NATURAL VS. ARTIFICIAL AGING: USE OF DIFFUSION THEORY TO MODEL ASPHALT AND FIBERGLASS-REINFORCED SHINGLE PERFORMANCE

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This paper examines the relationships between artificial, accelerated aging and natural exposure for fiberglass-reinforced shingles and asphalt coating. The artificial (i.e., accelerated) techniques employed in this study included the 70°C (158°F) dark oven, Atlas Weather-Ometer® and Q-Panel Q-U-V. Natural aging sites included Houston, Minneapolis, and Philadelphia. The aging behavior of the shingles is examined by determining the changes in asphalt chemical composition and in tensile and flexural properties of the shingle. Results indicate that the shingle or asphalt property of interest changes rapidly immediately after the onset of aging and then begins to stabilize over time until some equilibrium state is attained. This aging behavior is found to be similar among the three artificial methods but occurs at a much faster rate compared to the natural aging methods. A diffusional process initiated by heat is presented as the primary mechanism for asphalt and shingle degradation, regardless of the aging methodology. A mathematical model based upon diffusion theory is then derived and is found to describe the observed aging behavior. The statistical reliability of the mathematical models has provided a foundation for developing a correlation between the natural and artificial forms of aging.

KEYWORDS

Accelerated aging, artificial aging, asphaltenes, asphalt shingles, dark oven, diffusion, flexural modulus, mechanical property, natural exposure, thermal degradation, weathering.

INTRODUCTION

Manufacturers of asphalt roofing shingles who are concerned about the quality of their products will not dispute the important role of accelerated aging techniques in selecting raw materials or developing new products. From the perspective of understanding and predicting long-term shingle performance characteristics, the properties of the aged product are as crucial as the original properties. Because shingle warranty periods typically surpass 20 years, it is not practical for manufacturers to assess the performance of products after their useful life. Hence, the need to accelerate the aging process of roofing shingles in the laboratory is generally well recognized by most shingle manufacturers.

All roofing materials are subject to aging, and several processes may contribute to their degradation, namely—heat, radiation, moisture, chemical (pollution) and physical effects.[1] In the case of asphalt shingles, aging primarily refers to the oxidation and volatilization that occurs when shingles are exposed to the environment, either by natural weathering or artificially simulated by accelerated techniques. If they are to be truly useful, methods of accelerating the aging of shingles in the lab must indeed be 1) accelerated and 2) representative of the type of aging that the shingles will encounter during natural exposure. Among the techniques historically employed by the roofing industry to age raw materials such as asphalt or finished products are the Atlas Weather-Ometer® (WOM), the Q-Panel Q-U-V (QUV), and the dark 70°C (158°F) oven. Although these methods have been used to screen raw materials or to gauge the success of product development efforts, their utility lies primarily in the comparison of results (e.g., "Asphalt ABC failed after 60 cycles in the WOM while asphalt XYZ lasted 95 cycles; therefore, the latter asphalt is more durable.") Because the results of these accelerated forms of aging have traditionally been used in the comparative mode, there is little literature that attempts to translate these results into a real world, quantifiable, natural exposure life expectancy. The few attempts at making such correlations between natural and artificial methods of aging have resulted in little more than generalizations.[2]

Developing correlations between natural and accelerated forms of aging is not a trivial matter but one that has a direct impact on the development and marketing of future residential roofing products. The authors perceived the need for this type of data and in April 1994 instituted a study whose major objectives were: 1) to determine the value of the various artificial aging methods in simulating natural exposure and 2) to develop a mathematical relationship between the accelerated and natural forms of aging that would be useful for predicting specific shingle performance characteristics over time. Although the accelerated aging methodologies currently employed by the roofing industry do not address *all* factors affecting degradation, it has been assumed that accurate, reliable models can be developed that would enable one to predict a shingle performance characteristic (climate specific) based upon the product's performance in a laboratory test. This paper describes the materials and methodologies used to address the objectives listed above and presents specific mathematical models for predicting a mechanical property of fiberglass-reinforced shingles after aging under various accelerated and natural conditions.

ASPHALT/SHINGLE AGING: LITERATURE SURVEY

A common denominator among the accelerated forms of aging being discussed in this paper (and those, for example, that are not being discussed—pressure aging vessel, rolling thin film oven, etc.) is *heat.* Heat is certainly a factor in natural weathering. Rooftop temperatures on a clear, sunny day will considerably exceed ambient temperatures. In recent years, various authors have commented on the role of heat in the aging process of shingles. For example, Shuffleton and Still[3] and McLintock[4] have reported evidence that darker shingles will absorb more heat in summer, thereby raising their temperature and speeding up the aging process. James Wright[5] cites the work of Hubbard and Reeve, who demonstrated that the hardening of asphalt is due to volatilization and oxidation whereby the onset of hardening is slow at low temperatures but increases at high temperatures. Warford[1] contended that asphalt hardens progressively when subjected to roof temperatures. The softening point of the coating asphalt may increase by 27°C to 38°C (80°F to 100°F), even without direct solar radiation. Warford also stated that the granule covering used by roofing manufacturers has a beneficial effect on minimizing surface deterioration but has little or no effect in protecting the underlying asphalt. Aside from their aesthetic function, granules protect the surface layer of asphalt from harmful UV rays. Without granules, the surface layer of asphalt on the shingle may continue to erode, thereby exposing a fresh surface for UV rays to attack. However, despite the efforts of roofing manufacturers to select granules that block UV light (viz. light transmission test), degradation of shingle performance (i.e., mechanical) properties still occurs. Because the degradation caused by UV light is primarily a surface phenomenon, Wypych[6] contends, natural conditions can best be simulated by aging materials at elevated temperatures rather than exposing them to UV radiation. Maréchal's[7] work on thermo-oxidation also supports the claim that natural aging is best simulated by thermal degradation.

According to Kleinschmidt and Snoke,[8] the photo-oxidation of surface molecules by UV light causes the surface material to become water soluble. The loss of these water-soluble materials attributed to washing tends to imbalance the distribution of system components, thereby causing the migration of components in an attempt to restore new equilibrium. In 1961, Martin[9] also postulated that a process of migration or diffusion of oily constituents to the exposed surface to replace those constituents that had been photo-oxidized and leached out is a viable mechanism. The authors believe that the diffusion mechanism described by Martin is the one by which asphalts weather in the xenon arc WOM. For example, oils diffuse from the asphalt coating and are washed away until the material is sufficiently depleted to the point of cracking. One effect of the WOM's water spray is to wash away the water-soluble degradation products, thereby continually exposing a fresh surface for weathering. Another is that water induces thermal shock, which may help initiate cracks.[5]

Although much of the discussion so far has centered upon the role of UV light and water washing in initiating surface degradation and causing conditions leading to the migration of oily components, the authors have documentation that heat alone is sufficient to initiate and maintain this diffusion process. In a separate, unpublished study, the authors observed that over time, oils will diffuse and pool on the surface of asphalt coating specimens that have been aged in a 70°C (158°F) dark oven. Also, oil migration has been shown to manifest itself on fiberglass-reinforced shingles in the form of stained granules as the shingles age in a 70°C (158°F) dark oven. However, the relationship between the observed migration of oils and the change in asphalt composition or shingle performance has not been established in the literature. As a result, this study will attempt to link the heat-driven diffusion process and the aging behavior of asphalt and shingles using simple diffusion theory.

