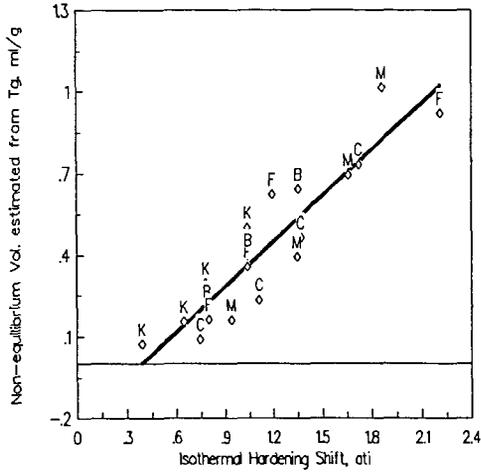


Figure 5. Correlation between hardening shift factors and the estimated deviation from equilibrium volume line.

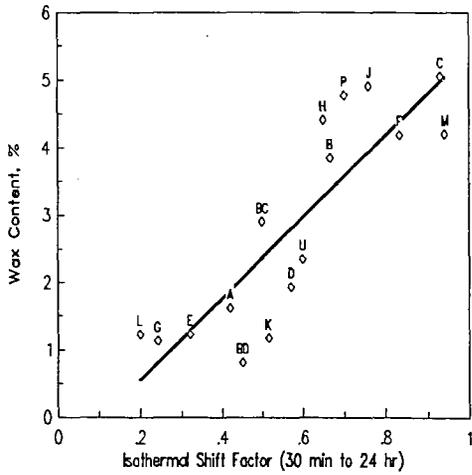
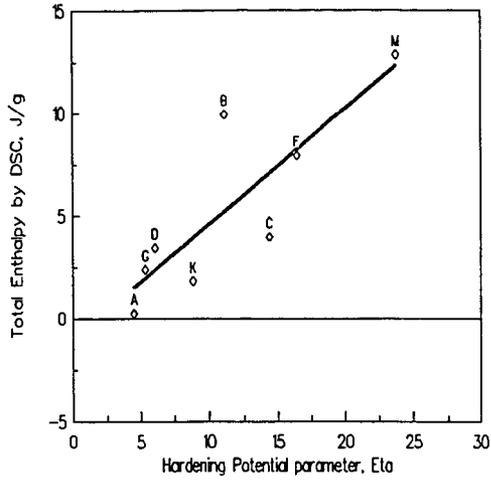


Figure 6. Correlation between hardening shift factor at -15°C and wax content for 16 SHRP asphalts.



**Figure 7.** Correlation between total endothermic enthalpy and hardening potential for 8 core SHRP asphalts