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# Surface free energy and moisture susceptibility evaluation of asphalt binders modified with surfactant-based chemical additive

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ABSTRACT

Warm mix additives are used to lower the production and application temperature of asphalt mixtures. Moisture damage is one of the main reported issues with warm mix asphalt due to its lower production temperature and the possible presence of moisture being trapped during the mixing process. This paper considers the use surface free energy evaluation as a fundamental material property to assess mixture performance. Cecabase® chemical surfactant additive was used to prepare warm mix asphalt binders. Contact angle measurements were determined with a Goniometer to evaluate surface free energy measures such as work of adhesion, work of debonding and compatibility ratio. The results show that the use of the surfactant-based additive reduces surface free energy. It increases after short-term (Rolling Thin Film Oven) and reduces after long-term (Pressure Aging Vessel) aging. The analytical measurements based on surface free energy results illustrate that the surfactant-based warm mix additive improves the spreadibility of asphalt binder over the aggregate particles. The work of adhesion slightly improves with the addition of Cecabase® content. Compatibility ratio is an indicator of moisture susceptibility and indicates that the granite aggregates are less resistant to moisture damage compared to the limestone aggregates used in this laboratory study.



## 1. Introduction

Warm mix asphalt (WMA) is now an important asphalt mix in many countries around the world. Compared to hot mix asphalt (HMA) it has qualities that make it attractive to the changing world in which we live. It has less environmental impact in terms of green-house gas emission. Less energy is required during mixing. It may be hauled greater conditions to site and compacted in cooler conditions (Hamzah et al., 2014). Increased amounts of Recycled Asphalt Pavement (RAP) may be used (Rubio et al., 2012, 2013). One of its most important benefits is that workers involved in manufacture and particularly laying are exposed to less potentially fumes compared to conventional HMA.

WMA is made and compacted at lower temperatures compared to HMA. There are three main methods to reduce mixing and laying temperatures (Capitão et al., 2012). They may reduce mixture viscosity of the bitumen using a foaming processes, which can either be water-based (direct method technologies) or water-containing (indirect method technologies) (Rubio et al., 2012). The use of organic or synthetic additives such as Sasobit and Asphamin add waxes to the mixture. Chemical additives such as Cecabase® contain combinations of emulsification agents, surfactants, polymers and adhesion promoting (anti-stripping agents) additives. These help to improve coating of the aggregate particles, workability and compaction (Rubio et al., 2012). Of these three main methods, the use of chemical additives has been found to be more practical and convenient as they can be added directly to the bitumen prior to mixing without any modification of the asphalt plant. It is also claimed, that unlike foaming or organic based WMA additives, the chemical surfactant-based additive does not significantly affect the mechanical/rheological properties of the bitumen i.e. its stiffness and low temperature properties (Oliveira et al., 2013).

In asphalt mixtures the purpose of bitumen is to bind the aggregates together and transfer the stresses of traffic loading during

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its in-service life (Hamzah et al., 2015). Good adhesion bond between bitumen and aggregate surface is therefore very important and anything that lessens this bond will reduce the life of the asphalt mixture layer. The development of a good bond between asphalt and aggregate is primarily dependent on the ability of the asphalt to wet the aggregate. The aggregate wettability increases when the surface tension or Surface Free Energy (SFE) of adhesion decreases (Kakar et al., 2015). The presence of water either contained within the aggregate particle or external to the bitumen coated particle is probably the main cause for failures at this critical interface (Bhasin and Little, 2009).

One of the main concerns relating to the durability of WMA is the potential for water/moisture induced failure of the bond. This is primarily due to issues with the lower temperatures involved during mixing that may not adequately reduce the aggregate moisture contents to an acceptable level. Despite extensive research to understand the behavior of WMA and its obvious beneficial characteristics, the risk of moisture damage related failure still remains a problem. The types of aggregates used in asphalt production are varied and reflect the many different types available. A simple classification is based on how they were formed i.e. igneous, sedimentary and metamorphic. Within each of these there are many different types that can be described in terms such as their overall bulk chemistry, mineralogy, grain size and degree of weathering. With regard to most aggregate/bitumen research, bulk chemistry is typically used to describe the aggregate. Mineral fillers such as fly ash are also used as adhesion promoter, however due to its increase in coating difficulty, fly ash is not recommended to mitigate the stripping problems (Pasandín et al., 2015).

In simple terms, the surface of different types of aggregate will have different chemical affinities with bitumen. For example, aggregates with higher $SiO_2$ contents such as granite and quartz are typically termed acidic. They are classified as hydrophilic or water loving and can be difficult to coat with bitumen. In contrast, basic aggregates with high $CaCO_3$ content such as limestone are hydrophobic. They tend to repel water and be less affected by moisture induced problems (Tarrer and Wagh, 1991).

