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Stripping at the bitumen-aggregate interface: A laboratory method to assess the loss of chemical adhesion

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Keywords:

Bitumen, stripping, kinetic, coated surface, imaging processing.

ABSTRACT

Moisture damage, cracking, and deformation are the three chief distresses caused by traffic and climate during the service life of an asphalt pavement. One manifestation of moisture damage is the loss of bond between bitumen and aggregate, resulting in the displacement of the bitumen in a process called stripping. While numerous tests try to evaluate moisture damage in the laboratory, most of them show poor correlation with field performance. A fuller understanding of stripping is still needed to enable paving technologists to predict and prevent the effects of moisture damage. This study aims to develop a new stripping resistance evaluation technique wherein adhesion is measured exclusively as a function of the chemical interaction between bitumen and aggregate. A key element of the evaluation technique discussed herein uses a time-lapse image analysis method to characterize the dynamic wetting of precisely applied bitumen droplets on the surfaces of polished mineral aggregates during immersion in a thermo-regulated water bath. At fixed water immersion temperatures, the applied bitumen droplets contract, and the image analysis technique allows measurement of the change with time in the surface area of the contracting bitumen droplet. Different bitumen-aggregate pairs were used in this study. This technique allows the bitumen-aggregate pairs to be ranked according to their resistance to moisture damage. This technique also allows calculation of stripping kinetics and loss of the bitumen-aggregate adhesive bond of nine samples in exactly the same conditions. Repeatability of the new method is reported. Lastly, the results of the dynamic stripping analyses are compared to the results from the boiling water test on loose mixture to compare ranking of performances according to the mineralogy.

1 INTRODUCTION

2 Individually or in combination, the mechanical, thermal, and oxidative stresses caused by traffic,
3 climate, respectively and aging may adversely alter the strength and viscoelastic properties of as-
4 phalt pavements, leading to deterioration in overall performance and durability [1]. Kiggundu
5 and Roberts [2] defined moisture damage as ‘the progressive functional deterioration of a pave-
6 ment mixture by loss of the adhesive bond between the asphalt cement and the aggregate surface
7 and/or loss of the cohesive resistance within the asphalt cement principally from the action of
8 water.

9 Moisture damage is considered as one of the most important factors in premature deterioration of
10 asphalt pavements and leads to an estimated annual \$54 billion in control and remediation costs
11 in America [3]. Because of that, most of the American transportation agencies specify minimum
12 standards in moisture susceptibility tests. In cases of low performance job mix formulas, 82% of
13 the agencies recommend the use of antistripping additives to prevent damage caused by moisture
14 damage [4].

15 During mixture production, precise control of both the quality of formulation ingredients (aggre-
16 gates, bitumen, and other materials) and plant operating conditions (e.g., temperature and mixing
17 time) ensures that mineral aggregate surfaces are fully coated by bitumen at the targeted layer
18 thickness. The wetting and coating of aggregate surfaces by bitumen during plant mixing is an
19 example of active adhesion. Likewise, during construction, low air voids are sought, in part, be-
20 cause the interfacial bond between bitumen and aggregate may be susceptible to weakening or
21 full rupture by water that intrudes into the pavement. The breaking of the adhesive bond between

1 bitumen and aggregate in compacted mixtures is known as stripping and is a form of passive ad-
2hesion. Thus, the strength and durability of the adhesive bond (passive and active) between bitu-
3men and an aggregate surface depends on numerous production and construction variables.

4 Traditionally, studies concerning moisture damage have aimed to identify the damage mecha-
5nism of road pavement materials in the presence of water and to develop or improve the tests for
6control and prevention in laboratories [5][6]. Indeed, there are numerous standardized laboratory
7test methods to measure moisture damage in use today [7]. Testing conditions and experimental
8procedures vary widely from test method to test method (duration of the water immersion cycle
9and water conditioning temperatures, required specimen air voids, saturation levels, etc). Though
10large in number and varied in procedural details, today's moisture sensitivity tests for bituminous
11materials can generally be divided into two broad categories. The first one comprises tests
12wherein thoroughly coated bituminous mixtures are evaluated for the percent of retained surface
13coating after immersion of the mixture in water. The percentage of the mineral aggregate surface,
14which remains coated after water conditioning, may be estimated visually as well as by instru-
15mental methods like image analysis [8][9]. Examples of these standardized test methods include
16ASTM D3625 [10] and XP T 66-043-2 [11]. The second category of standardized moisture sen-
17sitivity tests measures mechanical properties of compacted bituminous mixtures after condition-
18ing in water and compares the properties of the moisture-conditioned compacted specimens to
19the same mechanical properties of compacted specimens that have been stored in air or otherwise
20not exposed to moisture. Such test methods include NF EN 13967-12 [12] and AASHTO T283
21[13]. All the test methods within each of these two categories share a common purpose: to pro-
22vide the pavement technologist a predictive measure of the likelihood that a bitumen-aggregate
23pair is susceptible to the potentially damaging effects of moisture in the field.