MATERIALS/AGING METHODOLOGIES

The materials under study included three-tab fiberglass-reinforced shingles having an average weight of 10.8 kg/m^2 (222 lbs/square)and conforming to ASTM D 3462. The asphalt coating used in the manufacture of these shingles was catalytically air-blown from a Canadian roofers' flux to a nominal softening point of 101.7°C (215°F).

Shingle specimens measuring 127 mm by 38 mm (5 inches by 1.5 inches) were cut (transverse direction) from the exposed portion of the aforementioned shingles. These specimens were then equally divided among five forms of aging: 1) dark, 70°C (158°F) oven, 2) Atlas xenon arc Weather-Ometer® (WOM), 3) natural exposure in Houston, 4) natural exposure in Philadelphia, and 5) natural exposure in Minneapolis. Those samples reserved for oven aging were placed on aluminum trays and subjected to a 70±3°C (158±5°F) forced air, dark, dry environment. The shingles reserved for the WOM were mounted on aluminum panels using binder clips, placed in the WOM, and subjected to Cycle A.* Finally, those samples scheduled for outdoor exposure were stapled to 19-mm (0.75-inch), uninsulated, pressure-treated plywood decks and exposed at a ∠45° (southern exposure) to natural conditions in Houston, Minneapolis, and Philadelphia exposure farms. These locations were selected because of the diversity of their climates.†

In addition to the shingle samples, the Canadian shingle coating used in the manufacture of these shingles was applied to aluminum WOM panels to yield a nominal geometry of 127 mm by 51 mm by 0.64 mm (5 inches by 2 inches by 0.025 inches). Panels of this coating grade asphalt were then placed in the WOM (Cycle A), 70°C (158°F) oven, QUV‡ and also mounted to the exposure decks in Houston, Minneapolis, and Philadelphia. That is, the asphalt samples were allowed to weather or age alongside the corresponding shingle specimens.

*51 minutes light/9 minutes light and water spray; black panel temperature 60±3°C (140±5°F); water spray temperature 4.4°C (40°F); 50 percent relative humidity; utilizes a full-spectrum xenon light source (reference ASTM G 26, D 4798).

†The average monthly temperature for Houston, Philadelphia, and Minneapolis is plotted in Appendix A.

‡QUV operates in accordance with ASTM G 53 and a modified version of ASTM D 4799 (Cycle A), which provides alternating four-hour period of UV 8 light at 70°C (158°F) and condensation at 40°C (104°F).

SAMPLING/TESTING

Those shingle and asphalt coating specimens subjected to *artificial* aging were sampled and tested as early as one week after the onset of aging. During the first six months of the study, samples were taken frequently but at intervals that were influenced by the results achieved during its previous round of testing. Ultimately, the frequency of sampling was diminished to six-month intervals in order to preserve materials for the long-term portion of the study. Similarly, materials undergoing *natural* exposure were initially sampled after 35 days, but as the program progressed, the time between samples extended to a maximum of six months. The aged shingle bars were reserved for tensile and flexural testing. The aged asphalt coating was scraped from the aluminum panels and reserved for chemical analysis using the Corbett fractionation procedure and molecular weight determination using gel permeation chromatography (GPC).

The Corbett fractionation procedure employed in this study involved solvent deasphaltening for recovery of asphaltenes, followed by maltene elution-adsorption chromatography to yield saturates, naphthene aromatics, and polar aromatics. Asphaltene content was determined by solvent precipitation and filtration using n-heptane. The chromatography was performed using a 10- by 500-mm (0.4- by 19.7-inch) borosilicate column with a solvent delivery system composed of a low pressure pump, a rotary switching valve, and an injection valve. After the maltene injection, solvents of increasing polarity were pumped through the column bed of activated alumina. Fraction cut points were determined visually by color and/or volume of eluent. Saturates were released by n-heptane naphthene aromatics, the intermediate polarity fraction, were released by toluene without disturbing the extreme polar fraction. A 50:50 blend of toluene and methanol followed by trichloroethylene was used to solubilize and elute the polar aromatics. All four fractions were recovered by drying, and weight percentages were calculated.

Rather than being monodisperse, asphalt has a distribution of different length hydrocarbon chains, and therefore, a distribution of molecular weights can play a critical role in determining an asphalt's physical characteristics and performance. Gel permeation chromatography provides a method for determining molecular size and weight distributions. Chemical changes caused by aging can be detected by shifts in these distributions. Aged asphalts exhibit an increase in higher molecular size and weight fractions and a corresponding decrease in lower molecular size and weight fractions as compared to unaged asphalt.[10, 11, 12] The shift in quantity of both high and low molecular size fractions resulted in a higher average molecular weight. The GPC system utilized in this study included:

- DuPont Instruments 8800 Series HPLC microprocessor with an 850 Series Absorbance Detector and an 870 Series Gradient Pump
- Gateway 486DX2/33 computer with Polymer Laboratories PL Caliber GPC/SEC Version 5.2 software
- Two Polymer Laboratories PLgel 7.5- by 300-mm (0.3- by 11.8-inch) 5μm (0.2 mil) Mixed-D columns with manual injection
- Polymer Laboratories EasiCal PS-2 polystyrene narrow standards for column calibration

The system operating parameters included a tetrahydrofuran (ACS certified with 0.025 percent BHT preservative) mobile phase with a toluene flow detector, a flow rate of 1.0 ml/minute (0.0003 gallons/minute) at 35°C (95°F), UV absorbance at 254 nm, 0.10 percent sample concentration, 50-μ (0.000013-gallon) injection volume, and a 21-minute elution time.

Tensile and flexural tests (three-point bend) on the finished product were conducted on an Instron Model 1122 tensile test machine equipped with an environmental chamber for maintaining -1.1°C (30°F) and Series IX Automated Materials Testing System (Version 5.0). The crosshead speed for both mechanical tests was 5 mm/minute (0.2 inches/minute). Specimen gage length was 76 mm (3 inches) for the tensile test, and the span for the three-point bend test was 64 mm (2.5 inches). Test properties of interest included Young's modulus, elongation at break point, and toughness for the tensile specimens while the flexural modulus and energy at maximum load were recorded during the flexural test. The three-point bend apparatus used in this study is depicted in Figure 1.