Terms such as wettability and adhesion are used to explain the bitumen/aggregate interface mechanism (Wasiuddin et al., 2008). The interface can be explained using descriptive terms such as wettability of bitumen over aggregate, free energy of adhesion and solubility of adhesion bond. With respect to the chemical interactions occurring at the interface, the polar (hydrophilic) and non-polar (hydrophobic) nature of aggregate and bitumen control the wettability of bitumen over aggregate. Most types of bitumen are considered to be non-polar. Most basic and acid aggregate types have high polarity surfaces (Wasiuddin et al., 2010). Therefore, it is difficult to wet a polar aggregate surface with most non-polar types of bitumen. The wettability of most non-polar types of bitumen over polar aggregate can be improved by altering the aggregate surface from being polar to become non-polar i.e. hydrophilic to hydrophobic. This is best done by reducing the bitumen non-polar component and the polar component of the aggregate.

This paper uses SFE measurements to study the effects of WMA Cecabase® surfactant-based additive on the aggregate/bitumen bond. Since warm mix asphalt is a technology that produces asphalt mixtures at low temperature, which therefore reduces greenhouse gas emission and low fumes during pavement construction making it more environment friendly. Asphalt mixtures production at high temperatures can contribute to air quality problems due to the emission of reactive organic gases (ROGs) and particulate matter. The emissions released through asphalt plant stacks in the United States are regulated and controlled by the Environmental Protection Agency [EPA AP-42, Section 11.1 Hot-Mix Asphalt Plants (Kinsey, 1986)]. Reduction in reactive organic gases and nitrogen oxide emissions will reduce ozone formation potential in urban areas and subsequently this is a high priority nationwide. According to the California Air Resources Board (CARB) record, the largest source of ROG is emissions from light-duty vehicles and in 2005 accounted for 600 tons per day (tpd) or 24.6 percent of the total ROGs in the state (California Air Resources Board, 2015). In 2010, these emissions have decreased up to 400 tpd or 18.9 percent of the total ROGs. As emissions from these major sources decreased over time, emission reduction from smaller sources has become a higher priority for achieving clean air standards (Farshidi et al., 2013). Furthermore, research has been carried out for many years on health concerns with a recent focus on potential exposure to carcinogens with respect to asphalt fume exposure. A very important group of chemical carcinogens in asphalt is potentially represented by Polycyclic aromatic hydrocarbons (PAH). Many of the lower molecular weight PAH compounds might also be removed during the refinery process, but this depends on the crude oil source and the process used to refine it (Farshidi et al., 2013). Studies (Newcomb, 2007; D'Angelo et al., 2008) have proven that WMA plants would reduce $CO_2$ and $SO_2$ by 30%–40%, volatile organic compounds (VOC) by 50 percent, CO by 10%–30%, $NO_x$ by 60%–70% and dust by 20%–25%. Hence, in the context of warm mix asphalt which is also called green technology with sustainable asphalt production can be the prime interest of environmental protection agencies and pavement researchers. Two different aggregate with differing in-service moisture related performance were used in the calculations. Blends of Cecabase® were prepared with 2 different bitumen grades which were subjected to short and long term aging. Changes in SFE were investigated using the contact angle technique.

## 2. Surface free energy using the contact angle technique

Surface free energy (SFE or $\gamma$) is defined as the amount of external work done on a material to create a new unit surface area in a vacuum. SFE is normally presented in units of ergs per square centimeter (Bhasin et al., 2006). Four types of test equipment are available to measure SFE of bitumen and aggregate i.e. the Goniometer, the Wilhelmy Plate Device, the Micro-calorimeter and the Dynamic Vapor Sorption System. The measurement of contact angle with the bitumen using different probe liquids is performed using the Goniometer and the Wilhelmy Plate Device. The Micro-calorimeter and the Dynamic Vapor Sorption device are used to measure the heat of adhesion and adsorption of different probe liquids/vapours respectively with aggregate. The measurement of contact angle using the Goniometer is the most common and simple approach used to determine the SFE characteristics of bitumen and was the method used in this study.

The contact angle approach was described by Young to determine the SFE properties of a solid (Ahmad, 2011). The contact angle was defined by the three surface tensions (solid, liquid and air/vapour). Young's equation shown in Fig. 1 is used to summarize the calculations (Ahmad, 2011). Young's equation can be written as Eq. (1):

$$\gamma_{LA} \cos\theta + \gamma_{SL} = \gamma_{SA} \tag{1}$$

where L, S and A denotes liquid, solid and air respectively.

Van Oss et al. (1988) identified two main interactions of a surface energy components for a solid i.e. Lifshitz–Van der Waals interactions and Acid–Base interactions (Erbil, 2006). Polar components are divided into Lewis acid and base component, which encompass all the electron donor and electron acceptor type interactions (Van Oss et al., 1988).

The surface energy, $\gamma^T$, can be calculated from Eq. (2):