1 However, most of them are limited by their empirical nature, the dependence on the moisture
2 conditioning methodology and mostly their poor predictive power in field performance. If test
3 specimen manufacturing conditions in the laboratory are not representative of field mix produc-
4 tion and pavement construction conditions (for example, with regard to temperature control and
5 heat history), then the predictive utility of the lab test will be limited. Indeed, in one comparative
6 study it was found that the mixture, which was best according to the lab test, was not the best un-
7 der field conditions [14]. Additionally, it has been observed that procedures for water condition-
8 ing of laboratory specimens may not be representative of moisture exposure conditions in the
9 field [15]. A better understanding of the fundamental phenomena at the bitumen/aggregate inter-
10 face during moisture conditioning is needed, as this would enable researchers to understand strip-
11 ping of the bitumen film from the aggregate surface independent of the conditioning procedure.

12 To provide a more comprehensive understanding of stripping phenomena, an approach to evalu-
13 ating moisture susceptibility directly from the properties of the interface between aggregate and
14 bitumen has been developed during the last decade. Many researchers have studied various as-
15 pects of physico chemical characteristics (composition, surface properties) of the mix compo-
16 nents (bitumen and aggregates) and adhesive bond between them [16][17][18]. Measurement of
17 contact angles and calculation of the work of bitumen-aggregate adhesion in the absence of water
18 have been the topics of various research articles [19][20][21]. In the presence of water, bitumen-
19 aggregate bonds break and contact angles increase with time of immersion [22]. Basu shows this
20 phenomenon with bitumen drops on glass slides: the film of bitumen in contact with water be-
21 comes distorted and adopts a spherical shape to minimize interfacial energy [22]. The results of
22 these experimental approaches to measuring stripping are largely influenced by the chemical

composition of bitumen and mineral aggregates. It is well known that the mineralogy of the aggregate contributes to the strength and durability of the adhesive bond [1][23]. Indeed, research has shown bitumen interfaces with calcareous aggregate such as limestone generally show greater resistance to the intrusion of moisture than interfaces formed by bitumen and siliceous mineral aggregates.

THEORETICAL BASIS

Moisture damage is defined as the degradation of the mechanical performance of asphalt mixtures due to the presence of moisture. The damage phenomenon involves loss of adhesion between bitumen and aggregate. To understand the evolution of the bitumen-aggregate interface, it is important to explain the five different adhesive bond theories.

Rice and Thelen described the mechanism of adhesion using a lock and key model [24][25]. Their mechanical point of view was predicated on the well-known fact that at elevated temperatures, bitumen viscosity is sufficiently low to allow bitumen to thoroughly spread over the asperities of mineral aggregates surfaces and penetrate into the aggregate micro-pores. Thus, in this model, the quality and tenacity of the “lock” depends on the viscosity of the bitumen and the texture of the surface [2]. Considering aggregate angularity, interlock adhesion is promoted with high angularity [26].

The results of other research have advanced the theory that the bond between bitumen and aggregate is influenced by the forces of attraction between different chemical functionality in the bitumen and on the aggregate surface [16][27][28][29][30]. It is adhesion due to chemical reaction between bitumen and aggregate with the formation of a new material. Considering this theory, the characterization of the active functional groups in bitumen and on the aggregate surface is

essential. In the presence of water, it is important to identify which functional groups in bitumen are displaced by water. Hefer summarized three studies and showed that generally, the most strongly adsorbed functional groups are easily displaced by water, meaning that displacement of bitumen by water is chemically favored [17]. This theory is also useful to understand the action of additives in improving mix moisture resistance.

Adhesion also can result from other chemical interactions between aggregate and bitumen, but without formation of new material. Adhesive interactions can be electrostatic in nature, arising from Coulombic forces of attraction [31]. Water damage has been evaluated from the evolution of zeta potential at the aggregate/bitumen interface. Adhesive interactions can also be explained as the result of thermodynamic phenomenon, which depend on the surface free energy of the materials and the work needed to create a new unit surface area. Moisture susceptibility, in this theory, can be defined as the change in free energy when water displaces bitumen from the aggregate surface.

A final theory, which has been enlisted to explain stripping, is the weak boundary theory. According to this theory, the adhesive failure may occur due to the existence of an interface region of low cohesive performance [31].

The aim of this study is not to advance a new normalized test but to develop a new testing methodology for stripping resistance evaluation, wherein different contributions of the various chemical adhesion factors can be isolated. The first part of this paper discusses the characteristics of materials used, the sample preparation procedures, the laboratory experimental conditions, the measurement techniques, and the results obtained with this new methodology, which for simplicity is called Method 1. In the latter part of this paper, a comparison is made between the results

of Method 1 and the results of standardized tests for moisture susceptibility in loose materials (Method 2).