RESULTS

Asphalt Chemical Properties

The molecular weight distributions measured by GPC are plotted in Figure 2 as a function of elution time and detector response for both the natural and accelerated aging methods. The detector response, which is directly related to average molecular size* through a standard calibration curve, may be divided into three equal sections based on elution time of the peak.[13, 14] The section that elutes first is referred to as the large molecular size (LMS) fraction, the second as the medium molecular size (MMS) fraction, and the last as the small molecular size (SMS) fraction.

Focusing on the GPC profiles for the naturally aged specimens (Figure 2, lower), it is readily apparent that the peak

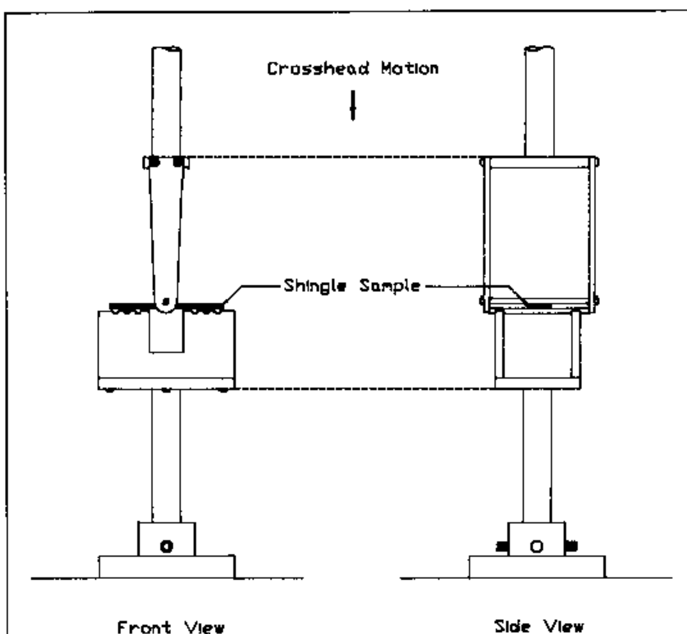


Figure 1.

* Molecular size is proportional to log molecular weight.

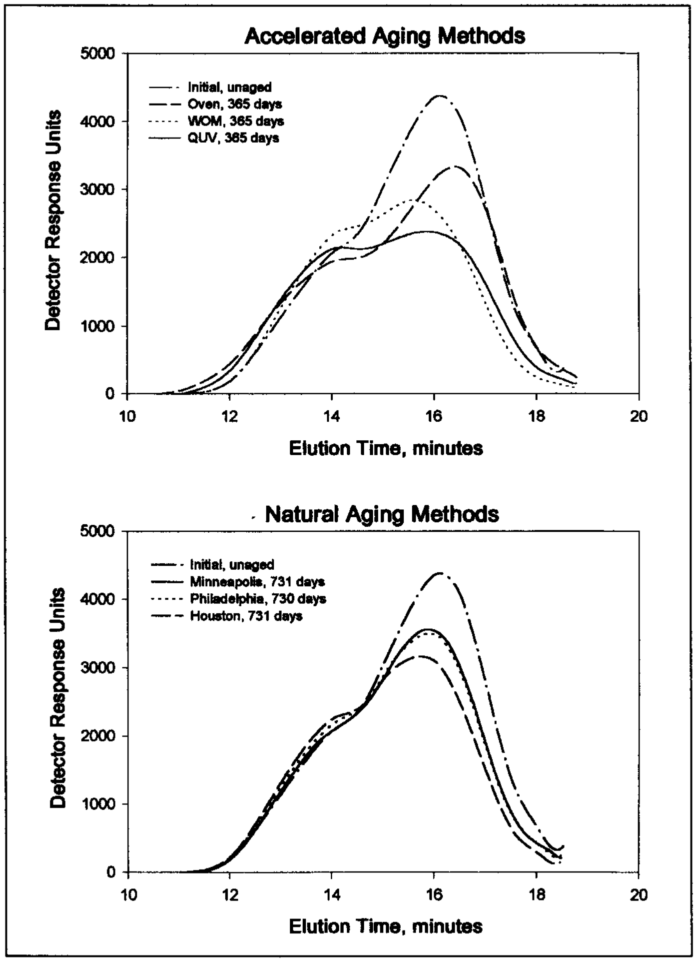


Figure 2. GPC profiles.

heights significantly decreased after aging. This decrease in height is primarily attributed to the loss in maltenes. Also, there is a slight tendency for the naturally aged samples to elute earlier (refer to 13 minutes) as compared to the initial, unaged samples. This shift to the left is in the direction of increasing molecular weight, toward the LMS region. Typically, the increase in the LMS region of the chromatogram is attributed to the increased formation of large polar molecules. A classic example is the increased formation of highly polar asphaltenes observed as a result of oxidation. The most pronounced changes (decrease in peak height, shift toward LMS region) occured with the Houston sample and is most likely attributed to the higher temperatures at this locale.

In contrast to the naturally aged asphalt samples, those that were aged in an accelerated mode (Figure 2, upper) exhibit a more pronounced change in their GPC profile. For example, the increased magnitude of the LMS region is readily apparent after just one year of accelerated aging among each of the artificial methods. In general, the WOM, QUV, and dark oven produce similar results (i.e., decreased peak height and a shift toward the LMS region) primarily because of the role of heat in promoting the formation of asphaltenes and because the volatilization of light ends. Although the data also suggest a more noticeable change in GPC profile associated with the WOM and QUV, it is believed that this may be attributed to the loss of low molecular weight substances due to surface washing effects that are characteristic to these modes of aging.

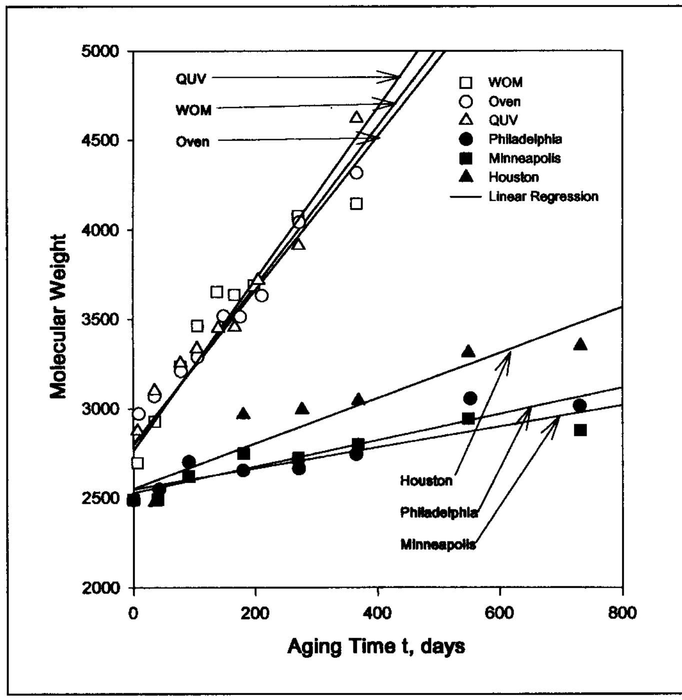


Figure 3. Molecular weight as a function of aging.

