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GRADUATE COLLEGE

EFFECT OF ADDITIVES ON SURFACE FREE ENERGY CHARACTERISTICS OF AGGREGATES AND BINDERS IN HOT MIX ASPHALT

A DISSERTATION

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degree of

Doctor of Philosophy

By

NAZIMUDDIN MOHAMMAD WASIUDDIN
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EFFECT OF ADDITIVES ON SURFACE FREE ENERGY CHARACTERISTICS OF AGGREGATES AND BINDERS IN HOT MIX ASPHALT

A DISSERTATION APPROVED FOR THE
SCHOOL OF CIVIL ENGINEERING AND ENVIRONMENTAL SCIENCE

BY

_____
Dr. Musharraf M. Zaman, Chairman

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Dr. Gerald A. Miller

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Dr. Tohren C. G. Kibbey

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Dr. Edgar A. O'Rear

_____
Dr. Douglas D. Gransberg

DEDICATION

To my parents

ACKNOWLEDGEMENTS

At first, I want to thank God, The Almighty, for blessing me with the opportunity and ability to complete this work.

I am very happy to have this opportunity to express my deepest appreciation and gratitude, and heartiest thanks to my doctoral committee chairman, Professor Musharraf M. Zaman, for his invaluable help, constant support and considerable patience throughout my doctoral studies. It was his guidance and encouragement that made me working in this challenging and novel arena of pavement materials. Without his dedication, effort and active involvement, this work would not have been possible. “Thank You”.

I would like to acknowledge Dr. Joakim G. Laguros for his help for some of my research works in the University of Oklahoma that are also partially related to this dissertation. Also, it is his personality that always took me to him. It was a privilege for me to work with him. I want to thank Dr. Edgar A. O’Rear for his technical help from the very beginning of this study. His encouragement was pivotal to me for being able to work in this multidisciplinary area.

I wish to thank Dr. Tohren C. G. Kibbey for serving in my doctoral committee. I greatly thank him for sharing his knowledge and ideas with me. Also, I gratefully thank Dr. Douglas D. Gransberg for being always supportive and for being a gracious external examiner in my committee. I thank Dr. Gerald A. Miller for his kindness in serving in

my committee. I must thank him for teaching me some of the basics in geotechnical engineering.

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The love, encouragement, support and prayers of my parents carried me through this time. I am indebted to them. This acknowledgement will be incomplete without mentioning my wife who was always beside me with her love and support. Many thanks to my friends for their best wishes.

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ABSTRACT

U.S. spends approximately $20 billion/year on asphalt pavements with disproportionately high maintenance costs of $9.3 billion/year. Better performance of asphalt pavements is crucial to reducing these maintenance costs. During the past two decades significant advances have been made in understanding the behavior of hot mix asphalt (HMA) and in improving the design of asphalt pavements. In spite of these efforts, moisture-induced damage (also called stripping) is still one of the most common (75% of total road damage in one of the states surveyed) and complex problems. In this study, a mechanism-based approach based on the surface free energy (SFE) characteristics of asphalt binders and aggregates was used to elucidate on the asphalt-aggregate interactions for moisture-induced damage mechanisms. Researchers at the Texas Transportation Institute (TTI) have been using the SFE method to evaluate different asphalt binders and aggregates for moisture-induced damages. In this study, asphalt binders and aggregates were evaluated for moisture-induced damage after being modified with four different types of additives, namely liquid amines, styrene-butadiene rubber (SBR) emulsion, commercial wax and synthetic zeolite. Based on their effects relative to control samples without additives, the moisture-induced damage mechanisms are explained. A chemical model was developed which can explain that basic chemical compounds such as amines in the form of anti-strip additives reduce the acid component of SFE and increase the base component of SFE of an asphalt binder and favor the adhesion between acidic asphalt binders and acidic aggregates. The model can be used to explain that the beneficial effect of anti-strip additives in acid-base characteristics of

asphalt binders is severely reduced by Rolling Thin Film Oven (RTFO) aging and Pressure Aging Vessel (PAV) aging. The analyses also provides an explanation that the acid SFE of acidic aggregate such as sandstone is significantly reduced and the base SFE is increased by SBR coating and thus, favors the adhesion between an acidic asphalt binder and an acidic aggregate. Besides the acid-base characteristics, the model can explain wettability (spreading coefficient), adhesion (free energy of adhesion) and moisture susceptibility (spontaneous change in free energy under water). One warm mix asphalt (WMA) additive, Sasobit® (a commercial wax) was found to increase the wettability and decrease the adhesion of asphalt binders significantly. No significant effect of the second WMA additive, Aspha-Min® (a synthetic zeolite) was observed. Therefore, the chemical model proposed in this study has a set of parameters, namely Lewis acid surface parameter, Lewis base surface parameter, wettability, adhesion and moisture susceptibility that were found to be important in explaining the asphalt-aggregate interaction mechanisms. In this dissertation, the effects of amine anti-strip, RTFO and PAV-aging, and SBR polymer coating are presented in Chapters 2, 3 and 4, respectively. Effects of Sasobit® and Aspha-Min® on the binder rheology and the SFE characteristics are presented in Chapters 5 and 6, respectively. The results of this study can be used as a tool for cataloging of materials to predict moisture-induced damage in asphalt pavement.

CHAPTER

1

There are therefore agents in nature able to make the particles of bodies stick together by very strong attractions. And it is the business of experimental philosophy to find them out. *I. Newton, 1730*

INTRODUCTION

Moisture-Induced Damage in Asphalt Pavements

Moisture-induced damage of asphalt mixtures can contribute to serious distress, reduced performance and increased maintenance of asphalt pavements. Localized bleeding, rutting, shoving and eventual failure of a pavement due to permanent deformation and cracking are examples of moisture-induced damages. One of the leading causes of such damages is the "stripping" of asphalt binder from aggregate and in some cases softening of the asphalt mix [1]. In spite of significant advances made during the past two decades on understanding the behavior of hot mix asphalt (HMA) and improved design of asphalt pavements, moisture-induced damage is still one of the most common and complex problems. The classic three stages of stripping evident on the road surface are: (1) deposition of water transported aggregate fines or dust from partially stripped aggregates on to road surface; (2) migration of asphalt binder to road surface or flushing; and (3) development of potholes in the flushed area. [2].

Extent of the Moisture-Induced Damage

In a survey under the National Co-operative Highway Research Program (NCHRP) in 1991, it was found that 37 out of 53 agencies reported moisture damage in

their pavements [3]. One of the agencies participating reported 75 percent of its pavements experienced moisture-induced damages.

In 2002, an attempt was made at the University of Oklahoma to present an overview of the state of knowledge on the moisture-induced damage in asphalt pavements focusing on the following aspects: mechanisms and related theories, influencing factors, consistent test methods, and use of anti-stripping additives or aggregate pretreatment [4]. In view of the objectives of that study, emphasis was given to the "surface free energy" aspect. The literature review conducted in that study clearly shows that moisture-induced damage has been a wide spread problem for a long time. The mechanisms of moisture-induced damage are still not clearly understood. All the factors that are responsible for moisture-induced damage are still not known, and their relationships with or contributions to stripping are not fully understood. New test methods for identifying moisture susceptible aggregates and mixtures are being pursued because of the lack of a representative test method. Also, use of anti-stripping additives and aggregate pretreatment issues are active research areas [3, 5].

More than a decade after the NCHRP survey, another survey under the American Association of State Highway and Transportation Officials (AASHTO) in 2002 reported that moisture-induced damage remains a national problem. This time 45 out of 55 agencies responding, require some sort of anti-strip treatment [5]. The impact of moisture sensitivity problems on pavement performance or pavement costs was not clearly defined, but 11 agencies continued to fund research to this problem.

Current Test Methods and Treatment

A number of tests have been developed, implemented and modified by the highway agencies to help identify moisture susceptible asphalt mixes. But a test method for truly predicting moisture susceptibility is still not available. New test methods are still evolving and modifications on the existing methods are being made. Use of the tensile test following the Modified Lottman procedure (AASHTO T 283) increased from 9 agencies in 1991 to 30 in 2002 [3, 5]. Some of the other test methods being used are immersion-compression, Lottman, wheel tracking, Tunnicliff and Root etc. Out of the 82% agencies that treat their asphalt mixes for moisture-induced damage, 56% uses liquid amines, 15% liquid amines or lime and 29% lime.

Surface Free Energy (SFE) Method for Moisture-Induced Damage

SFE of a solid (or liquid) is defined as the work required to increase a unit area of surface of that solid under vacuum. Consequently, the free energy of adhesion is the free energy required to create two interfaces from one interface consisting of two different phases in contact. The SFE of a solid (or liquid) mainly comprises of an apolar component (also called Lifshitz-van der Waals component) and an acid-base component. According to Good's postulation [6], the acid-base term can be decomposed to a Lewis acidic surface parameter and a Lewis basic surface parameter

Use of SFE method for adhesion science and technology is wide spread [6, 7]. Working mechanisms of coatings, surfactants and ink are based on SFE method. If applicable in asphalt mixes, this method can be used as a tool for predesign material selection. Elphingstone [7] from Texas Transportation Institute (TTI) first showed that the SFE measurements can be a good tool for predicting fatigue and moisture-induced

damage in HMA. Since then the researchers at TTI have been contributing in relating the SFE-based methods to different areas in asphalt pavement such as moisture-induced damage, fatigue cracking, moisture diffusion and microdamage healing [7-15]. A brief summary of the contribution from TTI in this field is given below.

Elphingstone [7] suggested that aggregates should be ranked based upon strength (receding work of adhesion in vacuum) and healing (advancing work of adhesion in vacuum). According to Elphingstone [7], aggregate is the largest contributor to the magnitude of adhesive bonds. Asphalt binder is less important than aggregate in this respect. It was suggested that asphalt binder should be ranked based on physical properties (aging, low temperature properties, etc.), cohesive healing (advancing work of cohesion in vacuum), strength (receding work of adhesion in vacuum), and water susceptibility (receding work of adhesion in water).

The fatigue process is viewed as the result of the competing processes of crack growth and crack healing. In 1999, Little et al. [8] explained healing based on the first principles of fracture and healing. These principles show that surface energy of the mixture constituents and mixture compliance must affect both fracture rate and healing rate. The impact of surface energy on the healing process was verified by comparing binder surface energies measured for various binders to the rate of healing of mixtures containing those binders.

In 2002, Cheng et al. [9] evaluated the SFE of different binders and aggregates and calculated the free energy of adhesion and free energy of cohesion of the mix with and without the presence of water. Their results were consistent with the accelerated moisture damage testing on asphalt-aggregate mixtures.

Cheng et al. [10] reported that SFE is a very important parameter in fatigue model based on the Schapery's fundamental law of fracture mechanics for a viscoelastic medium. Both the SFE of cohesion and adhesion are used in the model. It was observed that certain SHRP (Strategic Highway Research Program) core asphalt binders have longer fatigue life than others.

Zhiming et al. [11] demonstrated pseudo strain concept based on the extended nonlinear elastic-viscoelastic correspondence principle, to be an appropriate and efficient method to evaluate both microdamage and healing during the fatigue damage process. It was observed that pseudo stiffness can be used to monitor microdamage and healing during the fatigue test. The effects of hydrated lime on fatigue microdamage and healing have also been evaluated based on pseudo stiffness recovery.

In 2003, Cheng et al. [12] proposed two moisture damage models based on major moisture failure mechanisms. A moisture diffusion model was developed and was used to obtain the moisture diffusion characteristics of asphalt binders, including the amount of moisture than can permeate a binder and the diffusivity of the binder.

Kim et al. [13] used dynamic mechanical analysis (DMA) to successfully evaluate complex characteristics of fatigue damage and fracture of asphalt binders and mastics by measuring fundamental viscoelastic properties and damage characteristics. DMA is used to define the effect of moisture on fatigue damage in the asphalt mastic fraction. The effect of SFE is discussed by employing DMA fatigue test results.

Very recently, Bhasin et al. [14] quantified two bond energy related parameters based on the SFE concept; adhesive bond energy between the aggregate and binder, and reduction of free energy when binder debonds from the aggregate surface in the

presence of moisture. Results show significant differences in bond energies developed between various aggregates and a given binder. The methodology of using the energy related parameters to assess moisture sensitivity of HMA was also discussed.

Masad et al. [15] developed a methodology to provide an index that is directly related to crack growth in asphalt mixtures subjected to dynamic loading. This index is a function of bond energy, viscoelastic properties, and fracture properties. The developed methodology was used to evaluate a number of asphalt mixtures that exhibited good or poor performance in the field. The resistance of the field mixtures to moisture damage was found in most cases to be related to the mixtures' bond energies, the accumulated damage in DMA, and the crack growth index.

Background of the Present Study

If SFE method is applicable to moisture-induced damage (also called stripping) of asphalt mixes, it should be able to characterize the effects of anti-strip additives on asphalt binders. To this end, this study was undertaken to examine the effects of anti-strip additives on the SFE characteristics of asphalt binders. This would also help in understanding how anti-strip additives would work in resisting moisture-induced damage. Different chemicals may have different mechanisms against moisture-induced damage. Therefore, two different types of anti-strip additives namely, liquid amines and styrene-butadiene rubber emulsion, have been used in this study. Also, it was observed that the effect of aging on asphalt binders with anti-strip additives is not clearly understood. To this end, this study includes the effect of Rolling Thin Film Oven (RTFO) aging and Pressure Aging Vessel (PAV) aging on SFE components of asphalt binders. A commercial wax (Sasobit®) and a synthetic zeolite (Aspha-Min®) are

commonly used in warm mix asphalt (WMA). Sasobit® melts and reduces viscosity while Aspha-Min® releases water vapor and reduces workability. It is suspected that WMA is moisture susceptible. Therefore, effect of these two additives were evaluated using the SFE method.

Hypothesis and Objectives

The main hypothesis of this study is:

Measurement of the SFE components of aggregates and binders could be a good tool for evaluation of different additives used in asphalt mixes.

The specific objectives of this study are:

- Develop a test protocol for the binder SFE measurement of a binder
- Develop a test protocol for the aggregate SFE measurement of aggregates
- Measure the SFE components of selected binders
- Measure the SFE components of selected aggregates
- Evaluate the SFE characteristics of binders with amine-based anti-strip additives
- Characterize thermal degradation of amine-based anti-strip additives due to RTFO-aging and PAV-aging
- Evaluate the effect of polymeric aggregate treatment using styrene-butadiene rubber (SBR)
- Compare Sasobit® and Aspha-Min® based on SFE characteristics.

Outline of the Dissertation

This dissertation is focused on the effects of various additives on the SFE components and related properties of asphalt binders, aggregates and the mix. The

findings of this study are presented in this dissertation in the format of 5 journal publications (3 published, 1 under review and 1 just prepared). Each of the Chapters 2 to 6 contains one paper and Chapter 7 presents the overall conclusions.

Chapter 2 evaluates the effect of liquid amine anti-strip additives on the SFE characteristics of asphalt binders for moisture-induced damage potential. Two performance graded asphalt binders, namely, a PG 64-22 and a PG 70-28 and two amine-based liquid anti-strip additives, namely, AD-Here HP Plus and Redicote E-6 were evaluated at different percentages (0.25%, 0.75% and 1.5%). This chapter introduces the evaluation of surface acid-base characteristics of asphalt binders with and without anti-strip additives for moisture-induced damage potential. A chemical model of the asphalt-aggregate interaction was proposed explaining these acid-base interactions between the asphalt binder and the aggregate.

In Chapter 3, thermal degradation of amine-based liquid anti-strip additives was evaluated due to RTFO-aging and PAV-aging according to AASHTO T 240 and AASHTO R 28 test methods, respectively. The SFE characteristics of asphalt binders before and after aging were used as a tool in this evaluation. Two asphalt binders, namely a PG 64-22 and a PG 70-28, and two anti-strip additives, namely AD-Here HP Plus and Redicote E-6, were evaluated. Besides the thermal degradation, the effectiveness of the anti-strip additive mixing temperature was evaluated in this chapter. Finally, the chemical model of asphalt binder, proposed in Chapter 2, was expanded to include the SFE characteristics of asphalt binders due to aging.

In Chapter 4, the SFE characteristics of two Oklahoma aggregates with and without styrene-butadiene rubber (SBR) treatment were evaluated for moisture-induced

damage potential using a universal sorption device (USD). This chapter introduces two new parameters, namely wettability and adhesion for the evaluation of moisture-induced damage potential. Two commonly used aggregates in Oklahoma, namely a limestone and a sandstone, were selected for SFE measurements. The SBR coating was evaluated based on surface area, total SFE, non-polar SFE and acid-base components of SFE. Finally, the wettability and adhesion with and without the presence of water were evaluated.

Chapters 5 and 6 present the results on WMA. In recent years, environmental protection is increasingly becoming a major issue in transportation including asphalt mix production. WMA, which reduces the production temperatures (mixing and compaction) while maintaining the advantages of HMA, is becoming an attractive paving material. In Chapter 5, rheological properties of two commonly used binders (a PG 64-22 and a PG 70-28) were evaluated, with and without additives (Sasobit® and Aspha-Min®). Three selected percentages of (2%, 3% and 4%) of Sasobit® and three selected percentages of Aspha-Min® (0.2%, 0.3% and 0.4% based on weight of the asphalt-aggregate mix) were evaluated. Effect of viscosity and binder grading were evaluated. Finally, APA rut depths were measured in an attempt to correlate rutting factor $G^*/\sin(\delta)$ to the APA rut depths.

Chapter 6 presents the effect of Sasobit® and Aspha-Min® on the wettability and adhesion (between asphalt binders and aggregates) using the SFE method from dynamic contact angle measurements. The SFE and related properties were also measured for Sasobit® and paraffin wax. To investigate the effect of water in Aspha-Min®, the Aspha-Min® with water was heated at 150°C for 36 hrs and the SFE properties were

measured. Finally, the change in surface morphology with the addition of Sasobit® was noted.

Chapter 7 summarizes the important conclusions from this study. It also includes some recommendations for future studies.

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CHAPTER

2

Mechanical joints are only possible with porous materials…We find that a joint results between porous materials whenever any Liquid material solidifies in situ to form a solid film embedded in the pores. McBain and Hopkins, 1925

EFFECT OF ANTI-STRIP ADDITIVES ON SURFACE FREE ENERGY CHARACTERISTICS OF ASPHALT BINDERS FOR MOISTURE-INDUCED DAMAGE POTENTIAL[†]

ABSTRACT

In this study, the effect of anti-strip additives on asphalt binders was evaluated by both laboratory tests and a proposed chemical model of asphalt binder based on the Surface Free Energy (SFE) characteristics. Two performance graded asphalt binders, namely, PG 64-22 and PG 70-28 and two amine-based liquid anti-strip additives, namely, AD-Here HP Plus and Redicote E-6 were evaluated at different percentages (0.25%, 0.75% and 1.5%). It was found that 1.5% AD-Here HP Plus and 1.5% Redicote E-6 increased the total SFE of PG 64-22 by 67% and 208%, respectively. Also, the acid components of PG 64-22 and PG 70-28 are 2.9 dyne/cm and 2.5 dyne/cm, respectively, whereas, the corresponding base components are 0.4 dyne/cm for both. With the addition of 1.5% Redicote E-6 in PG 64-22, the acid component of the binder reduced by 92% and the base component of the binder increased by 1141%.

[†] This chapter or portions thereof has been published previously in the ASTM Journal of Testing and Evaluation under the title "Effect of Anti-Strip Additives on Surface Free Energy Characteristics of Asphalt Binders for Moisture-Induced Damage Potential", ASTM JTE, Vol. 35, Issue 1, 2007. The current version has been formatted for this dissertation.

Keywords: Asphalt Binder, Moisture-Induced Damage, Anti-Strip Additives, Surface Free Energy, Dynamic Wilhelmy Plate Method, Contact Angle, Acid, Base.

Introduction

Moisture-induced damage of asphalt pavement can lead to serious distress, reduced performance and increased maintenance of asphalt pavements. Localized bleeding, particle degradation, disintegration, potholes, shoving and structural failure of pavement due to permanent deformation and cracking are examples of moisture-induced damage [1]. Despite significant advances in the past two decades on understanding the behavior of Hot Mix Asphalt (HMA) and on improved design of asphalt pavements, moisture-induced damage continues to be one of the most common and complex problems. Currently, the performance of HMA due to moisture exposure is evaluated by the AASHTO (American Association of State Highway and Transportation Officials) Standard Method of Test for Resistance of Compacted Asphalt Mixtures to Moisture-Induced Damage (AASHTO T 283). This test, however, does not directly address any mechanisms that govern stripping, and is only an indicator of moisture-induced damage.

Hicks [2] attributed moisture-induced damage in asphalt pavements to the following mechanisms, among others: (i) loss of adhesion depicted in Figure 2.1(a), and (ii) loss of cohesion depicted in Figure 2.1(b). Loss of adhesion, also called stripping, is caused by heterogeneous breaking of the adhesive bond between the aggregate surface and the asphalt binder primarily due to the action of water and water vapor [1,3]. When the bond is broken, the asphalt pavement weakens and exhibits various types of macroscopic failure such as cracking and raveling [4]. Softening is a general loss of

stability of a mixture due to loss of cohesion by the action of moisture within the asphalt binder. These two mechanisms are often interrelated, and thus moisture-induced damage in asphalt pavements may be a combined result of cohesion and adhesion losses [2].

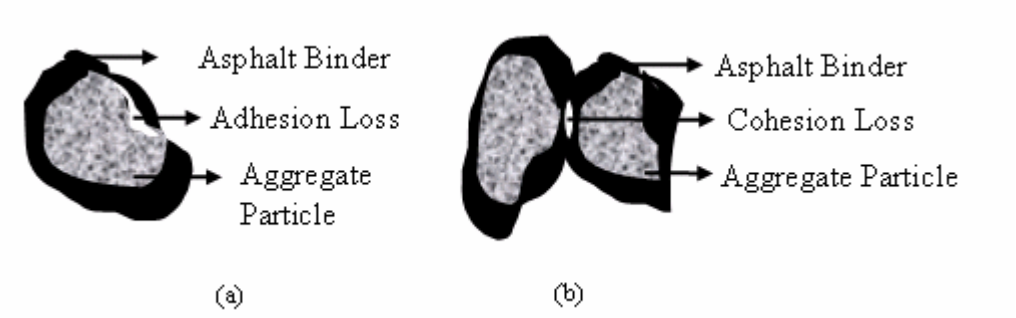

FIG. 2.1 - (a) Loss of adhesion and (b) Loss of cohesion.

Elphingstone [5] from Texas Transportation Institute first showed that the Surface Free Energy (SFE) measurements can be a good tool for predicting fatigue and moisture damage in HMA. The fatigue process is viewed as the result of the competing processes of crack growth and crack healing. In 1999, Little et al. [6] explained healing based on the first principles of fracture and healing. These principles show that surface energy of the mixture constituents and mixture compliance must affect both fracture rate and healing rate. The impact of surface energy on the healing process was verified by comparing binder surface energies measured for various binders to the rate of healing of mixtures containing those binders.

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presence of moisture. Results show significant differences in bond energies developed between various aggregates and a given binder. The methodology of using the energy related parameters to assess moisture sensitivity of HMA was also discussed.

Masad et al. [13] developed a methodology to provide an index that is directly related to crack growth in asphalt mixtures subjected to dynamic loading. This index is a function of bond energy, viscoelastic properties, and fracture properties. The developed methodology was used to evaluate a number of asphalt mixtures that exhibited good or poor performance in the field. The resistance of the field mixtures to moisture damage was found in most cases to be related to the mixtures' bond energies, the accumulated damage in DMA, and the crack growth index.

Liquid anti-strip additives are widely used for resisting moisture-induced damage. To this end, effects of liquid anti-strip additives on asphalt binders were evaluated in this study based on the SFE characteristics of asphalt binder, with and without anti-strip additives. The effect on acid-base characteristics of asphalt binder was also evaluated using the SFE method.

Surface Free Energy (SFE) of Asphalt Binder

SFE of a solid (or liquid) is defined as the work required to increase a unit area of surface of that solid under vacuum. Consequently, the free energy of cohesion (Fig. 2.2(a)) is the work done by a unit force acting along the surface of an asphalt binder at a right angle to any line of unit length against a cohesive force to create two interfaces from one (i.e., asphalt binder) under vacuum. Similarly, the free energy of adhesion (Fig. 2.2(b)) is the free energy required to create two interfaces from one interface consisting of two different phases in contact (aggregate and asphalt binder in this case).

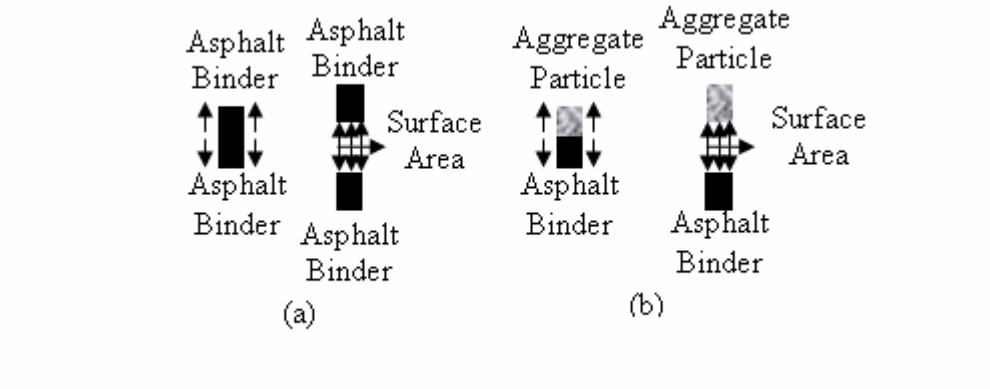

FIG. 2.2 - (a) Free energy of cohesion and (b) Free energy of adhesion.

The SFE of an asphalt binder mainly comprises of an apolar component (also called Lifshitz-van der Waals component) and an acid-base component, as shown in the following equation [14]:

$$\Gamma = \Gamma^{LW} + \Gamma^{AB} \tag{1}$$

where,

Γ = SFE of the asphalt binder,

Γ^{LW} = Lifshitz-van der Waals component of the SFE, and

Γ^{AB} = Acid-Base component of the SFE.

According to Good's postulation [14], the acid-base term can be decomposed to a Lewis acidic surface parameter and a Lewis basic surface parameter as follows:

$$\Gamma^{AB} = 2\sqrt{\Gamma^{+}\Gamma^{-}} \tag{2}$$

where,

Γ^{+} = Lewis acid component of surface interaction, and

Γ^{-} = Lewis base component of surface interaction.

Dynamic contact angles for different liquids can be used, as employed in this study, to evaluate these SFE components. The Dynamic Wilhelmy Plate method was used in this study to measure contact angles.

Dynamic Wilhelmy Plate Method (DWPM)

The measurement of dynamic contact angle by DWPM is based on kinetic force equilibrium when a thin plate is immersed and then withdrawn from a liquid solvent at a very slow and constant speed. The dynamic contact angle (see Fig. 2.3) between an asphalt binder and a liquid solvent obtained during the immersing process is called "Advancing Contact Angle" (ACA), while the dynamic contact angle during the withdrawal process is called "Receding Contact Angle" (RCA). As noted by Cheng et al. [7], the ACA, which is a wetting process, is associated with the asphalt binder's healing mechanism. In this study, only ACA was considered for analyses. It is difficult to measure RCA accurately, as reported by other researchers (see e.g., Elphingstone [5]). A microbalance measuring the change in force from tare, ΔF, during the immersion and withdrawal process is utilized. These forces, in combination with a buoyant force correction, are used to determine the dynamic contact angle applying the kinetic equilibrium equation, as shown below.

$$\cos\theta = (\Delta F + V_{im}(\rho_L - \rho_{air})g)/(P_t\Gamma_L) \tag{3}$$

where,

θ = Contact angle (degrees),

V_{im} = Volume immersed (cm^3),

ρ_L = Density of liquid solvent (gm/cm^3),

ρ_{air} = Density of air (gm/cm^3),

P_t = Perimeter of the sample (cm),

ΔF = Change in force (dyne), and

Γ_L = SFE of liquid (ergs/cm^2) or surface tension (dyne/cm).

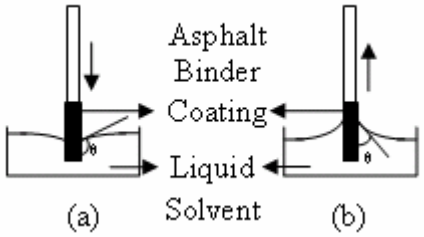

FIG. 2.3 - Dynamic Wilhelmy Plate Method for (a) advancing contact angle and (b) receding contact angle.