MATERIALS AND METHODS

1 Materials characterization

1.1 Surface energy

According to Owens-Wendt theory [32], surface tension or surface energy can be divided into two components, a polar component γ^P , including electron donor and acceptor interactions and a dispersion component γ^D , including Van der Waals interactions. The overall surface energy or surface tension, γ , according to Owens-Wendt theory is expressed in Equation 1.

$$\gamma = \gamma^P + \gamma^D \quad [1]$$

The Fowkes equation (Equation 2) expressing the interfacial tension γ_{SL} between a solid and a liquid in terms of the components of the surface energy of the solid γ_S and the surface tension of the liquid γ_L and Young equation (Equation 3), it is possible to calculate the solid surface energy and its components from contact angles of different reference liquids:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^D \gamma_L^D} - 2\sqrt{\gamma_S^P \gamma_L^P} \quad [2]$$

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta \quad [3]$$

Where γ_S^D and γ_L^D are dispersive components and γ_S^P and γ_L^P are polar components of respectively surface tension of the solid γ_S and the surface tension of the liquid γ_L [33]. γ_{SL} is the interfacial tension between the solid and the liquid.

By combining Equations 1, 2 and 3, one can calculate polar and dispersive components of a solid from reference liquid with known polar and dispersive components. Table 1 presents the values of γ_L^P and γ_L^D of four common liquids.

Table 1. Surface tension values of reference liquids and polar and dispersive components

Reference liquids	γ_L (mN/m)	γ_L^P (mN/m)	γ_L^D (mN/m)
Ethylene glycol	47.7	30.9	16.8
Glycerol	63.4	37.0	26.4
Water	72.8	21.8	51.0
Diiodomethane	50.8	50.8	0.0

A thermo-regulated drop tensiometer (DSA 100, Krüss GmbH) was used to determine the surface energy of aggregates at 25°C. Blocks of mineral aggregate were cored to 40-mm diameter, cylindrical specimens. These specimens were then cut under water using a diamond saw to obtain approximately 10 mm thick slides. For each aggregate, the 10-mm thick slides were ground to a smoothness of $\frac{1}{4}$ μ m and cleaned under distilled water, followed by air drying and storage in a dust-free and low-humidity environment into a calcium chloride desiccator. The delay between surface preparation of slides and contact angle measurements was seven days. Indeed, the influence of the delay between polishing and drop deposit has not been evaluated. For the reason of organization, the delay has been fixed at seven days.

Equal volumes of each of the four liquids in Table 1 were applied to the highly-polished, 10-mm thick aggregate slides. The volume of the deposited drops was approximatively 1 μ L for all the reference liquids. Contact angles of four different reference liquids were measured after 1.0 min of stabilization. For each aggregate, at least eight drops of one reference liquid were deposited on

three different slides, followed by contact angle measurements. The average of the repeat contact angles measurements was calculated.

Results for the difference aggregates of the study are presented in Figure 1. The surface energy of Limestone 2 has not been measured because a block of mineral was not available in the lab.

Figure 1. Polar and dispersion components of aggregates and ratio of polarity

1.2 Mineral characterization

Chemical composition of the surface of aggregate slides was determined via Micro X-ray Fluorescence. Major components are showed in Table 2. The characterization of Limestone 2 has not been measured because a block of mineral was not available in the lab.

Table 2: Aggregate characterization

Aggregates	Minerals composition					Roughness
	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Sa
	%	%	%	%	%	μm
Basalt	5.07	16.78	51.03	2.74	12.64	-
Limestone 1	1.73	0.17	0.03	0.00	97.75	112
Limestone 2	-	-	-	-	98.52	147
Limestone 3	0.57	0.59	3.00	0.07	95.35*	440
Diorite	0.19	11.65	68.30	10.95	3.21	-
Gneiss	0.00	12.50	75.40	8.89	0.83	-
Quartzite	0.00	0.97	98.08	0.87	0.00	-

* with microscope observation on aggregates slides, it has been observed carbonated mud in cracks for Limestone 3

1.3 Texture characterization

Three different limestones were studied. Roughness evaluation was realized from an optical 3D measurement device from Alicona. The Alicona high-resolution measuring device uses high-resolution (vertical resolution up to 10 nm) photography to create surface profiles. Photographs taken at precisely different altitudes above a surface are superposed to reconstitute surface profiles and allow measurement of surface roughness (S_a). Because the mineralogy of the three limestone is the same, one can assume that the surface chemistry is the same. Roughness measurement has been made only on limestone samples. The arithmetic mean S_a for the limestones is presented in Table 2.

2 Sample preparation and immersion for Method 2

The boiling water test, ASTM D3625, was conducted in this study. For this test, mixtures were formulated with 6/10 aggregate (i.e., a gradation cut between the 6 mm and 10 mm sieve sizes), which had been water washed and dried prior to treatment with a bitumen content of 2.9% (250 g of 6/10 sized aggregates and 7.5 g of bitumen). The retained bitumen coating result was evaluated visually after water immersion.