In Figure 3, the average molecular weight of asphalt as calculated from the GPC data is plotted as a function of aging time. The data provided in Figure 3 suggest that the linear relationship assumed between average molecular weight and aging time is quite appropriate. Notice the significant difference in molecular weight between the natural and accelerated aging methods. The steeper slopes associated with the artificial methods of aging demonstrate the more rapid rate of aging characteristic of these techniques. Although the initial molecular weight for the Canadian coating was 2464±110, there was a rapid rise in molecular weight for the samples aged in the QUV, WOM, or dark oven that took place seven to nine days after the onset of aging. This rapid rise, or spurt reaction, has been attributed to the asphalt's high reactivity with oxygen.[15] The spurt is then followed by a continually slowing rate of oxidation. Also of significance is the fact that the three accelerated aging methods (WOM, dark oven, and QUV) are practically superimposed, suggesting that their aging mechanisms are *not* significantly different. Because the common denominator among the three accelerated techniques is heat, this observation reinforces the role of heat in aging asphalt. Notice that among the natural exposure sites, the molecular weight of asphalt aged in Houston appeared to increase at a faster rate than the molecular weights of its counterparts. This acceleration may also be attributed to the overall warmer climate of Houston (see Appendix A).

In addition to higher temperatures, the data provided in Appendix B suggests that the Houston environment has a greater proportion of sunlight in comparison to Philadelphia or Minneapolis. Although more sunlight generally translates into increased UV exposure, one cannot ignore the fact that UV represents only five percent of the energy in sunlight.[16] Because the UV in natural sunlight is filtered by air mass, cloud cover, and pollution and is dependent upon sunlight intensity and angle of the sun, the spectral distribution of natural ultraviolet light is likely to be extremely variable.[17]

Because of this variability in UV light, the effect of heat is viewed as the *primary* catalyst for creating changes in the molecular weight distribution of the aged asphalt samples.

The increase in polar moieties, which occurs as a function of asphalt oxidation coupled with a decrease in oils, was determined using the Corbett procedure. The changes in asphaltenes and naphthene aromatics are plotted in Figures 4 and 5 after normalizing with their initial values. When processed to a 101.7°C (215°F) softening point, the Canadian coating included in this study had an asphaltene content of 32.6±0.93 percent and a naphthene aromatics content of 33.4±1.04 percent prior to accelerated or natural aging.

Once again, the severity of the accelerated methods is readily apparent as evidenced by the sharper change in chemical fractions, which indicates the rate of change in the chemical fractions is much faster in the accelerated modes as opposed to the natural exposure sites. As Figure 4 depicts, the development of asphaltenes is clearly accelerated when the asphalt coating is aged in either the WOM, QUV, or dark oven. Conversely, the rapid decrease in oils (Figure 5) is demonstrated. After artificial aging for one year, the naphthene aromatics content decreased 60 to 80 percent, depending upon the form of aging. Note, however, that the shape of the curves for the artificial and natural methods of aging is similar. That is, the chemical fractions change rapidly after the onset of aging and then the rate of change decelerates and tends to level off over time. This similarity of shape suggests that although the rate may be different, the aging mechanisms may be the same for both the natural and artificial methods. Indeed, other researchers have asserted that the same type of oxidation reaction takes place in both a dark and light environment.[18] The difference in rates between natural and artificial aging may be attributed to the more intense and consistent heat provided by the accelerated test methods. Under natural conditions, the effect of heat is again demonstrated by the proliferation of asphaltenes and loss of oils that occur at a faster rate in the warmer climate of Houston.

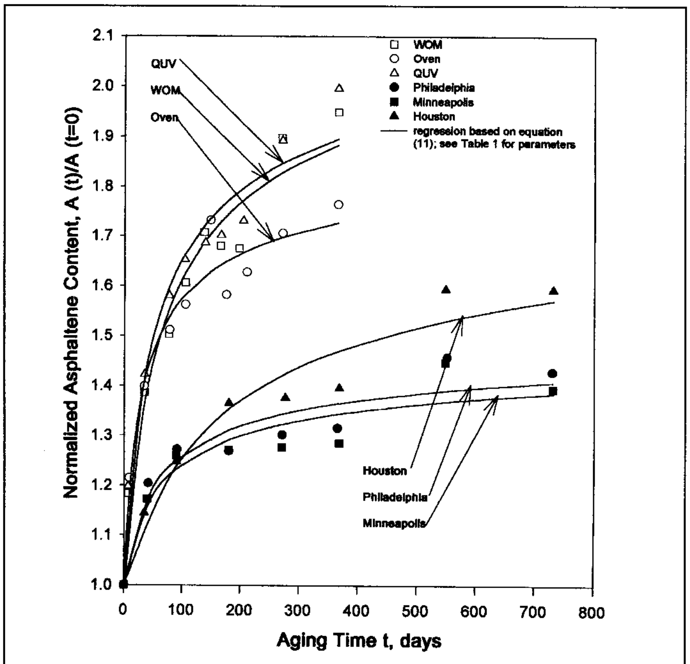


Figure 4. Asphaltene content as a function of time and aging method.

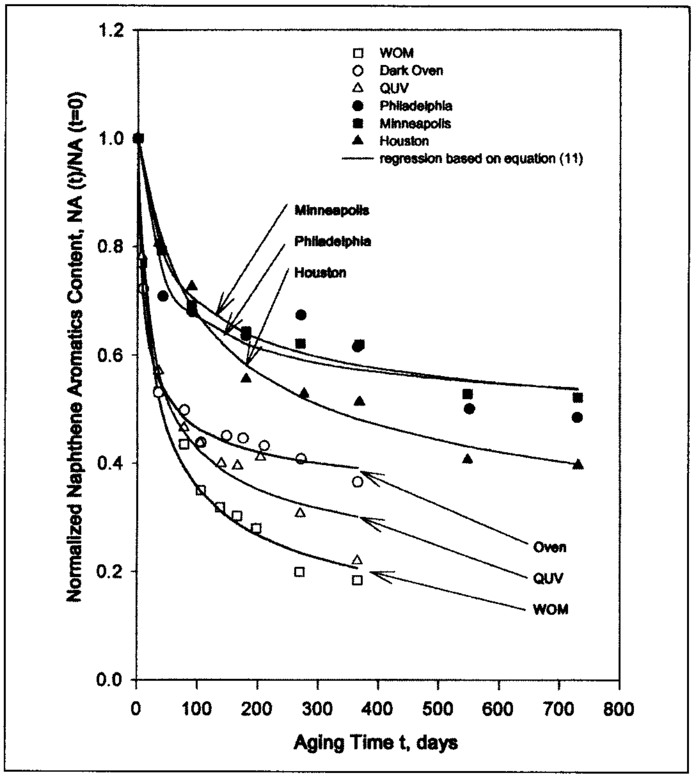


Figure 5. Naphthene aromatics as a function of time and aging method.