Calculation of SFE from Dynamic Contact Angle

Young's equation, which is essentially based on an energy balance of a drop of liquid (liquid solvent in this case) spreading on a flat solid (asphalt binder in this case) in the horizontal direction, can be used to evaluate the SFE characteristics associated with cohesion. Young's equation can be expressed as follows [14]:

$$\Gamma_{SV} = \Gamma_{SL} + \Gamma_{LV} \cos\theta_{SL} \tag{4}$$

where,

θ_{SL} = Contact angle between the solid and liquid measured through the liquid,

Γ_{SV} = SFE of solid in vacuum,

Γ_{SL} = SFE of solid in liquid, and

Γ_{LV} = SFE of liquid in vacuum.

Dupre's equation can be used to evaluate the free energy of adhesion, which represents the energy required to create two interfaces from two different phases in contact with a third medium [14]. Dupre's equation can be written as follows:

$$\Delta G_{12}^{a} = \Gamma_1 + \Gamma_2 - \Gamma_{12} \tag{5}$$

where,

ΔG^{a}_{12} = Free energy of adhesion,

Γ_1 = SFE of phase 1 (asphalt binder in this case),

Γ_2 = SFE of phase 2 (liquid solvent in this case), and

Γ_{12} = Interfacial SFE of phase 1 and phase 2.

Assuming that equilibrium film pressure is negligible for an asphalt binder, Young's equation and Dupre's equation can be combined with Good's postulate to obtain the so called Young-Dupre equation [14]. The resulting Young-Dupre equation can be expressed as follows:

$$\Gamma_L (1+\cos\theta) = 2\times\sqrt{\Gamma_S^{LW}\Gamma_L^{LW}} + 2\times\sqrt{\Gamma_S^{-}\Gamma_L^{+}} + 2\times\sqrt{\Gamma_S^{+}\Gamma_L^{-}} \quad (6)$$

where,

Γ_L^{LW}, Γ_L^{+}, and Γ_L^{-} = SFE components of liquid solvent,

Γ_S^{LW}, Γ_S^{+}, and Γ_S^{-} = SFE components of asphalt binder, and

θ = Contact angle.

In the above equation, the SFE components of an asphalt binder are given by the three unknowns (Γ_S^{LW}, Γ_S^{+}, and Γ_S^{-}). To obtain these unknowns, dynamic contact angles must be measured in at least three different liquid solvents. The SFE characteristics of these liquid solvents must be known a priori. Water, glycerin and formamide were used here as liquid solvents because of their relatively large SFE, immiscibility with asphalt binder, and differing SFE components [7].

Calculation of Free Energy of Adhesion from SFE

The free energy of adhesion (ΔG^A), as defined previously, has two components, Lifshitz- van der Waals or non-polar part of adhesion and acid-base or polar part of adhesion. The following equations are used to determine the non-polar and polar adhesion between an asphalt binder and an aggregate.

$$\Delta G^A = \Delta G^{aLW} + \Delta G^{aAB} = -2\sqrt{\Gamma_s^{LW}\Gamma_l^{LW}} - 2\sqrt{\Gamma_s^{+}\Gamma_l^{-}} - 2\sqrt{\Gamma_s^{-}\Gamma_l^{+}} \quad (7)$$

where,

ΔG^A = Free energy of adhesion,

ΔG^{aLW} = Non-Polar or Lifshitz-van der Waals part of adhesion, and

ΔG^{aAB} = Acid-base or polar part of adhesion,

Γ_L^{LW}, Γ_L^{+}, and Γ_L^{-} = SFE components of asphalt binder, and

Γ_S^{LW}, Γ_S^{+}, and Γ_S^{-} = SFE components of aggregate.

Experimental Setup and Procedure

Cheng et al. [7] evaluated the SFE of asphalt binders using DWPM and developed a testing protocol on the basis of their experience. In this study the DWPM was used with some modifications as described in this section. A Dynamic Contact Angle (DCA) analyzer, manufactured by Cahn Instruments, Inc., was used for measuring advancing contact angles using a Window-based application software, WinDCA. Cover glasses (plates) from Fisher Scientific (25 mm x 50 mm) were partially coated with an asphalt binder, with or without anti-strip additives. These coated plates are referred to as “samples” in this paper. The following experimental setup and procedure were used for sample preparation and contact angle measurements.

For cleaning, cover glass plate was placed into an oxygen flame, called flaming, horizontally along its length in a moving condition for at least three times. The flaming of a single cover glass plate did not take more than a few seconds.

For sample preparation, approximately 100 gm of asphalt binder was poured in a tin can, and the tin can was heated in a gravity oven for 2 h at 145˚C and 163ºC, respectively, for AD-Here HP Plus and Redicote E-6 based on their boiling points. The additives were mixed and stirred with a spoon at corresponding temperatures. The mix was then placed in an oven at 163ºC for 2 h. Each cover glass plate was dipped with a vertical orientation into the hot asphalt binder, to a depth of about 2 cm for approximately 5 s. After dipping, the sample was held above the asphalt binder for an additional 5 s to allow excess asphalt binder to drop into the tin can. Samples were then kept in a sample holder with coated end up for 2 min. Sample preparation was done inside a gravity oven with the help of forceps and a sample holder. The aforementioned method provided a uniform coating of at least 1 cm in length at the top end of the cover glass plate. Prepared samples were kept inside a desiccator overnight before thickness measurement (see Fig. 2.4). The thickness of the samples was measured using an Image Analyzer [15].

For contact angle measurement, triplicate samples were used for each of the three different solvents, namely, water, glycerin and formamide. No solvent was reused for any two samples. Both motor and balance of the DCA analyzer were calibrated at the beginning of each day the device was used. All measurements were made at room temperature. The sample was placed in the microbalance with the help of a sample holder such that it remained freely hanging in a vertical orientation for the duration of

measurements. Liquid solvent to be used for measuring contact angles was poured in a clean beaker and placed under the mounted sample. The distance between the surface of the liquid solvent and the bottom of the sample was maintained below 4 mm before the start of the test by moving the stage up and down, as desired. The beaker is then allowed to move vertically upward at 80 μm/s. No change in weight (force) data occurs before the sample touches the liquid solvent (see Fig. 2.5). A plus symbol inside a circle shows the ZDOI (Zero Depth of Immersion) in Figure 2.5. The sample was dipped into the liquid solvent up to 6 mm from the ZDOI at the same advancing rate. The sample is then held steady for 2 min (dwelling time) before withdrawing from the liquid solvent at the same speed. The lower portion of Figure 2.5 shows the weight (force) data for advancing contact angle, while the upper portion shows the same data for receding contact angle. The weight (force) data obtained from the microbalance were saved on the computer and used for the calculation of dynamic contact angle, using a Microsoft Excel program.

Test Matrix

The SFE components of two selected asphalt binders, namely PG 64-22 and PG 70-28 from Valero Refinery, Ardmore, Oklahoma, were determined separately from measurements of advancing contact angles. PG 70-28 used in this study is modified with the polymer Elvaloy® RET. Two amine-based liquid anti-strip additives, namely AD-Here HP Plus from Arr-Maz, Florida and Redicote E-6 from Akzo-Nobel, Chicago, were used. Three selected amounts (0.25%, 0.75% and 1.50%) of these additives were added to both the binders. If no rate is proposed by the manufacturer, the Oklahoma Department of Transportation (ODOT) recommends that the additives be mixed at the

rate of 0.5% by weight of the asphalt binder. The test matrix, including the number of samples used, for which the SFE components were evaluated is presented in Table 2.1.

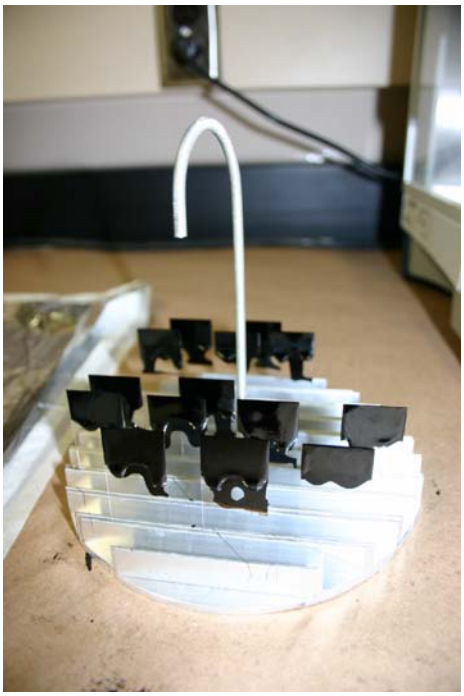

FIG. 2.4 - Samples in a sample holder.

Advancing Contact Angle of Asphalt Binders

Contact Angle with Water

The contact angle of original PG 64-22, without any anti-strip additive is, 109.4º (see Table 2.2). The contact angles of the same binder with 0.25%, 0.75% and 1.5% AD-Here HP Plus are 108.0º, 107.5º and 101.6º, respectively. The corresponding contact angles of PG 64-22 with Redicote E-6 are 109.4º, 106.3º and 94.8º. It is evident that contact angle decreases with an increase in additive content, the reduction in contact angle being more dominant for Redicote E-6 than for AD-Here HP Plus. The minimum contact angle of 94.8º is obtained for 1.5% Redicote E-6. This shows

significant effect of Redicote E-6 at 1.5%. The standard deviations in contact angle values were between 0.2º and 1.1º.

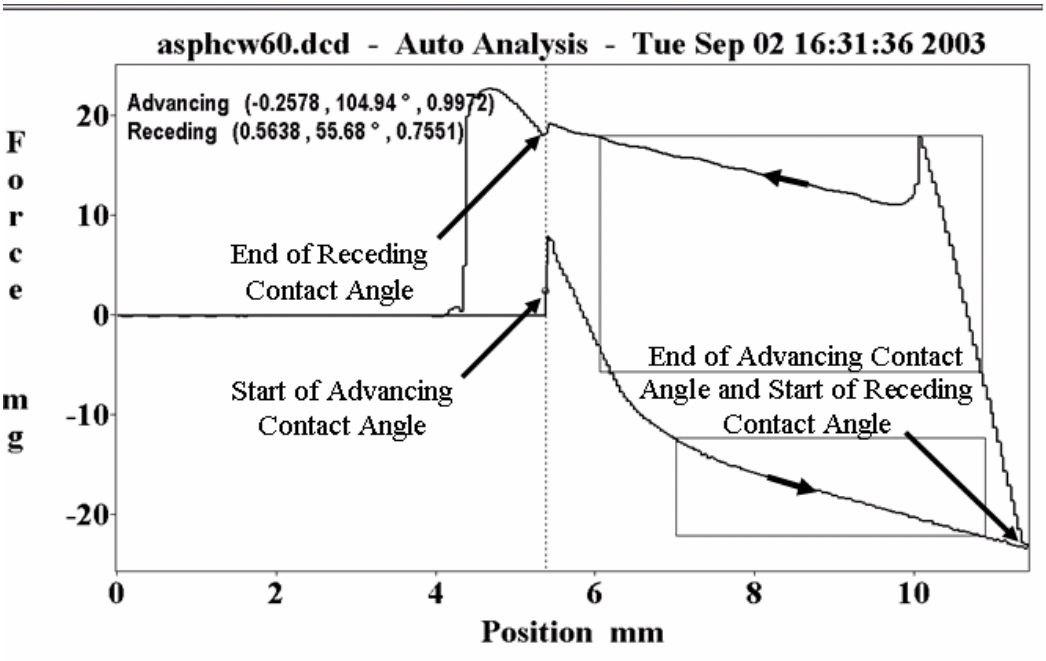

FIG. 2.5 - Wilhelmy Plate test results from DCA Analyzer.

TABLE 2.1 - Test matrix.

Types of Binder	Types of Anti-Strip Additives for Each Binder	Amount in Percent for Each Type of Additive	Types of Solvents for Each Percent of Additive	No. of Samples for Each Solvent
PG 64-22 PG 70-28	AD-Here HP Plus Redicote E-6	0% 0.25% 0.75% 1.5%	Water Glycerin Formamide	3

Comparatively, the contact angle of original PG 70-28, without any anti-strip additive is 108.1º, which is lower than the contact angle of original PG 64-22. The contact angles decrease with an increase in additive content, but the effect is not as pronounced as in the case of PG 64-22. The minimum contact angle is found to be

105.7º, with 1.5% AD-Here HP Plus. The standard deviations were between 0.1º and 0.9º.

TABLE 2.2 - Average contact angle with standard deviation.

Binders	Types of Additives	Percent of Additive	Contact Angle with Water (degree)		Contact Angle with Glycerin (degree)		Contact Angle with Formamide (degree)	
			Average	St. Dev.	Average	St. Dev.	Average	St. Dev.
PG 64-22		0	109.4	0.3	94.1	0.3	91.4	0.5
	AD-Here HP Plus	0.25	108.0	0.6	93.8	0.4	90.0	0.2
		0.75	107.5	0.9	95.1	0.2	90.3	0.2
		1.5	101.6	0.6	93.9	0.2	88.8	0.7
	Redicote E-6	0.25	109.4	0.3	94.6	0.1	90.6	0.3
		0.75	106.3	0.3	93.7	0.3	88.8	0.4
		1.5	94.8	1.1	91.9	0.7	82.9	1.4
PG 70-28		0	108.1	0.1	92.7	0.1	89.2	0.3
	AD-Here HP Plus	0.25	107.5	0.1	92.7	0.1	88.8	0.1
		0.75	107.2	0.2	92.5	0.8	88.4	0.3
		1.5	105.7	0.9	91.2	0.2	86.8	0.2
	Redicote E-6	0.25	107.5	0.8	92.3	0.1	88.8	0.7
		0.75	107.4	0.2	92.2	0.3	87.9	0.0
		1.5	106.2	0.4	91.6	0.1	87.0	0.5

Contact Angle with Glycerin

The contact angle of PG 64-22, without any anti-strip additive, is 94.1º. The contact angle for this case does not show any increasing or decreasing trend with increasing AD-Here HP Plus content. Comparatively, the contact angle decreases with an increase in the percent of Redicote E-6. The contact angle values reduced from 94.6º to 91.9º due to increasing the Redicote E-6 amount from 0.25% to 1.5%. Specifically, 1.5% Redicote E-6 significantly reduces the contact angle to 91.9º. The standard deviations in this case varied between 0.1º and 0.7 º.

The contact angle of PG 70-28, without any anti-strip additive, is 92.7º which is lower than the corresponding contact angle of PG 64-22. The contact angles are found to decrease slightly for both additives, with increasing amount of additives. The standard deviations vary between 0.1º and 0.8º.

Contact Angle with Formamide

The contact angle of original PG 64-22 for this solvent is 91.4º. No decreasing trend is observed with an increase in the percent of AD-Here HP Plus whereas, the contact angle decreases with an increase in the percent of Redicote E-6. The minimum contact angle is found to be 82.9º with 1.5% Redicote E-6. The standard deviation was some what higher (1.4º) in this case.

For original PG 70-28, the contact angle is 89.2 which is lower than that of original PG 64-22. A decreasing trend in contact angle was observed with an increase in additive content for both the additives. The standard deviation varies between 0.1º and 0.7º.

Effect of Anti-Strip Additives on SFE of Asphalt Binders

Increase in SFE with the Addition of Anti-Strip Additives (Surfactants)

Many researchers have reported that liquid anti-strip additives reduce the SFE of asphalt binders and therefore, increase the wetability of binders to the aggregate [16-18]. Increased wetability gives increased surface area to be wetted and promotes adhesion between the binder and the aggregate. To achieve this, surface active agents, the so-called "surfactants" are used as anti-strip additives. In this study, it was found that the surfactants (liquid anti-strip additives) do not decrease the SFE of an asphalt binder. Rather, it increases the SFE. This increased SFE increases the free energy of adhesion (adhesive strength) between the asphalt binder and the highly acidic aggregate such as granite according to Equation 7. The increased free energy of adhesion provides increased resistance to stripping. The more the SFE of an asphalt binder, the more the free energy of adhesion between the highly acidic aggregate and the binder.

Reasons for Increase in SFE with the Addition of Liquid Anti-Strip Additives (Surfactants)

Asphalt is a continuous phase of non-polar materials [19]. Non-polar solvents have received far less attention than polar solvents (i.e., water) with respect to the surfactant-action phenomenon. Surfactants of most types decrease surface tension of water (polar solvent) as the hydrocarbon tail groups are directed outward. In case of non-polar solvent, asphalt binder in this case, the polar head groups are directed outward. This actually results in an increase in surface tension [20-21] in asphalt binder.

Results

Table 2.3 shows the total SFE and its components obtained in this study. A general trend is that the total SFE increases with an increase in percent of additive, Redicote E-6 performing better than AD-Here HP Plus. Both additives are more effective in PG 64-22 than PG 70-28 with respect to increase in total SFE. Because it is a polymer-modified binder, the SFE of PG 70-28 is rather difficult to measure due to its relatively high viscosity.

PG 64-22 with AD-Here HP Plus - The total SFE of PG 64-22, without any anti-strip additive, is 9.3 dyne/cm. The total SFE increases to 11.4 dyne/cm, 13.5 dyne/cm and 15.5 dyne/cm, respectively, when 0.25%, 0.75% and 1.5% AD-Here HP Plus is added. The maximum (67%) increase occurs when the additive content is 1.5%.

PG 64-22 with Redicote E-6 - The total SFE of PG 64-22 increases from 9.3 dyne/cm to 11.2 dyne/cm, 14.1 dyne/cm and 28.6 dyne/cm, respectively, for 0.25%, 0.75% and 1.5% Redicote E-6, the maximum increase being 276% in case of 1.5% additive.

TABLE 2.3 - SFE components of asphalt binders with and without additives.[1]

Binders	Types of Additives	Percent of Additive	Total SFE, Γ (dyne/cm)	Lifitz-van der Waal Component, Γ^{LW} (dyne/cm)	Acid Component, Γ^{+} (dyne/cm)	Base Component, Γ^{-} (dyne/cm)	Acid-Base Component, Γ^{AB} (dyne/cm)
PG 64-22		0	9.3	7.0	2.9	0.4	2.3
	AD-Here HP Plus	0.25	11.4	9.2	2.0	0.6	2.1
		0.75	13.5	11.7	1.0	0.8	1.8
		1.5	15.5	13.1	0.5	2.9	2.4
	Redicote E-6	0.25	11.2	9.6	1.8	0.4	1.6
		0.75	14.1	12.2	1.0	0.9	1.9
		1.5	28.6	26.4	0.2	5.4	2.2
PG 70-28		0	10.9	8.8	2.5	0.4	2.1
	AD-Here HP Plus	0.25	11.8	9.7	2.1	0.5	2.1
		0.75	12.4	10.4	1.9	0.5	2.0
		1.5	13.5	11.3	1.8	0.7	2.2
	Redicote E-6	0.25	11.2	8.9	2.5	0.5	2.2
		0.75	12.5	10.7	1.9	0.4	1.8
		1.5	13.6	11.6	1.7	0.6	2.0

PG 70-28 with AD-Here HP Plus - The total SFE of original PG 70-28 is 10.9 dyne/cm. The total SFE increases to 11.8 dyne/cm, 12.4 dyne/cm and 13.5 dyne/cm, respectively, when 0.25%, 0.75% and 1.5% AD-Here HP Plus is added to the binder. The maximum increase (28%) here is much smaller than in case of PG 64-22.

PG 70-28 with Redicote E-6 - The total SFE of PG 70-28 increases from 10.9 dyne/cm to 11.2 dyne/cm, 12.5 dyne/cm and 13.6 dyne/cm, respectively, for 0.25%, 0.75% and 1.5% Redicote E-6, the maximum increase being 31%.

Effect of Anti-Strip Additives on Acid-Base Characteristics of Asphalt Binders

Acid-Base Characteristics of Asphalt Binders

Asphalt binder is acidic in nature. Carboxylic acid, anhydride, phenol, pyrrole etc. are generally the acidic functional groups in asphalt [22]. In an Ion Exchange

[1] See Appendix A for errors corresponding to these SFE values.

Chromatography (IEC) analysis on four Strategic Highway Research Program (SHRP) core asphalts, Kim and Branthaver [23] found that the mass fraction of strong acid varies between 3.9% and 9.55%, whereas, the mass fraction of strong base varies between 2.3% and 5.2%. Its acid value is between 0 and 4 mg KOH/g.

Acid-Base Characteristics of Aggregates

Acidic (also called hydrophilic) aggregates such as quartzite, granite and sandstone generally exhibit a high silica content. Basic (also called hydrophobic) aggregates, on the other hand, exhibit a low silica content. Carbonate rocks, such as limestone and dolomite, produce basic aggregates [24].

Interactions between Asphalt Binders and Aggregates

Basic aggregates such as limestone provide good bonding for acidic bitumen. In case of acidic aggregates such as granite, surface chemistry of Lewis acids and bases does not favor adhesion and a good bond between an acidic aggregate and acidic asphalt binder is very difficult to obtain [3].

Acid-Base Characteristics of Anti-Strip Additives

Liquid anti-strip additives are principally amines including protonated or alkylated amines (cationic surface active agents (surfactants)). Amines are organic compounds and are generally basic while protonated or alkylated amines are not. One percent aqueous solution of Redicote E-6 is basic according to the manufacturer. pH of Dyrek® BHMT-HP (Bis (hexamethylene) triamine-high purity), an additive not used in this study, is 12.6 (5% aqueous solution). Two major types of amine surfactants are used as anti-strip additives: fatty diamine/fatty acid salt and fatty amido-diamine/fatty acid salt.

Interactions between Aggregates and Asphalt Binders with Anti-Strip Additives

By using basic chemicals, such as amines and lime as anti-strip additives, a better adhesion can be achieved between an acidic asphalt binder and an acidic aggregate such as granite. Amines which are basic organics alter the surface of an acidic aggregate to provide better adhesion [18].

The amines consist of a long chain hydrocarbon and amine group. The amine group reacts with the aggregate surface, and the hydrocarbon portion, which is hydrophobic, is directed into the binder. The net effect is that the long hydrocarbon chain acts as a bridge between the hydrophilic aggregate and hydrophobic bitumen surfaces thus, encouraging a strong bond between them.

Results

The SFE components of binders with and without anti-strip additives are documented in Table 2.3. A general trend is that the acid component of SFE decreases with an increase in additive percent for both the additives. Another finding is that the base component decreases with an increase in additive percent for both the additives. In general, Redicote E-6 performs better than AD-Here HP Plus, while both the additives are more effective in PG 64-22 with respect to decreasing the acid component and increasing the base component.

PG 64-22 with AD-Here HP Plus - The acid component of original PG 64-22 is 2.9 dyne/cm. The acid component decreases to 2.0 dyne/cm, 1.0 dyne/cm and 0.5 dyne/cm, respectively, with the addition of 0.25%, 0.75% and 1.5% AD-Here HP Plus, the maximum reduction (83%) occurring for 1.5% additive content.

The base component of PG 64-22 without additive is 0.4 dyne/cm. The base component increases with an increase in additive amount. The maximum increase is 568% with 1.5% AD-Here HP Plus.

PG 64-22 with Redicote E-6 - The acid component of PG 64-22 is reduced from 2.9 dyne/cm to 1.8 dyne/cm, 1.0 dyne/cm and 0.2 dyne/cm, respectively, with the addition of 0.25%, 0.75% and 1.5% Redicote HP Plus, the maximum reduction (93%) taking place in case of 1.5% additive content. Redicote E-6 exhibited an excellent performance in terms of increasing the base component. The maximum increase in base component is 1142% for the additive content of 1.5%.

PG 70-28 with AD-Here HP Plus - The acid component of original PG 70-28 is 2.5 dyne/cm. The acid component reduces to 2.1 dyne/cm, 1.9 dyne/cm and 1.8 dyne/cm, respectively, with the addition of 0.25%, 0.75% and 1.5% AD-Here HP Plus, the maximum decrease being 28%. Comparatively, the component of original PG 70-28 (0.4 dyne/cm) increases to 0.5 dyne/cm, 0.5 dyne/cm and 0.7 dyne/cm, respectively, for 0.25%, 0.75% and 1.5% AD-Here HP Plus.

PG 70-28 with Redicote E-6 - The acid component of PG 70-28 with 0.25%, 0.75% and 1.5% Redicote E-6 are 2.5 dyne/cm, 1.9 dyne/cm and 1.7 dyne/cm, respectively. The maximum reduction of 33% is exhibited by 1.5% Redicote E-6. The base components of PG 70-28 are 0.5 dyne/cm, 0.5 dyne/cm and 0.7 dyne/cm, respectively, for 0.25%, 0.75% and 1.5% Redicote E-6, with the maximum increase being 39%.

In this study, the effect of anti-strip additives has been evaluated only by the acid-base characteristics of asphalt binder with and without anti-strip additives. It

should be noted that basic anti-strip additives such as amines have some other advantages besides altering the acidic aggregate surface to adhere with an acidic binder. Carboxylic acid is the most strongly adsorbed functional types on most mineral surfaces; however, it is also the functional type most easily displaced by water. Amine functionality has better water resistant capability than carboxylic acid functionality when adsorbed on aggregate surfaces [25].

Interaction of Acidic Binder with Acidic Aggregate

Asphalt binder is acidic in nature. The acid component of PG 64-22 and PG 70-28 are 2.9 dyne/cm and 2.5 dyne/cm, respectively, whereas the corresponding base component is only 0.4 dyne/cm for both. In the case of an acidic aggregate and an acidic binder, surface chemistry of Lewis acids and bases does not favor adhesion, and a good bond between an acidic aggregate and an acidic binder is very difficult to obtain, as previously found by other researchers. Basic chemical compounds such as amines in the form of anti-strip additives reduce the acid component and increase the base component of an asphalt binder. For example, with the addition of 1.5% Redicote E-6 in PG 64-22, the acid component reduces by 92% and base component increases by 1141%.

Comparison between PG 64-22 and PG 70-28

Comparison between PG 64-22 and PG 70-28 on Total SFE and SFE Components

The total SFE of PG 64-22 and PG 70-28 are 9.3 dyne/cm and 10.9 dyne/cm, respectively. The higher total SFE explains the good adhesion between aggregates and PG 70-28 without any additive. The acid component of PG 70-28 is lower than PG 64-22 and the base components are equal (see Table 2.3).

Comparison between PG 64-22 and PG 70-28 on the Effect of Anti-Strip Additives

1.5% AD-Here HP Plus increases the total SFE of PG 64-22 and PG 70-28 by 67% and 24%, respectively. Comparatively, 1.5% Redicote E-6 increases the corresponding SFE by 208% and 24%. Therefore, both the additives have greater influence on PG 64-22 than on PG 70-28 with respect to increase in total SFE. The same trend is observed for acid component and base component.

Proposed Chemical Model of Asphalt Binder

The chemical model proposed in this study is based on the SFE characteristics of asphalt binder with and without anti-strip additives. This model explains the behavioral characteristics of an asphalt binder related to anti-strip additives.

As noted by Robertson [19] asphalt binder is a collection of polar and non-polar molecules. The polar molecules tend to associate strongly to form organized structures throughout the continuous phase of the non-polar materials.

Asphalt binders are acidic in nature. In the case of an acidic aggregate and an acidic binder, surface chemistry of Lewis acids and bases does not favor adhesion, and a good bond between an acidic aggregate and an acidic binder is very difficult to obtain, as previously found by other researchers. Basic chemicals in the form of anti-strip additives reduce the acid component of SFE and increase the basic component of SFE of asphalt binders.

When cationic surfactants are added to an asphalt binder (non-polar solvent), it adsorbs onto the surface with polar head group directed outward. This actually results in an increase in surface tension of an asphalt binder.

Conclusions

The following conclusions can be drawn from the aforementioned results of this study.

- The total SFE of PG 64-22 and PG 70-28 increases with an increase in additive content. 1.5% AD-Here HP Plus and 1.5% Redicote E-6 increased the total SFE of PG 64-22 by 67% and 208%. The corresponding increases in total SFE of PG 70-28 are 23.6% and 24.4%, respectively.
- A chemical model of asphalt binder is proposed which explains this increase in total SFE. When cationic surfactants (such as amines) are added to an asphalt binder (non-polar solvent), it adsorbs onto the surface with polar head group directed outward. This actually results in an increase in surface tension of an asphalt binder.
- Asphalt binder is acidic in nature. The acid component of PG 64-22 and PG 70-28 are 2.9 dyne/cm and 2.5 dyne/cm, respectively whereas, the corresponding base components is 0.4 dyne/cm for both. Basic chemicals in the form of anti-strip additives (such as amines) can reduce the acid components of SFE and increase the basic components of SFE of asphalt binder. With the addition of 1.5% Redicote E-6 in PG 64-22, the acid component of the binder decreases by 92% and the base component increases by 1141%.
- The total SFE of PG 64-22 and PG 70-28 are 9.3 dyne/cm and 10.9 dyne/cm, respectively. The higher total SFE explains good adhesion between aggregates and PG 70-28. Both the additives have much greater

influence on PG 64-22 than PG 70-28 with respect to increase in total SFE. The same trend is observed for acid component and base component.