Aggregates and bitumen are heated to 150°C. After adding bitumen to aggregates, the mixture is stirred 1 min while maintaining the temperature at 150°C. After reducing their temperature to 85°C, coated loose materials are immersed in boiling water for 10 min. After allowing the boiled mixture to cool to room temperature, the retained bitumen coating result is evaluated visually.

It is known that stripping phenomenon depends on several parameters, including the physico-chemical properties of the bitumen and aggregate, the manner of mixture manufacturing, and the conditions of moisture exposure. The primary focus of this study, however, is to develop a new

stripping resistance evaluation test. Validation of the method is provided. Then influence of mineralogy of the aggregate on stripping is studied and results are compared to usual standardized test methods for moisture resistance.

EVALUATION OF DROP STRIPPING ON POLISHED AGGREGATE SURFACE – METHOD 1

This new method of stripping evaluation studies the dynamic changes in the shape (area) of a bitumen drop deposited on a highly-polished aggregate slide while the bitumen-treated slide is immersed in water at a fixed temperature. Indeed, in air the final droplet shape is reached when all the forces involved are equilibrated. The contact point between bitumen, air (or water) and aggregates is called triple point. When the equilibrium droplet shape is reached, the triple point does not move anymore. When the sample is immersed into water, the interfacial forces may change to reach a new equilibrium in water. This change is the stripping driving force. Forces in both water and air are described in Table 3.

Table 3. Forces active in the system of bitumen and aggregate in air and in water

In air		In water
Surface forces	Surface tension of bitumen	Interfacial tension between bitumen and water
	Adhesion forces between bitumen and aggregates	Adhesion forces between bitumen and aggregates
	Surface energy of aggregate	Interfacial tension between aggregate and water
Volume forces	Viscous forces	Viscous forces
	Gravitational forces	Gravitational forces
		Archimedes force

Difference in forces are due to evolution of surface forces and the addition of Archimedes (or buoyant) force. From the Young equation (Equation 3), the contact angle at the triple point can

be expressed in terms of the surface tensions, γ , between bitumen, aggregate, and air (or water). Expressions and order of magnitude of different physical quantities are presented in Table 4.

Table 4: Contact angle estimation from the Young equation

	In air	In water
Forces in triple point
Contact angle expression	$\cos \vartheta_1 = \frac{\gamma_A - \gamma_{BA}}{\gamma_B}$	$\cos \vartheta_2 = \frac{\gamma_{AW} - \gamma_{BA}}{\gamma_{BW}}$
Order of magnitude of physical properties	$\gamma_G \sim 50 - 250 \text{ mJ/m}^2 *$ $\gamma_B \sim 30 - 40 \text{ mN/m}^*$ $\gamma_G > \gamma_{BG}$	$\gamma_E = 72.8 \text{ mN/m}$ $\gamma_{BE} \sim 50 - 60 \text{ mN/m}$ $\gamma_{GE} < \gamma_{BG}$ $\gamma_{BE} < \gamma_E$
Order of magnitude of contact angle	$\cos \theta > 0$ θ is low	$\cos \theta < 0$ $\theta > 90^\circ$

*[1][34][35]

As shown in the schematic representation of forces acting at the triple point in Table 4, γ_G is the surface energy of aggregate, γ_B is the surface tension of bitumen, γ_{BG} is the interfacial tension between bitumen and aggregate, γ_{GE} is the interfacial tension between water and aggregate, γ_{BE} is the interfacial tension between water and bitumen. The contact angle formed by the bitumen droplet in air, Θ_1 , is smaller than the contact angle in water, Θ_2 . These differences in contact angles and surface energies of the two systems are responsible for the contraction of the bitumen drop during water immersion.

The experimental method allowed data acquisition on nine drop samples simultaneously. The step-by-step experimental protocol for aggregate polishing, droplet application, water immersion, and photographic treatment of the specimens are described in the following section. Then the analysis of experimental results is described.

1 Experimental protocol

1.1 Aggregate polishing

Four cleaned and dried aggregates of 6/10 sizes were rendered immobile by partial embedment in a curable liquid resin. For each aggregate, slides with four impregnated aggregates were ground as described in Table 5.

Table 5. Grinding and polishing protocol for thin aggregates slides

	Disk	Lubricant	Time (min)	Rotation speed (rpm)
Pre grinding	MD Piano 220	Water	8	250
	MD Piano 1200	Water	8	200
	MD Piano 4000	Water	8	200
Grinding	MD Dac	6 μm *	6	150
	MD Dac	3 μm *	6	150
	MA Nat	$\frac{1}{4}$ μm *	2	100

* Aqueous solution of polycrystalline diamond of 6, 3 and $\frac{1}{4}$ μm size.

Slides are cleaned under distilled water, followed by air drying and storage in a dust-free and low-humidity environment. The delay between polishing and bitumen drop deposit is seven days.