Shingle Mechanical Properties

In addition to nail pull and tear resistance (ASTM D 3462), tensile and flexural properties are common tests used to assess finished product performance. In this study, tensile properties were measured at -1.1°C (30°F) on the shingle samples, which had been aged using the methods previously described. Unfortunately, because of the large data scattering, the results were found to be inconclusive. This may be partially attributed to the fact that the tensile behavior of shingles may be dominated by the glass fiber mat. Also, it is noted that the dimensions of the specimens may change as they age and result in microcracking as they are placed in the loading fixture prior to testing.6

In contrast with the shingle tensile test, the determination of shingle flexural modulus at -1.1°C (30°F) using a three-point bend test fixture yielded more consistent results. The magnitude and variability of the flexural modulus data can be assessed in the graphs presented in Figures 6 and 7, in which the mean and standard error bars are plotted. Note again that the flexural modulus increases rapidly during the initial (first 100 days) aging period and then levels off as aging progresses. Based upon the 70°C (158°F) dark oven and WOM data presented in Figure 6, there does not appear to be a significant difference between these aging methods. When both natural and artificial methods are compared, one may note that the trend for the increase in flexural modulus is similar but the rate of the artificial methods appears to be significantly higher.

THEORY

In the diffusional model of asphalt aging, heat first promotes the migration of oils out of the asphalt. Then, some of these oils are volatilized, and others are washed away because of

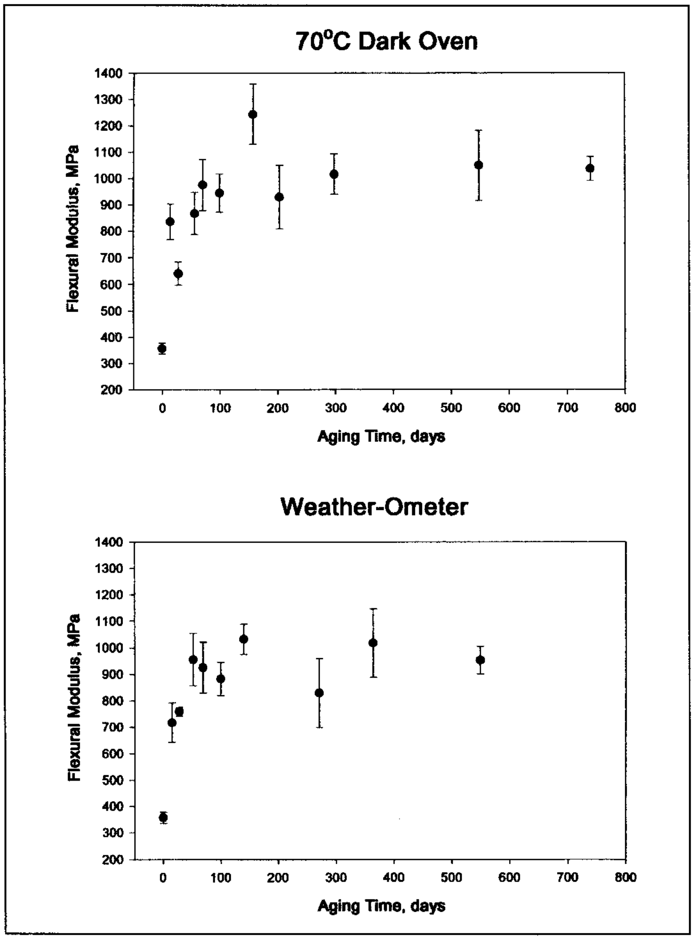


Figure 6. Flexural modulus—accelerated.

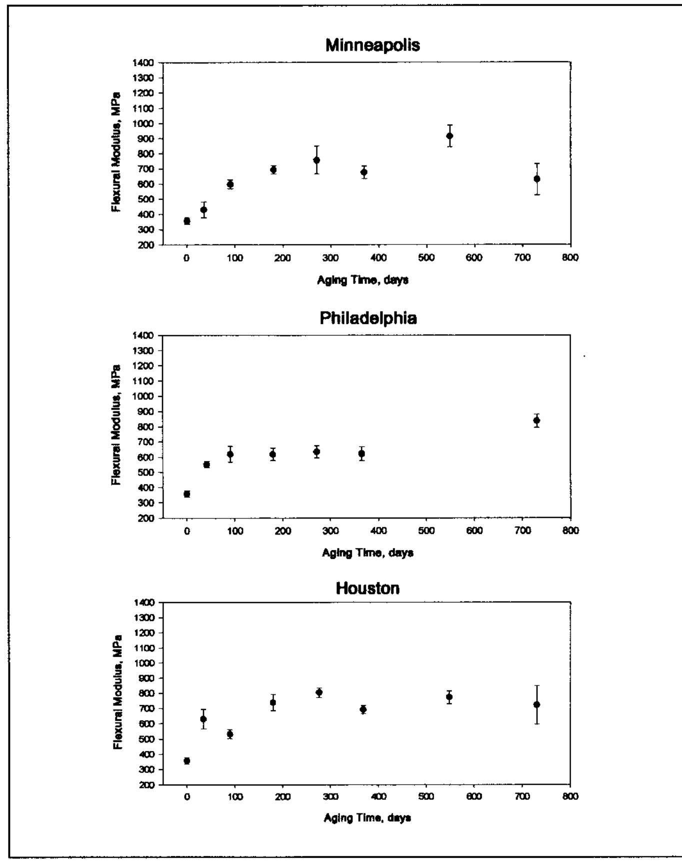


Figure 7. Flexural modulus—natural exposure.

photo-oxidation and subsequent solubility in water. Finally, oxygen migrates into the system, resulting in the formation of more heptane-insoluble, polar molecules known as asphaltenes.[19] As the aging progresses, these diffusion processes may lead to final failure of the system (typically, cracking) as the asphalt becomes harder and stiffer.