- Finally, in this study it was found that DWPM is an excellent tool for evaluating total SFE and acid-base components of SFE of asphalt binders with and without anti-strip additives. Effect of short term aging, long term aging and temperature susceptibility of anti-strip additives are currently under investigation.

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CHAPTER 3

Adhesive joints frequently posses an important mechanical component essential to the performance of the joint but this type of component cannot suffice as the sole mechanism whereby surfaces are joined. It must be enhanced by, just as it enhances, specific adhesion. W.C. Wake, 1976

CHARACTERIZATION OF THERMAL DEGRADATION OF LIQUID AMINE ANTI-STRIP ADDITIVES IN ASPHALT BINDERS DUE TO RTFO AND PAV-AGING[†]

ABSTRACT

In this study, thermal degradation of amine-based liquid anti-strip additives was evaluated due to RTFO-aging and PAV-aging according to AASHTO T 240 and AASHTO R 28 test methods, respectively. The surface free energy (SFE) characteristics of asphalt binders before and after aging were used as a tool for this evaluation. Two asphalt binders, namely PG 64-22 and PG 70-28, and two anti-strip additives, namely AD-Here HP Plus and Redicote E-6, were evaluated. It was observed for 0.75% AD-Here HP Plus in PG 64-22, mixing at 163°C is more effective than mixing at 145°C with respect to increase in SFE. Also, both RTFO and PAV-aging decrease the total SFE of asphalt binders; both the aging processes are more effective in PG 64-22. In addition, the beneficial effect of anti-strip additives in acid-base characteristics of asphalt binders is severely reduced by RTFO and PAV-aging. Finally,

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the chemical model of asphalt binder, proposed by Wasiuddin et al. [1], was expanded to include the SFE characteristics of asphalt binders due to aging.

Keywords: Asphalt Binder, Anti-Strip Additives, Thermal Degradation, RTFO-Aging, PAV-Aging, Surface Free Energy, Dynamic Wilhelmy Plate Method, Contact Angle, Acid, Base

Introduction

Surface active agents (surfactants) are widely used as liquid anti-strip additives in the United States [2]. Problems with some commercial anti-strip additives (surfactants) are heat instability (or thermal degradation) and long-term field performance [3]. The additive manufacturers, who responded to the inquiries of Tunnicliff and Root [4], all claim that their additives are heat stable at typical working temperatures. Theoretically, an additive that is heat stable does not become ineffective at production temperatures. The rate of becoming ineffective is significantly increased with increased temperature and time. Several researchers reported that some commercial anti-strip additives exhibit low heat stability regardless of manufacturer claims [5,6,7,8]. At present, no published data are available, to the authors' knowledge, on the effect of anti-strip additives on the long term field performance of asphalt pavements. In this study, the thermal degradation of selected anti-strip additives in selected asphalt binders was evaluated for both short term aging and long term aging. Short term aging was simulated by Rolling Thin Film Oven (RTFO) at 163°C for 85 min according to AASHTO T 240, while long term aging was simulated by Pressure Aging Vessel (PAV) at 100°C and 2.1 MPa for 20 h according to AASHTO R 28. The Surface Free Energy (SFE) method was used as a tool in this evaluation. No research

data is currently available for thermal degradation of anti-strip additives in asphalt binders due to short and long term aging. Because liquid anti-strip additives have boiling points as low as 149°C, effective mixing temperatures of anti-strip additives were also determined in this study.

Objectives

The objectives of this study are as follows:

- Application of SFE method to characterize the thermal degradation of anti-strip additives in asphalt binders.
- Characterization of thermal degradation of anti-strip additives in asphalt binders due to short term aging and long term aging.
- Determination of effective mixing temperature of anti-strip additives with asphalt binders.

Liquid Anti-Strip Additives (Cationic Surfactants)

Tunnicliff and Root [4] reported that all of the surfactants used as anti-strip additives are amines or chemical compounds containing amines, which are strongly basic compounds derived from ammonia. Historically, the most common types of anti-strip additives have been tallow diamine, polyamines based on bis-hexamethylene triamine (BHMT), and amidoamines [9]. The amines consist of a long chain hydrocarbon and amine group. The amine group reacts with the aggregate surface and forms ammonium salts with hydrogen ions in the aggregate, and the hydrocarbon portion, which is hydrophobic, is directed into the binder. The net effect is that the long hydrocarbon chain acts as a bridge between the hydrophilic aggregate and hydrophobic binder surfaces, thus, encouraging a strong bond between them [7,8,10,11].

Thermal Degradation of Anti-Strip Additives in Asphalt Binders

Dybalski [6] pointed out that some fatty diamines, which are used as anti-strip additives, thermally degrade to amides at 100ºC and above (see Dybalski [6] for the reaction mechanism and chemical structures). Subsequently, Tarrer and Wagh [7] reported that at 120ºC, 50 percent of the added amine may be inactivated within 24 h and at 180ºC, all the amines can be stored only for a few hours before losing their activity. The amine itself can, however, be stored at ambient temperatures indefinitely without a loss in efficiency [6,7]. In a different study, Yoon et al. [12] observed that all the anti-strip additives tested were capable of reacting with asphalt binder components at temperatures typical of binder handling (162.8°C). The concentrations of those additives reduced when stored (after mixing with an asphalt binder) at temperatures greater than 149ºC. Correspondingly, the effectiveness of the anti-strip additives tested was found to decrease after being held for some time in a hot asphalt binder in this temperature range. It was concluded that a positive correlation exists between the measured decrease in additive effectiveness and measured decrease in additive concentration with storage in a hot asphalt binder [12]. Very recently, Bagampadde [13] investigated the thermal stability of anti-strip additives by examining whether reaction occurs between the additives and the binders after mixing and storing at various times (1 h, 24 h and 72 h) and temperatures (25ºC, 100ºC, 140ºC and 150ºC). The total base number (TBN) calculated was proportional to the amount of basic amines present. It was observed that at 100°C, TBN of Redicote in asphalt binder reduces to 90%, 76% and 69% at 1 h, 24 h and 72 h, respectively. Therefore, this limitation (thermal degradation) on the use of amine-based anti-strip additives is important to recognize.

Test Methods for Characterization of Thermal Degradation

Tunnicliff and Root [14] identified three indicator tests, namely the bottle test, the color test and the chromatographic test, to identify qualitatively and quantitatively the thermal degradation of anti-strip additive in an asphalt binder. When used with an additive of known composition and known concentration, detection of a smaller amount would indicate decomposition or a chemical reaction between the additive and the asphalt binder.

In the bottle test, the asphalt binder is cut back by blending with naphtha or a similar diluent. The cutback asphalt is added with Ottawa sand, and the container is shaken vigorously for a few seconds. If an effective anti-strip additive is present, the sand and asphalt will be uniformly mixed. In the color indicator test, a sample of asphalt binder is placed in isopropyl alcohol. Bromophenol blue indicator is added in a quantity sufficient to bring pure isopropyl alcohol to a yellow color, at which point the test sample should be green or dark blue if an anti-strip additive is present. In a high performance liquid chromatography test, asphalt binder treated with an anti-strip additive is dissolved in a solvent and passed through a chromatographic column under high pressure. Only amide amines can be detected, and this test is not likely to be used in field laboratories.

In 1993, thermal degradation of anti-strip additive in asphalt binders was measured quantitatively using a Gilford ultraviolet and visible spectrophotometer (Model 250) by Yoon et al. [12]. Standard analytical anti-strip additive concentration versus absorbance curves were prepared and subsequently used to determine the additive concentrations of unknown asphalt binders. Very recently, Bagampadde [13]

used potentiometric titration and Fourier Transform Infrared spectroscopy for quantitative determination of thermal stability of anti-strip additives in an asphalt binder. Potentiometric titration was performed using grade reagents. The reagents were selected and mixed in accordance with the Swedish standard ISO 3771. The volume of titrant required to reach the end point was determined as maximum value. The total base number (TBN) expressed in mg KOH/g of a sample gives its basicity and was determined according to the Swedish ISO 3771 method. Although all the test procedures mentioned above offer the advantage of a quantitative determination of thermal degradation of anti-strip additives in asphalt binders, none of these can determine whether stripping will or will not occur.

Surface Free Energy Method

Surface free energy (SFE) measurements and concomitant bond energy calculations between asphalt binders and aggregates can be used as an effective tool to identify asphalt-aggregate pairs that are susceptible to premature moisture-induced damage [15]. It also explains causes for poor or good adhesion based on surface characteristics of aggregates and binders. Very recently, Masad et al. [16] proposed an index parameter related to bond energy based on the SFE method for the crack growth model. Also, Bhasin et al. [17] concluded that the SFE method can supplement the current mechanical tests for measuring moisture susceptibility with fundamental material properties. In a separate study, Wasiuddin et al. [18] used the SFE method to evaluate the acid-base characteristics of asphalt binders with and without anti-strip additives.

In this study, thermal degradation of anti-strip additives in an asphalt binder was evaluated by the SFE method using the van Oss-Chaudhury-Good (vOCG) analysis [19]. Details of the test methods and related theories were discussed previously by Wasiuddin et al. [1,18,20].

The SFE of a solid (or liquid) is defined as the work required to increase a unit area of surface of that solid under vacuum. Consequently, the free energy of cohesion is the work done by a unit force acting along the surface of an asphalt binder at a right angle to any line of unit length against a cohesive force to create two interfaces from one (i.e., asphalt binder) under vacuum. Similarly, the free energy of adhesion is the free energy required to create two interfaces from one consisting of two different phases in contact (aggregate and asphalt binder, in this case).

The SFE of an asphalt binder mainly comprises of an apolar component (also called Lifshitz-van der Waals component) and an acid-base component, as shown in the following equation [19]:

$$\Gamma = \Gamma^{LW} + \Gamma^{AB} \tag{1}$$

where,

Γ = SFE of the asphalt binder,

Γ^{LW} = Lifshitz-van der Waals component of the SFE, and

Γ^{AB} = Acid-base component of the SFE.

According to Good's postulate [19], the acid-base term can be decomposed to a Lewis acidic surface parameter and a Lewis basic surface parameter as follows:

$$\Gamma^{AB} = 2\sqrt{\Gamma^{+}\Gamma^{-}} \tag{2}$$

where,

Γ^+ = Lewis acid component of surface interaction, and

Γ^- = Lewis base component of surface interaction.

The so called Young-Dupre equation [19], in combination with Good's postulation, was used to calculate the SFE components of an asphalt binder, which can be expressed as follows:

$$\Gamma_L(1+\cos\theta) = 2\times\sqrt{\Gamma_S^{LW}\Gamma_L^{LW}} + 2\times\sqrt{\Gamma_S^-\Gamma_L^+} + 2\times\sqrt{\Gamma_S^+\Gamma_L^-} \quad (3)$$

where,

Γ_L^{LW}, Γ_L^+, and Γ_L^- = SFE components of liquid solvent,

Γ_S^{LW}, Γ_S^+, and Γ_S^- = SFE components of asphalt binder, and

θ = Contact angle.

In the above equation, the SFE components of an asphalt binder are given by the three unknowns (Γ_S^{LW}, Γ_S^+, and Γ_S^-). To obtain these unknowns, dynamic contact angles must be measured in at least three different liquid solvents. The SFE characteristics of these liquid solvents must be known a priori. Water, glycerin and formamide were used here as liquid solvents because of their relatively large SFE, immiscibility with asphalt binder, and differing SFE components [15]. Dynamic contact angles for different liquids can be used, as employed in this study, to evaluate these SFE components. The Dynamic Wilhelmy Plate method (DWPM), as described by Wasiuddin et al. [18], was used in this study to measure contact angles.

Another commonly used approach for measuring SFE is the Neumann's Equation of State (NES) method. In the NES method, only the total SFE is obtained as compared to the three SFE components in the vOCG analysis. Therefore, the contact

angle from only one liquid solvent is required to calculate the total SFE in the NES method. The total SFE can be obtained using the following equation [21]:

$$Cos\theta = \frac{(0.015\Gamma_S - 2)\sqrt{\Gamma_S\Gamma_L} + \Gamma_L}{\Gamma_L(0.015\sqrt{\Gamma_S\Gamma_L} - 1)} \quad (4)$$

where,

Γ_L = SFE of liquid solvent,

Γ_S = SFE of asphalt binder, and

θ = Contact angle.

Experimental Setup and Procedure

Cheng et al. [15,22] and other researchers in the Texas Transportation Institute (TTI) evaluated the SFE of asphalt binders using DWPM. In this study, the DWPM was used with some modifications in that protocol as described previously by Wasiuddin et al. [1,18,20]. A dynamic contact angle (DCA) analyzer, manufactured by Cahn Instruments, Inc., was used for measuring advancing contact angles using a Window-based application software, WinDCA. Cover glasses (plates) from Fisher Scientific (25 mm x 50 mm) were partially coated with an asphalt binder, with or without anti-strip additives. These coated plates are referred to as "samples" in this paper. The following experimental setup and procedure were used for sample preparation and contact angle measurements.

For cleaning, the cover glass plate was placed into an oxygen flame, called flaming, moving horizontally along its full length for at least three times. The flaming of a single cover glass plate did not take more than a few seconds.

For sample preparation, approximately 100 gm of asphalt binder was poured in a tin can, and the tin can was heated in a gravity oven for 2 h at 145˚C and 163ºC, respectively, for AD-Here HP Plus and Redicote E-6 based on their boiling points. The additives were mixed and stirred with a spoon at corresponding temperatures. The mix was then placed in an oven at 163ºC and stirred at every 5 min for 0.5 h. After 2 h, each cover glass plate was dipped with a vertical orientation into the hot asphalt binder to a depth of about 2 cm for approximately 5 s. After dipping, the sample was held above the asphalt binder for an additional 5 s to allow excess asphalt binder to drip into the tin can. Samples were then kept in a sample holder oriented vertically with coated end up for 2 min. Sample preparation was done inside a gravity oven with the help of forceps and a sample holder. The aforementioned method provided a uniform coating of at least 1 cm in length at the top end of the cover glass plate. Prepared samples were kept inside a desiccator overnight before thickness measurement. The thickness of the samples was measured using an image analyzer as described previously by Wasiuddin et al. [18,20].

For contact angle measurement, samples were prepared in triplicate for each of the three different solvents, namely, water, glycerin and formamide. No solvent was reused for any two samples. Both motor and balance of the DCA analyzer were calibrated at the beginning of each day the device was used. All measurements were made at room temperature. The sample was placed in the microbalance with the help of a sample holder such that it remained freely hanging in a vertical orientation for the duration of measurements. Liquid solvent to be used for measuring contact angles was poured in a clean beaker and placed under the mounted sample. The distance between the surface of the liquid solvent and the bottom of the sample was maintained below 4

mm before the start of the test by moving the stage up and down, as desired. The stage was then allowed to move vertically upward at 80 μm/s. No change in weight (force) data occurs before the sample touches the liquid solvent. The sample was dipped into the liquid solvent up to 6 mm from the ZDOI (Zero Depth of Immersion) at the same advancing rate. The sample was then held steady for 2 min (dwelling time) before being withdrawn from the liquid solvent at the same speed. The weight (force) data obtained from the microbalance were saved on the computer and used for the calculation of the dynamic contact angle using a Microsoft Excel program.

Test Matrix

The SFE components of two selected asphalt binders, namely PG 64-22 and PG 70-28 (Valero Refinery, Oklahoma) were determined separately from measurements of advancing contact angles. PG 70-28 used in this study is modified with the polymer Elvaloy® RET. Two amine-based liquid anti-strip additives, namely AD-Here HP Plus (Arr-Maz, Florida) and Redicote E-6 (Akzo-Nobel, Illinois) were used. For RTFO and PAV-aging, both PG 64-22 and PG 70-28 were evaluated and a selected amount (0.75%) of additive was added to these binders.

For determination of effective additive mixing temperatures, anti-strip additive was mixed at two different temperatures, one below the boiling point of the anti-strip additive and the other higher than the boiling point. According to the manufacturer, the boiling points of AD-Here HP Plus is >149°C. On the other hand, the Oklahoma Department of Transportation (ODOT) recommends 163°C for mixing the hot mix asphalt (HMA). Therefore, 145°C and 163°C were selected as the additive mixing temperatures for evaluation of an effective additive mixing temperature. In both the

cases, the asphalt binder was first heated at 145°C and then additive was added at this temperature. The binder-additive mixture was then stirred (mixed) at two different mixing temperatures (145ºC and 163°C) to find the effective additive mixing temperature. Only PG 64-22 was selected for evaluation as it undergoes significant changes in SFE due to the addition of anti-strip additives [18]. The boiling point of Redicote E-6 is >300°C. Therefore, it was not considered for effective additive mixing temperature evaluation. Two different percentages of anti-strip additives (0.75% and 1.5%) and one sample at each time interval were used for evaluation. The test matrix, including the number of samples used for which the contact angles as well as the SFE were evaluated, is presented in Table 3.1. For determination of degradation of anti-strip additives in asphalt binder due to RTFO and PAV-aging, the samples were prepared in the way as described in the experimental procedure section.

TABLE 3.1 - Test matrix.

For RTFO and PAV-Aged Samples					
Types of Binder	Types of Anti-Strip Additives for Each Binder	Amount in Percent for Each Type of Additive		Types of Solvents for Each Percent of Additive	No. of Samples for Each Solvent
PG 64-22 PG 70-28	AD-Here HP Plus Redicote E-6	0.75%		Water Glycerin Formamide	3
For Mixing Temperature Evaluation Samples					
Types of Binder	Types of Anti-Strip Additives for Each Binder	Amount in Percent for Each Type of Additive	Mixing Temperature (°C) (Heated at 145°C before Mixing)	Solvent	Time at which Samples were Taken (min)
PG 64-22	AD-Here HP Plus	0.75	163	Water	30,56,80,143,165,178,210
			145		30,55,85,143,165,211
		1.5	163		30,80,143,166,198
			145		30,55,79,114,177,209

Additive Mixing Temperature Evaluation (NES Analysis)

Table 3.2 shows the contact angles obtained for different mixing temperatures at different time intervals. In the case of 0.75% AD-Here HP Plus, contact angles obtained for 145°C samples are higher than contact angles obtained for corresponding (approximately the same time) 163°C samples. Another observation is that contact angles are relatively lower after 30 min of mixing. For 1.5% AD-Here HP Plus, contact angles of 163°C samples are higher than corresponding 145°C samples at the beginning. After about 100 min, contact angles of 145°C samples become higher than corresponding 163°C samples, as observed in the case of 0.75% AD-Here HP Plus.

TABLE 3.2 - Contact angles and SFE of mixing temperature evaluation samples.

Binder	Additive	Additive Percent	Mixing Temperature (°C)	Time (min)	Contact Angle (degree)	SFE (dyne/cm)
PG 64-22	AD-Here HP Plus	0.75%	163	30	102.2	21.8
				56	105.7	19.4
				80	106.9	18.6
				143	105.8	19.3
				165	106.1	19.1
				178	105.9	19.2
				210	106.4	18.9
			145	30	104.3	20.3
				55	106.9	18.6
				85	107.5	18.2
				143	107.4	18.3
				165	107.8	18
				211	107.3	18.3
		1.5%	163	30	102.2	21.8
				80	104.7	20
				143	103.4	20.9
				166	103.3	21
				198	102.0	21.9
			145	30	101.9	22
				55	102.1	21.8
				79	103.9	20.6
				114	104.8	20
				177	104.8	20
				209	105.4	19.6

Figure 3.1 shows the SFE of asphalt binders with different percentages of anti-strip additives at different temperatures. The SFE was evaluated using NES analysis as discussed earlier. It was observed for 0.75% AD-Here HP plus that mixing at 163°C is more effective than mixing at 145°C, because the purpose of anti-strip additives is to increase SFE [1] and mixing at 163° produces samples with higher SFE than those prepared at 145°C. In the case of 1.5% AD-Here HP Plus, the same is observed after about 2 h of heating. Therefore, in this study, anti-strip additive was mixed at 163°C for RTFO and PAV-aged samples. This conclusion needs to be implemented carefully because anti-strip strip additives become ineffective when stored at high temperatures (after mixing with an asphalt binder) for a long period of time. On the other hand, asphalt binder is a viscous material and a high additive mixing temperature is desirable for proper mixing as found in this study. Therefore, a high mixing temperature for a reasonably short period of time is expected to give the optimum results.

Advancing Contact Angles of RTFO and PAV-Aged Samples

From Table 3.3, the contact angle of original PG 64-22 (without any anti-strip additive) in water is 109.4°. The contact angle of the same binder with 0.75% AD-Here HP Plus and 0.75% Redicote E-6 reduces to 107.5° and 106.3°, respectively. It was found in this study that the contact angle of asphalt binder with anti-strip additive increases due to RTFO and PAV-aging. For example, for PG 64-22 with 0.75% AD-Here HP Plus, the contact angles of RTFO and PAV-aged samples are 109.6° and 109.0°, respectively, which are higher than the contact angle of original PG 64-22 with 0.75% AD-Here HP Plus. The corresponding contact angles of PG 64-22 with 0.75% Redicote E-6 are 107.5° and 109.2°. A similar trend is observed in the case of contact

angles with formamide. For glycerin, the changes in contact angle due to RTFO and PAV-aging are relatively small and no specific trend is observed in this case. The standard deviations in contact angle values were between 0.1° and 0.9°.

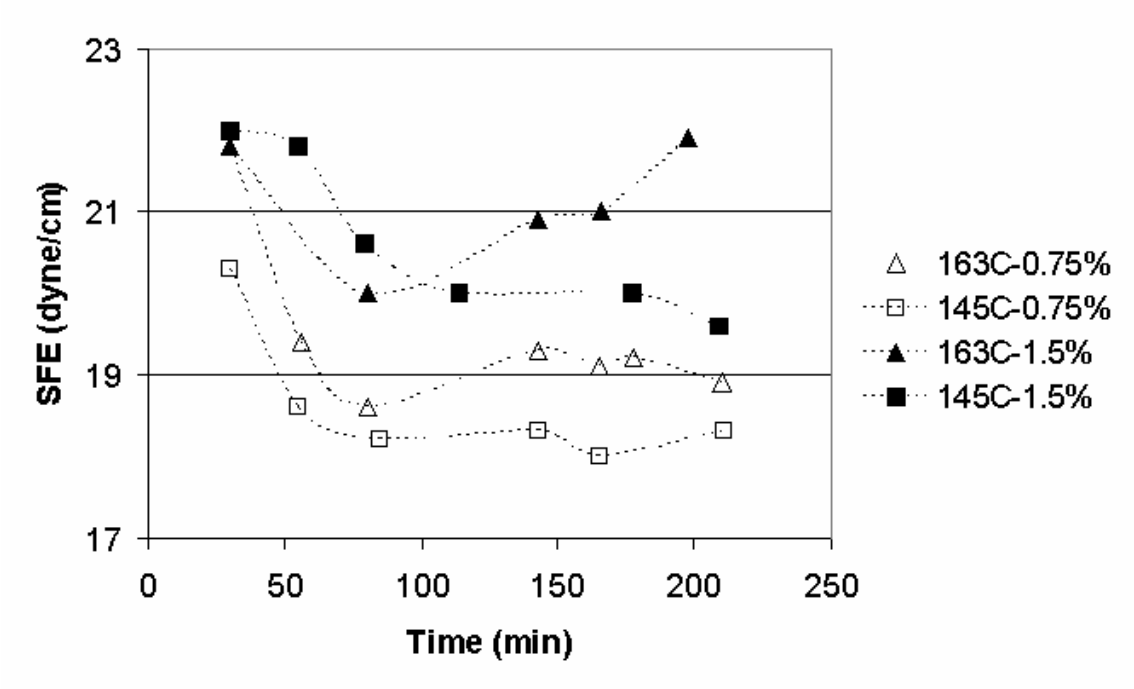

FIG. 3.1 – Effect of additive mixing temperature on SFE.

The contact angle of original PG 70-28 without any anti-strip additive is 108.1° in water, which is lower than the contact angle of original PG 64-22. A small reduction in contact angles is observed due to RTFO-aging, while a significant reduction is shown by the PAV-aged samples. A similar trend in contact angles is observed in the cases of glycerin and formamide. The standard deviations in this case were found to be between 0.1° and 1.9°.

TABLE 3.3 - Average contact angles of RTFO and PAV-aged samples.

			Contact Angle (Degree)					
		Solvent	Original Sample		RTFO-Aged Sample		PAV-Aged Sample	
			Average	Std. Dv.	Average	Std. Dv.	Average	Std. Dv.
PG64-22	0.0%	Water	109.4	0.3	109.5	0.1	109.5	0.3
		Glycerin	94.1	0.3	94.2	0.2	94.6	0.2
		Formamide	91.4	0.5	91.1	0.4	91.4	0.1
	0.75% AD-Here HP Plus	Water	107.5	0.9	109.6	0.1	109.0	0.2
		Glycerin	95.1	0.2	94.5	0.2	94.2	0.3
		Formamide	90.3	0.2	90.9	0.4	90.8	0.5
	0.75% Redicote E-6	Water	106.3	0.3	107.5	0.9	109.2	0.3
		Glycerin	93.7	0.3	93.9	0.4	94.6	0.5
		Formamide	88.8	0.4	89.5	0.6	91.3	0.4
PG70-28	0.0%	Water	108.1	0.1	107.9	1.4	105.4	1.9
		Glycerin	92.7	0.1	92.9	0.1	90.2	0.8
		Formamide	89.2	0.3	89.1	0.2	86.7	0.7
	0.75% AD-Here HP Plus	Water	107.2	0.2	107.3	0.1	101.1	0.6
		Glycerin	92.5	0.8	92.2	0.1	84.9	0.6
		Formamide	88.4	0.3	88.3	0.3	82.4	0.3
	0.75% Redicote E-6	Water	107.4	0.2	106.4	0.3	104.5	0.3
		Glycerin	92.2	0.3	91.3	0.2	89.8	0.5
		Formamide	87.9	0.1	87.5	0.2	86.4	0.3

Thermal Degradation due to Aging (vOCG Analysis)

Degradation in Total SFE

Wasiuddin et al. [18] reported that anti-strip additives increase the total SFE of asphalt binders whereas, in this study it was observed that both RTFO and PAV-aging decrease the total SFE of asphalt binders. Both the aging processes were more effective in PG 64-22. A general trend is that when subjected to aging (both RTFO and PAV), the total SFE of asphalt binders with anti-strip additives reduces almost to its total SFE without any anti-strip additives. Table 3.4 shows the SFE of asphalt binders before and after subjected to aging, obtained by the vOCG analysis.

The total SFE of PG 64-22 without any anti-strip additive is 9.3 dyne/cm. The total SFE increases by 45.1% and 52.2%, respectively, when 0.75% AD-Here HP Plus and 0.75% Redicote E-6 are added to the asphalt binder. Conversely, RTFO and PAV-

aging reduces the total SFE by 32.3% and 33.9%, respectively, for 0.75% AD-Here HP Plus. The corresponding reductions are 15.1% and 27.5% in the case of 0.75% Redicote E-6.

For PG 70-28, the increases in total SFE by the addition of 0.75% AD-Here HP Plus and 0.75% Redicote E-6 are only 13.3% and 15%, respectively. The changes due to RTFO and PAV-aging are also insignificant, the maximum reduction being 4.3% and 4% by the addition of 0.75% AD-Here HP Plus and Redicote E-6, respectively. Due to polymer modification, understanding the chemical behavior of PG 70-28 is more difficult than PG 64-22. Also, the SFE of PG 70-28 is difficult to measure because of its high viscosity. Therefore, this study focused mainly on the thermal degradation of PG 64-22.

TABLE 3.4 - SFE of original and aged asphalt binders.