1.2 Drop deposit

A drop tensiometer (DSA 100, Krüss GmbH) was used to deposit bitumen drops. Specimens were positioned on a manual table, which was movable in the x, y and z-axes. Solid samples af- fixed to the manual table were precisely oriented along the desired optical axis. Key features of

the optical instrument included a halogen light source, a frame grabber camera with a 780×580 pixel resolution, and a zoom/focus mode. A glass syringe was used to precisely apply and form the bitumen droplets on the polished aggregate slides.

The thermal cell of this tensiometer allows for precise temperature control during testing. Polished aggregates are placed in an oven at the aggregate temperature and are equilibrated for 3 h prior to beginning the experiment. The syringe was also equilibrated at the bitumen deposit temperature. Test bitumen samples were added in the 10-mL glass dosing syringe (with a 2.1-mm diameter needle) only 15 min to be sure that there was no aging phenomenon.

The syringe was introduced in the dosing cell, and the polished aggregate was placed in the measurement cell. The piston of the syringe was fixed to a micrometric screw to enable precise and accurate control of drop volume. Bitumen temperature T_b is chosen so that the bitumen viscosity is 0.2 Pa.s, which is a common coating viscosity used in the asphalt paving industry. Aggregates temperature T_a is chosen at 40°C under bitumen temperature, which is not representative of realistic industrial methods. However, this lower aggregate temperature was employed to simulate low adhesion condition during the droplet coating and spreading process; consequently, stripping is favored. One bitumen drop was deposited on each test aggregate. On average, four drops of one bitumen per aggregate slide could be studied simultaneously. After depositing the drop, the samples were covered with a protective bell jar to prevent dust contamination.

All contact angles were measured using DSA software (Krüss GmbH), following axisymmetric drop shape analysis (ADSA). Two numerical approaches can be used: Tangent-Method 1 and Circle fitting. The first one is based on the mathematical equation of an ellipse, while the second

one consists of the resolution of a higher-order polynomial equation. These are standard numerical analysis procedures for drop shape analysis and permit highly precise drop volume measurement.

1.3 Sample immersion

One day (24 h) after the bitumen drops were deposited on the polished mineral aggregate samples, the test specimens were pre-heated to the chosen water temperature for 3 h. An image of the drop-aggregate specimens was taken before water immersion. After immersion of the test specimens in hot distilled water, photographs were taken every five min for the first hour, then every 20 min, and to finish every 90 min during 20 h. In this studied, the temperature of the water is 70°C.

Photographs are taken from an overhead vantage point to measure the drop surface instead of taking photographs of the droplet profile, as with contact angle measurement. Indeed, in case of droplets on non-homogeneous and/or rough surfaces, contact angles are not constant and can vary significantly from one profile photograph to the other.

1.4 Pictures treatment

Photographs taken during water immersion were analyzed using a free, online software, Image J. The software was used to detect all drops on the picture, measure the surface area of each one, and report the results in units of mm². The photographs were converted from color to gray-scale, employing 255 shades of grey. A filter was applied to establish which grey shades corresponded to bitumen, and which corresponded to the aggregate. The filtered images were then completely

converted to black and white images. Figure 2 shows the evolution of the photographs during the treatment.

Figure 2. Evolution of the sample photographs a) samples in water; b) 8-bit image; c) black and white image; and d) drop detection

From this image analysis using Image J, the initial area (at time, $t = 0$) of the bitumen droplet was defined as $S(t=0)$. The area of the bitumen droplet at some time t was defined as $S(t)$. A plot of $S(t)/S(t=0)$ is shown in Figure 3 for three different polished aggregate specimens (dotted line).

2 Data analysis

A plot of $S(t)/S(t=0)$ is shown in Figure 3 for three different polished aggregate specimens. It can be seen in Figure 3 that equilibrium values for $S(t)$ were reached after around 120 min. From an analysis of results like those shown in Figure 3, Equation 4 is derived as a theoretical description of the dynamic evolution of the relative change in droplet surface area with time of immersion.

$$\frac{S(t)}{S(t=0)} * 100 = A - (A - 100)e^{-\frac{t}{\tau}} \quad [4]$$

The term A stands for the equilibrium value of the percent of residual drop surface. The term τ represents a time constant and the term t is the immersion time.

Figure 3 shows very good fit between the theoretical equation (Equation 4) and the measured data. Theoretical data are represented by the continuous line in Figure 3; measured data are individual points on the graph.

Figure 3. Evolution of the relative surface with immersion time

High values of the term A are synonymous with good resistance to the effects of water. The applied bitumen droplet did not contract significantly during water immersion.

A dimensional (or unit) analysis in Equation 5 shows that τ depends on three properties: 1) bitumen viscosity η , 2) interfacial tension between bitumen and water γ_{BW} , and 3) initial bitumen drop surface area $S(t=0)$:

$$\tau = f \left(\frac{\eta \sqrt{S_0}}{\gamma_{BW}} \right) \quad [5]$$

Values for A and τ were obtained by the method of least squares. It has been observed that when A is very high, above 90%, error in the value of τ can be very important. Indeed, the time constant describes the behavior of the bitumen/aggregate interface at very short time of immersion.

