

Laboratory Study on Photo-oxidative Aging of Asphalt

Shengjie Liu

School of Highway, Chang'an University, Xi'an 710064, Shaanxi Province, P.R. China

Corresponding author: Email: lsjwork@126.com

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Asphalt aging is an important factor on the degradation of bitumen. Photo-oxidation is one of the main causes for road asphalt aging. In this study, the effects of photo-oxidation of bitumen were investigated by exposing pressed thin films of bitumen using physical properties and chemical group composition as an indicator of performance. The results indicated that both oxidation and UV aging occurred during exposure in the UV radiation oven test for the asphalt. Photo-oxidative aging had a significant effect on the physical properties and chemical group composition of bitumen properties.

Key Words: Asphalt, Aging, Photo-oxidative, Laboratory tests.

INTRODUCTION

The performances of asphalt pavement have been studied for many years to determine the roles of material, environmental factors that affects the properties of bitumen. Among the many factors, aging of asphalt binders and hot mix asphalt mixes can lead to the development of several types of distresses such as fatigue and thermal cracking¹⁻³. Hardening of original asphalt binder due to plant mixing and lay-down operation (short-term aging) and *in situ* aging (long-term aging) are extremely complex phenomena because of numerous factors influencing the rate of aging⁴. During the service life of the pavement, the long-term ageing of asphalt occurs, which process is slow, but continuous. The aging cause hardening of the asphalt, which decreases its flexibility and consequently deterioration takes place.

The physical-chemical factors of asphalt could provide a useful tool for characterizing the durability of asphalt cements after aging. Various laboratory accelerated aging tests have been developed to simulate the actual aging. Long-term age-hardening testing of asphalt in these laboratories has been a quite promising approach to investigating the durability of asphalts. At present the standard long-term age-hardening testing is the RTFOT followed by PAV, but the RTFOT mainly focused on the thermal-oxidative aging, it cannot generally reflect particularly for binders that are susceptible to photo-oxidative aging⁵. Especially for binders which are used in high latitude regions where the solar radiation is expected to be very high. So it may be necessary to combine photochemical aging techniques with extended oxidative procedures to

simulate long-term field aging of bituminous pavements in these areas. Therefore, attention should be given to laboratory aging tests that include UV radiation. Although the impact of photo-oxidation aging on the degradation of bitumen has been extensively studied⁶. So far the quantitative effects of Photo-Oxidative on the degradation of paving bitumen have not been determined. Therefore, the aim of this study is to investigate the relative effects of photo-oxidation and the levels of oxidative degradation of bitumen.

This paper describes a study of the effects of UV radiation and oxidative on the physical properties and chemical group composition from the photo-oxidation of bitumen films. A press-sampling method was devised and applied to demonstrate the physical and chemical effects on the bitumen caused by the photo-oxidation aging.

EXPERIMENTAL

In this study, the selected asphalt binder were AH-90 and AH-60, which obtained from a commercial petro leum company, The basic physical properties and chemical group composition of asphalt binders as per (JTJ052-2006) are shown in Table-1.

Analysis of the composition: There are several methods for analysis of the chemical composition. The four components of SARA is very practical in the research of analysis of the composition. The basic principle of the four components is the SARA analysis separates the sample in saturated, aromatics, resins and asphaltenes compounds through the action of *n*-alkane solvents, toluene and dichloromethane and the interaction between the oil with a stationary phase.

TABLE-1 CHARACTERISTICS OF ORIGINAL BITUMEN			
Item		Value (AH-70)	Value (AH-90)
Physical properties	Penetration (25 °C, 0.1 mm)	78.2	48.3
	Softening point (°C)	51.2	98.4
	Ductility (15°C, cm)	> 150	> 150
Chemical components	Saturated (%)	25.86	22.65
	Aromatics (%)	33.27	46.29
	Resins (%)	29.11	21.92
	Asphaltenes (%)	11.66	8.13

The SARA analysis starts with the precipitation of asphaltenes in *n*-alkane solvents such as pentane or heptane. Subsequently, the de-asphalted oil is separated by chromatography methods with the help of different stationary phases and solvents of varied polarity.