SFE of PG 64-22 (dyne/cm)									
	0.0% Additive			0.75% AD-Here HP Plus			0.75% Redicote E-6		
SFE Components	Original	RTFO-Aged	PAV-Aged	Original	RTFO-Aged	PAV-Aged	Original	RTFO-Aged	PAV-Aged
Total SFE	9.3	9.6	9.9	13.5	10.5	10.3	14.1	12.7	10.2
Lifitz-van der Waal	7.0	7.6	7.9	11.7	8.7	8.3	12.2	10.8	8.1
Acid	2.9	2.7	2.4	1.0	2.1	2.3	1.0	1.4	2.3
Base	0.4	0.4	0.4	0.8	0.4	0.5	0.9	0.6	0.5
Acid-Base	2.3	2.0	2.0	1.8	1.8	2.1	1.9	1.9	2.1
SFE of PG 70-28 (dyne/cm)									
	0.0% Additive			0.75% AD-Here HP Plus			0.75% Redicote E-6		
SFE Components	Original	RTFO-Aged	PAV-Aged	Original	RTFO-Aged	PAV-Aged	Original	RTFO-Aged	PAV-Aged
Total SFE	10.9	11.5	12.2	12.3	11.9	12.6	12.5	12.1	12.3
Lifitz-van der Waal	8.8	9.6	9.5	10.4	9.8	8.2	10.7	9.8	9.3
Acid	2.5	2.1	2.6	1.9	2.2	4.5	1.9	2.3	2.7
Base	0.4	0.5	0.7	0.5	0.5	1.1	0.4	0.6	0.9
Acid-Base	2.1	2.0	2.7	2.0	2.0	4.4	1.8	2.3	3.1

Degradation in Acid-Base Components

Asphalt binders are acidic in nature. The acid component of SFE of PG 64-22 is 2.9 dyne/cm, whereas the corresponding base component is only 0.4 dyne/cm. In the case of an acidic aggregate and an acidic binder, the surface chemistry of Lewis acids and bases do not favor adhesion. Consequently a good bond between an acidic aggregate and an acidic asphalt binder is very difficult to obtain, as previously reported by other researchers (e.g., [23]). Basic chemical compounds such as amines, in the form of anti-strip additives, are found to reduce the acid component and increase the base component of asphalt binders. With the addition of 0.75% AD-Here HP Plus and 0.75% Redicote E-6 in PG 64-22, the acid component is reduced by as much as 67% and 65%, respectively. The corresponding increases in base components are 86% and 105%.

Conversely, this beneficial effect of anti-strip additives on acid-base characteristics of asphalt binder is severely reduced by RTFO and PAV-aging due to thermal degradation. For 0.75% AD-Here HP Plus in PG 64-22, the 67%-decrease in the acid component becomes a 28%-decrease after RTFO-aging and a 20%-decrease after PAV-aging. A similar trend is observed for the acid component of 0.75% Redicote E-6 in PG 64-22. In the case of the base component of SFE, the maximum increase of 105% was observed for 0.75% Redicote E-6 in PG 64-22. Due to RTFO and PAV-aging the base component reduces by 58% and 98%, respectively.

In the case of anti-strip additives in PG 70-28, a polymer-modified asphalt binder, both acid and base components are found to increase due to RTFO and PAV-aging. It was observed that PAV-aging is more effective than RTFO-aging in increasing the acid and base components of SFE. For example, for 0.75% AD-Here HP Plus, the

acid component of the original binder is 1.9 dyne/cm. The acid component increases to 2.2 dyne/cm after RTFO-aging, while the acid component increases to 4.5 dyne/cm after PAV-aging. In the case of the base component, no significant increases are observed after RTFO-aging, while the change is 129% after PAV-aging. A similar trend is observed for acid and base components of 0.75% Redicote E-6 in PG 70-28.

Causes for Thermal Degradation

Many anti-strip additives are known to be susceptible to heat, and thus, with storage in asphalt binders, the effectiveness of these additives can be severely reduced [12]. Amines in anti-strip additives are basic compounds. On the other hand, asphalt binders contain varying amounts of acidic compounds which can react with fatty amines. These reactions proceed very slowly at temperatures below 100°C but are accelerated at higher temperatures; eventually reaching the stage where no improvement in adhesion is detectable [7]. Dybalski [6] found that two major types of surfactants are in commercial use as adhesion-prompting anti-strip additives, namely diamine and amido-diamine (and their fatty acid salts). When their reactive amino hydrogen is present, these salts are susceptible to thermal degradation at temperature of 100°C and above to a non-functional fatty amide form.

In hot asphalt binders, the initial reaction between fatty amine and the asphalt binder results in the formation of salts which are still active as anti-strip additives; this does not influence the overall efficiency, provided they remain unchanged [7]. According to Dybalski [6], reactive amino hydrogen is still present at this stage in both diamine and amido-diamine salts. However, prolonged storage leads to further reactions producing inert compounds showing no adhesion properties. At this stage, no reactive

amino hydrogen is present. Their reactive amino hydrogen is replaced by a chemical substitution reaction with alkyl radicals causing thermal degradation at normal asphalt binder storage temperatures.

Besides temperature and storage time, Bagampadde [13] also reported acidity of the binder and basicity of the anti-strip additive to be the causes for thermal degradation. It was observed that the usefulness of anti-strip additives reduces considerably when a more alkaline additive was mixed with a highly acidic binder. The interaction level reduces significantly when a less alkaline additive was blended with a low acidic binder.

In addition, at a high temperature range (100°C), active components of anti-strip additives can interact chemically or physically with components within the additive or with some other components in the asphalt binder to form inactive complexes [12]. These inactive complexes cannot act as surfactants and do not provide any improvement in asphalt-aggregate bonding. It should also be noted that additives containing primary amines have relatively high vapor pressures and may vaporize at elevated temperatures.

Aging or oxidation increases polar materials in asphalt binders. An aliphatic carbon next to an aromatic ring is known as benzyl carbon and, is an example of a readily oxidizable site. Sites such as these oxidize to form ketones or aldehydes. Most severe oxidation may result in formation of carboxylic acids. Among others, carboxylic acid anhydrides (typically called anhydrides), quinolones and sulfoxides are typically found in aged asphalt binders [24]. Acids, thus formed, can also contribute to the thermal degradation of basic anti-strip additives.

Proposed Chemical Model of Asphalt Binder

The chemical model proposed by Wasiuddin et al. [1] is based on the SFE characteristics of asphalt binders with and without anti-strip additives. In this study, this model was expanded to include the SFE characteristics of asphalt binders with and without anti-strip additives before and after RTFO and PAV-aging. This model explains only the behavioral characteristics of an asphalt binder that is not polymer modified.

As noted by Robertson [24] an asphalt binder is a collection of polar and non-polar molecules. The polar molecules tend to associate strongly to form organized structures throughout the continuous phase of the non-polar materials.

Asphalt binders are acidic in nature. In the case of an acidic aggregate and an acidic binder, the surface chemistry of Lewis acids and bases do not favor adhesion. Consequently, a good bond between an acidic aggregate and an acidic asphalt binder is very difficult to obtain as previously reported by other researchers (e.g., [23]). Basic chemicals in the form of anti-strip additives reduce the acid component and increase the basic component of asphalt binders [1]. Conversely, in this study it was found that both RTFO and PAV-aging increase the acid component of SFE and decrease the base component of SFE, minimizing the beneficial effect of anti-strip additives. The most common types of anti-strip additives have been tallow diamine, polyamines based on bis-hexamethylene triamine (BHMT), and amidoamines [9]. In hot asphalt binders, the initial reaction between fatty amine and the asphalt binder results in the formation of fatty acid salts which are still active as anti-strip additives; this does not influence the overall efficiency, provided they remain unchanged [7]. According to Dybalski [6], reactive amino hydrogen is still present at this stage in both diamine/fatty acid salt and

amido-diamine/fatty acid salt. However, prolonged storage leads to further reactions producing inert compounds (non functional fatty diamide) showing no adhesion properties. At this stage, no reactive amino hydrogen is present. Their reactive amino hydrogen is replaced by a chemical substitution reaction with alkyl radicals causing thermal degradation at normal asphalt binder storage temperatures.

When cationic surfactants are added to an asphalt binder (non-polar solvent), it adsorbs onto the surface with the polar head group directed outward. This actually results in an increase in surface tension of an asphalt binder which enhances the adhesion energy between the acidic aggregate and the binder [1].

Conclusions

The following conclusions can be drawn from this study.

- The mixing of anti-strip additives at 163°C is more effective than mixing at 145°C, because the purpose of anti-strip additives is to increase SFE [1] and mixing at 163° produces samples with higher SFE than those prepared at 145°C. This conclusion needs to be viewed carefully because anti-strip strip additives become ineffective when stored at high temperatures (after mixing with an asphalt binder) for a long period of time. On the other hand, asphalt binder is a viscous material and a high additive mixing temperature is desirable for proper mixing as found in this study. Therefore, a high mixing temperature for a reasonably short period of time is expected to give the optimum results.
- Thermal degradation of anti-strip additives was observed due to RTFO-aging at 163°C for 85 min according to AASHTO T 240 and PAV-aging at

- Asphalt binders are acidic in nature. Basic chemicals in the form of anti-strip additives reduce the acid component and increase the basic component of asphalt binders. Conversely, this beneficial effect of anti-strip additives is severely reduced by RTFO and PAV-aging due to thermal degradation. As an example, in the case of the base component of SFE, the maximum increase of 105% was observed for 0.75% Redicote E-6 in PG 64-22. Due to RTFO and PAV-aging the base component reduces by 58% and 98%, respectively.

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CHAPTER 4

All experimental findings may be criticized, and no Experimental finding need be taken as crucial confirmation or disconfirmation of a theory. *New History and Sociology of Science School of Thought*

POLYMERIC AGGREGATE TREATMENT USING STYRENE-BUTADIENE RUBBER (SBR) FOR MOISTURE-INDUCED DAMAGE POTENTIAL[†]

ABSTRACT

The surface free energy (SFE) characteristics of two Oklahoma aggregates with and without styrene-butadiene rubber (SBR) treatment were evaluated for moisture-induced damage potential using a universal sorption device (USD). SBR coating altered the aggregate surface from hydrophilic to hydrophobic and thereby, increased the wettability of asphalt binder over aggregate. Significant reductions in interfacial energy were also observed for both the aggregates for increased wettability. SBR markedly reduced the total SFE, polar SFE and increased the non-polar SFE of aggregates and made the aggregate surface more hydrophobic for increased wettability. The acid SFE of acidic sandstone is significantly reduced and the base SFE is increased by SBR treatment and thus, favors the adhesion between an acidic asphalt binder and an acidic aggregate. The free energy of adhesion is increased by SBR coating with sandstone performing better than limestone. Aside from this, plugging of air-trapped fine pores

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with SBR coating reduced surface area which may help in increasing the interlocking and decreasing the asphalt binder content of the mix.

Keywords: Styrene-Butadiene Rubber (SBR), Surface Free Energy (SFE), Polymeric Aggregate Treatment, Wettability, Adhesion

Introduction

Asphalt binder is generally acidic in nature. Carboxylic acid, anhydride, phenol etc. are generally the acidic functional groups in asphalt binder [1]. In an Ion Exchange Chromatography (IEC) analysis on four Strategic Highway Research Program (SHRP) core asphalts, Kim and Branthaver [2] found that the mass fraction of strong acid varies between 3.9% and 9.55%, whereas, the mass fraction of strong base varies between 2.3% and 5.2%. Its acid value is between 0 and 4 mg KOH/g. On the other hand, acidic (also called hydrophilic) aggregates such as quartzite, granite and sandstone generally exhibit a high silica content. Basic (also called hydrophobic) aggregates exhibit a low silica content. Carbonate rocks, such as limestone and dolomite, produce basic aggregates [3]. Basic aggregates provide good bonding for acidic bitumen although some adhesive bonds such as carboxylic acid salts are easily water replaceable. In case of acidic aggregates surface chemistry of Lewis acids and bases does not favor adhesion and a good bond between an acidic aggregate and an acidic asphalt binder is difficult to achieve [4]. On the contrary, water has much higher affinity for an acidic surface. Therefore, anti-strip additives such as lime and amines are most commonly used to provide a good bond against moisture. Lime reacts with carboxylic acids in asphalt binder and forms insoluble calcium salts while amines react with acidic surface to produce insoluble ammonium salts to resist moisture damage.

A survey (including 50 states) conducted by Aschenbrener [5] indicated that 25 states use a liquid anti-strip additive, 13 states use hydrated lime, and 7 states use either a liquid anti-strip additive or hydrated lime. Lime is corrosive on equipment in bag houses at batch plants and also causes problems with dusting and subsequent worker exposure [6]. Odor is the major problem with amines, while reduced viscosity was reported by some others.

An attractive alternate method that received limited attention in the literature or market place for treating aggregate to reduce or eliminate stripping is to use polymer such as styrene-butadiene rubber (SBR). Emission test data showed that polymer systems are environmentally as safe as anti-strip additives for aggregates. The application of polymer to HMA is relatively simple, and consists of spraying diluted polymer directly on the aggregate as it is conveyed into the drum mixer. The mixing action of the drum is generally adequate to obtain coating [6]. An additional benefit of the polymer treatment is that it shows a significant decrease (0.4-0.85%) in the asphalt binder content as compared to the untreated and lime treated mixtures [7]. The SBR latex is applied directly to the aggregate and forms a rubber coating on the surface of the aggregate. It provides a protective barrier on the aggregate which repels water and water proofs the aggregate while providing an improved bonding with the asphalt binder [8].

Tarrer and Wagh [9] reported that aggregate which is coated with polymer has a decreased tendency to strip. Dunning et al. [6] performed laboratory and field trials and compared the performance of SBR with lime and amines. It was concluded from this study that SBR performed as good as an amine-treated control in the immersion-

compression test. In field tests, the polymer increased resistance to stripping and decreased the temperature susceptibility of the resilient modulus. Sebaaly et al. [7] used SBR, commercially available as UP-5000 from Ultrapave, GA, to evaluate its effectiveness compared to lime-treated and untreated aggregates. It was concluded from their study that UP-5000 is as effective as lime in eliminating the moisture sensitivity of a severe stripping aggregate, while significantly improving the performance of a marginal aggregate. Williams and Miknis [10] used Environmental Scanning Electron Microscope (ESEM) to study the effectiveness of anti-strip additives. A targeted point on the sample was observed after each freeze-thaw cycle to assess qualitatively the degree of stripping along the binder-aggregate interface of each sample. The reduced binder-aggregate separation in the SBR treated samples indicated that SBR treatments decrease separation at the binder-aggregate interface. The SBR treatment was more effective than the amine treatment, which was more effective than the lime treatment.

Objectives

The objectives of this study are to evaluate the effect of SBR treatment on the surface free energy (SFE) components (acid, base and non-polar) and related properties of selected aggregates and thereby elucidate the moisture-induced damage mechanisms. The specific objectives are as follows:

- Determine SFE components of SBR treated and untreated aggregates.
- Determine surface area, spreading coefficients and interfacial energy.
- Evaluate adhesive bond with and without the presence of water.
- Provide a better understanding of the chemical model of binder-aggregate interactions. Discuss moisture-induced damage potential with and without SBR

treatment with respect to wettability of asphalt binder over aggregate, adhesion (free energy of adhesion) between asphalt binder and aggregate, and solubility of the adhesive bond.

Surface Free Energy Method

Surface free energy (SFE) measurements and concomitant bond energy calculations between asphalt binders and aggregates can be used as an effective tool to identify binder-aggregate pairs that are susceptible to premature moisture-induced damage [11]. It also explains causes for poor or good adhesion based on surface characteristics of aggregates and binders. Very recently, Bhasin et al. [12] concluded that the SFE method can supplement the current mechanical tests for measuring moisture susceptibility with fundamental material properties. In a separate study, Wasiuddin et al. [13-14] used the SFE method to evaluate the acid-base characteristics of asphalt binders with and without anti-strip additives. In another study, Wasiuddin et al. [15] reported the thermal degradation of anti-strip additives due to rolling thin film oven (RTFO) aging and pressure aging vessel (PAV) aging based on the SFE method using the van Oss-Chaudhury-Good (vOCG) analysis [16]. Details of the test methods and related theories were discussed previously by Wasiuddin et al. [13-15].

The SFE of a solid (or liquid) is defined as the work required to increase the surface area of the solid under vacuum by unit length squared. Consequently, the free energy of cohesion is the work done by a unit force acting along the surface of an asphalt binder at a right angle to any line of unit length against a cohesive force to create two interfaces from one under vacuum. Similarly, the free energy of adhesion is

the free energy required to create two asymmetric interfaces from a boundary within a heterogeneous material (aggregate and asphalt binder, in this case).

The SFE of an aggregate mainly comprises of a non-polar component (also called Lifshitz-van der Waals component) and an acid-base component, as shown in the following equation [16]:

$$\Gamma = \Gamma^{LW} + \Gamma^{AB} \tag{1}$$

where,

Γ = SFE of the aggregate,

Γ^{LW} = Lifshitz-van der Waals component of the SFE, and

Γ^{AB} = Acid-base component of the SFE.

According to Good's postulate [16], the acid-base term can be decomposed to a Lewis acidic surface parameter and a Lewis basic surface parameter as follows:

$$\Gamma^{AB} = 2\sqrt{\Gamma^{+}\Gamma^{-}} \tag{2}$$

where,

Γ^{+} = Lewis acid component of surface interaction, and

Γ^{-} = Lewis base component of surface interaction.

The free energy of adhesion (ΔG^{A}), as defined previously, has two components, Lifshitz- van der Waals or non-polar part of adhesion and acid-base or polar part of adhesion. The following equations are used to determine the non-polar and polar adhesion between an asphalt binder and an aggregate:

$$\Delta G^{A} = \Delta G^{aLW} + \Delta G^{aAB} = -2\sqrt{\Gamma_s^{LW}\Gamma_l^{LW}} - 2\sqrt{\Gamma_s^{+}\Gamma_l^{-}} - 2\sqrt{\Gamma_s^{-}\Gamma_l^{+}} \tag{3}$$

where,

ΔG^{A} = Free energy of adhesion,

ΔG^{aLW} = Non-Polar or Lifshitz-van der Waals part of adhesion, and

ΔG^{aAB} = Acid-base or polar part of adhesion,

Γ_L^{LW}, Γ_L^{+}, and Γ_L^{-} = SFE components of asphalt binder, and

Γ_S^{LW}, Γ_S^{+}, and Γ_S^{-} = SFE components of aggregate.

Also, the following equation was used to calculate the adhesion of asphalt binder with aggregate in the presence of water where subscripts 1, 2 and 3 represent asphalt binder, aggregate, and water, respectively. If the value of free energy of adhesion is negative, it means the two phases of the material tend to bind together and the more it is negative the higher the bonding strength.

$$\begin{aligned} Adhesion = -(&2\Gamma_3^{LW} + 4\sqrt{\Gamma_3^{+}\Gamma_3^{-}} - 2\sqrt{\Gamma_1^{LW}\Gamma_3^{LW}} - 2\sqrt{\Gamma_1^{+}\Gamma_1^{-}} - 2\sqrt{\Gamma_1^{-}\Gamma_3^{+}} \\ &- 2\sqrt{\Gamma_2^{LW}\Gamma_3^{LW}} - 2\sqrt{\Gamma_2^{+}\Gamma_3^{-}} - 2\sqrt{\Gamma_2^{-}\Gamma_3^{+}} + 2\sqrt{\Gamma_1^{LW}\Gamma_2^{LW}} + 2\sqrt{\Gamma_1^{+}\Gamma_2^{-}} + 2\sqrt{\Gamma_1^{-}\Gamma_2^{+}}) \end{aligned} \quad (4)$$

where,

Γ_1^{LW}, Γ_1^{+}, and Γ_1^{-} = SFE components of asphalt binder,

Γ_2^{LW}, Γ_2^{+}, and Γ_2^{-} = SFE components of aggregate, and

Γ_3^{LW}, Γ_3^{+}, and Γ_3^{-} = SFE components of water.

The methodology established by Cheng et al. [11] was followed in this research, which is based on the van Oss-Choudhury-Good [16] postulation for the analysis of the SFE components of aggregate. The methodology and theory used for measuring the SFE components of an aggregate with the Universal Sorption Device (USD) are as follows.

- Three gas solvents, n-hexane (non-polar), MPK (methyl propyl ketone/2-pentanone, mono-polar), and water (bi-polar) were selected whose SFE components are known.
- The specific amount of solvent adsorbed on the surface of the absorbent (aggregate) was measured and simultaneously the vapor pressure at the surface of the aggregate was measured.
- The specific surface area of the aggregate was calculated using the following BET (after Brunauer, Emmet and Teller) equation:

$$\frac{P}{n(P_0 - P)} = \left(\frac{c-1}{n_m c}\right)\frac{P}{P_0} + \frac{1}{n_m c} \tag{5}$$

where,

P = Vapor pressure,

P_0 = Saturated vapor pressure of solvent,

n = Specific amount adsorbed on the surface of the absorbent,

n_m = Specific amount adsorbed on the monolayer, and

c = Constant.

- The spreading pressure at saturation vapor pressure was calculated for each solvent using the Gibbs adsorption equation, as follows:

$$\pi_e = \frac{RT}{A}\int_0^{P_0}\frac{n}{P}dP \tag{6}$$

where,

π_e = Spreading pressure at saturation vapor pressure of solvent,

R = Universal gas constant,

T = Absolute temperature, and

A = Specific surface area of absorbent.

- The work of adhesion of a liquid on a solid, W_A, was expressed in terms of the surface tension (surface energy) of the liquid, Γ_l, and the equilibrium spreading pressure of adsorbed vapor on the solid surface, π_e, as shown in the following equations:

$$W_A = \pi_e + 2\Gamma_l = \Delta G_{sl} \tag{7}$$

$$\Delta G_{sl} = \Delta G_{sl}^{LW} + \Delta G_{sl}^{AB} = 2\sqrt{\Gamma_s^{LW}\Gamma_l^{LW}} + 2\sqrt{\Gamma_s^{+}\Gamma_l^{-}} + 2\sqrt{\Gamma_s^{-}\Gamma_l^{+}} \tag{8}$$

$$\pi_e + 2\Gamma = 2\sqrt{\Gamma_s^{LW}\Gamma_l^{LW}} + 2\sqrt{\Gamma_s^{+}\Gamma_l^{-}} + 2\sqrt{\Gamma_s^{-}\Gamma_l^{+}} \tag{9}$$

- The following equation was used to calculate the non-polar component of the SFE from a non-polar solvent:

$$\Gamma_s^{LW} = \frac{(\pi_e + 2\Gamma_l)^2}{4\Gamma_l^{LW}} \tag{10}$$

One monopolar basic liquid vapor (subscript, m) and one known bipolar liquid vapor (subscript, b) were selected to calculate the acid-base components of the SFE using the following equations:

$$\Gamma_s^{+} = \frac{(\pi_e + 2\Gamma_{lm} - \sqrt{\Gamma_s^{LW}\Gamma_{lm}^{LW}})^2}{4\Gamma_{lm}^{-}} \tag{11}$$

$$\Gamma_s^{-} = \frac{(\pi_e + 2\Gamma_{lb} - 2\sqrt{\Gamma_s^{LW}\Gamma_{lb}^{LW}} - 2\sqrt{\Gamma_s^{+}\Gamma_{lb}^{-}})^2}{4\Gamma_{lb}^{+}} \tag{12}$$

The total SFE of the aggregate was calculated using the following equation:

$$\Gamma_s = \Gamma_s^{LW} + 2\sqrt{\Gamma^{+}\Gamma^{-}} \tag{13}$$

Material Description

Two commonly used aggregates in Oklahoma, namely limestone and sandstone, were selected for SFE measurements. The corresponding sources of the selected aggregates were Sawyer and Vinita. Polymeric anti-strip system styrene-butadiene rubber (SBR), commercially available as UP-5000, was collected from Ultrapave, GA. The UP-5000 (SBR) was received in an emulsion form at 15% solids. The 15% solids emulsion was mixed with the aggregate at 0.67% by dry weight of aggregate. This corresponds to 0.1% solids (not emulsions) by dry weight of aggregate. The SBR coated aggregate was then put in the oven at 150ºC for 2 h.

Experimental Setup and Procedure

A Universal Sorption Device (USD) from VTI Corporation was used to produce isotherms of different organic liquids and thereby, the SFE components were determined according to the equations described above. The major components of the USD are a microbalance, a dew point analyzer, a mass flow controller and a water bath. Approximately 15 g of an aggregate passing #4 sieve and retaining on #10 sieve (US Standard) was washed thoroughly with deionized water and put into the oven at 110°C for 24 h. The sample was then put in a desiccator and used in USD test after cooling. A test program was prepared using the VTI software. The aggregate sample was put in the USD for drying at 25°C for 600 min as set in the program. The test started with the increment of the relative humidity from water vapor. A relative humidity step of 10% was set in the program. The relative humidity will change after the sample reaches an equilibrium condition (forms a plateau) at that relative humidity level. Two different equilibrium conditions can be set in the program. One is based on percent change in

sample weight and the other on a specified time. An equilibrium condition can be set by combining the two. The USD obtains the percent change in weight data with respect to the change in relative humidity. Equilibrium (plateau) was reached at each relative humidity step.

Test Results

Adsorption isotherms of n-hexane, MPK and water vapors for both limestone and sandstone were collected at different humidity levels using the USD. It was observed that limestone has higher adsorption than sandstone with all the three vapors. This was expected because in general limestone has a much greater surface area than sandstone.

Figure 4.1 shows the adsorption of n-hexane, MPK and water at different relative pressures of different vapors on sandstone with and without SBR treatment. It can be observed that adsorption of n-hexane increased with SBR treatment. It was expected because SBR provides a relatively non-polar coating which increases the adsorption of non-polar n-hexane. The adsorption of MPK is significantly reduced with the SBR treatment (Fig. 4.1). It could be due to the fact that MPK (having a very high base SFE) repels SBR-treated aggregate (having increased base SFE due to SBR treatment as will be seen in a subsequent section). In the case of water vapor, SBR treatment reduced adsorption to sandstone, which should be helpful in resisting moisture damage. Finally, spreading pressure, specific surface area, spreading coefficient, interfacial energy and SFE components were calculated from the adsorption data, as will be discussed in the following sections. Also, all these parameters were

discussed with respect to their effect on wettability of asphalt binder over aggregate, adhesion (free energy of adhesion) and solubility of adhesive bond.

Effect on Hydrophobic/Hydrophilic Characteristics

Zettlemoyer [17] defined a surface hydrophobic (water-repelling) if water does not spread on it. Instead, the water stands up in the form of drops and a contact angle can be measured from the plane of the surface, tangent to the water surface at the three phase boundary line. It is believed that hydrophobic aggregates (considered to be basic) provide better resistance to stripping of asphalt binder films than hydrophilic aggregates (water-loving, considered to be acidic). Carbonate rocks, such as limestone, usually produce hydrophobic aggregates [3], while sandstone exhibits hydrophilic characteristics due to high silica content.

In this study, a syringe drop of water was placed on a limestone aggregate and a sandstone aggregate (both passing #4 sieve and retaining on #10 sieve) and was observed that the drop of water immediately spreads over both the dry aggregates (Fig. 4.2(b)). Spreading of the drop of water was expected for the sandstone as it exhibits hydrophilic surface. The drop of water spreads over the hydrophobic limestone aggregate perhaps due to the adsorbed layers of water molecules from the air. Both the limestone and the sandstone aggregates were then treated with SBR and it was observed that the water from the syringe formed a stable drop on both the aggregate surfaces (Fig. 4.2(c)). It was evident from this simple test that UP-5000 (SBR) polymeric aggregate treatment turns a hydrophilic aggregate (likes water) into a hydrophobic aggregate (dislikes water and likes oil), increasing the water resistance potential of the HMA. This

is consistent with the immiscible nature of aliphatic and aromatic hydrocarbon with water.

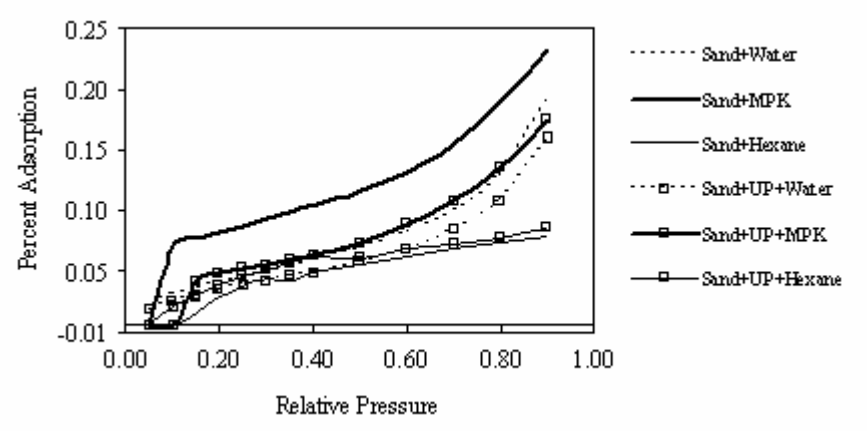

FIG. 4.1 - Adsorption of n-hexane, MPK and water at different relative pressure on sandstone with and without SBR treatment.