When the drop surface remains constant, there is no single, unique value for τ , which fits well all

the data, but rather a range of values. Consequently, values for the time constant, τ , are not determined if the value of A is above that 90%.

Based on the results with the materials and test parameters used in this study, one can conclude that a high value of A is a frequent occurrence. To evaluate the influence of this parameter on stripping rates, Equation 6 is used:

$$v(t_i) = \frac{S(t_{i+1}) - S(t_i)}{t_{i+1} - t_i} \quad [6]$$

$v(t_i)$ is the rate of stripping, $S(t_{i+1})$ is the drop area at time t_{i+1} and $S(t_i)$ the drop area at time t_i . The rate of stripping $v(t_i)$ approaches zero because, after a long time of immersion, the equilibrium droplet shape in water is reached, and the triple line (at intersection of bitumen, aggregate and water) does not move anymore. The initial rate of stripping is used to compare bitumen/aggregate.

3 Validation of Method 1

To evaluate the influence of bitumen drop volume and the repeatability of the test, a homogeneous substrate is used. Tests are performed on bitumen-glass pairs with the following conditions: Bitumen temperature $T_b = 150^\circ\text{C}$, glass slide temperature $T_a = 110^\circ\text{C}$, water temperature $T_w = 65^\circ\text{C}$.

3.1 Influence of drop volume

To rank bitumen/aggregates pairs from one to another, speeds are compared for a given contact angle. In this study, drops are considered as partial spheres because the drop radius is inferior to the capillary length, as described in Equation 7:

$$\kappa^{-1} = \sqrt{\frac{\gamma_B}{g\rho_B}} \quad [7]$$

With γ_B the interfacial tension between bitumen and water, g is the gravitational constant and ρ_B is the bitumen density. In case of bitumen, κ^{-1} is approximatively 1.9 mm. Gravitational forces are taken into account when $\kappa^{-1} \ll R$, the radius of the drop.

A plot of A value versus bitumen drop volume is shown in Figure 4. Nine drops were studied with volumes ranging from 2.2 μL to 29.0 μL .

Figure 4. Influence of Bitumen Drop Volume on A Value

In the volume range studied, increasing drop volume seems to have a small, downward influence on A value. Indeed, the higher the volume drop, the lower is the A value.

A plot of stripping rate versus immersion time is shown in Figure 5.

Figure 5. Evolution of stripping rate vs immersion in water for different drop volumes (μL)

For drop volumes from 6.3 to 24.7 μL , initial rate of stripping $v(t_0)$ is in a range between 6.3 and 8.9 mm^2/min . For a 2.2 μL drop and for a 29.0 μL drop, the stripping rates are, respectively, significantly higher and lower for a very short time of immersion.

Based on the results in Figure 4, Figure 5 and based on the fact that mineral substrates are more heterogeneous than glass slides, the volume of the bitumen droplets in this study were fixed at $9 \pm 3 \mu\text{L}$.

3.2 Repeatability

Two set of four drops were studied for repeatability of the tests on glass. Preparation techniques and immersion parameters are those described above. All the values for A and τ are presented in Figure 6.

Figure 6. Values for A and τ for the Eight Tested Specimens

The average value for A is 23.7 ± 3.4 % (error rate is 14%) and for $\tau = 7.9 \pm 1.2$ min (error rate is 15%).

A plot of the stripping rates versus immersion time for the eight specimens is shown in Figure 7.

The standard deviation is decreasing with immersion time. The rate of stripping at the initial time is 8.3 ± 1.0 mm²/min. The error rate is smaller than 15% which is satisfying. This new method appears suitable to evaluate adhesion forces of different bitumen/aggregate pairs.

Figure 7. Evolution of Stripping Rate vs Immersion Time for eight specimens studied

3.3 Summary

The described method allows one to simplify evaluation of the dynamics of a bitumen/substrate interface having a very clean and smooth substrate surface. Good experimental repeatability is obtained because preparation conditions use precise droplet volume application techniques and immersion conditions and measurement techniques are also precisely and accurately controlled.

To compare and rank different pairs of bitumen/aggregate surface, two indicators are used:

- The A value, which is the area of the retained coated surface, reflects the intensity of stripping phenomenon
- And, the time constant and more notably, the rate of stripping, $v(t_i)$, for a given contact angle allows one to evaluate the kinetics of the stripping phenomenon for a given bitumen/aggregate pair.

COMPARISON WITH METHOD 2

1 Evaluation of coated surface after immersion by binary photographic (image) analysis

Coated aggregates are inserted into rectangle based container, which is situated on a jack. A camera is positioned at 70 cm from the specimen, and spotlights are directed onto the specimen at a small incident angle to limit light reflection. A photograph is taken of each side of the container.