To describe the diffusion process, the authors start with Fick's Second Law of Diffusion:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \qquad [1]$$

where *C* is the concentration, *t* is the time, *x* refers to the distance travelled by the molecules, and *D* represents the diffusion coefficient. Because the diffusional process is also thermally activated, one may describe the diffusion coefficient by the Arrhenius equation as:

$$D = D_0 e^{\frac{-E}{kT}} \qquad [2]$$

where D_0 is the frequency factor that is characteristic of the material and/or its failure mechanism. The activation energy, *E*, represents the energy barrier that must be overcome in order for diffusion to take place, *k* denotes Boltzman's constant, and *T* is temperature (°K).

In order to evaluate the functional dependence of a diffusional process on asphalt aging, one may consider the general solution of Equation 1 to a semi-infinite surface with the following initial conditions:

$$C_t\,(at\ x = 0)\ C_\infty \wedge C_t\,(at\ x = \infty) = C_0 \qquad [3]$$

where C_∞ is the concentration at equilibrium and C_0 represents the initial concentration. The solution has the general form[20] of:

$$C_t = C_\infty - (C_\infty - C_0)\ erf\left(\frac{h}{2\sqrt{Dt}}\right) \qquad [4]$$

where *h* is the length parameter related to a reference point under consideration and is analogous to the thickness of the specimen (in this case) and *erf* is the error function given by:

$$erf\,(t) = \frac{2}{\sqrt{\pi}}\int_0^t e^{-\mu^2} d\mu \qquad [5]$$

In the diffusional model of asphalt/shingle aging, two situations may exist: 1) oils diffuse *out* [where the $(C_\infty\text{-}C_0)$ term is negative) *and* 2) oxygen diffuses *in* [where the $(C_\infty\text{-}C_0)$ term is positive] to facilitate the creation of asphaltenes. Letting *A(t)* represent the asphaltene content at time *t*, *O(t)* the oil content at time *t*, and assuming that the mechanical property P(t) at time t is proportional to both the concentration of oil and asphaltenes and that the additive law may apply, one may write:

$$P_t \propto O_t + A_t \qquad [6]$$

or in a form similar to Equation 4 one can write:

$$P(t) = P_\infty - (P_\infty - P_0)\ erf\left[\frac{h}{2\sqrt{Dt}}\right] \qquad [7]$$

To further simplify the treatise, the *erf* function may be approximated by an exponential function in the form of:

$$erf\,(x) \cong 1 - e^{-\xi x} \qquad [8]$$

where ξ is a constant with a value of about 1.7 (obtained from least-squares fitting). Figure 8 compares the error function with the exponential function used as an approximation in Equation 8. For engineering purposes, the close match of the two curves demonstrates the practicality of using the exponential to approximate the error function. Substituting Equation 8 into the general solution of Equation 7, it is possible to then derive:

$$P(t) \cong P_0 + (P_\infty - P_0)\ e^{\frac{-\xi h}{2\sqrt{Dt}}} \qquad [9]$$

or

$$\frac{P(t)}{P_0} \cong 1 + \left(\frac{P_\infty}{P_0} - 1\right) e^{\frac{-\xi h}{2\sqrt{Dt}}} \qquad [10]$$

Combining Equations 2 and 10, results in:

$$\frac{P_t}{P_0} \cong 1 + \alpha e^{-\beta/\sqrt{t}} \qquad [11]$$

where

$$\alpha = \left(\frac{P_\infty}{P_0} - 1\right) \qquad [12]$$

and

$$\beta = \frac{\xi h}{2[D_0 e^{-E/kT}]^{0.5}} \qquad [13]$$

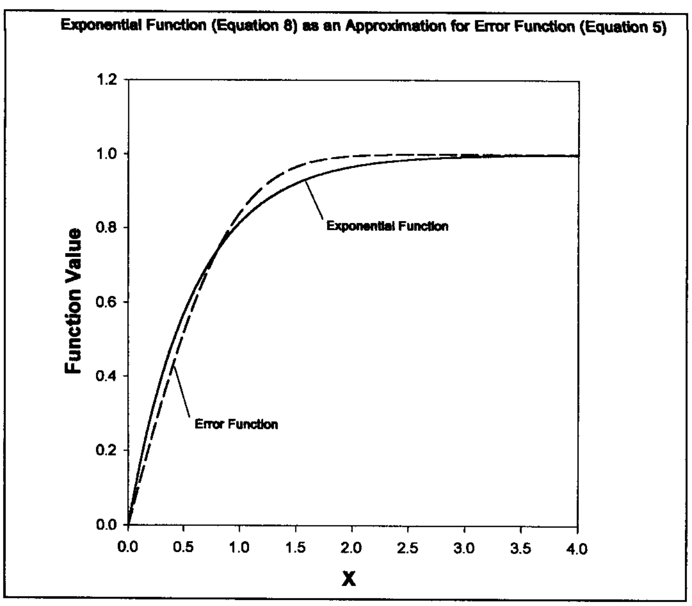


Figure 8. Functional plot.

The diffusion model presented in Equation 11 with parameters $\propto$ and β describes the effect of aging on the mechanical properties of asphalt roofing shingles due to the diffusion of oil and oxygen molecules. As will be seen later, the above model was found to adequately describe the observed aging behavior of asphalt coating.

It is interesting to note that Equation 11 predicts that the system will approach some equilibrium state as the aging progresses and that α is a material-dependent parameter resulting from the final product of aging. The rate of aging is largely influenced by the parameter β, which depends on the material's chemical structure for diffusivity and activation energy. That is, some asphalts will age faster than others at a given temperature. The effect of temperature is clearly demonstrated in Equation 11 through the strong dependence of mechanical properties on temperature in the exponential term. Similar conclusions have also been reached by other researchers,[21] and their efforts have resulted in the establishment of a thermal load map for design and prediction of roofing performance.[22]

THEORECTICAL APPLICATION

After normalizing the asphaltene and aromatics data, the Marquardt-Levenberg algorithm was used to fit the data to Equation 11. Table 1 summarizes the parameters calculated from fitting Equation 11 to the asphaltene and naphthene aromatics data as shown in Figures 4 and 5. The coefficient of determination (R^2) provided in the table clearly suggests that the diffusion model is useful for explaining *at least* 90 percent of the variability in the asphaltene and naphthene aromatic data as a function of aging methodology. Once again, the severity of the accelerated methods is readily apparent as evidenced by the steeper slopes of the regression curves as shown in Figures 4 and 5 and results in much smaller values β.

In Figure 9, the flexural modulus data for the artificial and natural exposure aging methods are compared after fitting to Equation 11. The model parameters, α and β, along with various statistics to assess the "goodness of fit" of the models are presented in Table 2. Notice that each of the models are statistically significant and that *at least* 71 percent of the variability in the flexural modulus data can be explained by the diffusion theory of Equation 11.