Effect on Surface Area

On the basis of purely mechanical considerations, large areas of aggregate interfacial contact with asphalt binder provide good adhesion and reduced moisture susceptibility. Limestone is porous and thereby, has greater surface areas than some other aggregates [18]. It appears to exhibit stronger bonds with asphalt binder than do aggregates having fewer or smaller surface pores such as quartz [19]. Table 4.1 shows the surface areas of limestone and sandstone used in this study. It was observed that limestone has about two times greater surface area than sandstone as measured by each of the three solvent vapors namely, n-hexane, MPK and water.

In addition to the greater surface areas, porous aggregate such as limestone provides greater interlock. Conversely, when asphalt binder coats a rough surface that has fine pores instead of large pores, the beneficial effect of porosity is reduced, air is trapped and the asphalt binder can hardly penetrate the fine pores. Yoon and Tarrer [18]

observed that dolomite with fine pores performed worse than limestone with large pores, probably because, only a fraction of the aggregate's apparent surface area was actually in contact with asphalt binder. In general, the depth of penetration of the asphalt binder depends on the size of the pore, as well as the viscosity and SFE of the asphalt binder at the temperature of mixing [18].

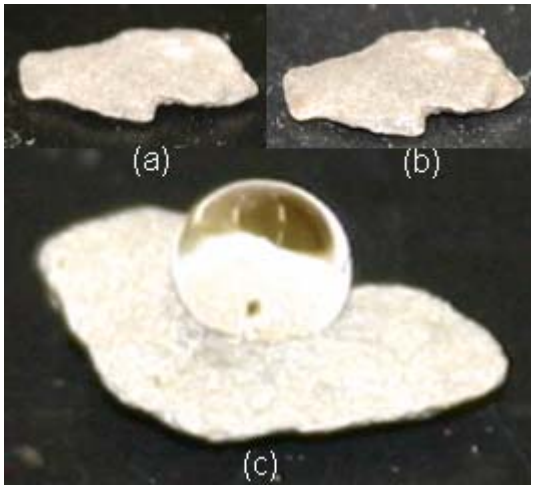

FIG. 4.2 – (a) A dry limestone (between #4 and #10), (b) Drop of water spreads on a limestone, and (c) Water drop retains on a SBR coated limestone.

The mechanism by which UP-5000 (SBR) works is that SBR coats the surface of the aggregate and penetrates the fine pores of the aggregate surface providing a strong mechanical bond. Thereby, it works as a bridging material between the aggregate surface inside the fine pores to the depth to which asphalt binder can penetrate. Thus, SBR reduces the aggregate surface area by filling up the fine pores which otherwise trap air. Table 4.1 shows that for each of the three solvent vapors, SBR reduces surface area for both limestone and sandstone. The reductions in surface areas for limestone and sandstone are 6.3% and 12% in case of water vapor, 23.3% and 33.4% for MPK, and

11.6% and 18.6% for n-hexane, respectively. The reductions are higher for limestone. It was expected because limestone has higher amount of fine pores than sandstone. Aside from this, a significant decrease in asphalt binder content of HMA with SBR treated aggregate compared to the untreated and lime treated aggregates, as found by other researchers [6-7], could be due to the reduced surface area of the SBR treated aggregates. Thus, reduced surface area explains two important mechanisms of SBR treatment, better mechanical interlocking and reduction in asphalt binder content.

Effect on Spreading Coefficient

Asphalt binder is generally hydrophobic in nature and aggregates are more or less hydrophilic [9]. Therefore, it is difficult to wet hydrophilic aggregates with a hydrophobic asphalt binder. Spreading coefficient is a quantitative measure of wetting. In this study the spreading coefficient for asphalt binder over aggregate with and without SBR treatment was calculated. The SFE components of a PG 64-22 binder was obtained from a previous study (Table 4.1) by the authors [13-14]. Spreading coefficient (SL/S) of a liquid over a solid is simply the reduction in SFE on losing the bare solid surface and forming the new solid/liquid and liquid/vapor interface [17]. It can be calculated according to the following equation:

$$S_{L/S} = \Gamma_S - \Gamma_{SL} - \Gamma_{LV} \quad (14)$$

where,

$S_{S/L}$ = Spreading coefficient of liquid L on solid S,

Γ_S = SFE of solid S, ergs/cm^2,

Γ_{SL} = Solid-liquid interfacial energy, ergs/cm^2, and

Γ_{LV} = SFE of liquid L, ergs/cm^2.

From the above equation, the free energy change of spreading coefficient will be positive for spontaneous spreading. Table 4.1 shows the spreading coefficient of a PG 64-22 binder over both the limestone and the sandstone with and without SBR (UP-5000) treatment. It was observed that SBR treatment increased the wetting of asphalt binder over both the aggregates. It improved the sandstone surface better than the limestone. These findings are consistent with the observed hydrophobic character of the SBR treated aggregate in the water droplet test and with the known relative wetting properties of sandstone and limestone.

Table 4.1 also shows that water wets the aggregate surface better than the asphalt binder as all the spreading coefficients of water over aggregates are higher than the ones for asphalt binder over aggregates. SBR treatment performed better for the sandstone reducing the wettability of water on its surface. The spreading coefficient of asphalt binder over sandstone increased from 103.8 ergs/cm^2 to 111.2 ergs/cm^2 whereas, the spreading coefficient of water over sandstone decreased from 207.7 ergs/cm^2 to 203.6 ergs/cm^2 due to SBR treatment.

Effect on Interfacial Surface Energy

Aggregates have a highly polar surface while asphalt binders have a continuous phase of non-polar materials with organized and structured polar molecules [20]. Therefore, it becomes difficult to wet polar aggregate surface with mostly non-polar asphalt binder.

The factor that affects wetting of the aggregate surface by asphalt binder is the interfacial surface energy between the asphalt binder and the aggregate [19]. Some of the additives can be extremely beneficial by reducing the surface energy, promoting

wetting, and facilitating close contact between the asphalt binder and the aggregate surface. However, the effectiveness of an additive, particularly an anti-strip additive, varies with the type of the additive, as well as with the asphalt binder and aggregate [19]. Aside from this, interfacial energy plays an important role in emulsification. When two immiscible liquids need to be mixed, a surface active agent (surfactant) is added whose molecules tend to be oriented between the two faces with the polar ends in the polar phase and the non-polar end in the non-polar phase, which lower interfacial tension. This results in miscibility of the two liquids. Therefore, changes in binder-aggregate interfacial energy due to SBR treatment were calculated in this study using the following equations [16]:

$$\Gamma_{SL} = \Delta G_{SL}^{a} + \Gamma_S + \Gamma_L \tag{15}$$

$$\Gamma_{SL}^{LW} = \Delta G_{SL}^{aLW} + \Gamma_S^{LW}\Gamma_L^{LW} \tag{16}$$

$$\Gamma_{SL}^{AB} = \Delta G_{SL}^{aAB} + \Gamma_S^{AB}\Gamma_L^{AB} \tag{17}$$

where,

Γ_S, $\Gamma^{LW}{}_S$ $\Gamma^{AB}{}_S$= Total, non-polar and polar SFE of aggregate,

Γ_L, $\Gamma^{LW}{}_L$ $\Gamma^{AB}{}_L$= Total, non-polar and polar SFE of asphalt binder,

Γ_{SL}, $\Gamma^{LW}{}_{SL}$ $\Gamma^{AB}{}_{SL}$= Total, non-polar and polar SFE of interfacial energy, and

$\Delta G^{a}{}_{SL}$, $\Delta G^{aLW}{}_{SL}$, $\Delta G^{aAB}{}_{SL}$= Total, non-polar and polar free energy of Adhesion.

Table 4.1 shows that limestone used in this study has much lower interfacial energy with PG 64-22 than does the sandstone. It was expected because limestone in general is a better performer than sandstone in resisting moisture-induced damage. SBR coating significantly decreased the interfacial energy of both limestone and sandstone

for increased wettability by asphalt binder. It was observed that with SBR treatment, the limestone-PG 64-22 interfacial energy reduced from 106.8 ergs/cm^2 to 70.6 ergs/cm^2, while the sandstone-PG 64-22 interfacial energy reduced from 180.6 ergs/cm^2 to only 66.7 ergs/cm^2. Therefore, it can be concluded that SBR coating markedly decreases the binder-aggregate interfacial energy for increased wettability and hence, better adhesion.

Effect on Total SFE (Γ) of Aggregates

In order to have a good bond between hydrophobic asphalt binder and hydrophilic aggregate the nature of the aggregate surface must be changed. The surface tension should be decreased so that the aggregate becomes more hydrophobic [9]. Table 4.1 shows the effect of SBR treatment on the total SFE of limestone and sandstone. It was observed that the total SFE of sandstone is higher than limestone and SBR treatment reduced the total SFE of both the aggregates. The total SFE of sandstone decreased significantly from 293.7 ergs/cm^2 to 187.2 ergs/cm^2 for improved wettability and adhesion. One important finding is that SBR treatment reduced the total SFE of limestone (219.9 ergs/cm^2) and sandstone (293.7 ergs/cm^2) to nearly the same level (196.2 ergs/cm^2 and 187.2 ergs/cm^2, respectively). This implies the SBR encapsulates the aggregate particles so that the effectiveness of SBR on reducing the total SFE does not depend on the aggregate mineralogy. The reduction in total SFE by styrene-butadiene rubber (SBR) coating can be explained by the fact that in general polymer, especially one with no heteroatoms, has much lower total SFE than aggregates.

TABLE 4.1 – Specific surface area, spreading coefficient, interfacial energy, SFE components and free energy of adhesion.

		Limestone	Limestone +SBR	Sandstone	Sandstone +SBR	PG 64-22*
Specific Surface Area (m^2/gm)	n-Hexane	2.24	2.10	1.30	1.15	
	MPK	3.23	2.47	1.51	1.01	
	Water	2.31	2.04	1.23	1.00	
Spreading Coefficient (ergs/cm^2)	Binder on Aggregate	103.7	116.3	103.8	111.2	
	Water on Aggregate	193.1	219.0	207.7	203.6	
Interfacial Energy (ergs/cm^2)	Binder-Aggregate Interface	106.8	70.6	180.6	66.7	
	Water-Aggregate Interface	-45.8	-95.4	13.4	-89.0	
SFE Components (ergs/cm^2)	Total SFE (Γ)	219.9	196.2	293.7	187.2	9.28
	Non-Polar SFE (Γ^{LW})	51.9	62.8	43.5	63.1	7.025
	Acid SFE (Γ^{A})	13.0	6.5	28.2	6.3	2.91
	Base SFE (Γ^{B})	540.7	687.7	555.2	610.5	0.44
	Acid-Base (Polar) SFE (Γ^{AB})	168.0	133.4	250.3	124.0	2.256
Free Energy of Adhesion (ergs/cm^2)	Binder-Aggregate	-122.3	-134.8	-122.4	-129.8	
	Water-Aggregate	-338.3	-364.2	-352.9	-348.8	
	Binder-Aggregate in Water	119.3	132.7	133.9	122.3	

*Wasiuddin et al. [*13-14]*

Effect on Non-Polar SFE (Γ^{LW}) of Aggregates

Aggregates have highly polar surface making it very difficult for mostly non-polar asphalt binder to wet. SBR treatment alters the aggregate surface increasing its non-polarity for increased wettability. It was observed (Table 4.1) that limestone (51.9 ergs/cm^2) has higher non-polar SFE than sandstone (43.5 ergs/cm^2) which was expected because limestone performs better against moisture-induced damage. As in the case of the total SFE, SBR treatment increased the non-polar SFE of both the limestone and the sandstone to the same level (62.8 ergs/cm^2 and 63.1 ergs/cm^2, respectively).

Good [16] reported comparatively higher non-polar SFE and lower polar SFE of some polymers. On the other hand, aggregates are known to have high polarity.

Therefore, styrene-butadiene rubber coating increases the non-polar SFE of aggregates and thereby, increases the wettability of asphalt binder.

Effect on Acid SFE (Γ^A) and Base SFE (Γ^B) of Aggregates

Asphalt binder generally is acidic in nature [13, 21]. As mentioned earlier, surface chemistry of Lewis acids and bases does not favor the bond between an acidic asphalt binder and an acidic aggregate. Also, zeta potential measurements by Hagen et al. [21] indicated that both the asphalt binder and the aggregates have an overall negative charge in the presence of water.

Table 4.1 shows that SBR treatment reduced the acid SFE and increased the base SFE of both the aggregates and thereby, favors the adhesion. The acid SFE of sandstone reduced significantly from 28.2 ergs/cm^2 to 6.3 ergs/cm^2, while the base SFE increased from 555.2 ergs/cm^2 to 610.5 ergs/cm^2. Once again, SBR is more effective in sandstone and it reduced the acid SFE of both the limestone and sandstone to the same level (6.5 ergs/cm^2 and 6.3 ergs/cm^2). This further proves that the performance of SBR does not depend on aggregate mineralogy.

One important point to note (Table 4.1) is that the base SFE of the selected aggregates are much higher than the acid SFE irrespective of the mineralogy of the aggregates. The same observation was noted by Bhasin et al. [12]. As found by previous researchers [12] that a high base SFE (relative to acid SFE of the same aggregate) is a manifestation of the selected scale proposed by this method. The base SFE of an aggregate obtained from this method cannot be compared with the acid SFE of that particular aggregate and can only be compared with the base SFE of any other aggregate. So comparing the acid SFE of different aggregates with and without SBR

treatment is acceptable. The same is true for comparison of base SFE. Therefore, though the base SFE of aggregate is higher than the acid SFE of the corresponding aggregate, aggregates like sandstone are considered to be acidic.

Effect on Acid-Base (Γ^{AB}) or Polar SFE of Aggregates

Zeta potential measurements of aggregates by Yoon and Tarrer [18] showed that aggregates having a relatively high surface electrical potential exhibit a high susceptibility to stripping. Peltonen [22] conducted SFE measurements of aggregates and found that the increase in the silica dioxide content causes an increase in the polarity of the aggregate surface and the adhesion is decreased. Table 4.1 shows that the acid-base (polar) SFE of the limestone (168.0 ergs/cm^2) is much lower than the sandstone (250.3 ergs/cm^2). It was expected as limestone performs better than sandstone in general. A significant decrease in the polar SFE of sandstone was observed with SBR treatment (from 250.3 ergs/cm^2 to 124.0 ergs/cm^2). The SBR treated limestone and sandstone exhibited similar polar SFE values.

Effect on Free Energy of Adhesion

Besides the wettability of asphalt binder over aggregate, adhesion (free energy of adhesion) is a very important factor for moisture-induced damage in HMA. According to Good [16], the free energy of adhesion is negative and the more negative the free energy of adhesion the better the bond. It was observed (Table 4.1) that SBR treatment improved the adhesion between the asphalt binder (PG 64-22 in this case) and the selected aggregates. It is important to note that binder-aggregate bonds (-122.3 ergs/cm^2 and -122.4 ergs/cm^2 for limestone and sandstone, respectively) are much weaker than water-aggregate bonds (-338.3 ergs/cm^2 and -352.9 ergs/cm^2 for limestone

and sandstone, respectively). It was expected because of the fact that water is a highly polar liquid and has high affinity for the aggregate surface.

As was expected, it was found that breaking of binder-aggregate bond and formation of water-aggregate bond is a spontaneous process. It is due to the positive free energy of adhesion for all the binder-aggregate bonds in the presence of water. Table 4.1 shows that limestone performs comparatively better as its free energy of adhesion is lower in the presence of water. SBR treatment performed well with sandstone reducing its free energy of adhesion in the presence of water (from 133.9 ergs/cm^2 to 122.3 ergs/cm^2).

Effect on Water Solubility of the Adhesive Bond

Wettability of asphalt binder over aggregate, adhesion (free energy of adhesion) between asphalt binder and aggregate, and water solubility of adhesive bond are the three major factors for moisture-induced damage. Performance enhancement after SBR treatment can be attributed to increased wettability and adhesion. However, improved mechanical interlocking due to plugging of fine pores by SBR was also discussed.

Yoon and Tarrer [18] reported that the water solubility of the binder-aggregate bond is the main factor affecting stripping of asphalt binder from the aggregate surface. Curtis et al. [19] found that acidic groups, carboxylic acids and sulfoxides to have the highest adsorptions, while ketone and nonbasic nitrogen groups had the least. Conversely, the sulfoxide and carboxylic acids were most susceptible to desorption in the presence of water. Such adhesive bonds are water soluble and thereby, moisture susceptible. Styrene-butadiene rubber (SBR) is not soluble, rather it repels water.

Thereby, improvement against moisture susceptibility by SBR treatment as found by previous studies can be justified.

Proposed Chemical Model of the Binder-Aggregate Interactions

The binder-aggregate interactions can be explained with respect to wettability of asphalt binder over aggregate, adhesion (free energy of adhesion) and solubility of the adhesive bond. Wettability of the asphalt binder over aggregate is controlled by the polar (hydrophilic) and non-polar (hydrophobic) nature of the aggregate and the binder. It can be calculated from the changes in polar and non-polar SFE, spreading coefficient, interfacial tension, etc. Alteration of polar aggregate surface (hydrophilic) to non-polar aggregate surface (hydrophobic) is an important mechanism for increased wettability with mostly non-polar asphalt binder. Reduction in total SFE and polar SFE will increase wettability, but may decrease the free energy of adhesion between aggregate and the asphalt binder. Therefore, wettability and adhesion need to be balanced carefully.

Both the carbonaceous and siliceous aggregate surfaces have high polarity. In case of siliceous aggregates, polarity increases with an increase in the amount of silica dioxide [22]. On the other hand, asphalt binders have a continuous phase of non-polar materials with organized and structured polar molecules [20]. Therefore, it becomes difficult to wet the polar aggregate surface with mostly non-polar asphalt binder. SBR treatment increases the non-polar SFE and reduces the polar SFE of aggregates significantly and thereby increasing wettability.

Asphalt binder surfaces are not absolutely non-polar. Wasiuddin et al. [13-14] reported that polar or acid-base SFE (2.26 ergs/cm^2) of a PG 64-22 binder is much

lower than non-polar SFE (7.03 ergs/cm^2) making the asphalt binder mostly non-polar. Conversely, aggregates (i.e., sandstone) have much higher polar or acid-base SFE (250.3 ergs/cm^2) than non-polar SFE (43.5 ergs/cm^2) although aggregate polarities are one order of magnitude higher than the asphalt binder polarities. Hagen et al. [21] reported that both the asphalt binders and the siliceous aggregates have an overall negative charge as observed from zeta potential measurements and can be considered acidic [13-14]. In this study, it was found that SBR treatment reduces the acid SFE and decreases the base SFE significantly to almost the same level for limestone and sandstone, and therefore favors the adhesion between an acidic aggregates and an acidic binder. It should be mentioned here that with SBR treatment reduction in total SFE and polar SFE did not cause a reduction in free energy of adhesion rather it increased the free energy of adhesion.

Adhesive bonds with carboxylic acids and sulfoxides are water soluble and thereby, moisture susceptible [19]. Acid-base adhesion between asphalt binder and aggregate could be strong but may be water soluble [18]. SBR is water insoluble and creates a hydrophobic barrier against water.

Among the three factors, wettability, adhesion and solubility, increased wettability can be obtained by other anti-strip additives such as lime, amines and organosilanes. Increased wettability in all these cases is obtained altering the hydrophilic aggregate surface to hydrophobic surface as in the case of SBR in this study. In the case of lime, Ca^{+2} migrates to aggregate surface to replace H^+, Na^+, K^+ and other cations which are comparatively more water susceptible. Mg^{+2} and Ca^{+2} ions are relatively hydrophobic and thereby increase the wettability of hydrophobic asphalt

binder over aggregate [22-23]. The amines consist of a long chain hydrocarbon and amine group. The amine group reacts with the aggregate surface, and the hydrocarbon portion, which is hydrophobic, is directed into the binder. The net effect is that the long hydrocarbon chain acts as a bridge between the hydrophilic aggregate and hydrophobic bitumen surfaces thus, encouraging a strong bond between them. Sometimes a newly crushed aggregate when used in an asphalt paving mixture exhibits a poor stripping resistance as compared to the same aggregate after it has been stockpiled (or aged) for some period of time [9]. Upon aging, the outermost adsorbed water molecules may become partially replaced or covered by organic contaminants present in air, such as fatty acids and oils, and this increases the wettability and thereby reducing the stripping potential of the aggregate.

Conclusions

The following conclusions can be drawn from this study.

- Styrene-butadiene rubber (SBR) coating alters hydrophilic aggregate surface to hydrophobic and thereby repelling water as seen from a drop of water. It plugs the fine pores of aggregates and work as a bridging material between aggregate surface inside the fine pores and asphalt binder to increase interlocking. This also reduces the surface area of aggregates as has been found in this study. Reduced surface area may help in reducing asphalt binder content.
- SBR increases spreading coefficient and interfacial tension and thereby increasing wettability of asphalt binder over aggregate.

- SBR significantly reduces the total SFE and polar SFE, and increases the non-polar SFE of aggregates and makes the aggregate surface more hydrophobic. This helps increase the wettability.
- The acid SFE of acidic sandstone is significantly reduced and base SFE is markedly increased by SBR treatment. The Lewis acid-base chemistry does favor the adhesion between acidic asphalt binder and acidic aggregate with SBR treatment.
- The free energy of adhesion is increased by SBR coating with sandstone performing better than limestone.
- Finally, SBR increases wettability of asphalt binder over aggregate, adhesion (free energy of adhesion) between asphalt binder and aggregate, and decreases solubility of binder-aggregate bond. It improves both the limestone and the sandstone to the same level and thereby, is independent of the aggregate mineralogy.

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CHAPTER

5

The conclusions of science are true and the judgment of man has nothing to do with them. *Galileo Galilei*

A COMPARATIVE LABORATORY STUDY OF SASOBIT® AND ASPHA-MIN® IN WARM MIX ASPHALT†

ABSTRACT

Warm mix asphalt (WMA), which reduces the production temperatures (mixing and compaction) while maintaining the advantages of hot mix asphalt (HMA), is becoming an attractive paving material. In this study, rheological properties of two commonly used binders (PG 64-22 and PG 70-28) were evaluated, with and without additives (Sasobit® and Aspha-Min®). For PG 64-22, 2%, 3% and 4% Sasobit® reduced the mixing temperature of the pure binder from 163ºC to 147ºC (i.e., by 16ºC). In case of the PG 70-28, the reductions are 10ºC, 12ºC and 13ºC, respectively, for 2%, 3% and 4% Sasobit®. No significant decrease in mixing temperature by Aspha-Min® was observed using rotational viscometer. Evaluation of binder based on the G*/sin(δ) demonstrates no negative effect on high temperature grading due to high temperature viscosity reduction. With the addition of 4% Sasobit® the high temperature binder grading of PG 64 (actually PG 65) increases to PG 69, while 4% Sasobit® improves the PG 70

† This chapter or portions thereof has been accepted for publication in the Transportation Research Record, Journal of the Transportation Research Board, 2007. The current version has been formatted for this dissertation.

(actually PG 75) to PG 80. No significant changes in grading were observed with the addition of Aspha-Min®. In fact, reduction in binder viscosity and improvement in binder grading without increasing the viscosity indicates a two-way reductions (both direct and indirect) in production temperatures by Sasobit®. Finally, Sasobit® is found to decrease the APA rut depths significantly, and these rut depths correlate well with the rutting factor G*/sin(δ). It was also observed that rutting potential decreases with decreasing mixing and compaction temperatures. Comparatively, a smaller reduction in rut depths was observed by adding Aspha-Min®.

Keywords: Warm Mix Asphalt, Sasobit®, Aspha-Min®, Viscosity, Binder Grading, APA Rut

Introduction

In recent years, environmental protection is increasingly becoming a major issue in transportation including asphalt production. Although hot mix asphalt (HMA) is widely used in the United States, some recent studies suggest using another process that reduces the production and placement temperature of asphalt mixes, while maintaining the advantages of HMA. This technology is called the warm mix asphalt (WMA), and is used mostly in European countries. Among the advantages of WMA, the most important one is the reduction of asphalt binder temperature during production (mixing and compaction) that leads to reduced energy consumption, compared to that of HMA. The reduction in energy consumption offers other benefits including reduced emission from burning of fuels at the plant, reduced fumes at the paving site, and reduced odor. These benefits as well as improvements in air quality can be significant [*1-3*].

Based on the review of literature and a survey of web sites, it is evident that several technologies have been used by the European countries in recent years to produce WMA [*1, 4*]. One technology uses a two-component binder system called WAM-Foam® (Warm Asphalt Mix Foam) at different stages during plant production, which acts as a soft and hard foamed binder that help maintain the desired viscosity and workability of a mix at reduced temperature. It may be difficult to foam effectively and safely in a laboratory setting.

A second approach uses additives, either organic or mineral, to achieve similar goals. Among organic additives, Sasobit®, a Fischer-Tropsch paraffin wax, and Asphaltan B®, which is a low molecular weight esterified wax, have shown success [*1, 3-4*]. Among mineral additives, a synthetic zeolite, called Aspha-Min®, is added during plant mixing to create a foaming effect in the binder [*2*].

The field of warm mix asphalt (WMA) is relatively new and evolving. Although it shows significant promise, laboratory and field data are significantly lacking in terms of rheological properties of modified binders as well as strength, stiffness and performance-related properties of the mix. This study is being pursued to fill this gap, at least partly.

Scope

This study was pursued to evaluate and compare performances of two organic and mineral additives, namely Sasobit® and Aspha-Min®, in producing warm mix asphalt in a laboratory setting. Specifically, these additives were mixed with two performance graded asphalt binders, PG 64-22 and PG 70-28, and their effect on the rheological properties of binders was examined. Also, the properties and performances

of the resulting WMA specimens were evaluated and compared with those of pertinent HMA specimens. The specific objectives of this study are listed below.

- Evaluate changes in viscosity (using a rotational viscometer) at mixing and compaction temperatures and thereby, determine the reduction, if any, in the production temperature (mixing and compaction).
- Evaluate changes in G*/sin(δ), if any, at pavement service temperatures using a Dynamic Shear Rheometer (DSR) of the original and the aged (using a Rolling Thin Film Oven) binders. Determine changes in binder grading, if any.
- Measure rut depth using an Asphalt Pavement Analyzer. Correlate, if possible, the rutting factor, G*/sin(δ) at service temperatures with APA rut depth. This also justified the improvement in binder grading, if any.

Material Description

Sasobit® is a product of Sasol Wax, South Africa. It is a modifier or an "asphalt flow improver." This paraffin wax is a fine crystalline material with long chain hydrocarbons, produced by the Fischer-Tropsch (FT) synthesis. This long chain is made with 40 to 115 carbon atoms. According to the Sasol Wax, the melting point of Sasobit® is approximately 100ºC and is completely soluble in asphalt binders at temperatures in excess of 115ºC. It produces a reduction in the binder viscosity and thereby a reduction of the production temperatures by 10°C - 30°C. At temperatures below its melting point, Sasobit® forms a lattice structure in the asphalt binder that is the basis for the increased resistance to rutting at service temperatures [1]. In addition, Sasol Wax is reported to enhance the "compactibility" of a mix, compared to unmodified asphalt

mixes. Sasol Wax recommends adding Sasobit® at 3 percent by weight of the asphalt binder to gain the desired reduction in viscosity and it should not exceed 4 percent by weight due to the possible nonbeneficial or harmful impact on the low temperature properties of the binder [*4*].

Aspha-Min® is a product of Eurovia Services GmbH, Bottrop, Germany. It is a very fine white powder and a synthetic zeolite, which is added during mixing in order to create a foaming effect in the binder and to reduce the binder viscosity that allows a reduction of the production temperatures by 30°C - 35°C [*5*]. Eurovia Services GmbH recommends adding Aspha-Min® at 0.3 percent by weight of the mix to gain the desired reduction in viscosity. A 30°C reduction in production temperature is equivalent to about 30 percent reduction in fuel consumption. Aspha-Min® can be added to pre-heated aggregates at the same time as the asphalt binder without any modifications in the mix preparation process. A water-based vapor is then created [*1*].