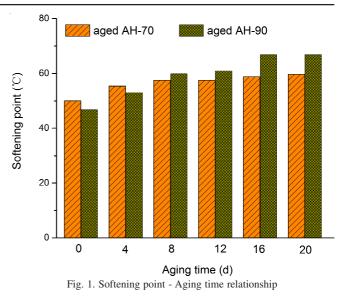
Performance testing: The penetration, ring and ball softening point, ductility were tested following the standard test methods of Bitumen and Bituminous Mixtures for Highway Engineering (JTJ 052-2006). The viscosity was tested using rotational viscometer at a temperature of 135 °C.

Infrared spectra: The infrared absorption spectra was obtained from the infrared spectrometer at different aging times, which was used to analysis the structure changes of aging asphalt.

Design and testing procedures: To analysis the performance of asphalt after long-term photo-oxidative aging. Firstly, the asphalt (about 50 ± 1 g) was heated until became fluid in an iron container and then the asphalt were pour into the flat bottom container (ξ 140 mm × 9.5 mm), the asphalt membrane is about 3.2 mm.Then the experimental has been carried out under the conditions of 85 °C temperature and ambient pressure, using the 500 W high pressure mercury lamp as light resource. The distance between samples and light resource was 45 cm. And the experimental would be taken in the due time.

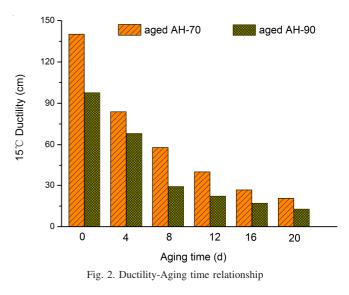
RESULTS AND DISCUSSION

Effect of photo-oxidation Aging on softening point: The variation law of the softening point at different aging time as shown in Fig. 1. It can be seen in Fig. 1 that with the prolonging of aging time, two kinds of asphalt softening point are rising, especially in the aging time is 4 days, softening point rise greatly; at the aging time 4-12 days, the increased rate of softening point decreases relatively. The softening point is the temperature at which the bitumen begins to show fluidity. It is defined as the temperature at which a bitumen sample can no longer support the weight of a 3.5-g steel ball. The related research have shown that the softening point increased as the contents of resins and asphaltenes increasing, but in contrast, softening point decreased as the contents of saturated and aromatics increasing. The former research findings in this study have found that in the 0-4 days of aging time, the resins, asphaltenes had an obvious increase and the saturated, aromatics reduced obviously. So in this period, the softening point had a significant rise. But in the 4-12 d aging time, the contents of resins reduce significantly, which leaded the slowly increasing rate of softening point. Since then, The changes of each component became slowly down, but the incremental accumulation of asphaltenes made the softening point raise.



From the Fig. 1, it can be found that the softening point of AH-90 had a high growth rate than that of AH-70,which indicated the capability of anti-photo-oxidative aging of AH-70 was greater than that of AH-90.

Effect of photo-oxidative aging on ductility: The variation law of the ductility (15 °C) at different aging time as shown in Fig. 2. It can be seen from Fig. 2, as the aging time increasing, the ductility of both asphalt showed a downward trend. Ductility is a performance index that evaluates adhesion and tenacity of asphalt. The acquisition of ductility dues to the colloidal structure and the ring and chain structure of asphalt, as the flexibility of molecular chain, the sample can bear the tensile without fracture. Ductility is mainly affected by the saturated and aromatic compounds. The long alkyl side chain and little condensation degree of aromatic compounds makes the molecular chain flexibility. It only has benefit to the matching ability of each component. In the aging process, the contents of aromatics both asphalt had been reducing, which resulted in the ductility decrease.