Focusing on the initial portion of these curves (Figure 9), it appears that shingles stiffen at a faster rate when aged in the WOM or dark oven. The consistent, intense heat associated with these accelerated methods is primarily responsible for the rate of change in the performance property and, hence, results in a smaller value of β. This work is reinforced

Aging Methodology	Asphaltenes			Naphthene Aromatics		
	α	β	R^2	α	β	R^2
Dark Oven	0.938	4.880	0.962	-0.701	2.691	0.992
QUV	1.264	6.587	0.966	-0.866	4.104	0.974
WOM	1.315	7.600	0.960	-0.998	4.365	0.991
Houston	0.915	12.770	0.954	-0.862	9.712	0.986
Minneapolis	0.505	7.370	0.900	-0.596	6.768	0.983
Philadelphia	0.531	7.182	0.915	-0.562	5.273	0.911

Table 1. Asphaltene and naphthene aromatics content as a function of aging.

Aging Methodology	α	β	MSE	R^2	Sig. Level
Dark Oven	2.198	2.829	0.092	0.797	0.000
WOM	1.900	2.190	0.043	0.873	0.000
Houston	1.264	4.116	0.043	0.782	0.000
Minneapolis	1.666	9.275	0.078	0.717	0.000
Philadelphia	1.415	7.758	0.033	0.830	0.000

Table 2. Flexural modulus as a function of aging

Aging Methodology	Time (Days) Required for Flexural Modulus to Increase by 75%
70°C (158°F) Dark Oven	7
WOM	6
Houston	62
Minneapolis	135
Philadelphia	149

Table 3.

by others who claim that heat is a major culprit in reducing the service life of shingles.[23] Secondly, the model reveals that shingles aged in Philadelphia or Minneapolis appear to lag behind Houston in the promotion of stiffness or degradation. Again, the overall hotter environment associated with Houston appears to give rise to a faster rate of degradation. Although the Minneapolis curve appears to exceed the Philadelphia curve by a small margin, this may be attributed to the perhaps overly influential data point at 548 days (see Figure 7, upper portion) with an average flexural modulus of 915 MPa (0.133 lbf/in^2). As additional data are collected, the effect of this potential "outlier" will be minimized.

Unlike the data for asphaltene and naphthene aromatics, which are continuing on their trend towards equilibrium, the flexural modulus data seems to have reached equilibrium for those materials aged in the WOM and 70°C (158°F) dark oven. Although additional data will be collected as the study continues, it appears probable that the equilibrium value of α for flexural modulus may lie between 2.1 and 2.4.

Because the reliability of the regression models has been demonstrated, they can be used to predict values of the response variable, flexural modulus. It is possible to ask, "How long will it take for the flexural modulus to increase by 75 percent of its original value?" Referring to Figure 9, notice that this question is plausible because those shingles aged in a natural environment have already achieved this state. Making predictions beyond a value of Y_t/Y_0=1.75 is not recommended at the present time because this involves extrapolation beyond the relevant range of the data. Table 3 summarizes the time required for the modulus to increase by 75 percent. The data in the table indicates that one week in the dark oven is comparable to approximately nine weeks in an environment such as Houston. Similarly, a week in a 70°C (158°F) dark oven corresponds to 19 and 21 weeks in Minneapolis and Philadelphia, respectively.

As additional data is collected, the reliability of predictions can be refined and the forecasting capability of the models can be extended to include situations in which the flexural modulus doubles or increases by more than 100 percent. One should be reminded, however, that this is only an estimate based upon Equation 11. Future work in linking the diffusion model of Equation 11 to various thermal histories experienced by the shingles using the time-temperature superposition principle will be attempted to establish a more

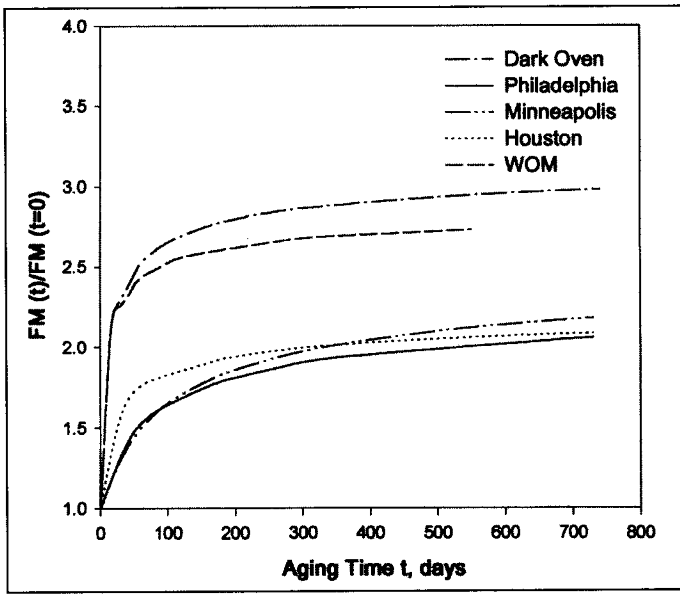


Figure 9: Flexural modulus as a function of time and aging method (regression curves based on Equation 11).

precise prediction as other geographical thermal loadings are considered.

CONCLUSIONS

In this study, fiberglass roofing shingles and coating grade asphalt were subjected to accelerated aging in a dark 70°C (158°F) oven, Atlas xenon arc Weather-Ometer®, Q-Panel Q-U-V and to the natural environments of Houston, Philadelphia, and Minneapolis. The changes in asphalt composition as well as the tensile and flexural properties of the shingles were measured as a function of aging time.

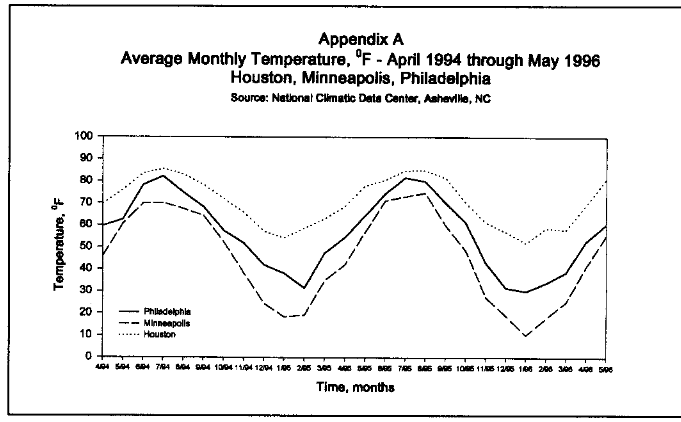
The results indicate that the reaction mechanism based on the almost identical data curves for the accelerated and natural techniques is similar, though reaction rates vary significantly between artificial and natural methods. This is most vividly noticed in the molecular weight data, in which the dark oven, WOM, and QUV regression curves are virtually superimposed. The corresponding regression for the natural sites significantly lags behind the accelerated methods, with Houston leading Minneapolis and Philadelphia in the increase in average molecular weight. These data suggest the primary effect of heat in initiating and promoting degradation, despite the presence of ultraviolet light and moisture, which are characteristic of the natural climates. Even among the natural exposure sites, the increase in asphaltenes and shingle flexural modulus and the decrease in naphthene aromatics are found to occur at a faster rate in Houston because of its hotter climate.