Both the asphalt binders, PG 64-22 and PG 70-28, used in this study were obtained from Valero Refinery, Ardmore, Oklahoma. PG 64-22 is an unmodified binder, whereas PG 70-28 is a polymer-modified binder with Styrene Butadiene Styrene (SBS). Limestone and mine chat for the HMA mix designs were obtained from APAC-Oklahoma near Vinita and from the Kenoyer North Chat Pile in Ottawa County, respectively.

Laboratory Testing

As noted earlier, two binders, a PG 64-22 and a PG 70-28, were evaluated in this study. Three selected percentages of Sasobit® (2%, 3% and 4% by weight of the asphalt binder) and three selected percentages of Aspha-Min® (0.2%, 0.3% and 0.4% by weight

of the mix) were added to each binder to evaluate their effects on the rheological properties of each binder and to determine the desired additive amount.

An electric hand-held blender at 135°C was used to mix these additives with PG 64-22. A higher temperature (150°C) was used for PG 70-28. Rotational Viscometer (RV) tests, following AASHTO T 316-02, were performed at three different temperatures (135°C, 150°C and 180°C) for each additive content and each binder to evaluate the effect on viscosity at production temperatures, and to find the associated reduction in temperature using viscosity charts [*6*].

It is important to evaluate the effect of additives on the rutting parameter, G*/sin(δ) due to the reduction in viscosity at production temperatures (mixing at 163ºC and compaction at 150ºC). Therefore, the rutting parameter, G*/sin(δ) was determined at pavement service temperatures using a Dynamic Shear Rheometer (AASHTO T 315-02) on both un-aged and aged (Rolling Thin Film Oven or RTFO) binders for each additive content. The effect of additives on the high temperature performance grading of binders was also evaluated. It is reported in the literature that the lower the ratio between viscosity of aged binder and viscosity of original binder, the better the road life [*7*]. Accordingly, RTFO tests (AASHTO T 240-03) were performed to determine the effect of adding Sasobit® and Aspha-Min® on this factor (called "aging factor" in this study).

Also, previous studies have related G*/sin(δ) to rutting [8]. Therefore, rut tests (OHD L-43) were performed using an Asphalt Pavement Analyzer (APA). An S5-type Superpave surface mix (9.5-mm nominal maximum size), designed for more than three million ESALs, was used to prepare rut samples. The specifications set by the

Oklahoma Department of Transportation (ODOT) were followed [9]. Reduced mixing and compaction temperatures determined from the RV tests were used to prepare rut samples, as discussed subsequently.

Experimental Results

Effect on Viscosity at Production Temperatures

Figure 5.1 shows the rotational viscometer test results for PG 64-22. For both PG 64-22 and PG 70-28, Sasobit® reduces the viscosity significantly (Table 5.1), while the reductions in viscosity are insignificant with the addition of Aspha-Min® as found by the rotational viscometer. The following paragraphs describe the specific changes in asphalt binder viscosity.

TABLE 5.1 - Rotational viscosity results.

	PG 64-22				PG 70-28			
	Rotational Viscosity for Aspha-Min® (mPa.s)				Rotational Viscosity for Aspha-Min® (mPa.s)			
Temp.(°C)	Pure	0.2%	0.3%	0.4%	Pure	0.2%	0.3%	0.4%
135	475	479	475	475	958	869	890	883
150	250	246	242	254	502	458	458	465
180	100	88	96	100	179	150	156	154
	Rotational Viscosity for Sasobit® (mPa.s)				Rotational Viscosity for Sasobit® (mPa.s)			
Temp.(°C)	Pure	2%	3%	4%	Pure	2%	3%	4%
135	475	344	335	317	958	850	763	663
150	250	175	175	175	502	390	373	360
180	100	63	67	67	179	142	125	117

For PG 64-22, it is evident that the addition of Sasobit® reduces the viscosity significantly (Table 5.1). The viscosity of 2% Sasobit® modified binder is 175 mPa·s at 150°C. Comparatively, the viscosity of pure PG 64-22 binder is 250 mPa·s at the same temperature. The desired viscosity for proper mixing of asphalt binder is 170±20 mPa·s (AASHTO T 312-01). However, all the three percentages of Sasobit® reduced the mixing temperature (163°C as recommended by the ODOT) by 16°C (see Table 5.2).

For Aspha-Min®, an insignificant change in rotational viscosity was observed when added to PG 64-22.

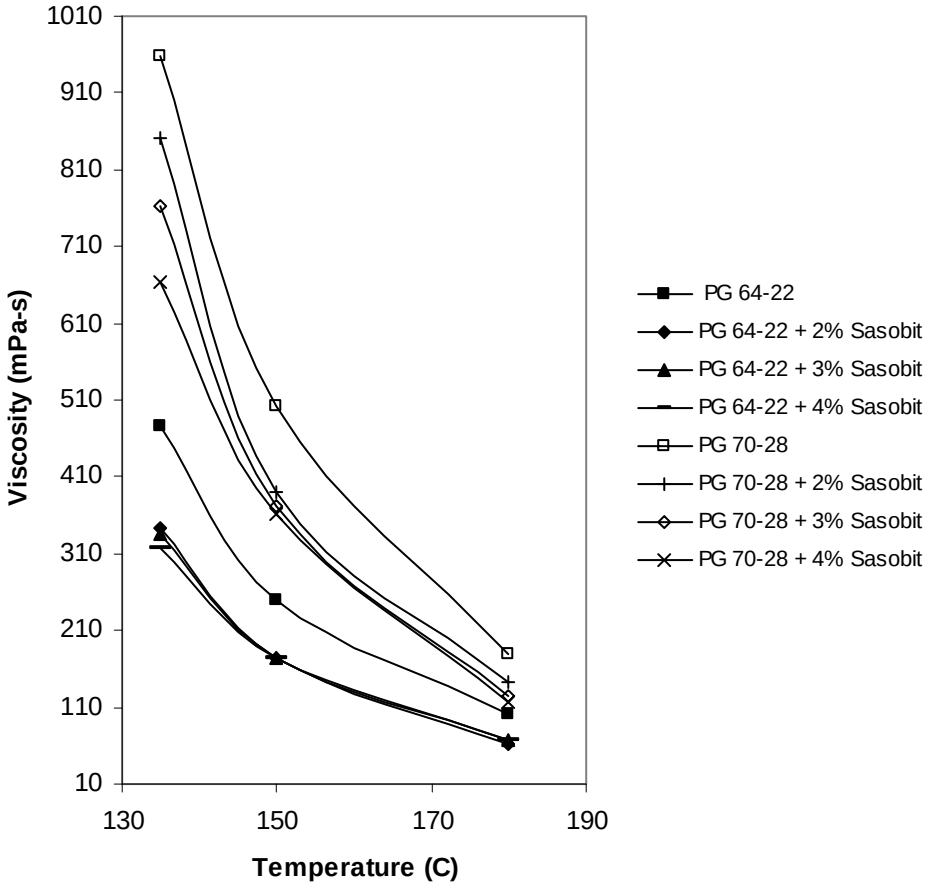

FIG. 5.1 - RV results for PG 64-22.

For PG 70-28, the viscosity of pure PG 70-28 is about 502 mPa.s at 150°C whereas, the viscosity of PG 70-28 with 2%, 3% and 4% Sasobit® are about 390 mPa.s, 373 mPa.s and 360 mPa.s, respectively, at the same temperature (Table 5.1). These reductions correspond to a drop in mixing temperatures by 10°C, 12°C and 13°C, respectively, from 163°C (Table 5.2). In case of the PG 70-28 with Aspha-Min®, 0.2%, 0.3% and 0.4% Aspha-Min® reduces the binder viscosity by 4ºC, 3ºC and 3ºC, respectively.

Effect on High Temperature Stiffness G/sin(δ) at Service Temperatures*

Both the original binder (un-aged) and the RTFO-aged binders were tested using a DSR. Each test was conducted three times, according to the AASHTO T 315-02 method, to ensure reproducibility of data. The temperatures considered were 60ºC, 64ºC and 70ºC for PG 64-22 and 60ºC, 70ºC and 80ºC for PG 70-28.

TABLE 5.2 - Changes in mixing and compaction temperatures.

	PG 64-22			PG 70-28		
Percent of Aspha-Min®	0.20%	0.30%	0.40%	0.20%	0.30%	0.40%
Reduction in Mixing Temperature (163ºC), °C	1	1	0	4	3	3
Reduction in Compaction Temperature (150°C), °C	0	1	0	2	2	1
Percent of Sasobit®	2%	3%	4%	2%	3%	4%
Reduction in Mixing Temperature (163ºC), °C	16	16	16	10	12	13
Reduction in Compaction Temperature (150°C), °C	7	7	8	4	5	7

Original Binders - The DSR results for this series of tests are presented in Table 5.3. The G*/sin(δ) of the original PG 64-22 with 2% Sasobit® is 1.21 kPa at 64°C. The G*/sin(δ) of the same binder with 3% and 4% Sasobit® are 1.47 kPa and 1.90 kPa, respectively, at the same temperature. Comparatively, the G*/sin(δ) of the original binder is 1.13 kPa. It is evident that the addition of Sasobit® increased the G*/sin(δ) with an increase in percent of Sasobit®.

A similar comparison can be done for PG 70-28 modified with Sasobit® (see Table 5.3). Overall, the addition of Sasobit® in the binder increases the G*/sin(δ) in the temperature range considered, 60°C to 80°C. The increase in G*/sin(δ) at service temperatures causes a significant improvement in stability and resistance to deformation of an asphalt mix under operational conditions of high ambient temperature and heavy traffic [8, 10].

TABLE 5.3 - Average G*/sinδ for original binders and RTFO-aged binders.

G*/sin(δ) for Original Binders (kPa)														
	PG 64-22							PG 70-28						
		Sasobit®			Aspha-Min®				Sasobit®			Aspha-Min®		
T(°C)	Pure	2%	3%	4%	0.2%	0.3%	0.4%	Pure	2%	3%	4%	0.2%	0.3%	0.4%
60	1.91	2.07	2.53	3.29	1.58	1.59	1.60	5.03	6.92	10.1	11.5	4.99	4.63	4.21
64	1.13	1.21	1.47	1.90	0.91	0.92	0.93	NA	NA	NA	NA	NA	NA	NA
70	0.49	0.57	0.70	0.87	0.44	0.44	0.45	1.97	2.66	4.01	4.34	1.92	1.78	1.63
80	NA	NA	NA	NA	NA	NA	NA	0.83	1.02	1.46	1.51	0.77	0.72	0.66
G*/sin(δ) for RTFO-Aged Binders (kPa)														
	PG 64-22							PG 70-28						
		Sasobit®			Aspha-Min®				Sasobit®			Aspha-Min®		
T(°C)	Pure	2%	3%	4%	0.2%	0.3%	0.4%	Pure	2%	3%	4%	0.2%	0.3%	0.4%
60	4.93	4.90	7.75	10.2	3.57	3.73	3.92	7.62	12.5	13.5	15.1	9.5	8.93	7.86
64	2.84	2.69	4.17	5.56	2.06	2.13	2.28	NA	NA	NA	NA	NA	NA	NA
70	1.3	1.15	1.64	2.11	0.95	0.99	1.00	3.01	4.92	5.31	5.71	3.66	3.42	3.04
80	NA	NA	NA	NA	NA	NA	NA	1.29	2	2.09	2.15	1.46	1.38	1.23

Comparatively, Aspha-Min® does not change the G*/sin(δ) in a noticeable manner. The G*/sin(δ) of original PG 64-22 is 1.13 kPa at 64°C. At this temperature, the G*/sin(δ) of this binder changes to 0.91 kPa, 0.92 kPa and 0.93 kPa, respectively, with the addition of 0.2%, 0.3% and 0.4% Aspha-Min® (Table 5.3).

For original PG 70-28, the G*/sin(δ) is approximately 1.97 kPa at 70°C. At this temperature the G*/sin(δ) reduces slightly with an increase in percent of Aspha-Min® (Table 5.3).

Aged Binders - In addition to temperature effects, an asphalt binder ages during the construction process and over the service life of a pavement. Heating the asphalt binder to mixing temperature and blending it with aggregates, causes rapid oxidation and volatilization [*6*]. The RTFO is generally used to simulate the change in binder characteristics during construction. The RTFO tests were conducted in this study according to the AASHTO T 240-03 method. The aged binders were tested with DSR so as to compare the changes in G*/sin(δ) due to short-term aging. A significant change

in the binder's G*/sin(δ) can make an asphalt mix brittle and it may crack prematurely [7]. The DSR results are summarized in Table 5.3.

The G*/sin(δ) (after RTFO aging) of PG 64-22 modified with 2% Sasobit® is 2.69 kPa at 64°C. With 3% and 4% Sasobit®, the corresponding G*/sin(δ) values are 4.17 kPa and 5.56 kPa, respectively. Comparatively, the G*/sin(δ) (after aging) of the same binder with 0.2%, 0.3%, and 0.4% Aspha-Min® added are 2.06 kPa, 2.13 kPa and 2.28 kPa, respectively. The minimum requirement of G*/sin(δ) after RTFO aging is 2.2 kPa (AASHTO M 320-03).

Both Sasobit® and Aspha-Min® performed well in case of PG 70-28. All three percentages of each of the additives, Sasobit® and Aspha-Min®, passed the minimum requirement of 2.2 kPa (AASHTO M 320-03) (see Table 5.3).

Effect on Aging Factor

In a National Cooperative Highway Research Program study, it was found that RTFO aging changes the molecular size distribution [7]. The asphaltenes increase, while the resins and the oils decrease. Resins turn into asphaltenes and the net effect is a small increase in molecular weight. The G*/sin(δ) increases greatly with a small increase in molecular weight. This explains the increase in G*/sin(δ) between original and aged binders. But, it is also reported that large increases in G*/sin(δ), induced by aging, and hardness of a binder are associated with pavement cracking. To this end, the "aging factor" (ratio between G*/sin(δ) of aged binder and G*/sin(δ) of original binder) is compared in Table 5.4. Generally, the lower the aging factor, the better the pavement life.

Table 5.4 shows that the aging factor for original PG 64-22 is 2.52 at 64°C. The corresponding factors for 2%, 3% and 4% Sasobit® are 2.21, 2.84, and 2.92. In case of Aspha-Min®, the aging factors are 2.25, 2.32 and 2.45, respectively, for 0.2%, 0.3% and 0.4% Aspha-Min®.

TABLE 5.4 - Aging factor between original and RTFO-aged binder G*/sin(δ).

PG 64-22							
		Sasobit®			Aspha-Min®		
Temp. (ºC)	Pure	2%	3%	4%	0.2%	0.3%	0.4%
60	2.58	2.37	3.06	3.13	2.26	2.34	2.46
64	2.52	2.21	2.84	2.92	2.25	2.32	2.45
70	2.63	2.02	2.36	2.43	2.14	2.24	2.25
PG 70-28							
		Sasobit®			Aspha-Min®		
Temp. (ºC)	Pure	2%	3%	4%	0.2%	0.3%	0.4%
60	1.51	1.81	1.34	1.31	1.9	1.93	1.87
70	1.53	1.85	1.32	1.32	1.91	1.92	1.87
80	1.55	1.96	1.43	1.42	1.9	1.92	1.86

For PG 70-28, addition of Sasobit® decreases the aging factor with an increase in percent of Sasobit®. The aging factor of the pure PG 70-28 is 1.53 at 70ºC while, the aging factors are 1.91, 1.92 and 1.87 for 0.2%, 0.3% and 0.4% Aspha-Min®, respectively (Table 5.4).

Effect on Binder Grading

It can be seen from Table 5.3 and Table 5.5 that G*/sin(δ) of PG 64-22 with Sasobit® increases with an increase in percent of Sasobit® for both original and RTFO-aged binders. Therefore, 4% Sasobit® increases the binder grading significantly from PG 64 (actual grading PG 65) to PG 69. Aspha-Min® does not change the PG 64 grading significantly.

TABLE 5.5 - Changes in binder grading.

	PG 64-22				PG 70-28			
	Effect on Binder Grading by Aspha-Min®				Effect on Binder Grading by Aspha-Min®			
	Pure	0.2%	0.3%	0.4%	Pure	0.2%	0.3%	0.4%
Unaged	65	63	63	63	79	78	77	76
Aged	66	63	64	64	75	77	76	75
Combined	65	63	63	63	75	77	76	75
	Effect on Binder Grading by Sasobit®				Effect on Binder Grading by Sasobit®			
	Pure	2%	3%	4%	Pure	2%	3%	4%
Unaged	65	66	68	69	79	80	82	82
Aged	66	66	69	70	75	79	80	80
Combined	65	66	68	69	75	79	80	80

For PG 70-28, the overall grading improvement based on $G^*/\sin(\delta)$ of both the original binder and RTFO aged binder is significant for all the Sasobit® percentages. It was found that the actual grading of PG 70 is PG 75. With the addition of 2%, 3% and 4% Sasobit®, the binder grading increases to PG 79, PG 80 and PG 80, respectively. Comparatively, 0.2% Aspha-Min® increases the binder grading to PG 77.

Effect on low temperature binder grading was examined using a Bending Beam Rheometer (AASHTO T 313). It was observed that both the PG 64-22 with 3% Sasobit® and PG 70-28 with 3% Sasobit® failed to meet the Superpave specified minimum m-value requirement of 0.3. However, in both the cases, the creep stiffness values were below the maximum limit of 300 MPa. Further study is needed with other percentages of Sasobit® and different percentages of Aspha-Min®.

Effect on APA Rut Depth

Rut tests were conducted on compacted cylindrical specimens prepared with mixes containing un-modified and modified binders. Tables 5.6 and 5.7 present a summary of these results for the two binders after 8,000 loading cycles. A general trend is that rut depth decreases with an increase in percent of Sasobit® in PG 64-22. The APA rut depth for PG 64-22 without additive is 5.8 mm. The rut depths with 2%, 3%

and 4% Sasobit®-modified binders are 4.7 mm, 4.0 mm and 3.5 mm, respectively. Comparatively, 0.2% and 0.3% Aspha-Min® reduces the rut depth to 5.0 mm and 5.8 mm, respectively (Fig. 5.2). A number of researchers correlated G*/sin(δ) with rut depth and thereby called the G*/sin(δ) as a rutting parameter [*8, 10*]. In this study, it was found that for PG 64-22, the rutting parameter G*/sin(δ) for different percentages of Sasobit® has a good correlation (Fig. 5.3) with APA rut depth ($R^2 = 0.8$).

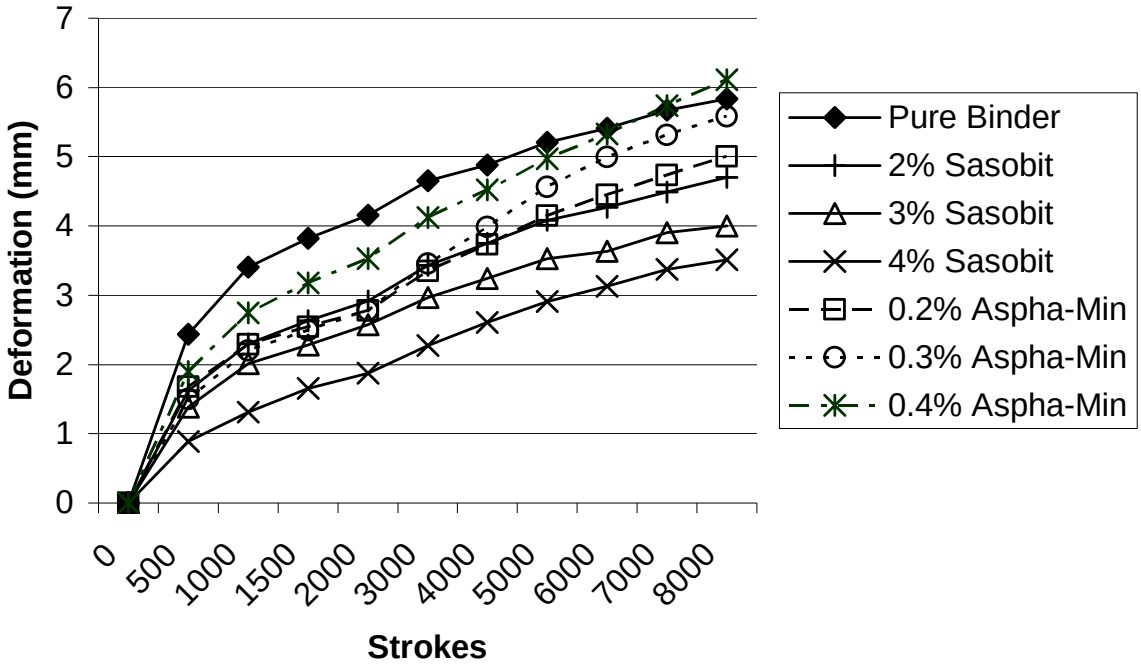

FIG. 5.2 - Rut results for PG 64-22.

TABLE 5.6 - APA rut depths after 8,000 cycles.

	Number of Loading Cycles : 8,000						
	Rut (mm)						
	Pure Binder	2% Sasobit®	3% Sasobit®	4% Sasobit®	0.2% Aspha Min®	0.3% Aspha Min®	0.4% Aspha Min®
PG 64-22	5.8	4.7	4.0	3.5	5.0	5.6	6.1

TABLE 5.7 - Rut depths for reduced mixing and compaction temperatures.

Binder	Additive	Mixing Temp.(°C)	Compacting Temp. (°C)	Rut Depth, mm
PG 70-28	Pure	163	149	6.85
	3% Sasobit®	153	139	2.41
	3% Sasobit®	143	129	2.95
	0.3% Aspha-Min®	153	139	4.85
	0.3% Aspha-Min®	143	129	3.59

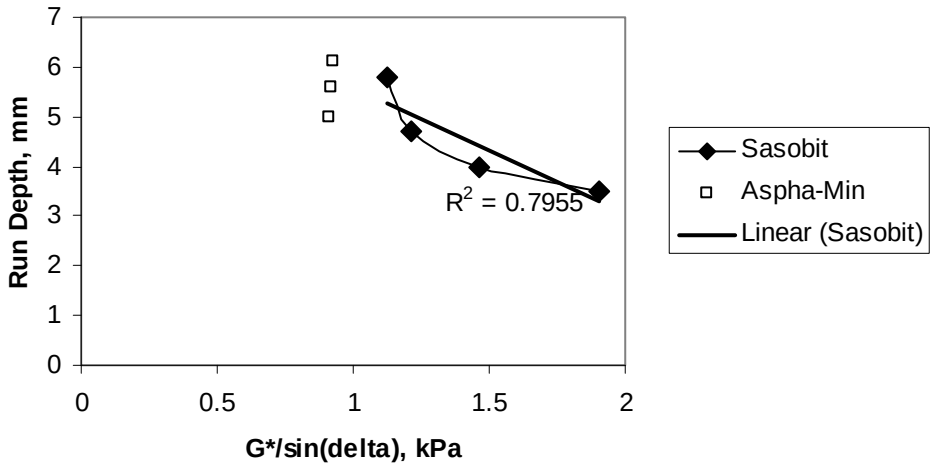

FIG. 5.3 - Relationship between G*/sin(δ) and rut depth.

As far as PG 70-28 is concerned, a different approach was followed to observe the effect of reduced mixing and compaction temperatures on the workability/compactibility of the warm mix asphalt. Rut samples were prepared at different mixing (163°C, 153°C and 143°C) and compaction (149°C, 139°C and 129°C) temperatures with a desired percentage of each of the WMA additives (see Table 5.7). As noted above, all the three percentages of Sasobit® increased the binder grading from PG 75 to at least PG 79. This increase in high temperature stiffness was reflected in rut test. It was found that 3% Sasobit® decreased the rut depth significantly from 6.9 mm to 2.95 mm when mixed at 143°C and compacted at 129°C. For 0.3% Aspha-Min®, the rut depth decreased to 3.6 mm from 6.9 mm (see Table 5.7). Rutting potential decreases with a decrease in mixing and compaction temperatures for both Sasobit® and Aspha-

Min® (Table 5.7). The reduction in temperature was 20°C for both mixing and compaction.

Conclusions

From the results presented above, the following conclusions can be drawn.

- For PG 64-22, all the three percentages of Sasobit® (2%, 3% and 4%) reduced the mixing temperature and compaction temperature based on the rotational viscosity. The reduction in mixing temperature is 16ºC from 163°C (as recommended by the ODOT) for all the three percentages of Sasobit®. No beneficial effect in temperature reduction was observed with the addition of Aspha-Min® in PG 64-22 based on rotational viscometer. In the case of PG 70-28, 2%, 3% and 4% Sasobit® reduced the ODOT mixing temperature by 10ºC, 12ºC and 13ºC, respectively, from 163ºC. A similar trend is observed for reduction in compaction temperature. For PG 70-28, a maximum of 4ºC reduction in mixing temperature was observed for 0.2% Aspha-Min®.
- A general trend is that Sasobit® increased the high temperature binder grading for both the binders. In the case of the PG 64-22, 4% Sasobit® increases the binder grading significantly from PG 64 (actual grading PG 65) to PG 69. The most significant improvement was exhibited by Sasobit® in PG 70. The actual high temperature grading of PG 70 is PG 75. With the addition of 2%, 3% and 4% Sasobit®, the grading increases to PG 79, PG 80 and PG 80, respectively. However, both the PG 64-22 with 3% Sasobit® and PG 70-28 with 3% Sasobit® failed to meet the Superpave specified

minimum m-value requirement of 0.3. Further study should be performed with other percentages of Sasobit®. Among the Aspha-Min® percentages, 0.2% increased the binder grading to PG 77.

- Sasobit® decreases the rut depth significantly for PG 64-22 and these rut depths correlate well with the rutting factor, G*/sin(δ) value ($R^2 = 0.8$). In the case of PG 70-28, 3% Sasobit® decreased the rut depth significantly from 6.9 mm to 2.4 mm. For 0.3% Aspha-Min®, the rut depth is decreased to 3.6 mm from 6.9 mm. Rutting potential decreases with a decrease in mixing and compaction temperatures for both Sasobit® and Aspha-Min®.
- Overall, Sasobit® helps in decreasing the production temperatures in both direct and indirect ways. Sasobit® decreases the mixing and compaction temperatures for both PG 64-22 and PG 70-28. Also, it upgrades the binder without increasing the viscosity of the binder. Reduction in viscosity at high temperature does not increase rut depth at service temperature. Rather, addition of Sasobit® decreases the rut depth significantly which justifies the improvement in high temperature binder grading. Comparatively, a significant direct decrease in production temperatures with Aspha-Min® was not achieved in this study perhaps due to rotational viscometer.

Recommendations

Research is underway to analyze the other rheological properties of asphalt binder such as DSR of PAV-aged samples, moisture sensibility, permeability, and fatigue. Other additives used in the field include Sasolink®, Sasoflex®, etc. Some of these additives can be used in future studies. Most importantly, field data is needed

documenting successes and failures of warm asphalt mixes in actual practice. Then only the promises of this new material can be fully utilized.

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CHAPTER

6

In the world of surface science, a pound of experiment is worth a ton of theory. *W. Zisman*

EFFECT OF SASOBIT® AND ASPHA-MIN® ON WETTABILITY AND ADHESION BETWEEN ASPHALT BINDERS AND AGGREGATES

ABSTRACT

The influence of natural wax in asphalt binders and hot mix asphalt (HMA) has been studied for decades, considering both negative and positive effects. Recent advances in warm mix asphalt (WMA) have spurred interests in the use of commercial waxes such as Sasobit® and Asphaltan B® as additives in asphalt binders to achieve certain positive effects. In spite of a number of previous studies, the effect of Sasobit® on wettability and adhesion between asphalt binders and aggregates are not fully understood. Likewise, the effect of water vapor released from Aspha-Min®, another WMA additive at production temperatures is not adequately understood although such water may negatively influence the behavior of WMA. In the present study, the effect of Sasobit® and Aspha-Min® on wettability and adhesion is investigated using the surface free energy (SFE) method. Dynamic advancing/wetting contact angles were measured for wettability (coating) and dewetting/receding contact angles were measured to evaluate adhesion. It is observed that Sasobit® increases the wettability of asphalt binders over aggregates significantly, as indicated by the change in the spreading coefficient.

Conversely, a general trend is that Sasobit® reduces the adhesion (free energy of adhesion) between asphalt binders and aggregates. In this study, moisture susceptibility is defined as the amount of spontaneously released free energy due to the breaking of binder-aggregate bond with water. For PG 64-22, small or no reduction in moisture susceptibility and for PG 70-28 an increase in moisture susceptibility were observed. In case of the Aspha-Min®, the overall SFE results are insignificant.