As previously mentioned, the software used for the photographic image analysis is ImageJ. Color photographs (Figure 8.a) were converted into black and white ones (Figure 8.b). The “black and white” photographs contained 255 shades of grey. Again, as described above, a filter was applied

to assign certain grey shades as black, corresponding to the bitumen, and certain shades to be white, corresponding to the mineral aggregate.

Figure 8. a) Original Picture; b) Binary Picture for Coated Surface

Once the percent of black in the selected photographed area was calculated by the ImageJ software, the corresponding percent of retained bitumen coating could be calculated.

2 Influence of the mineralogy

The influence of mineralogy on stripping resistance was studied via this image analysis using two different substrates: 1) on model materials, studying the stripping of a bitumen drop on a polished aggregate, and 2) on loose mineral aggregate.

2.1 Results using Method 2

Standard boiling test adhesion was used to evaluate the susceptibility of the bitumen-aggregate bond to stripping [10]. Specimens were immersed 10 min in boiling water. The results are reported as the percentage of aggregate surface coated with bitumen after test and after the loose, boiled mixture had been allowed to stand for 10 h at room temperature. This retained coated surface is obtained with the photographic treatment previously described. The results are presented in Table 6.

Quartzite displayed the lowest percent of retained coated surface after immersion with 24.2% of aggregate having a residual bitumen coating after boiling. In contrast, Limestone 2 displayed the highest percentage of retained aggregate surface coating, with 74.8% after boiling.

Table 6. Results of boiling test on loose materials

Aggregate	Average (%)	ANOVA ranking
Quartzite	24.2 ± 3.6	A
Gneiss	32.1 ± 1.2	B
Diorite	32.6 ± 2.3	B
Basalt	51.0 ± 0.7	C
Limestone 3	52.2 ± 4.3	C
Limestone 1	57.2 ± 3.1	C
Limestone 2	74.8 ± 1.9	D

The higher the percent of residual coated surface after 10 min in boiling water in the static immersion condition, the better the resistance of the bitumen-aggregate pair to stripping. Gneiss and Diorite are not significantly different. Moreover Basalt has the same behavior of Limestone 3 and 1. These results are in accordance with research results from other scientists [8][23]. Acidic aggregates with high silica content show low resistance to water intrusion. Indeed, carboxylic acids of bitumen are strongly adsorbed on surface due to hydroxyl group but easily displaced by water [16].

On the contrary, basic aggregates with high carbonate content react with carboxylic acids to form a water-insoluble calcium carbonate salt.

With this test, it was possible to discriminate between the three limestone samples studied. Indeed Limestone 2 is significantly different from the others. Regarding the roughness measurements, there is no significant difference in Sa values between Limestone 1 and Limestone 2. The Sa value is more important for Limestone 3. One might hypothesize that during conditioning in a boiling water test, higher roughness makes the bitumen/aggregate interface more susceptible to water intrusion. For example, during mix preparation, micro-pockets of air might be trapped between the bitumen film and the asperities of a rough aggregate surface. A weak bond at those points would facilitate intrusion of moisture.

2.2 Results using Method 1

Contrary to the previous method where the roughness and macro texture of the aggregate in the static immersion test is a potential variable in stripping resistance, Method 1 used polished aggregate.

The change in bitumen drop area (on a polished aggregate surface) was measured as a function of immersion time in heated distilled water as a means of characterize passive stripping. Table 7 shows the equilibrium retained surface area A for one bitumen on the seven different polished aggregate surfaces after immersion in water at 70°C and the value of the constant time for acid (quartzite and gneiss) and heterogeneous aggregate (diorite and basalt).

The lowest A value at 70°C was measured with quartzite and gneiss (under 20%), whereas all the different limestone showed a high percent of residual surface (more than 90%). Diorite and bas-

alt aggregate showed intermediate behavior, with respectively 50.8% and 77.6%. As noted previously, a high percentage of retained droplet surface area (a high A value) indicates good resistance to water. The bitumen drop boundary did not recede for the three limestone systems, or in other words, the triple line did not move in the presence of water. The bitumen-limestone interfacial bond is more resistant to water intrusion than the bond formed between bitumen and quartzite or bitumen and gneiss.

Table 7. Results of drop stripping after 15 h of static immersion in water at 70°C

Aggregate	A (%)	ANOVA ranking	Final contact angle in water (°)	Tau (min)	$V_{(t=0)}$ (mm ² /min)
Quartzite	14.9	A	132.5	10.6	6.9
Gneiss	16.9	A	126.9	14.9	5.0
Diorite	50.8	B	64.4	83.2	0.6
Basalt	77.6	C	49.5	20.0	1.4
Limestone 3	93.0	D	38.8	-	1.0
Limestone 1	94.7	D E	41.5	-	0.8
Limestone 2	95.3	E	44.4	-	0.3

The final contact angle at the triple point in water was measured from the drop profile. Values for these final contact angles are presented in Table 7. The higher the contact angle, the more the bitumen droplet receded (or stripped) during water immersion. With quartzite and gneiss, the contact angle exceeded 100°, meaning that interface of the aggregate with water increased at the expense of bitumen-aggregate interfacial area. In contrast, the contact angle on limestone was around 40°, meaning a higher affinity of the bitumen for the limestone than for the water.