Effect of photo-oxidative aging on penetration: The variation law of the penetration (25 °C) at different aging time as shown in Fig. 3. As illustrated in the Fig. 3, as the aging



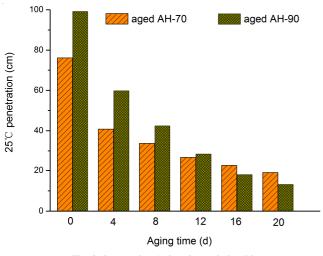
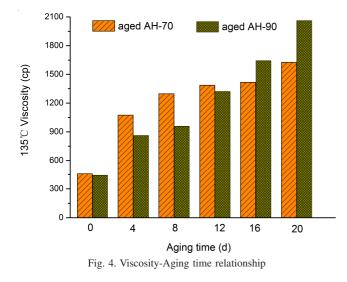


Fig. 3. Penetration-Aging time relationship

time increasing, the penetration of both asphalt showed the downward trend. Penetration is a performance index that evaluates hardness and consistency of asphalt. During the four components, the asphaltenes had the greatest impact on the penetration and then the resins, aromatic and saturated compounds. The penetration will decrease as asphaltenes content increase, in addition, following the resins, aromatics, saturated increasing, penetration showed the upward trend. Asphaltene content had been increasing and the aromatics and resins had been decreasing while the saturated content almost unchanged during the whole aging time. The penetration decreased was inspired by many factors of which the asphaltenes is the dominant. In the late aging time, the penetration change of AH-70 was slow.

Effect of photo-oxidative aging on viscosity: The variation law of the asphalt at different aging time as shown in Fig. 4 as it can be seen that following the aging time increasing, the viscosity of both asphalt showed the increase trend. With the aging time growing,the content of aromatics and resins continuous reduced,which weakened the adhesion property and peptization property with the asphaltenes. On the other hand, the increased asphaltene needed more solute to dissolve and absorb and this promoted the colloidal structure from solution-gel to gel, which leaded the viscosity of asphalt increased.



Effect of photo-oxidative aging on asphalt structure: The ultraviolet absorption peak of aromatic hydrocarbon of asphalt is near ultraviolet region (200- 400 nm), when the molecular of asphalt absorbed ultraviolet light, the electronic turned into excited state from ground state due to the electron transition. Oxidation is main factor of asphalt aging, but the oxidation of asphalt is very complex, under the action of temperature and ultraviolet, the methylene in the unsaturated chain are oxidated to form ketone and the alkyl connected with the benzene ring were oxidated to form carboxylic acid. The absorption peak relative area of asphalt was shown in Fig. 5 when after different aging times. As can be seen from the Fig. 5, the typical absorption bands of carbonyl gradually strengthened with the aging time and the concentration of carbonyl compound was increasing constantly, which showed that the aging degree was continually deepening. In the first 4 d aging time, the concentration of carbonyl increased most rapidly.

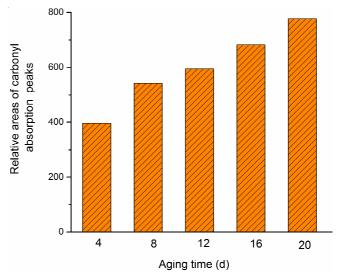


Fig. 5. Relative areas of carbonyl absorption peaks-Aging time relationship

Conclusion

Ultraviolet light can significantly accelerate the aging of asphalt. In the aging process, the rate of aromatics transformed into resins and resins transformed into asphaltenes had remarkable speed up,accordingly,the changing rate of asphalt performance had the same speed up.

During the aging process, the aromatic and asphaltene had the significantly changes and the smallest changes was saturated, which only had a little volatile.

With the time growth, the content of aromatics and resins reduced and the ductility decreased significantly. As the asphaltene content increasing continuously, the ability of anti-aging of asphalt decreased.

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