Keywords: Warm Mix Asphalt, Sasobit®, Aspha-Min®, Wettability, Adhesion, Surface Free Energy

Introduction

Due to its environmental friendliness, warm mix asphalt (WMA) is becoming an increasingly popular material for the construction of roadways. Several warm mix technologies are available for reducing asphalt mixing and compaction temperatures, thereby saving energy and reducing emission problems. Among the available technologies, the use of organic additives such as commercial wax and mineral additives such as synthetic zeolites show significant promises. Improved compaction was noted at temperatures as low as 88°C for both (wax and zeolites) of these technologies [1, 2]. Results show that lower plant temperatures can lead to a significant reduction, up to 30 percent, in energy consumption [3]. Also, reduced production temperature leads to a reduction in emission, making WMA an environmentally attractive material. According to previous studies, the reduction in emissions represents a significant cost savings, considering that 30-50 percent of overhead costs at an asphalt plant can be attributed to emission control [3].

The influence of natural wax as an additive in asphalt binder and hot mix asphalt (HMA) has been under discussion for decades, implying both negative and positive effects. However, natural wax in asphalt binder is low in content now a days and of a kind not likely to be harmful to binder or HMA properties [4]. Therefore, the use of commercial waxes as additive to asphalt binder in WMA, in order to gain certain positive effects, can be of great interest. Commercial waxes such as Fischer-Tropsch (FT) paraffin wax (Sasobit®) and montan wax (Asphaltan B®) are commonly used in WMA. Sasobit® is a product of Sasol Wax GmbH (Germany) and Asphaltan B® is a product of Romonta, GmbH (Germany). Sasobit® is produced in FT synthesis, where carbon monoxide is converted into higher hydrocarbons in catalytic hydrogenation, followed by a distillation process. The end product consists of mainly fine crystalline long chain aliphatic polymethylene hydrocarbon chains with 40–100 carbon atoms [5]. By comparison, macrocrystalline bituminous paraffin waxes have carbon chain lengths ranging from 25 to 50 [6]. The longer carbon chains in the Sasobit® lead to a higher melting point, and the wider wax molecule distribution results in broader melting temperature range and increased plasticity span. In the range of 60°C to 90°C, natural asphalt wax is normally completely melted out whereas, the melting temperatures of asphalt with Sasobit® are higher (between approximately 100°C and 130°C) [6].

Effects of Sasobit® in asphalt binders and HMA have been studied previously by several researchers [1, 4-8]. Sasobit® is known to improve flow of asphalt mixes (viscosity depressant) and to reduce the mixing and compaction temperatures by about 18-54°C [1, 7, 9]. In addition, Sasobit® reportedly improved resistance to deformation at higher temperatures for asphalt binder and HMA (rutting) thereby, significantly

increasing the high temperature grading of an asphalt binder [1, 7]. However, increase in creep stiffness and reduction in creep rate (m) may be a concern for low temperature grading, specifically in the case of overdosing [5, 7]. Moreover, a lower mixing and compaction temperature can result in incomplete drying of the aggregate. The resulting water trapped in the coated aggregate may cause moisture damage [1]. Also, reduced-aging property of Sasobit® was reported by some researchers [1, 5]. Despite significant research in the past few decades on the effect of commercial wax such as Sasobit® on asphalt binder and HMA and increasing recent interests on WMA, an understanding of the effects of the commercial wax on wettability of binder over aggregate and on the adhesion between binder and aggregate is still seriously lacking [4]. Wasiuddin et al. [10] previously studied the effect of amine anti-strip additives on the surface free energy (SFE) components (acid, base and non-polar) of asphalt binders for moisture-induced damage potential of HMA. In a separate study, the thermal degradation of anti-strip additives due to aging was also characterized by Wasiuddin et al. [11]. These researchers also proposed the evaluation of wettability and adhesion, based on the SFE method, of polymer treated aggregates for moisture-induced damage potential of HMA [12]. As moisture-induced damage is a major concern in WMA [1-2], the present study is undertaken to evaluate the wettability and adhesion characteristics of HMA based on their SFE values.

Aspha-Min®, a mineral additive used in WMA, is a manufactured synthetic zeolite (sodium aluminum silicate) from Eurovia Services, GmbH, Germany. It is hydro-thermally crystallized. Zeolites are framework silicates with large empty spaces in their structures that allow the presence of large cations, such as sodium, calcium and

water [2]. Aspha-Min® is added to the mix at the same time as the binder. Water vapor released by Aspha-Min® creates a volume expansion of the binder that results in asphalt foam which leads to increased workability and aggregate coating at a lower temperature than that of HMA. Aspha-Min® contains approximately 21 percent water by mass and is released in the temperature range of 85-182°C. As much as 30°C reduction in mixing and compaction temperatures were reported [9].

Very limited literature is available currently on the effect of Aspha-Min® on binder and HMA. A recent study by Wasiuddin et al. [7] reported no detection of reduction in viscosity by the Brookfield rotational viscometer [7]. Effects on aging, binder grading and performance of HMA were not fully understood from those studies [2, 7]. The addition of Aspha-Min® does not increase the rutting potential of HMA [7]. However, the long term pavement performance data is lacking. Like Sasobit®, it may increase the potential for moisture damage because of the retention of moisture due to lower heating temperature of aggregates.

The present study is focused on understanding the effect of Aspha-Min® on the SFE characteristics of binder with and without the presence of water. The results are expected to shade lights on moisture-induced damage potential.

Objectives

The objectives of this study are to evaluate the effect of Sasobit® and Aspha-Min® on the SFE components (acid, base and non-polar) and related properties (wettability and adhesion) of selected binders and thereby elucidate the moisture-induced damage mechanisms of HMA. The specific objectives are as follows.

- Evaluation of the SFE components of asphalt binders with and without Sasobit® and Aspha-Min®.
- Evaluation of the SFE components of Sasobit®.
- Evaluation of the wettability of asphalt binders (with and without Sasobit® and Aspha-Min®) over aggregates and the adhesion between asphalt binders (with and without Sasobit® and Aspha-Min®) and aggregates.
- Discussion of moisture-induced damage potential of WMA with respect to wettability and adhesion.

Surface Free Energy (SFE) Method

The SFE of an asphalt binder mainly comprises of an apolar component (also called Lifshitz-van der Waals component) and an acid-base component which can be decomposed to Lewis acidic surface parameter and a Lewis basic surface parameter, as shown in the following equation [13]:

$$\Gamma = \Gamma^{LW} + 2\sqrt{\Gamma^{+}\Gamma^{-}} \quad (1)$$

where,

Γ = SFE of the asphalt binder,

Γ^{LW} = Lifshitz-van der Waals component of the SFE,

Γ^{+} = Lewis acid component of surface interaction, and

Γ^{-} = Lewis base component of surface interaction.

In this study, the Young-Dupre equation [13] along with Good's postulation was used to calculate the SFE components of an asphalt binder. The resulting equation can be expressed as follows:

$$\Gamma_L(1+\cos\theta) = 2\times\sqrt{\Gamma_S^{LW}\Gamma_L^{LW}} + 2\times\sqrt{\Gamma_S^{-}\Gamma_L^{+}} + 2\times\sqrt{\Gamma_S^{+}\Gamma_L^{-}} \quad (2)$$

where,

Γ_L^{LW}, Γ_L^{+}, and Γ_L^{-} = SFE components of liquid solvent,

Γ_S^{LW}, Γ_S^{+}, and Γ_S^{-} = SFE components of asphalt binder, and

θ = Contact angle.

In the above equation, the SFE components of an asphalt binder are given by the three unknowns (Γ_S^{LW}, Γ_S^{+}, and Γ_S^{-}). To obtain these unknowns, dynamic contact angles must be measured in at least three different liquid solvents of known SFE characteristics. The dynamic contact angles for different liquids can be used, as employed in this study, to evaluate these SFE components. The Dynamic Wilhelmy Plate method (DWPM), as described by Wasiuddin et al. [10, 11], was used here to measure the desired contact angles.

Test Matrix

The SFE components of two selected asphalt binders, namely a PG 64-22 and a PG 70-28 from Ardmore, Oklahoma, were determined separately from measurements of both advancing/wetting and receding/dewetting contact angles. The PG 70-28 binder used in this study is modified with Styrene-Butadiene-Styrene (SBS) polymer. The SFE components of these binders were also evaluated at three selected percentages of Sasobit® (2%, 4% and 8%) and Aspha-Min® (1%, 4% and 6%) based on the weight of the binder. The SFE components of Sasobit® and paraffin wax were also evaluated. Sasobit® was collected from Sasol Wax, America in the form of prills and Aspha-Min® was obtained in the form of very fine powder (Figure 6.1) from PQ Corporation,

America. The test matrix, including the number of samples used for which the SFE components were evaluated, is presented in Table 6.1.

TABLE 6.1 - Test matrix.

Types of Binder	Types of Additives	Amount in Percent for Each Type of Additive	Types of Solvents for Each Percent of Additive	No. of Samples for Each Solvent
PG 64-22 PG 70-28 (SBS)	Sasobit® Aspha-Min® Paraffin Wax	0%, 2%, 4% and 8% Sasobit® 0%, 1%, 4% and 6% Aspha-Min® 8% and 100% Paraffin Wax	Water Glycerin Formamide	3

Effect on SFE

Table 6.2 shows the SFE components of PG 64-22 and PG 70-28 with and without the addition of Sasobit®. A general trend is that Sasobit® reduces the advancing/wetting total SFE and the receding/dewetting total SFE of both the asphalt binders. An increase in the amount of Sasobit® is found to reduce the receding/dewetting total SFE significantly, while the reductions are relatively small in the case of the advancing/wetting total SFE. The receding/dewetting total SFE of PG 64-22, Sasobit® and paraffin wax are 41.4-42.3 dyne/cm, 22.8-24.4 dyne/cm and 10.6-11.6 dyne/cm, respectively. This explains a reduction in receding/dewetting total SFE with an increase in percent of Sasobit®. Therefore, it is evident from this study that Sasobit® reduces the total SFE, as reported previously [5]. This reduction in total SFE can significantly affect the adhesion between asphalt binders and aggregates, as will become evident from the subsequent paragraphs.

The effect of Sasobit® on the surface acid-base characteristics of asphalt binders is also found to be significant (Table 6.2). In general, the acid component of SFE increases with an increase in the amount of Sasobit® for both the advancing/wetting

SFE and the receding/dewetting SFE. A similar trend is observed for the ratio between the acid component of SFE and the base component of SFE. The increase in acid component of SFE with the addition of Sasobit® will affect the contact angle of glycerin and formamide (both have higher base component of SFE than their acid component of SFE), as will be discussed in the following paragraphs related to wettability.

Effect of Aspha-Min® on the SFE characteristics is insignificant for both the binders, as evident from both the advancing/wetting and receding/dewetting SFE components (Table 6.3). As noted previously, Aspha-Min® releases water vapor at HMA production temperature. In order to investigate the effect of water vapor on the SFE components of asphalt binders, the PG 64-22 with 4% Aspha-Min® was heated at 150°C for 36 hrs (selected arbitrarily) and the SFE components were evaluated. It is evident from Table 6.3 that water in Aspha-Min® does not have significant effect on the SFE components even after 36 hrs of heating.

(a) (b)

FIG. 6.1 - (a) Sasobit® and (b) Aspha-Min® in the scoop.

TABLE 6.2 - SFE Components of Asphalt Binders with Sasobit®.

SFE components of PG 64-22 with Sasobit® from advancing contact angle						
Binder	Γ	Γ^{LW}	Γ^{+}	Γ^{-}	Γ^{AB}	Ratio$^{+/-}$
Sasobit® (Set1)	11.3	9.6	1.4	0.5	1.7	2.8
Sasobit® (Set2)	10.7	8.6	1.3	0.8	2.1	1.5
Wax (Set1)	6.5	5.3	1.8	0.2	1.1	10.3
Wax (Set2)	5.7	4.7	2.3	0.1	1.0	21.5
PG 64-22 (Set1)	12.5	11.2	0.7	0.6	1.3	1.2
PG 64-22 (Set2)	12.1	10.6	0.8	0.7	1.5	1.2
PG 64-22 + 2% Sasobit®	10.5	7.8	2.1	0.9	2.7	2.4
PG 64-22 + 4% Sasobit®	10.4	7.7	2.5	0.7	2.7	3.4
PG 64-22 + 8% Sasobit®	10.3	7.9	2.5	0.6	2.4	4.2
PG 64-22 + 8% Paraffin Wax	8.9	7.6	1.3	0.3	1.3	3.8
SFE components of PG 64-22 with Sasobit® from receding contact angle						
Binder	Γ	Γ^{LW}	Γ^{+}	Γ^{-}	Γ^{AB}	Ratio$^{+/-}$
Sasobit® (Set1)	22.8	17.6	2.2	3.1	5.2	0.7
Sasobit® (Set2)	24.4	19.7	1.9	2.9	4.7	0.7
Wax (Set1)	11.6	4.8	4.7	2.5	6.9	1.8
Wax (Set2)	10.6	4.4	5.4	1.8	6.2	3.0
PG 64-22 (Set1)	42.3	25.6	3.3	21.2	16.8	0.2
PG 64-22 (Set2)	41.4	23.5	3.6	22.1	17.9	0.2
PG 64-22 + 2% Sasobit®	34.1	17.1	4.6	15.7	17.1	0.3
PG 64-22 + 4% Sasobit®	28.1	13.5	4.8	11.1	14.6	0.4
PG 64-22 + 8% Sasobit®	25.7	11.2	4.5	11.6	14.5	0.4
PG 64-22 + 8% Paraffin Wax	13.9	2.3	9.5	3.6	11.7	2.7
SFE components of PG 70-28 with Sasobit® from advancing contact angle						
Binder	Γ	Γ^{LW}	Γ^{+}	Γ^{-}	Γ^{AB}	Ratio$^{+/-}$
PG 70-28	12.5	11.3	0.8	0.4	1.2	1.9
PG 70-28 + 2% Sasobit®	10.5	8.6	1.8	0.5	1.9	3.7
PG 70-28 + 4% Sasobit®	10.7	8.6	1.9	0.6	2.1	3.3
PG 70-28 + 8% Sasobit®	9.5	6.4	3.0	0.8	3.1	3.7
PG 70-28 + 8% Paraffin Wax	10.2	9.2	0.6	0.4	1.0	1.5
SFE components of PG 70-28 with Sasobit® from receding contact angle						
Binder	Γ	Γ^{LW}	Γ^{+}	Γ^{-}	Γ^{AB}	Ratio$^{+/-}$
PG 70-28	44.8	26.8	3.8	21.2	17.9	0.2
PG 70-28 + 2% Sasobit®	38.4	28.6	1.3	18.4	9.9	0.1
PG 70-28 + 4% Sasobit®	35.2	25.8	1.5	15.3	9.5	0.1
PG 70-28 + 8% Sasobit®	29.1	21.5	1.5	9.6	7.5	0.2
PG 70-28 + 8% Paraffin Wax	14.1	4.1	8.0	3.1	10.0	2.6

Effect on Wettability

Asphalt binder is generally hydrophobic in nature and aggregates are mostly hydrophilic [14]. Therefore, it is difficult to wet hydrophilic aggregates with a

hydrophobic asphalt binder. Spreading coefficient is a quantitative measure of wettability. In this study, the spreading coefficient of asphalt binders over aggregates with and without WMA additives was evaluated. Spreading coefficient ($S_{L/S}$) of a liquid over a solid is simply the reduction in SFE on losing the bare solid surface and forming the new solid/liquid and liquid/vapor interface during the advancing/wetting process [15]. The spreading coefficient was measured using the following equation, as previously used by Wasiuddin et al. [12]:

$$S_{L/S} = \Gamma_S - \Gamma_{SL} - \Gamma_{LV} \quad (3)$$

where,

$S_{L/S}$ = Spreading coefficient of liquid L on solid S,

Γ_S = Advancing/wetting SFE of solid S, ergs/cm^2,

Γ_{SL} = Advancing/wetting solid-liquid interfacial energy, ergs/cm^2, and

Γ_{LV} = Advancing/wetting SFE of liquid L, ergs/cm^2.

From the above equation, the free energy change of spreading coefficient will be positive for spontaneous spreading. From the definition of the work of adhesion and cohesion [12], the spreading coefficient can be obtained from the difference between the work of adhesion of S to L and the work of cohesion of L, as shown in the equation below:

$$S_{L/S} = W_{SL} - W_{LL} \quad (4)$$

where,

$S_{L/S}$ = Spreading coefficient of liquid L on solid S,

W_{SL} = Advancing/wetting work of adhesion of S and L, ergs/cm^2, and

W_{LL} = Advancing/wetting work of cohesion, ergs/cm^2.

TABLE 6.3 - SFE Components of Asphalt Binders with Aspha-Min®.

SFE components of PG 64-22 with Aspha-Min® from advancing contact angle						
Binder	Γ	Γ^{LW}	Γ^{+}	Γ^{-}	Γ^{AB}	Ratio$^{+/-}$
PG 64-22 (Set1)	12.5	11.2	0.7	0.6	1.3	1.2
PG 64-22 (Set2)	12.1	10.6	0.8	0.7	1.5	1.2
PG 64-22 + 1% Aspha-Min®	9.5	6.9	2.3	0.7	2.6	3.3
PG 64-22 + 4% Aspha-Min®	10.6	8.8	1.5	0.5	1.8	3.0
PG 64-22 + 4% Aspha-Min®	10.0	7.9	1.9	0.6	2.1	3.4
PG 64-22 + 6% Aspha-Min®	10.2	8.4	1.7	0.4	1.7	3.9
SFE components of PG 64-22 with Aspha-Min® from receding contact angle						
Binder	Γ	Γ^{LW}	Γ^{+}	Γ^{-}	Γ^{AB}	Ratio$^{+/-}$
PG 64-22 (Set1)	42.3	25.6	3.3	21.2	16.8	0.2
PG 64-22 (Set2)	41.4	23.5	3.6	22.1	17.9	0.2
PG 64-22 + 1% Aspha-Min®	41.1	27.1	2.6	19.0	13.9	0.1
PG 64-22 + 4% Aspha-Min®	40.4	17.5	6.3	20.8	22.9	0.3
PG 64-22 + 4% Aspha-Min®	37.8	24.1	2.7	17.2	13.7	0.2
PG 64-22 + 6% Aspha-Min®	41.6	29.2	2.0	19.0	12.4	0.1
SFE components of PG 70-28 with Aspha-Min® from advancing contact angle						
Binder	Γ	Γ^{LW}	Γ^{+}	Γ^{-}	Γ^{AB}	Ratio$^{+/-}$
PG 70-28	12.5	11.3	0.8	0.4	1.2	1.9
PG 70-28 + 1% Aspha-Min®	13.0	12.0	0.7	0.4	1.0	1.8
PG 70-28 + 4% Aspha-Min®	11.7	10.5	1.0	0.3	1.2	3.0
PG 70-28 + 6% Aspha-Min®	13.5	12.7	0.5	0.4	0.9	1.3
SFE components of PG 70-28 with Aspha-Min® from receding contact angle						
Binder	Γ	Γ^{LW}	Γ^{+}	Γ^{-}	Γ^{AB}	Ratio$^{+/-}$
PG 70-28	44.8	26.8	3.8	21.2	17.9	0.2
PG 70-28 + 1% Aspha-Min®	44.2	20.6	7.0	19.9	23.6	0.4
PG 70-28 + 4% Aspha-Min®	44.6	23.8	5.6	19.4	20.8	0.3
PG 70-28 + 6% Aspha-Min®	43.8	22.5	6.3	18.2	21.4	0.3

Table 6.4 shows the wettability with respect to spreading coefficient of asphalt binders, with and without Sasobit®, over limestone and granite. The SFE components of two selected Oklahoma aggregates, a limestone and a sandstone, were obtained from a previous study by Wasiuddin et al. [12]. It can be seen from Table 6.4 that the wettability of PG 64-22 with 8% Sasobit® increases from 70.9 dyne/cm and 70.3 dyne/cm to 98.7 dyne/cm and 98.8 dyne/cm, respectively, for limestone and sandstone. The increase in wettability is even greater for PG 70-28. A general trend is that wettability increases with an increase in percent of Sasobit® for both the binders.

However, it was pointed out by the authors and by other researchers that due to the addition of wax (in this case Sasobit®), the ability to wet the aggregate may reduce because of the hydrophobic character of the wax [5]. It is evident from Table 6.4 that Sasobit® itself has higher wettability than the asphalt binder. Therefore, addition of Sasobit® is likely to increase the wettability, whereas 8% paraffin wax reduces the wettability.

TABLE 6.4 - Wettability and adhesion between aggregates and binders with Sasobit®.

	PG 64-22					
	Wettability (dyne/cm)		Adhesion with Limestone (ergs/cm^2)		Adhesion with Sandstone (ergs/cm^2)	
Binder	Limestone	Sandstone	In Air	In Water	In Air	In Water
Sasobit® (Set1)	82.0	81.3	-141.9	123.0	-143.7	135.7
Sasobit® (Set2)	80.2	80.5	-140.5	125.0	-141.7	138.4
Wax (Set1)	85.9	85.3	-143.2	108.0	-147.3	118.5
Wax (Set2)	92.3	91.6	-147.9	101.5	-151.4	112.7
PG 64-22 (Set1)	68.6	67.7	-190.8	114.2	-201.4	118.2
PG 64-22 (Set2)	70.9	70.3	-192.1	112.7	-203.4	116.1
PG 64-22 + 2% Sasobit®	93.8	94.4	-188.2	105.1	-197.9	109.9
PG 64-22 + 4% Sasobit®	99.1	99.6	-178.8	104.2	-187.0	110.6
PG 64-22 + 8% Sasobit®	98.7	98.8	-171.7	108.3	-180.5	114.2
PG 64-22 + 8% Paraffin Wax	78.2	77.4	-178.7	78.6	-185.2	86.7
	PG 70-28					
	Wettability (dyne/cm)		Adhesion with Limestone (ergs/cm^2)		Adhesion with Sandstone (ergs/cm^2)	
Binder	Limestone	Sandstone	In Air	In Water	In Air	In Water
PG 70-28	70.4	69.1	-198.5	108.8	-209.0	112.9
PG 70-28 + 2% Sasobit®	88.9	88.6	-161.5	136.2	-170.2	142.1
PG 70-28 + 4% Sasobit®	90.3	90.2	-157.8	134.2	-165.6	141.0
PG 70-28 + 8% Sasobit®	104.0	105.0	-145.9	133.9	-151.5	142.9
PG 70-28 + 8% Paraffin Wax	65.0	64.0	-173.7	84.7	-179.0	94.0

The smaller the advancing/wetting contact angle the higher the wetting tendency. Table 6.5 shows that addition of Sasobit® slightly reduces the advancing/wetting contact angle of water for both the asphalt binders. The reduction in advancing/wetting contact angle is significant for glycerin and formamide. Addition of

8% Sasobit®, however, reduces the glycerin advancing/wetting contact angle by 4.2° and 3.3°, respectively, for PG 64-22 and PG 70-28. The increased wettability (reduction in advancing/wetting contact angle) by glycerin and formamide can be explained from the values of the SFE components. Both glycerin and formamide have much higher base component of SFE than acid component, and Table 6.2 shows that Sasobit® increases the acid component of SFE of a binder. Therefore, the complementary interaction between the acid component of SFE of the binder and the base component of SFE of the glycerin and the formamide increases with an increase in percent of Sasobit®, thereby increasing the wettability.

The increase in wettability is also evident from the increased hydrophilic characteristics of asphalt binder with the addition of Sasobit®. Addition of Sasobit® increases the advancing/wetting polar (acid-base) component of SFE by 1.4 dyne/cm and 1.9 dyne/cm from 1.3 dyne/cm and 1.2 dyne/cm, respectively for PG 64-22 and PG 70-28 (Table 6.2). Increase in polar SFE increases the hydrophilic characteristics of asphalt binder thereby increasing the wettability of the asphalt binder over hydrophilic aggregate. According to the manufacturer of Sasobit® (Sasol Wax, America), it reduces the total SFE and therefore, increases the wettability. It was observed in this study (Table 6.2) that Sasobit® reduces the total SFE for both the binders.

Table 6.6 shows the effect of Aspha-Min® on wettability of asphalt binders with respect to the change in spreading coefficient. An increase in wettability was observed for PG 64-22, but no significant change was observed for PG 70-28. An insignificant change in wettability of PG 70-28 can be explained from the negligible changes in advancing/wetting contact angle (Table 6.7). However, the increase in wettability of PG

64-22 does not correlate to the advancing/wetting contact angle as the changes in advancing/wetting contact angle are insignificant. Therefore, Aspha-Min® does not have any significant effect on the wettability of the two binders used in this study.

TABLE 6.5 - Contact angles of asphalt binders with Sasobit®.

Advancing Contact Angles of PG 64-22 with Sasobit®						
Binder	Water	St.Dev.	Glycerin	St.Dev.	Formamide	St.Dev.
Sasobit® (Set1)	109.9	0.9	96.4	0.3	92.2	0.2
Sasobit® (Set2)	109.8	0.9	98.1	1.7	94.3	1.0
Wax (Set1)	117.3	1.3	103.6	0.6	100.9	0.3
Wax (Set2)	117.9	0.3	103.2	0.2	100.9	0.5
PG 64-22 (Set1)	110.2	0.4	98.0	0.5	93.0	0.3
PG 64-22 (Set2)	110.0	0.4	98.1	0.6	93.4	0.3
PG 64-22 + 2% Sasobit®	108.1	0.5	95.1	0.4	92.0	0.0
PG 64-22 + 4% Sasobit®	107.8	0.2	93.8	0.1	90.8	0.1
PG 64-22 + 8% Sasobit®	108.3	0.5	93.8	0.1	90.7	0.3
PG 64-22 + 8% Paraffin Wax	114.2	0.2	101.3	0.2	97.6	0.2
Receding Contact Angles of PG 64-22 with Sasobit®						
Binder	Water	St.Dev.	Glycerin	St.Dev.	Formamide	St.Dev.
Sasobit® (Set1)	90.6	0.5	77.1	0.0	71.6	0.6
Sasobit® (Set2)	90.2	21.8	76.0	1.3	69.9	0.4
Wax (Set1)	101.5	0.2	89.6	0.2	88.8	0.4
Wax (Set2)	102.9	0.6	89.2	0.5	88.6	0.8
PG 64-22 (Set1)	57.2	2.1	50.4	1.6	43.6	0.4
PG 64-22 (Set2)	57.4	0.6	51.4	0.9	45.5	0.1
PG 64-22 + 2% Sasobit®	67.7	0.9	59.5	0.8	55.7	0.3
PG 64-22 + 4% Sasobit®	76.2	0.6	66.8	0.3	63.9	0.2
PG 64-22 + 8% Sasobit®	78.6	1.1	71.8	0.6	67.4	1.5
PG 64-22 + 8% Paraffin Wax	96.6	0.1	83.1	0.0	84.8	0.3
Advancing Contact Angles of PG 70-28 with Sasobit®						
Binder	Water	St.Dev.	Glycerin	St.Dev.	Formamide	St.Dev.
PG 70-28	110.6	0.5	97.6	0.5	92.7	0.2
PG 70-28 + 2% Sasobit®	109.8	0.1	95.9	0.1	92.3	0.3
PG 70-28 + 4% Sasobit®	109.2	0.5	95.4	0.1	91.8	0.1
PG 70-28 + 8% Sasobit®	108.1	1.0	94.3	0.6	91.9	0.4
PG 70-28 + 8% Paraffin Wax	114.3	0.7	101.1	2.7	98.1	0.2
Receding Contact Angles of PG 70-28 with Sasobit®						
Binder	Water	St.Dev.	Glycerin	St.Dev.	Formamide	St.Dev.
PG 70-28	55.5	0.7	45.3	1.0	39.2	0.3
PG 70-28 + 2% Sasobit®	63.8	1.2	59.2	0.9	51.4	1.2
PG 70-28 + 4% Sasobit®	68.8	1.4	63.0	0.9	56.0	0.1
PG 70-28 + 8% Sasobit®	78.8	1.1	71.0	0.8	64.8	0.4
PG 70-28 + 8% Paraffin Wax	95.8	0.2	68.4	22.6	81.9	0.3

TABLE 6.6 - Wettability and adhesion between aggregates and binders with Aspha-Min®.