1 The constant time was calculated for all the aggregate except the limestone because A is higher
2 than 90% (see Paragraph 2. Data analysis). According to the initial stripping rate, one can con-
3 clude, the lower tau value, the faster is the rate of bitumen withdrawal. Thus, stripping is signifi-
4 cant and rapid for quartzite and gneiss, whereas it is very slow for diorite.

5 From all the measured values, it is possible to classify the bitumen-aggregate pairs according to
6 their stripping resistance. Quartzite and gneiss showed the same behavior. Diorite and Basalt are
7 significantly different. Limestone 3 and Limestone 2 are considered as different even if the re-
8 sults are very close. Limestone 1 is not significantly different from the other limestones.

10 ***2.3 Comparison between Method 1 and Method 2***

11 Differences between the drop test on polished aggregate and the boiling water test include the
12 following. Aggregate in the boiling test are not polished. The Method 1 was conducted at 70°C
13 whereas the Method 2 was conducted at boiling temperature. Despite these differences, there was
14 a common trend in overall ranking of stripping resistance. Figure 9 shows this commonality.
15 Generally both methods gave results, which indicated that stripping was more significant the
16 higher the silica content of the mineral aggregate.

17 It is worth pointing out also that the values for the percent retained coating in the drop test
18 (Method 1) are lower than those values obtained in the static immersion test (Method 2) for acid
19 aggregates (Quartzite and gneiss) due to aggregate smoothness differences and due to the lack of
20 mechanical action in the Method 1 drop test.

Figure 9. Correlation of Residual Coated Surface with Silica Content

One can surmise that with Method 1, adhesion is the result of chemical adhesion, because aggregate surfaces are polished to minimize the surface roughness and texture. Indeed, Alicona characterization has been realized on polished surface and S_a is very low (from 13 to 27 μm) compared to the value for unpolished aggregate presented in Table 2. Polishing contributed to the fact that the value of the coefficient of determination, R^2 , in Figure 9 is higher for Method 1 than for Method 2.

In contrast, while Method 1 cannot discriminate between the three limestones ($A = 94.4 \% \pm 1.3$), Method 2 allows one to consider Limestone 2 as better mineral aggregate in terms of moisture resistance. Because the mineralogy of the three limestones is the same, one can assume that the surface chemistry is the same, and therefore, Method 1 allows one to measure chemical adhesion without taking into account aggregate micro-texture. The aggregates in this study have been chosen because their mineralogy are significantly different. The selected aggregate are representative of those found in Western Europe.

CONCLUSION

Water damage and stripping resistance are influenced by numerous parameters. The aim of this work was to develop a new stripping resistance evaluation method which can isolate chemical adhesion from mechanical adhesion.

This study introduced a new small-scale test method for moisture sensitivity. The method uses optical image analysis to quantify the strength of bitumen film adhesion to polished aggregate exposed to water at varying temperatures. A precise volume (around 9 μL) of test bitumen is deposited as a drop on a polished aggregate surface. The area of droplet is measured using optical image analysis. The optically-determined area of the droplet was then measured as a function of time of immersion in water at a range of temperatures. The ratio of the droplet surface area after the immersed sample reached equilibrium (expressed as $S(t)$) to the initial surface area of the droplet ($S(t=0)$) was a reliable measurement of the resistance of the bitumen film to moisture-induced stripping.

Moreover, by carefully characterizing the petrographic characteristics of the polished aggregate surface, the retained surface area ratio ($S(t)/S(t=0)$) could be correlated with physicochemical properties of the bitumen and aggregate interfaces, such as silica content. Results highlighted different families of mineralogy. For example, it was shown that basic aggregates such as limestone showed a good resistance to water whereas acid ones, with high silica content, were very susceptible to water. Comparing the result with those of Boiling Test, the impact of roughness is reduced and the kinetic can be evaluated.

The impact of bitumen rheological properties is not presented in this paper. However, it is reasonable that bitumen rheology, at the temperature of water during the immersion, might have an

1 impact on A value, the time constant value, τ , and the rate of stripping. The higher the water tem-
2 perature, the lower is the A value and the faster the rate of stripping.

3 The results of the new test method allow researchers to identify bitumen/aggregate pairs resistant
4 to water. Further, the technique discussed herein is a promising tool for the evaluation aggre-
5 gate/additive compatibility. In case of good compatibility between additives and aggregates, A
6 value increase and stripping kinetic reduce. A limit of 90% on A value has been decided to con-
7 sider additives as useful.

8 In future work, the practical utility of this method (Method 1) will be demonstrated further by
9 comparison with results of other standard moisture resistance test for compacted bituminous
10 mixtures.

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