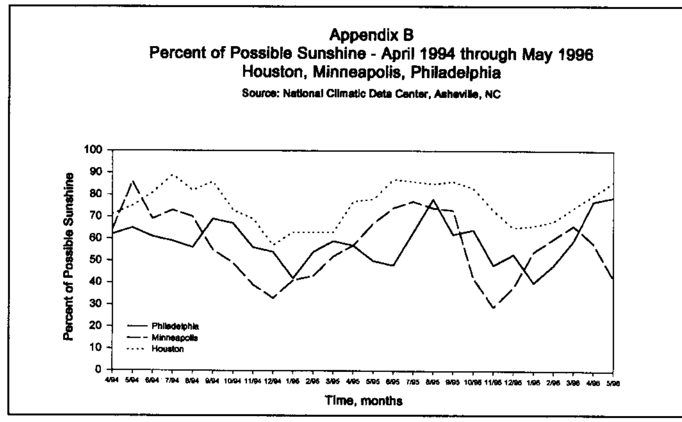
Using diffusion theory, an aging mechanism was postulated in which heat initiates the reaction and alters the equilibrium of the shingle or asphalt sample by promoting the migration of oils out of the specimen and by incorporating oxygen into the system. Changes in the chemical fractions of the asphalt were found to occur rapidly after the onset of artificial or natural aging, before slowing down and approaching some equilibrium value. These changes have been described successfully by the derived diffusional model in which the effect of temperature is clearly reflected in the model parameter β. Likewise, changes in the flexural modulus [measured at -1.1°C (30°F)] of fiberglass-reinforced shingles were found to mimic this behavior.

The statistical reliability of the diffusion models provides an opportunity for using them as a tool for predicting shingle flexural modulus, asphaltene, or naphthene aromatics content. A relationship detailing the correlation between one week in a 70°C (158°F) dark oven and corresponding time in Houston, Minneapolis, and Philadelphia was thus incorporated. Together with all of these efforts, the authors have established evidence that the accelerated methods of artificially aging asphalt or shingles are indeed accelerated and that each of these methods is representative of the reaction mechanism occurring in the field.

LITERATURE CITED

1. Warford, M. "What Aging Does to Roofing Materials," *Roofer* magazine, July 1988, 12-16.
2. Janicke, D. and P. Fitlante. "Quality Asphalt Key to Durability," *Contractors Guide*, February 1993, 44-46.
3. Shuffleton, J. D. and M. Still. "Fiberglass shingles: How Fast Do They Age?" *RSI*, May 1990, 44-48.
4. McLintock, M. "Roof Color of Choice Not Black and White," *Contractors Guide*, April 1991, 48-49.
5. Wright, J. R. "Weathering: Theoretical and Practical Aspects of Asphalt Durability," edited by A. J. Hoiberg, *Bituminous Materials: Asphalts, Tars and Pitches*, 1979, 249-306.
6. Wypych, G., ed. *Handbook of Material Weathering*, 2nd ed., 1995.
7. Maréchal, J., G. Ghaleb, and D. Bonnet. *Aging of Waterproofing Coatings Made of SBS Elastomeric Asphalt*, CSTB Studies and Research, March 1983.
8. Kleinschmidt, L. R. and H. R. Snoke. "Effect of Light and Water on the Degradation of Asphalt," *Journal of Research of the National Bureau of Standards*, Vol. 63C, No.1, July-September 1959, 31-36.
9. Martin, K.G. "Review of the Durability of Roofing Bitumens," *Journal of the Institute of Petroleum*, Vol. 47, No. 454, October 1961, 321-388.
10. Brule, B. "Contribution of Gel Permeation Chromatography (GPC) to the Characterization of Asphalts," *Liquid Chromatography of Polymers and Related Materials II*, 1980.
11. Graham, R. T. *Gel Permeation Chromatography Analysis of Asphalt-Based Joint Sealants*, U.S. Department of Transportation and Federal Aviation Administration, 1993.
12. Kirkland, W. and D. Bly. *Modern Size Exclusion Liquid Chromatography*, 1979.
13. Jennings, W. "Workshop-Prediction of Asphalt Performance by HP-GPC," *Proceedings of the Association of Asphalt Paving Technologists*, Vol. 54, 1985.
14. Jennings, W. "Advanced High Performance Gel Permeation Chromatography Methodology," *SHRP Report #A-630*, 1993.
15. Petersen, J. C., P. M. Harnsberger, and R. E. Robertson. "Factors Affecting the Oxidation and Age Hardening Kinetics of Asphalt and the Relative Effects of Oxidation Products on Asphalt Viscosity," presentation during 1996 Petersen Asphalt Research Conference, Laramie, WY.
16. Grossman, D. M. *Know Your Enemy: The Weather and How to Reproduce it in the Laboratory*, The Q-Panel Company, November 1989.





17. Fedor, G. and P. Brennan. "Correlation of Accelerated and Natural Weathering of Sealants," *Adhesives Age*, May 1990.
18. Knotnerus, J. "Bitumen Durability-Measurement by Oxygen Absorption," *Industrial Engineering and Chemistry*, Vol. 11, No. 4, 1972, 411-422.
19. Greenfield, S. "Report on the Evolution of Twenty-One Coating Grade Roofing Asphalts," *National Bureau of Standards Report*, July 1956.
20. Porter, D. A. and K. E. Easterling. *Phase Transformations in Metals and Alloys*, 1981.
21. Koike, M. and K. Tanaka. "Weatherability of Elastomeric Roofing Membranes Part 3)—Thermal Aging Tests Based on the Theory of Chemical Reaction Rate," *Transactions of Architectural Institute of Japan*, No. 255, 1977.
22. Tanaka, K., H. Hashida, T. Kuibira, and M. Koike. "Development of Thermal Degradation Load Map for Elastomeric Roofing Sheets in Japan," *Report of the Research Laboratory of Engineering Materials*, Tokyo Institute of Technology, 1990.
23. Kummer, K. L. "Roof Color Doesn't Affect Energy Use," *Eight-Penny News*, March 1991.