	PG 64-22					
	Wettability (dyne/cm)		Adhesion with Limestone (ergs/cm^2)		Adhesion with Sandstone (ergs/cm^2)	
Binder	Limestone	Sandstone	In Air	In Water	In Air	In Water
PG 64-22 (Set1)	68.6	67.7	-190.8	114.2	-201.4	118.2
PG 64-22 (Set2)	70.9	70.3	-192.1	112.7	-203.4	116.1
PG 64-22 + 1% Aspha-Min®	96.0	96.6	-180.9	120.8	-190.3	126.0
PG 64-22 + 4% Aspha-Min®	84.3	83.9	-209.9	93.5	-221.8	96.2
PG 64-22 + 4% Aspha-Min® (36hrs Heating)	90.0	90.0	-177.7	119.6	-186.8	125.1
PG 64-22 + 6% Aspha-Min®	87.1	86.7	-175.5	126.2	-184.6	131.7
	PG 70-28					
	Wettability (dyne/cm)		Adhesion with Limestone (ergs/cm^2)		Adhesion with Sandstone (ergs/cm^2)	
Binder	Limestone	Sandstone	In Air	In Water	In Air	In Water
PG 70-28	70.4	69.1	-198.5	108.8	-209.0	112.9
PG 70-28 + 1% Aspha-Min®	66.9	65.3	-220.8	86.3	-232.0	89.6
PG 70-28 + 4% Aspha-Min®	74.1	72.7	-212.0	94.8	-222.4	98.9
PG 70-28 + 6% Aspha-Min®	61.1	59.3	-215.6	89.9	-225.9	94.3

Effect on Adhesion

Advancing/wetting contact angle is related to the wettability, as discussed in the previous paragraphs. The relation between the receding/dewetting contact angle (results of the contact angle hysteresis) and the adhesion (free energy of adhesion) is not yet clearly understood [16-17]. However, some researchers correlated adhesion (free energy of adhesion) with receding/dewetting contact angle as breaking of bond occurs during the receding/dewetting process (in the cases of receding/dewetting contact angle greater than zero). Extrand [17] noted that receding/dewetting free energies are analogous to fracture energies of solid systems. Therefore, in the present study, adhesion (free energy of adhesion) was calculated from the SFE components obtained from receding/dewetting process. The adhesion (free energy of adhesion) in the presence of

water was also calculated in order to elucidate on the moisture-induced damage mechanisms.

TABLE 6.7 - Contact angles of asphalt binders with Aspha-Min®.

Advancing Contact Angles of PG 64-22 with Aspha-Min®						
Binder	Water	St.Dev.	Glycerin	St.Dev.	Formamide	St.Dev.
PG 64-22 (Set1)	110.2	0.4	98.0	0.5	93.0	0.3
PG 64-22 (Set2)	110.0	0.4	98.1	0.6	93.4	0.3
PG 64-22 + 1% Aspha-Min®	109.5	0.5	96.2	0.1	93.4	0.6
PG 64-22 + 4% Aspha-Min®	110.3	0.7	97.0	0.1	93.1	0.2
PG 64-22 + 4% Aspha-Min® (36hrs Heating)	110.1	1.0	96.6	0.2	93.2	0.3
PG 64-22 + 6% Aspha-Min®	110.7	0.4	96.9	0.2	93.2	0.1
Receding Contact Angles of PG 64-22 with Aspha-Min®						
Binder	Water	St.Dev.	Glycerin	St.Dev.	Formamide	St.Dev.
PG 64-22 (Set1)	57.2	2.1	50.4	1.6	43.6	0.4
PG 64-22 (Set2)	57.4	0.6	51.4	0.9	45.5	0.1
PG 64-22 + 1% Aspha-Min®	60.3	1.3	53.3	0.8	45.9	0.5
PG 64-22 + 4% Aspha-Min®	58.7	0.7	50.3	0.5	46.9	0.6
PG 64-22 + 4% Aspha-Min® (36hrs Heating)	64.2	0.9	57.1	0.5	50.8	0.6
PG 64-22 + 6% Aspha-Min®	60.2	0.6	53.8	0.3	45.6	0.1
Advancing Contact Angles of PG 70-28 with Aspha-Min®						
Binder	Water	St.Dev.	Glycerin	St.Dev.	Formamide	St.Dev.
PG 70-28	110.6	0.5	97.6	0.5	92.7	0.2
PG 70-28 + 1% Aspha-Min®	110.8	0.5	97.8	0.6	92.5	0.2
PG 70-28 + 4% Aspha-Min®	111.4	0.4	97.9	0.3	93.1	0.2
PG 70-28 + 6% Aspha-Min®	111.1	0.6	98.5	0.9	92.8	0.3
Receding Contact Angles of PG 70-28 with Aspha-Min®						
Binder	Water	St.Dev.	Glycerin	St.Dev.	Formamide	St.Dev.
PG 70-28	55.5	0.7	45.3	1.0	39.2	0.3
PG 70-28 + 1% Aspha-Min®	55.3	0.7	43.1	0.8	38.3	0.4
PG 70-28 + 4% Aspha-Min®	55.6	0.5	43.9	0.4	37.6	0.1
PG 70-28 + 6% Aspha-Min®	56.7	0.6	43.9	0.6	38.1	0.2

The use of receding/dewetting contact angle is limited. Lack of repeatability, stick-slip property and dependency on the speed of receding/dewetting process are some of the major reasons for this [13]. In this study, no stick-slip nature of the redecing/dewetting contact angle was observed. Tables 6.5 and 6.7 show that the receding/dewetting contact angles are repeatable relative to the effect of Sasobit® on

asphalt binders. Among the three liquids used in this study, glycerin has the highest viscosity. Therefore, advancing/wetting and receding/dewetting contact angles were obtained at different receding/dewetting speed in order to investigate the effect of speed on contact angle. The effect of speed on advancing/wetting contact angle is negligible whereas, the effect on receding/dewetting contact angle is small relative to the effect of Sasobit® on asphalt binders. The advancing/wetting and receding/dewetting speed in this study was 80μm/sec.

The free energy of adhesion (ΔG^A), has two components, Lifshitz- van der Waals or non-polar part of adhesion and acid-base or polar part of adhesion. The following equations were used to determine the non-polar and polar adhesion between an asphalt binder and an aggregate:

$$\Delta G^A = \Delta G^{aLW} + \Delta G^{aAB} = -2\sqrt{\Gamma_s^{LW}\Gamma_l^{LW}} - 2\sqrt{\Gamma_s^+\Gamma_l^-} - 2\sqrt{\Gamma_s^-\Gamma_l^+} \quad (5)$$

where,

ΔG^A = Free energy of adhesion,

ΔG^{aLW} = Non-polar or Lifshitz-van der Waals part of adhesion, and

ΔG^{aAB} = Acid-base or polar part of adhesion,

Γ_L^{LW}, Γ_L^+, and Γ_L^- = SFE components of the asphalt binder, and

Γ_S^{LW}, Γ_S^+, and Γ_S^- = SFE components of the aggregate.

Also, the following equation was used to calculate the adhesion of asphalt binder with aggregate in the presence of water where subscripts 1, 2 and 3 represent asphalt binder, aggregate, and water, respectively. If the value of free energy of adhesion is negative, it means the two phases of the material tend to bind together and the more it is negative the higher the bonding strength.

$$Adhesion = -(2\Gamma_3^{LW} + 4\sqrt{\Gamma_3^+\Gamma_3^-} - 2\sqrt{\Gamma_1^{LW}\Gamma_3^{LW}} - 2\sqrt{\Gamma_1^+\Gamma_1^-} - 2\sqrt{\Gamma_1^-\Gamma_3^+}$$
$$- 2\sqrt{\Gamma_2^{LW}\Gamma_3^{LW}} - 2\sqrt{\Gamma_2^+\Gamma_3^-} - 2\sqrt{\Gamma_2^-\Gamma_3^+} + 2\sqrt{\Gamma_1^{LW}\Gamma_2^{LW}} + 2\sqrt{\Gamma_1^+\Gamma_2^-} + 2\sqrt{\Gamma_1^-\Gamma_2^+}) \quad (6)$$

where,

Γ_1^{LW}, Γ_1^+, and Γ_1^- = SFE components of asphalt binder,

Γ_2^{LW}, Γ_2^+, and Γ_2^- = SFE components of aggregate, and

Γ_3^{LW}, Γ_3^+, and Γ_3^- = SFE components of water.

Tables 6.4 and 6.6 show the adhesion (free energy of adhesion) between aggregates and asphalt binders with and without the presence of water. If the value of adhesion (free energy of adhesion) is negative, it means that the two materials tend to bind together, and the larger the magnitude of this negative value of adhesion the higher the bond strength. If the value of adhesion (free energy of adhesion) is positive, it means that the two materials spontaneously separate and the larger the positive value the higher the moisture susceptibility.

It is evident from Table 6.4 that the adhesion (free energy of adhesion) between the PG 64-22 and the aggregates reduces with an increase in percent of Sasobit®. A similar trend was observed in case of PG 70-28. This was expected. Edwards and Redelius [5] noted that commercial wax (in this case Sasobit®) may reduce the adhesion (free energy of adhesion) between asphalt binders and aggregates.

In another study, Garby et al. [16] established a relationship between the tensile stress values obtained by the pull-off test and the polar interaction values measured during receding/dewetting. From Table 6.2, it is evident that Sasobit® reduces the polar component of SFE (receding/dewetting) for both the asphalt binders. Therefore, Sasobit® reduces the polar component of SFE (receding/dewetting) as well as the

adhesion (free energy of adhesion from receding/dewetting), thereby reducing the tensile stress.

In the presence of water, the adhesion (free energy of adhesion) between the asphalt binder and the aggregate becomes positive, which indicates that no bond exists between the asphalt binder and the aggregate. This also implies that the process is spontaneous. In case of PG 64-22, small or no reduction in moisture susceptibility (spontaneous change in free energy under water) was observed whereas, Sasobit® was found to significantly increase the moisture susceptibility of PG 70-28. Overall, Sasobit® reduces the adhesion (free energy of adhesion) and increases the moisture susceptibility.

For Aspha-Min®, no trend was observed on increase or reduction of adhesion (free energy of adhesion) in the case of PG 64-22. Like wettability, no significant effect on adhesion (free energy of adhesion) of the asphalt binder was observed due to heating with Aspha-Min® for 36 hrs. For PG 70-28, Aspha-Min® increases the adhesion (free energy of adhesion) and reduces the moisture susceptibility.

Effect on Asphalt Morphology

Wettability of a liquid (in this case an asphalt binder) over a solid surface is strongly influenced by the surface roughness of the solid. Using an Atomic Force Microscopy (AFM) Miller et al. [18] demonstrated that even nanometer size surface roughness strongly influences the wetting behavior of water on the surface of polytetrafluoroethylene (PTFE) thin films. Loeber et al. [19] observed nano-scale “bee” structured surface roughness on the surface of the asphalt binders using AFM and Scanning Electron Microscopy (SEC). Recently, Lu et al. [20] investigated the wax

morphology in asphalt binders using Differential Scanning Calorimetry (DSC). It was reported that non-waxy asphalt binder displays no structure or crystals whereas, waxy binders display a large variation in structures. They vary from tiny needles, elongated needles, flakes and even crescent shaped structures. The morphology of the wax crystals is highly dependent on crystallization temperature as well as temperature history. In the present study, changes in asphalt binders' morphology were observed visually with the addition of Sasobit®. Sketches drawn in Figure 6.2 shows how the surface of the asphalt binders changes with an increase in percent of Sasobit®. It is highly likely that both the advancing/wetting and receding/dewetting contact angles are influenced by the surface morphology that varies from nanometer size bee structures [19, 20] to the visual roughness, as observed in this study (Figure 6.2).

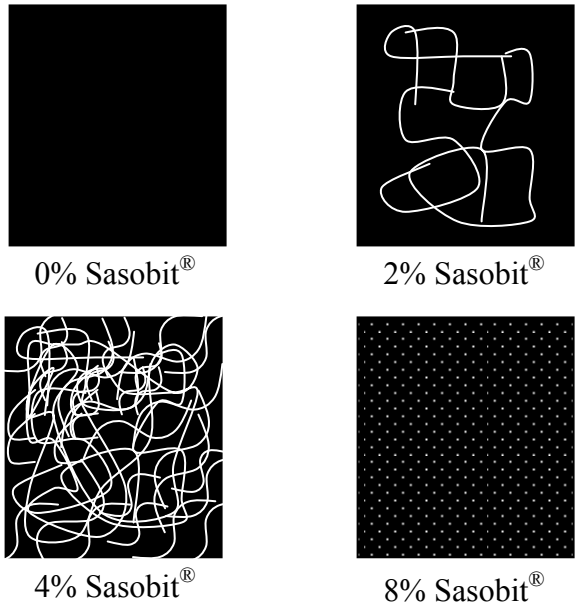

FIG. 6.2 - Effect of Sasobit® on the morphology of the asphalt binder.

Conclusions

The following conclusions can be drawn from this study.

- From both advancing/wetting and receding/dewetting contact angles, it is evident that Sasobit® reduces the total SFE of asphalt binders. Also, it increases the acid component of SFE thereby increasing the ratio between the acid component of SFE and the base component of SFE. On the other hand, effect of Aspha-Min® on SFE components of asphalt binders is insignificant.

- Sasobit® increases the wettability of asphalt binders over aggregates significantly. For example, addition of 8% Sasobit® increases the wettability of PG 64-22 from 70.3 dyne/cm to 98.8 dyne/cm, as measured by the spreading coefficient. Increase in wettability is also exhibited by the reduction in contact angle of glycerin and formamide. For Aspha-Min® no significant changes in wettability were observed. Heating of PG 64-22 with 4% Aspha-Min® for 36 hrs also has negligible effect on wettability.

- A general trend is that Sasobit® reduces the adhesion (free energy of adhesion) between asphalt binders and aggregates, as calculated from the receding/dewetting contact angle measurements. For PG 64-22, small or no reduction in moisture susceptibility and for PG 70-28, an increase in the moisture susceptibility were observed. For Aspha-Min® no trend was observed in the case of PG 64-22, however, for PG 70-28, Aspha-Min® increases the adhesion (free energy of adhesion) and reduces the moisture susceptibility.

- The surface morphology of the asphalt binders changes with the addition of Sasobit®. The effects of these changes on contact angles and related properties were not evaluated in this study.

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CHAPTER 7

Decisions about the status of experimental findings are not dictated by the findings: scientists' judgments may be informed by commitments to certain accounts of what the natural world contains and by (considerations) usually thought of as 'external' to science. *New History and Sociology of Science School of Thought*

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

This chapter summarizes the major findings of this overall study. Specific conclusions pertaining to specific topics were included in individual chapters. The hypothesis of this study is that measurement of the surface free energy (SFE) characteristics of aggregates and binders could be a useful tool for the evaluation of the effectiveness of different additives used in asphalt mixes. The pertinent conclusions are summarized in the following bulleted points.

1. It was observed that liquid amine anti-strip additives can significantly change the SFE characteristics of an asphalt binder. For example, addition of 1.5% AD-Here HP Plus increased the total SFE of the PG 64-22 binder used by 67%. According to the Good's postulate, an increase in binder SFE indicates an increase in adhesion (free energy of adhesion) between a binder and an aggregate.
2. The effect of liquid amine anti-strip additives on surface Lewis acid-base characteristics of binders can be evaluated adequately using the SFE method. For example, 1.5% AD-Here HP Plus increased the base component of SFE of the PG 64-22 used by 568%. In the case of an acidic aggregate and an acidic

binder, the surface chemistry of Lewis acids and bases does not favor adhesion, consequently a good bond between an acidic aggregate and an acidic binder is very difficult to obtain, as previously found by other researchers. For example, it is know that acidic granite is more susceptible to stripping than basic limestone. Therefore, an increase in the base component of SFE of asphalt binders with the addition of anti-strip additives indicates an increase in adhesion between the binders and the aggregates according to the Good's postulate.

3. The effect of aging on amine anti-strip additives was evaluated in this study. It was shown that both Rolling Thin Film Oven (RTFO) aging and Pressure Aging Vessel (PAV) aging change the SFE characteristics of asphalt binders with liquid amine anti-strip additives. The beneficial effect of anti-strip additives in acid-base characteristics of asphalt binders is severely reduced by RTFO and PAV-aging (in case of the base component of SFE of PG 64-22 with 0.75% Redicote E-6, the reductions are 58% and 98%, respectively for RTFO and PAV-aging).
4. The SFE method was also used to evaluate an aggregate with and without styrene-butadiene rubber (SBR) polymer treatment. It was observed that the SBR treatment increases the spreading coefficient and reduces the interfacial energy significantly, thereby increasing the wettability of asphalt binders over aggregates. As in the case of the asphalt binder, the effect on surface Lewis acid-base characteristics of aggregates due to SBR treatment can be evaluated adequately using the SFE method. It was observed that the acid SFE of acidic sandstone is significantly reduced and the base SFE is increased by SBR

treatment and thus, favoring the adhesion between an acidic asphalt binder and an acidic aggregate. For example, in case of the PG 64-22 used, the adhesion (free energy of adhesion) is increased by 10% and 6% respectively, for limestone and sandstone by SBR treatment.

5. The rheological properties of asphalt binders with and without warm mix additives (Sasobit® and Aspha-Min®) were evaluated in this study. The Rotational Viscometer results show that Sasobit® significantly reduces (as much as 16°C for the PG 64-22 binder used) the mixing and compaction temperatures whereas, viscosity reduction with Aspha-Min® was not observed. In addition, Sasobit® increases the high temperature binder grading (4°C in case of the PG 64-22 binder used), while Aspha-Min® does not have any significant effect. Moreover, Sasobit® was found to decrease the APA rut depths significantly, and these rut depths correlate well with the rutting factor $G^*/\sin(\delta)$ in case of PG 64-22. For example, in the case of the PG 64-22 used, 4% Sasobit® decreased the rut depth significantly from 5.8 mm to 3.5 mm.
6. The effect of Sasobit® (a commercial wax) and Aspha-Min® (a synthetic zeolite) on asphalt binders was examined using the SFE method. An important finding is that Sasobit® (a commercial wax) increases the wettability (increased wettability indicates improved coating of aggregates by binders thereby, reducing moisture propensity) of asphalt binders significantly. For example, addition of 8% Sasobit® increases the wettability of the PG 64-22 from 70.3 dyne/cm to 98.8 dyne/cm, as indicated by the change in free energy (spreading coefficient) due to wetting. For Aspha-Min®, no significant changes in wettability were

observed. A general trend is that Sasobit® reduces the adhesion (free energy of adhesion) between asphalt binders and aggregates, as calculated from the receding/dewetting contact angle measurements. For the PG 64-22 binder used here, a small or no reduction in moisture susceptibility (spontaneous release of energy due to work of adhesion from aggregate and binder to aggregate and water) was observed. However, for the PG 70-28 binder, an increase in the moisture susceptibility, due to addition of Sasobit®, was observed.

7. A chemical model is proposed based on the SFE characteristics of asphalt binders and aggregates which explains the mechanisms of asphalt binder-aggregate interactions with and without the addition of additives. When cationic surfactants (amine-based additive in this study) are added to an asphalt binder (non-polar solvent), it adsorbs onto the surface with polar head group directed outward. This actually results in an increase in surface energy of an asphalt binder, as observed in this study. The chemical model also explains that the basic chemical compounds, namely amines in anti-strip additives, in the context of this study, reduce the acid component of the SFE and increase the base component of the SFE of an asphalt binder and increases the adhesion between binders and aggregates according to the Good's postulate. The chemical model (for un-aged binders) was expanded to include the SFE characteristics of asphalt binders due to aging. The expanded model explains that the beneficial effect of anti-strip additives in acid-base characteristics of asphalt binders is severely reduced by RTFO and PAV-aging. The chemical model was further expanded to include the surface acid-base SFE characteristics

of an aggregate with and without SBR polymer coating. It explains that the acid SFE of acidic sandstone is significantly reduced and the base SFE is increased by SBR treatment and thus, favoring the adhesion between an acidic asphalt binder and an acidic aggregate. In this model, the parameters used to explain binder-aggregate interaction are Lewis acid surface parameter, Lewis base surface parameter, wettability (spreading coefficient), adhesion (free energy of adhesion) and moisture susceptibility (spontaneous change in free energy under water).

Besides the above conclusions on theoretical aspects of binder-aggregate interaction, the following application oriented conclusions can be drawn from this study.

1. It was revealed that mixing of amine anti-strip additives at 163°C is more effective than mixing at 145°C. However, a short duration of mixing of additives is required to reduce thermal degradation of additives.
2. Because of the same reason, amine anti-strip additives should be mixed to asphalt binders just before mixing the asphalt binders with the aggregates. Also, the asphalt mix containing anti-strip additives should not be kept in the silos for long time.
3. SBR coating reduces the moisture susceptibility of sandstone used. However, limestone without SBR coating is better than sandstone with SBR coating with respect to moisture susceptibility. SBR coating increases the moisture susceptibility of limestone used.

4. Sasobit® reduces the binder viscosity and increases the binder high temperature grading, thereby reducing the rut depth.

Four different types of additives (liquid amine, polymer emulsion, commercial wax, synthetic zeolite) were evaluated in this study using the SFE method in order to elucidate the mechanisms of asphalt-aggregate interaction. The results of this study can be used as a tool for cataloging of materials[2]. Also, the knowledge gained in this study will contribute to developing performance based parameters for assessment of moisture-induced damage in pavement using the SFE method.

Recommendations for Future Research

The most important recommendations from this study are as follows.

1. The parameters used in this study namely, acid component of SFE, base component of SFE, wettability (spreading coefficient) and adhesion (free energy of adhesion) with and without the presence of water should be evaluated with performance tests in the laboratory. Currently, researchers at the Turner-Fairbank Highway Research Center (T-FHRC) of the Federal Highway Administration (FHWA) are conducting adhesion test using Pneaumatic Adhesion Tensile Testing Instrument (PATTI). A study to correlate the SFE characteristics with the PATTI test data, namely adhesion, should be pursued in a future study.
2. The binders and the aggregates used in the moisture damaged roads should be collected for the evaluation of the SFE characteristics.

[2] See Appendix B for details.

3. This study was focused on developing the SFE measurement protocols and on the effect of additives. It is recommended that binders and aggregates from different sources be evaluated. This will help establish the SFE method as the tool for cataloging of materials.
4. Hydrated lime is a commonly used anti-strip additive. Effect of hydrated lime on SFE characteristics of binders/aggregates should be evaluated.
5. Different types of chemicals are used as de-icing and anti-icing materials. The effect of these chemicals (salts) on SFE characteristics should be evaluated for moisture-induced damage potential.
6. Finally, researchers at the Texas Transportation Institute (TTI) and the Technical University of Delft (TU Delft) are developing numerical modeling tools (fatigue models, moisture damage models, etc.) for predicting pavement performance. The SFE characteristics are fundamental properties of materials. As such, they should be included in the development of pavement performance models.

APPENDIX

A

PROPAGATION OF ERROR FROM CONTACT ANGLES TO SFE COMPONENTS

In this study the standard deviation of the contact angles were measured and used to calculate the standard deviations of the SFE components. Equation 6 in Chapter 2 was used for this purpose. Rearranging this equation we get the following equation:

$$1+\cos\theta = +\frac{2\times\sqrt{\Gamma_{Sol}^{LW}}}{\Gamma_{Sol}}\sqrt{\Gamma_{Asp}^{LW}} + \frac{2\times\sqrt{\Gamma_{Sol}^{+}}}{\Gamma_{Sol}}\sqrt{\Gamma_{Asp}^{-}} + \frac{2\times\sqrt{\Gamma_{Sol}^{-}}}{\Gamma_{Sol}}\sqrt{\Gamma_{Asp}^{+}} \quad (1)$$

The general equation[3] for propagation of error is given by:

$$S_x^2 = S_u^2\left(\frac{\delta x}{\delta u}\right)^2 + S_v^2\left(\frac{\delta x}{\delta v}\right)^2 + S_w^2\left(\frac{\delta x}{\delta w}\right)^2 \quad (2)$$

where s is the standard deviation and x is a function of independent variables u, v and w. Applying Equation 2 in Equation 1 we get,

$$S_\theta \sin\theta = +\frac{2\times\sqrt{\Gamma_{Sol}^{LW}}}{\Gamma_{Sol}} S_{\sqrt{\Gamma_{Asp}^{LW}}} + \frac{2\times\sqrt{\Gamma_{Sol}^{+}}}{\Gamma_{Sol}} S_{\sqrt{\Gamma_{Asp}^{-}}} + \frac{2\times\sqrt{\Gamma_{Sol}^{-}}}{\Gamma_{Sol}} S_{\sqrt{\Gamma_{Asp}^{+}}} \quad (3)$$

$$\text{where, } S_{\sqrt{\Gamma_{Asp}}} = \frac{S_{\Gamma_{Asp}}}{2\times\sqrt{\Gamma}_{Asp}} \quad (4)$$

[3] Source: Wikipedia, the Free Encyclopedia (online)

Soling Equation 3 for three different solvents will give the error in SFE components. Finally, the error in the total SFE can be calculated from the errors in the SFE components from the following equation:

$$S_{\Gamma}^2 = S_{\Gamma^{LW}}^2 + S_{\Gamma^+}^2 \frac{\Gamma^-}{\Gamma^+} + S_{\Gamma^-}^2 \frac{\Gamma^+}{\Gamma^-} \tag{5}$$

Table A.1 provides the error in the SFE components pertaining to the data presented in Table 2.3. It can be seen that the standard deviations are relatively small.

TABLE A.1 - Errors in SFE components provided in Table 2.3.

Binders	Types of Additives	Percent of Additive/ Standard Deviation	Total SFE, Γ (dyne/cm)	Lifitz-van der Waal Component, Γ^{LW} (dyne/cm)	Acid Component, Γ^+ (dyne/cm)	Base Component, Γ^- (dyne/cm)	Acid-Base Component, Γ^{AB} (dyne/cm)
PG 64-22	No	0	9.3	7.0	2.9	0.4	2.3
		St.Dev.	0.04	0.04	0.01	0.00	0.00
	AD-Here HP Plus	0.25	11.4	9.2	2.0	0.6	2.1
		St.Dev.	0.02	0.02	0.01	0.01	0.01
		0.75	13.5	11.7	1.0	0.8	1.8
		St.Dev.	0.03	0.00	0.00	0.03	0.03
		1.5	15.5	13.1	0.5	2.9	2.4
		St.Dev.	0.27	0.26	0.03	0.01	0.07
	Redicote E-6	0.25	11.2	9.6	1.8	0.4	1.6
		St.Dev.	0.04	0.04	0.01	0.00	0.00
		0.75	14.1	12.2	1.0	0.9	1.9
		St.Dev.	0.01	0.01	0.00	0.00	0.00
		1.5	28.6	26.4	0.2	5.4	2.2
		St.Dev.	0.80	0.78	0.03	0.02	0.15
PG 70-28	No	0	10.9	8.8	2.5	0.4	2.1
		St.Dev.	0.03	0.03	0.01	0.00	0.00
	AD-Here HP Plus	0.25	11.8	9.7	2.1	0.5	2.1
		St.Dev.	0.00	0.00	0.00	0.00	0.00
		0.75	12.4	10.4	1.9	0.5	2.0
		St.Dev.	0.17	0.16	0.09	0.00	0.05
		1.5	13.5	11.3	1.8	0.7	2.2
		St.Dev.	0.04	0.00	0.00	0.02	0.04
	Redicote E-6	0.25	11.2	8.9	2.5	0.5	2.2
		St.Dev.	0.31	0.31	0.11	0.01	0.05
		0.75	12.5	10.7	1.9	0.4	1.8
		St.Dev.	0.06	0.06	0.02	0.00	0.01
		1.5	13.6	11.6	1.7	0.6	2.0
		St.Dev.	0.15	0.15	0.03	0.00	0.02

APPENDIX

B

CATALOGING OF MATERIALS

Based on the results obtained in this study, an attempt has been taken for cataloging of materials as presented in Table B.1.

Table B.1 – Cataloguing of materials used in this study.

Additives		Binders	Aggregates
Anti-Strip for Binders	AD-Here HP Plus	Perform better with PG 64-22 than PG 70-28 (Elvaloy)	
	Redicote E-6	1) Perform better with PG 64-22 than PG 70-28 (Elvaloy) 2) Redicote E-6 is more effective than AD-Here HP Plus	
Anti-Strip for Aggregates	UP 5000		1) Effective for Sandstone and Limestone 2) Performs better for Sandstone than Limestone
Warm Mix Additives	Sasobit®	Perform better with PG 64-22 than PG 70-28	
	Aspha-Min®	No significant effect	